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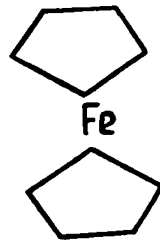
STUDIES OF FERROCENE IN THE USSR

Ferrocene or dicyclopentadienyliron ($C_5H_5FeC_5H_5$) was discovered in 1951 by Kealy and Pauson (1).

The unusual chemical and physical properties of this compound at once attracted the attention of chemists in many countries.

These properties prompted Woodward and co-workers in 1952 (2) to ascribe to it a three-dimensional structure of a pentagonal antiprism or the so-called sandwich structure (I) with an atom of iron placed between two parallel five-membered rings.

All studies (both chemical and physical) of ferrocene and of its analogues with other transitional metals confirmed configuration I.



The nature of the linkage between the cyclopentadienyl rings and the iron atom is not clear as yet. Several hypotheses have been advanced on this score, more or less substantiated by quantum mechanical calculations.

In any case the chemical and physical properties of ferrocene favour the assumption that the linkage between the organic part of the molecule and the iron atom is effected by means of the π -electrons of the cyclopentadienyl rings and the d-electrons of the atom of the transitional metal.

Ferrocene is an orange-coloured, crystalline substance with a melting point of $174^\circ C$. It is diamagnetic, its dipole moment being zero. Ferrocene is readily soluble in most organic solvents, it is insoluble in water, and can be distilled with water vapours; its sublimation temperature is about $100^\circ C$.

The most characteristic properties of ferrocene are: a) exceptional thermal stability (it is not destroyed up to $450^\circ C$); b) the stability of the linkage between the cyclopentadienyl radicals and iron (it withstands boiling with concentrated HCl, and is resistant to alkalis); c) exceptional sensitivity to the action of oxidizing agents (sulphuric and nitric acids, halogens, silver sulfate, quinone, peroxides) which transform ferrocene into the unstable ferrocinium cation $[(C_5H_5)_2 Fe^+]$ and eventually completely destroy it; d) total absence of reactions to double bonds of cyclopentadienyl rings; e) a tendency to enter into substitution reactions in the cyclopentadienyl rings

All these properties characterize ferrocene, on the one hand, an organometallic compound of a new type with an unusual linkage between the organic radicals and metal, and as a new system on the other.

In the USSR, studies of ferrocene were begun in 1953 in the laboratory of Academician A. Nesmeyanov. The subject of these studies was the reactivity of the organic part of the ferrocene molecule. It is these studies that yielded most of the data confirming the aromatic nature of the new organometallic compound.

The results of the researches carried out so far are represented at the exhibition in the form of a diagram, accompanied by samples of the substances obtained.

As studies of ferrocene were undertaken simultaneously and independently in several countries, there has been an inevitable overlapping in the directions of research. Such instances are referred to in the prospectus.

In 1954 A. Nesmeyanov, E. Perevalova, R. Golovnya and O. Nesmeyanova (3) effected mercuriation, metallation with butyl lithium and arylation of ferrocene.

These early experiments demonstrated that in substitution reactions ferrocene behaves like benzene or rather like such superaromatic systems as furan or thiophene. This is borne out by mercuriation with mercuric acetate under mild conditions which resulted in a mixture of di- and monomercuriated ferrocenes. No mercuriation of benzene is possible under such conditions. The same applies to metallation with butyl lithium, which cannot be accomplished with benzene, while in the case of ferrocene it produces a mixture of di- and monolithium derivatives of ferrocenes.

Arylation of ferrocene with aromatic diazonium salts was carried out under the conditions of Homberg's reaction.

Somewhat later metallation with butyl lithium (4) and arylation of ferrocene (5, 6) were reported by British and American authors.

Three reactions described in the first report proved to be highly fruitful from the viewpoint of synthesis. Further studies in the arylation of ferrocene with diazonium salts (7, 8) resulted in the synthesis of a whole series of mono- and diarylferrocenes. Some of these were obtained not by direct arylation but by secondary transformations (aminophenylferrocenes from nitrophenylferrocenes, and p-ferrocenylanizol from p-ferrocenylphenol).

A study of the properties of arylferrocenes revealed the nature of ferrocenyl as a substituent in the benzene ring. A measurement of dissociation constants of ferrocenylanilines, ferrocenylphenols, ferrocenylbenzoic acids and ferrocenylamine and a comparison thereof with the dissociation constants of the respective biphenyl compounds revealed that ferrocenyl is a strong electron-donor substituent.

A. Nesmeyanov, E. Pervakova and O. Nesmeyanova used mercuric derivatives of ferrocene possessing the usual properties of organo-mercury compounds (symmetrization reaction, splitting off of mercury by boiling in concentrated HCl) to synthesize some ferrocene derivatives which could not be obtained otherwise.

Thus, by action of bromine and iodine on mercuriated ferrocenes iodo-, bromo-, diiodo- and dibromoferrocenes were obtained (10). Action of free rhodan produced rhodanide, which, however, was reduced to diferrocenyl disulphide in the process of separation (11). Action of chlormercuriferrocene on triphenylchloromethane resulted in the synthesis of triphenylferrocenilmethane (11). The latter reaction demonstrates the mobility of mercury in the ferrocene nucleus.

A study of the properties of halogenoferrocenes revealed that the halogen in the ferrocene nucleus is even more inert than an aromatic halogen.

Lithium and later obtained sodium derivatives (12) of ferrocene made it possible to synthesize ferrocene mono- and dicarboxylic acids and, what is of special interest, ferrocenylamine (9). The latter was obtained by the method of K. Kocheshkov by reaction of ferrocenyllithium with the benzyl ester of hydroxylamine.

Almost simultaneously ferrocenylamine was synthesized by Arimoto and Haven (13) from the azide of ferrocenecarboxylic acid.

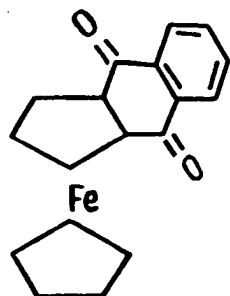
Despite the preliminary data obtained by some authors (14), in 1956 A. Nesmeyanov and N. Kochetkova (15) effected alkylation of ferrocene with alkyl halides in the presence of aluminum chloride. It was demonstrated that alkylation of ferrocene, like that of benzene, results in mixtures of mono-, di-, and poly-substituted products.

Separate alkyl ferrocenes were obtained by A. Nesmeyanov and N. Volkenau (16) by reduction of acylferrocenes using Clemensen's method. Dimethylferrocene was synthesized by reduction of dimethyl ester of ferrocenedicarboxylic acid with lithium aluminum hydride (12). Esters and ketons of the ferrocene series are in general easily reduced by lithium aluminum hydride producing hydroxyderivatives and then alkyl derivatives of ferrocene (12).

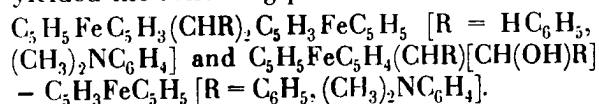
A detailed study of acylation (the first substitution reaction carried out for ferrocene) was also made by Soviet chemists.

Thus, it was demonstrated (3) that acylation of ferrocene takes place not only in the presence of aluminum chloride, but unlike that of benzene, also in the presence of stannic tetrachloride, under milder conditions. By using various modifications of the Friedel-Crafts method a considerable number of ketones and ketoacids of the ferrocene series were synthesized (16, 17, 18).

Highly interesting is intramolecular acylation achieved within the ferrocene series. In 1956 A. Nesmeyanov, N. Volkenau and V. Vilchevskaya (18) carried out cyclization of di-(ω -carboxypropyl) ferrocene by means of polyphosphoric acid. As a result, di-(~~ketotetrahydroindenyl~~-iron was obtained and its structure ascertained by reducing it to di-(tetrahydroindenyl)-iron, obtained earlier by Fischer (19). The synthesis and the establishment of the structure (20) of ketotetrahydroindenyl-(cyclopentadienyl)-iron from ω -carboxypropyl-ferrocene and of a ferrocene analogue of antraquinone (II) from *o*-carboxybenzoyl-ferrocene confirmed that cyclization proceeds into the same cyclopentadienyl ring which already has the substituent in it.



In 1956 A. Nesmeyanov and I. Kritskaya demonstrated the condensation of ferrocene with aldehydes in the presence of sulfuric acid (21). Interaction between ferrocene and formaldehyde, benzaldehyde and *p*-dimethylaminobenzaldehyde yielded the following products:



By means of infrared spectra and by destructive bromination it was shown that the compounds thus produced contained unsubstituted cyclopentadienyl rings, i. e., that condensation takes place twice into the same cyclopentadienyl ring.

Interaction between ferrocene and formaldehyde and benzaldehyde had been achieved somewhat earlier by Weinmayr (22) in the presence of anhydrous HF, and later by Riemschneider and Helm (14).

The instability of ferrocene to the action of oxidizing agents makes it impossible to involve it in the most characteristic reactions of electrophilic substitution, such as nitration and halogenation.

In 1955 A. Nesmeyanov, E. Perevalova and S. Churanov (23) succeeded in sulfonation of ferrocene with pyridine sulfotrioxide, obtaining di- and monosulfonic acids of ferrocene. Esters and chlorides of these sulfonic acids were also synthesized. Chloride of ferrocene monosulfonic acid was reduced to diferrocenyldisulfide (23).

Sulfonic acids of ferrocene were synthesized independently by Weinmayr (22) who had used concentrated sulfuric acid in acetic anhydride as a sulfonating agent.

Soviet chemists are conducting researches aimed at establishing the effects of substituents on the reactivity of cyclopentadienyl rings

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in ferrocene. In this connection A. Mesmeyanov and E. Perevalova with a group of co-workers (24) developed two methods for ascertaining the structure of ferrocene compounds: a) destructive bromination and b) destructive hydrogenation. The first method involving the action of excess bromine on the compound investigated, makes it possible to establish the presence of an unsubstituted cyclopentadienyl ring in the molecule by the formation of pentabromocyclopentane. The second method—hydrogenation under rigid conditions over Raney nickel—reduces the compound investigated to known cyclopentane derivatives.

By now, some information has been collected indicating that alkyl substituents have a certain activating effect, and acyl substituents, a certain deactivating effect on ferrocene in electrophilic substitution reactions (17).

There are also some preliminary indications that the effect of substituent is transmitted from one cyclopentadienyl ring to another through the iron atom (25).

Thus, the integrated researches, the results of which are represented at the exhibition in a nutshell, were directed at investigating ferrocene as a new aromatic system.

The information obtained clearly illustrates this aspect of the new compound. According to this information, ferrocene behaves as a superaromatic compound in many typical substitution reactions.

A. N. Nesmeyanov and E. G. Perevalova, *Uspekhi Khimii*
 27, 3 (1958).

CYCLOPENTADIENYL COMPOUNDS OF METALS AND
 RELATED COMPOUNDS

In spite of many attempts, it has not been possible up to the present time to obtain alkyl and aryl organometallic compounds for the majority of the transition metals. The few representatives of this class of compounds described in the literature are distinguished by great instability^{1,2}.

Thus all attempts to isolate ferro-organic compounds were unsuccessful³⁻⁷. The assertion of Afanasyev and Tsyganov⁸ that they obtained a mixture of diethyl and monoethyl iron bromides as a result of the reaction of metallic iron with ethyl bromide is completely without basis.

Allyl (and benzyl) organometallic compounds are usually much less stable than alkyl and aryl compounds. Jaffe and Doak⁹ believe that the difficulty in obtaining organic compounds of transition elements is explained by the slight stability of pure covalent bonds between metal and carbon; at the same time these bonds can not be very ionic because of the insufficiently great difference in electronegativities between transition elements and carbon.

Therefore the discovery in 1951-1952 of the class of organometallic compounds, unique in both properties and structure, namely the dicyclopentadienyl derivatives of transition metals, was completely unexpected.

The first representative of this new class of compounds was dicyclopentadienyliron--an iron-organic compound obtained first in 1951 by Kealy and Pauson¹⁰, and then independently in 1952 by Miller, Tebboth, and Tremain¹¹.

Kealy and Pauson¹⁰ in the attempt to synthesize dicyclopentadienyl, $C_5H_5-C_5H_5$ by the reaction of ferric chloride with cyclopentadienylmagnesium bromide, obtained instead of the expected hydrocarbon a crystalline, extraordinarily stable, orange-colored compound which contained carbon, hydrogen, and iron and corresponded in elemental analysis to dicyclopentadienyliron.

This compound, which later according to the suggestion of Woodward and coworkers¹² came to be called ferrocene, immediately attracted the attention of chemists of a number of countries (the Soviet Union, the United States, Germany, and others). The study of the properties of ferrocene provided the start of the investigation of a new field of organometallic compounds--the chemistry of dicyclopentadienyl derivatives of transition metals.

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Investigations in this field began to develop in two directions:

- (1) the obtaining of dicyclopentadienyl derivatives of various metals and the establishment of their structures and
- (2) multilateral study of the reactions of ferrocene.

Soon after the discovery of ferrocene, dicyclopentadienyl derivatives of practically all transition elements were synthesized, and there were also obtained diindenyl compounds, cyclopentadienyl-carbonyls, and cyclopentadienylnitrosyls of some metals, and also compounds of metals with benzene (dibenzenechromium and others). Up to the present time, more than 200 works have been devoted to ferrocene and compounds similar to it. This interest was aroused by the great singularity of the structure and properties of this type of compound.

Ferrocene and some other dicyclopentadienyl derivatives of transition elements are unusually stable for organometallic compounds. In spite of the great formal unsaturation, addition reactions are unknown for these compounds. For ferrocene itself, a wide circle of reactions of electrophilic substitution, typical of aromatic systems, has been found.

Earlier investigations in the field of the chemistry of organometallic compounds played a great role in the formulation of a theory of valence, and in connection with the study of dicyclopentadienyl derivatives of transition metals, the question again arises as to the limits of applicability of the classical postulate of valence.

Several reviews¹³⁻¹⁶ of dicyclopentadienyl derivatives of metals were published in 1955, but at the present time they are already far from including all the literature on this question.

I. METHODS OF OBTAINING DICYCLOPENTADIENYL COMPOUNDS OF METALS

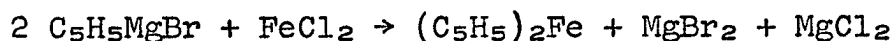
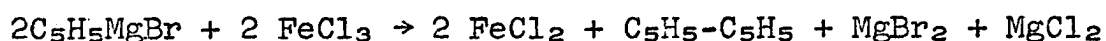
Dicyclopentadienyl derivatives of transition metals are obtained by the action of salts or acetylacetonates of these metals on cyclopentadienylmagnesium bromide, on cyclopentadienyllithium or sodium, or also by the immediate reaction of cyclopentadiene with the salt or carbonyl of the corresponding metal. Each of these methods is briefly characterized below.

In table 1 there are listed all the dicyclopentadienyl derivatives of metals synthesized as of the present time, with indication of the formal valence of the metal in them, the means of obtaining the compound, the yield (when indicated in the article), and the literature references. The means of synthesis are indicated by corresponding letters A, B, C, etc.; the nature of the method is set forth in the text.

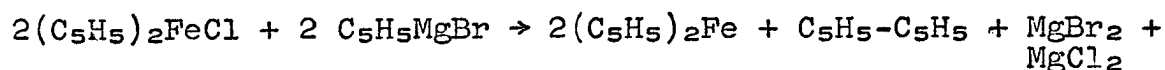
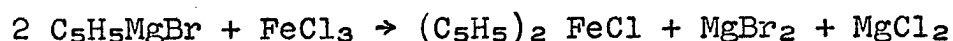
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A. The reaction of cyclopentadienylmagnesium bromide with the halide of the metal is a convenient method of obtaining dicyclopentadienyl derivatives of metals. The reaction is carried out in ether or ether-benzene solution. Thus, in the reaction of ferric chloride with cyclopentadienylmagnesium bromide in ether solution Kealy and Pauson¹⁶ first obtained ferrocene (yield 34%), later Riemschneida and Helm¹⁷ raised the yield to 52% by carrying out the reaction in ether-benzene medium. Probably the ferric chloride first is reduced by the organomagnesium compound to ferrous, which then reacts with another molecule of cyclopentadienylmagnesium bromide:



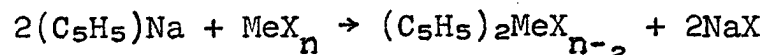
Such a reaction mechanism has in no way been proved; therefore the possibility is not excluded that the first step is formation of dicyclopentadienylferric chloride, which then is reduced by an excess of the Grignard reagent:



By this method there have been obtained dicyclopentadienyl compounds of cobalt,¹⁸ titanium,¹⁹ zirconium,¹⁹ vanadium,^{19,20} and others (see table 1).

B. The reaction of cyclopentadienylmagnesium bromide with the acetylacetonates of metals has been used with success in the case of metals whose halides are difficultly soluble in ether.¹⁹ Thus, dicyclopentadienyl compounds of iron,²¹ nickel,¹⁹ cobalt,²² ruthenium,²³ rhodium,²⁴ and iridium²⁴ have been obtained.

C. The reaction of cyclopentadienylsodium (or lithium) with halides²⁵ allowed one to obtain in good yields dicyclopentadienyl compounds of iron,²⁶ titanium,²⁰ vanadium,²⁰ molybdenum,²⁷ tungsten,²⁷ tantalum²⁰ and manganese:²⁵



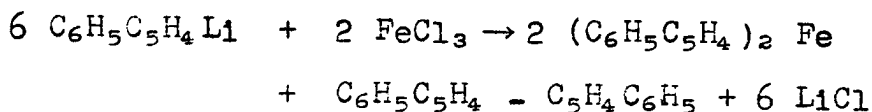
By this same method tricyclopentadienyl compounds of scandium, yttrium, and the lanthanides were obtained^{28,29}:



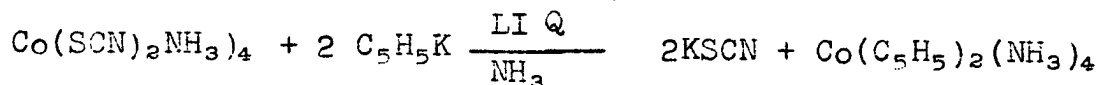
Tetrahydrofuran or ethylene glycol dimethyl ether served as solvent.^{20,26,27}

Pauson³⁰ used a method analogous to this for the synthesis of diphenyl-, polyphenyl- and dibenzhydrylferrocene. He obtained the lithium derivative of the substituted cyclopentadiene and brought it into reaction with ferric chloride in ether solution:

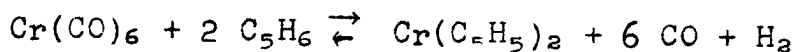
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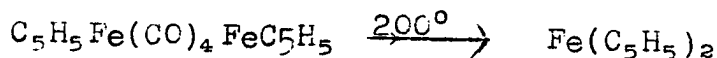
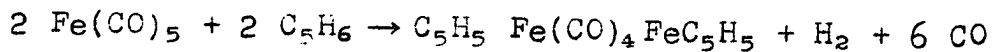
D. Dicyclopentadienyl compounds are obtained in high yields, except in the case of chromium and molybdenum, by the reaction of cyclopentadienyllithium, sodium, or potassium with the thiocyanatoamines of metals and subsequent thermal dissociation of the dicyclopentadienylmetal ammine⁽³¹⁻³³⁾.



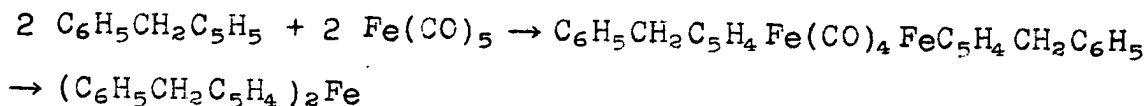
E. Cyclopentadiene reacts with carbonyls of transition metals at 250-350°, yielding dicyclopentadienyl compounds, it is true, in low yields, (10-30%)^(31, 34). The reaction for some metals is reversible⁽³⁵⁾:



Intermediate products are mixed cyclopentadienyl-carbonyls of the metals, which are usually obtained by this method^(36; 37). (See the section "Cyclopentadienylcarbonyls and cyclopentadienyl-nitrosyls of metals.")



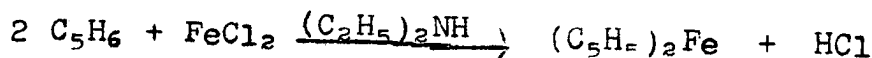
Hallam and Pauson³⁸ suggested the carbonyl method for the synthesis of substituted ferrocenes. By the reaction of benzylcyclopentadiene with iron pentacarbonyl, they obtained 1,1'-dibenzylferrocene; during this process there is first formed bis (benzylcyclopentadienyliron)-tetracarbonyl:



By the same method, 1,3,1',3'-tetraphenylferrocene was synthesized from 1,3-diphenylcyclopentadiene, however in this case it was not possible to isolate the carbonyl compound.

Bis (cyclopentadienyliron)-tetracarbonyl, $\text{C}_5\text{H}_5 \text{ Fe}(\text{CO})_4 \text{ FeC}_5\text{H}_5$, was used by Hallam and Pauson³⁸ for the obtaining of derivatives of ferrocene with substituents in one cyclopentadienyl ring. By the reaction of benzylcyclopentadiene and 1,3-diphenylcyclopentadiene with bis (cyclopentadienyliron) tetracarbonyl, they prepared benzylferrocene and 1,3-diphenylferrocene, respectively.

F. In the presence of organic bases cyclopentadiene reacts with halides^{26, 39}:



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By this method ferrocene is obtained in a yield of 84-88%²⁶.

G. Ferrocene was obtained as well by the reaction of cyclopentadiene with reduced iron in the presence of oxides of various metals¹¹.

Dicyclopentadienylmercury reacts with powdered iron yielding ferrocene⁴⁰ in 24-30% yield.

As of the present time dicyclopentadienyl compounds of almost all the transition metals, and also of some elements of non-transition groups, have been synthesized (see Table I). The latter are organometallic compounds of the usual type with a very reactive C-metal bond.

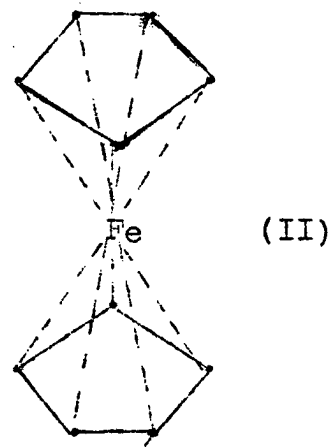
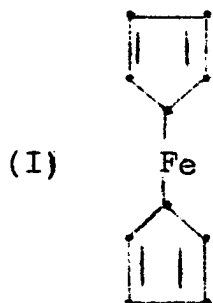
II. PROPERTIES OF FERROCENE

Physical Properties and Structure of Ferrocene

The first investigations of the properties of ferrocene showed that the structure (II), which was at first suggested, quite naturally, by Pauson, does not agree at all with the physical and chemical properties. Ferrocene is stable in air, does not decompose upon being heated to 470°, sublimes at 100°, is steam distillable, melts without decomposition at 173-174°¹⁰, dissolves in organic solvents, and withstands heating with concentrated hydrochloric acid and with alkali.

Ferrocene is diamagnetic. The infrared spectrum^{21,41} indicates the presence of C-H bonds of only one type. The dipole moment is virtually zero.^{41,59}

In 1952 Wilkinson and coworkers⁴¹ suggested for ferrocene the structure of a pentagonal antiprism, the "sandwich"-structure (II). The iron is located in the center of symmetry of the molecule, which has only one type of C-H bond.



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Further investigations of the chemical and, above all, of the physical properties of ferrocene showed the correctness of the "sandwich" structure (II).

Quantum mechanical calculations by the method of molecular orbitals⁽⁶⁰⁻⁶⁴⁾ also shows that there do not exist great hindrances to the free rotation of the cyclopentadienyl rings around the axis of symmetry inasmuch as the energy of interaction does not depend on the mutual rotation of the rings. Steric interaction of the carbon atoms of different rings favors the antiparallel centrally symmetrical configuration which is found in the ferrocene crystal. Experimental investigations show that in the crystalline state the cyclopentadienyl rings undergo oscillations around an axis of the fifth order, but the average configuration with time proves to be centrally symmetrical⁽⁶⁰⁻⁶⁵⁾. Free reciprocal rotation of the rings in the vapor phase at 400° has been proven by electronographic investigation⁶⁶ of ferrocene. In solutions, rotation is somewhat hindered⁶⁷.

Some chemical arguments in support of free rotation of the rings will be presented in examining the acylation of ferrocene.

Investigation of the magnetic properties of ferrocene showed that the ferrocene molecule is diamagnetic,^{41,68,69} and consequently does not have unpaired electrons. Ferricinium salts are paramagnetic. The paramagnetic moment of the picrate^($\mu_{\text{eff}} = 2.26$ Bohr magnetons) indicates the presence of one unpaired electron, as in the ferrocyanide ion ($\mu_{\text{eff}} = 2.33$ Bohr magnetons)⁴¹. For ferrocene the nuclear magnetic resonance spectrum has also been taken⁷⁰

The results of x-ray diffraction studies of ferrocene crystals^{60, 65, 71, 73} support the "sandwich" structure. The presence of a center of symmetry in the ferrocene molecule definitively determines the antiprismatic structure (II).

Data on electron diffraction studies of ferrocene⁶⁶ also supports the "sandwich" structure. Bond lengths found by this method agree well with those obtained on the basis of x-ray diffraction analysis.

The C-C bond distances in ferrocene (1.43 Å) and in benzene (1.39 Å) are very close. The distance between the rings (3.25 Å) is very close to the distance between the layers in graphite (3.35 Å). Consequently, there is very little direct bonding between the rings⁶⁶

Spectroscopic investigations. It has already been mentioned above, that in the infrared spectrum only one frequency has been detected for the C-H bond, which allows one to assert^{21,41} that

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in ferrocene there is only one type of C-H bond, in agreement with structure (II). The basic lines in the infrared spectrum, characteristic for ferrocene, are maintained, although with changes in intensity, in the spectra of ferricinium salts²⁰ and monosubstituted ferrocenes (see below). This permits one to detect the presence of the unsubstituted ring in derivatives of ferrocene^{13,30,74}. In the Raman spectrum⁶⁷ there is also only one C-H bond frequency.

Absorption spectra of ferrocene and ferricinium salts differ markedly^{13,75}. The absorption spectra have been investigated for ferrocene in the crystalline state^{76,77}. The infrared spectrum has been taken for a monocrystal²⁶.

Kauer⁷⁸ and Boke^{79,80} investigated the x-ray absorption spectra of ferrocene and of other cyclopentadienyl derivatives. These works are considered in detail in the review by Dyatkina⁸¹.

Investigation of mass spectra, carried out by Friedman, Irsa, and Wilkinson⁸² shows that they differ sharply from spectra of ionic as well as covalent organometallic compounds.

Thermochemical investigations. Cotton and Wilkinson⁸³ determined the heat of combustion of ferrocene from the elements ($\Delta H_f^{\circ}{}_{298} = 33.8 \pm 1.3$ kcal/mole). The heat of formation of ferrocene gas from gaseous metal and C_5H_5 radical equals $\Delta H_{298} = -147$ kcal/mole²¹. The heat of sublimation is 16.8 kcal/mole⁷⁵.

The bond energy between the metal and the C_5H_5 radical in ferrocene and nickelocene is 286 and 211 kcal/mole, respectively⁶¹.

Polarographic investigations^{20,41,84}. The oxidation-reduction potential of the system:

$(C_5H_5)_2Fe^{\overline{2}} \rightleftharpoons (C_5H_5)Fe^+$ in 90% alcohol equals + 0.30 V. The system is reversible. An aqueous solution of ferricinium perchlorate has a half wave potential of + 0.16 V with reference to the normal calomel electrode. The shift of the half-wave potential in going from an alcoholic to an aqueous solution confirms the chemical findings that ferricinium in neutral aqueous medium partially decomposes forming ferrocene. The determination of the amount of electricity required for electrolysis shows that the oxidation of ferrocene to ferricinium is a mono-electronic process.

The polarographic data show that ferrocene and other cyclopentadienyl compounds are distinct in their behavior from corresponding ions of the metal and related complex ions with the same degree of oxidation^{13,20}.

The electronic structure of dicyclopentadienyl derivatives of transition metals presents great interest, on the one hand from the

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point of view of explaining the valence state of the metal in these compounds, and on the other for an understanding of the reasons behind the phenomenon of aromatic properties.

The question of the special nature of the electronic structure of ferrocene and similar compounds is thoroughly discussed in the review of Dyatkina ⁸¹, therefore, we limit ourselves to a mention of the two directions existing for the solution of the problem.

Fischer and coworkers ^{16, 71, 85-88} look upon ferrocene and similar compounds as complexes in which all the II^- electrons of the cyclopentadienyl rings take part in the formation of the bond with iron. Much ^{89, 90} offers a theoretical basis for this point of view. In the opinion of Fischer and coworkers, ^{18, 71, 72, 85-87} ferrocene is a complex analogous to the hexacyanoferrate ions, with a central divalent iron. All 6 II^- electrons of each cyclopentadienyl ring (in the form of the anion C_5H_5^-) form approximately octahedrally directed coordinate covalent bonds with the free d^2sp^3 orbitals of the metal ion Fe^{++} ³¹. Around the central metal atom there is formed the stable 36-electron configuration of the noble gas krypton, which gives the compound its great stability. Such a hypothesis regarding bonding is applied by Fischer to all cyclopentadienyl and benzene derivatives of transition metals. ^{16, 18, 31, 86, 87}.

Jaffe ⁶³, Dunitz and Orgel ^{60, 61, 91-93} Moffitt ^{62, 94} and a number of other authors ^{64, 95-98} approach the electronic structure of ferrocene on the basis of the method of molecular orbitals and believe that in the formation of the bond with iron only a part of the II^- electrons of the cyclopentadienyl rings participate. The indicated authors consider the possible combinations of orbitals of the metal with molecular orbitals of each cyclopentadienyl radical as a whole, and not with separate carbon atoms.

CHEMICAL PROPERTIES OF FERROCENE

As has already been noted, ferrocene possess a thermal stability surprising for an organometallic compound, but still more unusual are the various chemical transformations of ferrocene, and above all its distinctly expressed tendency toward reactions involving substitution of the hydrogens of the cyclopentadienyl rings, and the absence of properties characteristic for unsaturated compounds.

The reactions of ferrocene can be divided into three groups: 1) oxidation; 2) reactions involving cleavage of iron-carbon bonds; 3) substitution of hydrogens in the cyclopentadiene rings (so-called reactions of "aromatic" substitution).

1. Oxidation

In ferrocene the iron is formally divalent but in air ferrocene is completely stable and does not oxidize either in the crystalline

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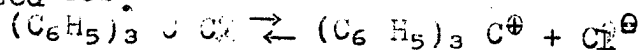
state or in solution. The oxidation of ferrocene takes place easily upon electrolysis (anode process) and also by means of such oxidants as halogens ^{11, 17}, ferric chloride, ceric sulfate, silver sulfate or p-quinone in organic solvents in the presence of acid ^{41, 88}. Ferrocene is also oxidized by sulfur dioxide in anhydrous hydrogen fluoride at 100° and a pressure of 7 atm. ⁹⁹ and by N-bromosuccinimide in acetic acid ¹³.

In acid solutions ferrocene is oxidized by the oxygen of the air. Upon solution of ferrocene in sulfuric ^{10, 100} or nitric acid ^{10, 41} oxidation also takes place.

Ferrocene reduces the triphenylmethyl cation to triphenylmethyl radical and is oxidized thereby to the ferricinium cation

$$(C_5H_5)_2 Fe + (C_6H_5)_3 C^+ \rightarrow (C_5H_5)_2 Fe^+ + (C_6H_5)_3 C\cdot$$

The reaction was carried out with a solution of triphenylmethyl chloride in nitromethane, in which triphenylmethyl chloride is ionized ¹⁰².



In benzene, the oxidation of ferrocene by $(C_6H_5)_3 C Cl$ takes place only in the presence of small quantities of phenol, which probably facilitates the ionization of triphenylmethyl chloride ¹⁰⁴.

Upon oxidation, ferrocene is converted into the blue, water-soluble ferricinium cation, $(C_5H_5)_2 Fe^+$, which is easily reduced by $SnCl_2$ ⁴¹, sodium sulfite or thiosulfate, ascorbic acid ^{99, 100}, $Ti_2(SO_4)_3$ ¹⁰³, and other reductants. Upon addition of alkali, aqueous solutions of the cation evolve ferrocene ⁷¹.

Salts of the ferricinium cation with such anions as Cl^- , Br^- , NO_3^- , SO_4^{--} , ClO_4^- , are water soluble: the cation can be precipitated in the form of the tetrachlorogallate, $(C_5H_5)_2 Fe Ga Cl_4$, and the picrate, as well as the silicotungstate, reineckeate, tetraphenylborate, $(C_5H_5)_2 Fe B(C_6H_5)_4$ ^{41, 71} and others ^{18, 88}.

Salts of the ferricinium cation are paramagnetic. The paramagnetic moment of the picrate $\mu_{eff} = 2.26$ Bohr magnetons which indicates the presence of one unpaired electron ⁴¹.

The ease of conversion of ferrocene into a much less stable cation ^{12, 41} is perhaps one of the reasons why no one has succeeded in nitrating or halogenating ferrocene ¹². Besides, the presence of a positive charge on the ferricinium cation can hinder electrophilic attack. Dunitz and Orgel ⁶¹ believe that in cations of dicyclopentadienyl compounds the d-orbitals of the central atoms are much more stable than the π -orbitals of the rings, and hence in the ferricinium cation the bonds are shifted to a greater degree toward the ionic state. These discussions are in complete agreement with the observed decrease in stability of the ferricinium cation (particularly toward hydrolysis) in comparison with ferro-

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cene, and allow one to suggest that the cation will be inert in reactions of electrophilic substitution.

2. Reactions Involving Cleavage of the Bonds Between Iron and the Cyclopentadiene Rings

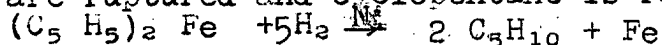
Ferrocene, as has already been noted, is distinguished by its unusual stability for an organometallic compound. Thus, ferrocene does not react with water, 10% aqueous sodium hydroxide, or concentrated hydrochloric acid even upon boiling ¹⁰. The inertness of the iron-carbon bond in ferrocene is apparent also in the absence of exchange of iron atoms upon treatment of a salt of isotopically labeled iron ²⁵.

In the vapor phase ferrocene is stable and does not undergo pyrolysis at 470° ^{41, 75}.

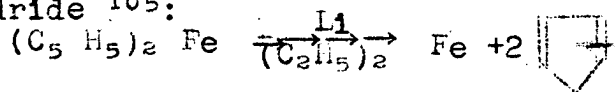
The complete decomposition of ferrocene into iron oxide and unidentified products takes place upon heating an aqueous suspension of it in a closed system at 350°; in 36% hydrofluoric acid ferrocene decomposes at 100° ⁹⁹.

The properties characteristic for compounds with conjugated double bonds are not evinced by ferrocene. Thus, it does not react with maleic anhydride, is not hydrogenated in the presence of platinum ^{12, 86}, and also is not hydrogenated in the presence of Raney nickel at 140° and 150 atm. pressure ^{16, 86}.

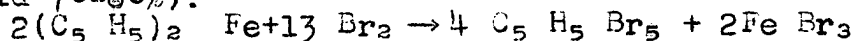
However, Nesmeyanov, Perevalova, Golovnya, Nikitina and Simykova ¹⁰⁴ hydrogenated ferrocene under very severe conditions - in the presence of Raney nickel at 280 atm. and 300-340°; under these conditions the bonds between the cyclopentadiene rings and iron are ruptured and cyclopentane is formed in 67% yield:



In contrast to the severe conditions for catalytic hydrogenation, the cleavage of the ferrocene nucleus by means of solutions of alkali metals in liquid ammonia or amines takes place very readily; the reaction goes best with lithium in diethylamine. In this reaction iron and cyclopentadiene are formed, the latter being isolated in good yield in the form of its adduct with maleic anhydride ¹⁰⁵:



The iron-carbon bonds in ferrocene are easily broken by the action of bromine ¹⁰⁴. Ferrocene forms a complex compound with bromine ^{17, 104, 106} which upon brief heating in CCl₄ with excess bromine decomposes with the formation of pentabromocyclopentane (yield 70-80%):



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Chlorine (in C_2Cl_4 solution) cleaves ferrocene at 0° with the formation of pentachlorocyclopentane (yield 90%)¹⁰⁴:

$$2(C_5H_5)_2Fe + 13 Cl_2 \rightarrow 4 C_5H_5Cl_5 + 2Fe Cl_3$$

The cleavage of the ferrocene nucleus by hydrogenation and by the action of halogens was used by A.N. Nesmeyanov and co-workers¹⁰⁴ as a proof of the structures of derivatives of ferrocene (see the following section).

3. Substitution Reactions of Ferrocene

As a result of intensive investigations in recent years, a wide circle of reactions of electrophilic and homolytic substitution have become known for ferrocene and are discussed in detail below:

a) Acylation

Soon after the discovery of ferrocene Woodward and co-workers¹² found that this organo-iron compound reacts with acid chlorides in the presence of aluminum chloride in a way analogous to aromatic compounds. Thus, by the reaction of ferrocene with acetyl chloride, diacetyl ferrocene was obtained, a substance which crystallizes well and has a characteristic dark-red color:

$$(C_5H_5)_2Fe : 2 CH_3CO \xrightarrow{AlCl_3} (CH_3CO C_5H_4)_2 Fe + 2HCl$$

By analogous means these same authors¹² obtained di- β -chloropropionylferrocene (along with diacryloylferrocene) and di- α -carboxybenzoylferrocene, characterized via its dimethyl ester. Nesmeyanov and Vplkenau¹⁰⁷ synthesized dipropionyl-, dibutyryl-, dibenzoyl-, and acetylbenzoylferrocene¹⁵⁴ (yields 40-70%).

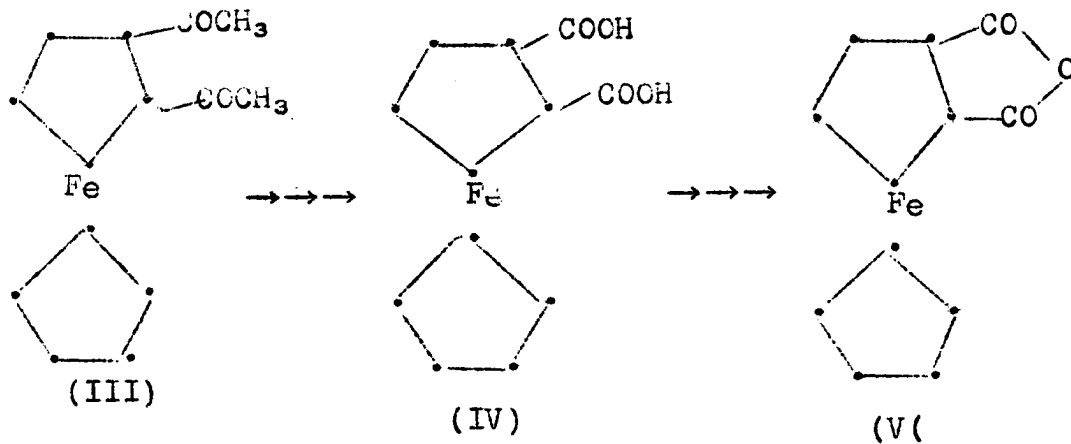
The acyl groups in diacylferrocenes are located in different rings of the ferrocene nucleus. The structure was proved by hydrogenation¹⁰⁴ based on the example of diacetylferrocene; (only ethylcyclopentane was isolated, while diethylcyclopentane was not detected):



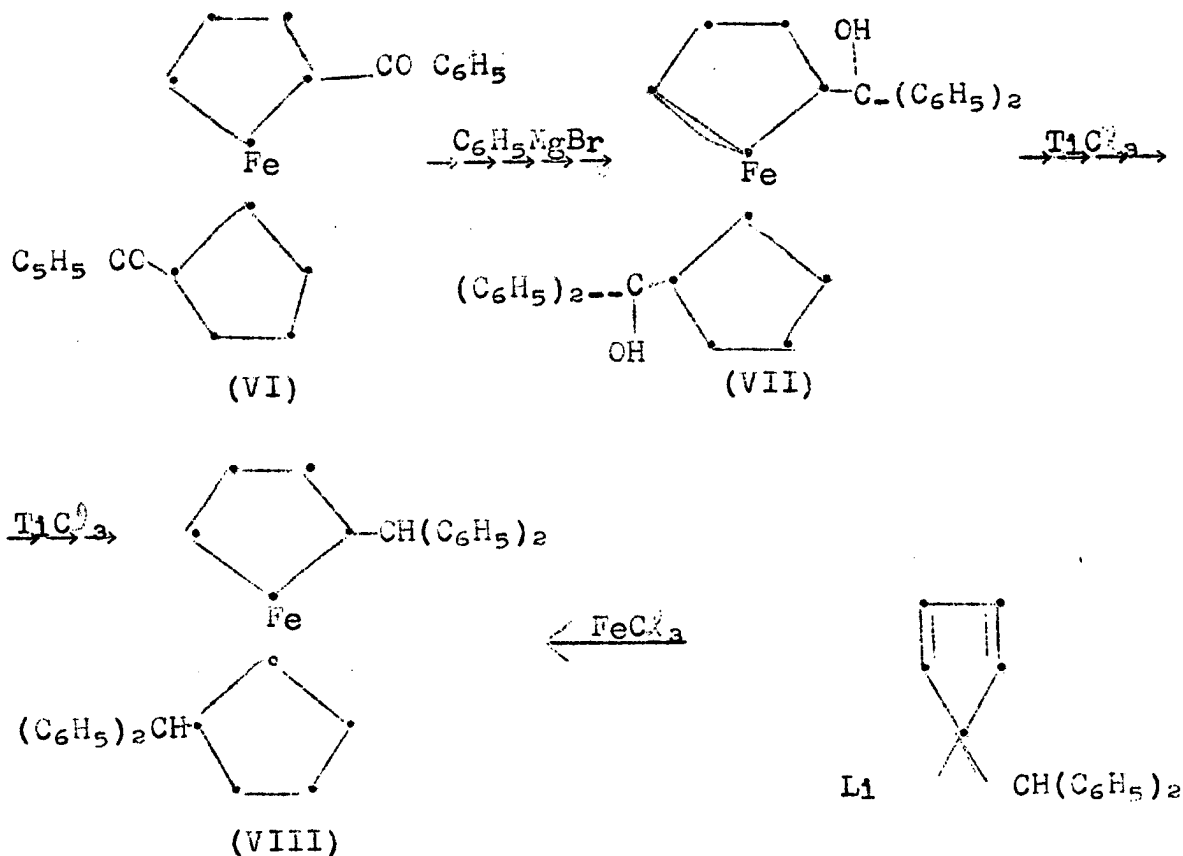
However, during acetylation along with 1,1'-diacetyl-ferrocene, there is formed a small quantity (about 3% of the isolated diacylated products) of the homoannular 1,2-diacetylferrocene (III), the structure of which was proved by oxidation with sodium hypochlorite to 1,2-ferrocenedicarboxylic acid (IV), which upon treatment with N,N'-dicyclohexylcarbodiimide is converted to the anhydride (V)¹⁰⁸

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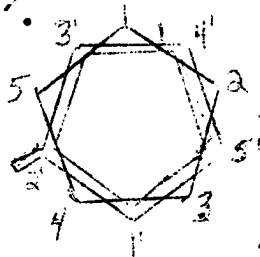
For dibenzoylferrocene (VI) it has also been rigorously shown that the benzoyl groups are located in different rings: upon reduction of the carbinol (VII) which is formed by reaction of dibenzoylferrocene with phenylmagnesium bromide, dibenzhydrylferrocene is obtained (VIII), identical with that synthesized from benzhydrylicyclopentadiene^{13, 30}.



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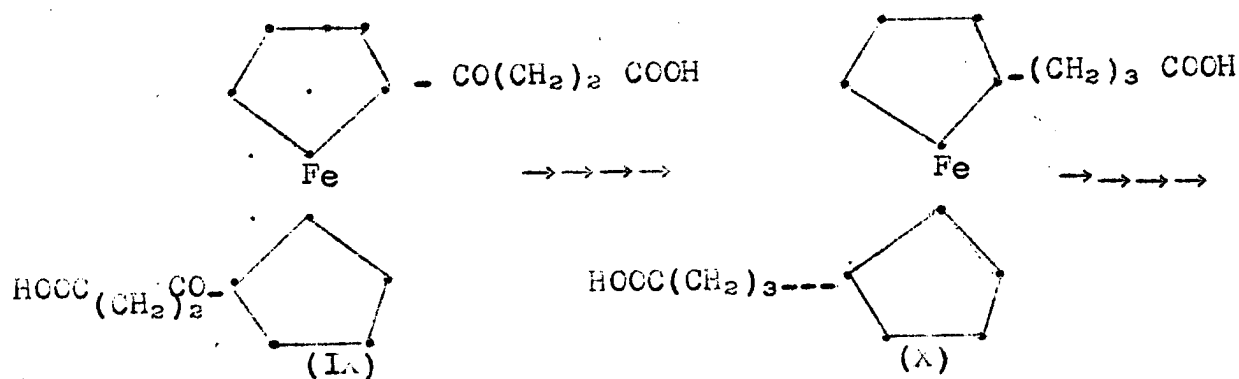
X-ray crystallographic studies, carried out by Struchkov⁷³,
109, showed that in crystals of dibenzoylferrocene the benzoyl
groups occupy the positions 1, 2'.



The interatomic distances in dibenzoylferrocene agree with those
found for ferrocene. Diacetyl- and dibutylferrocene probably
have the 1,2'-configuration as well^{73, 109}.

In solutions, probably, free rotation of the substituted cyclo-
pentadiene rings is possible, which is in accord with the fact that
only one isomer is obtained in independent syntheses of ferrocene
derivatives disubstituted in different rings. Richmond and
Freiser¹¹⁰ believe that the existence of free rotation is indica-
ted by the presence of a dipole moment in diacetylferrocene.*

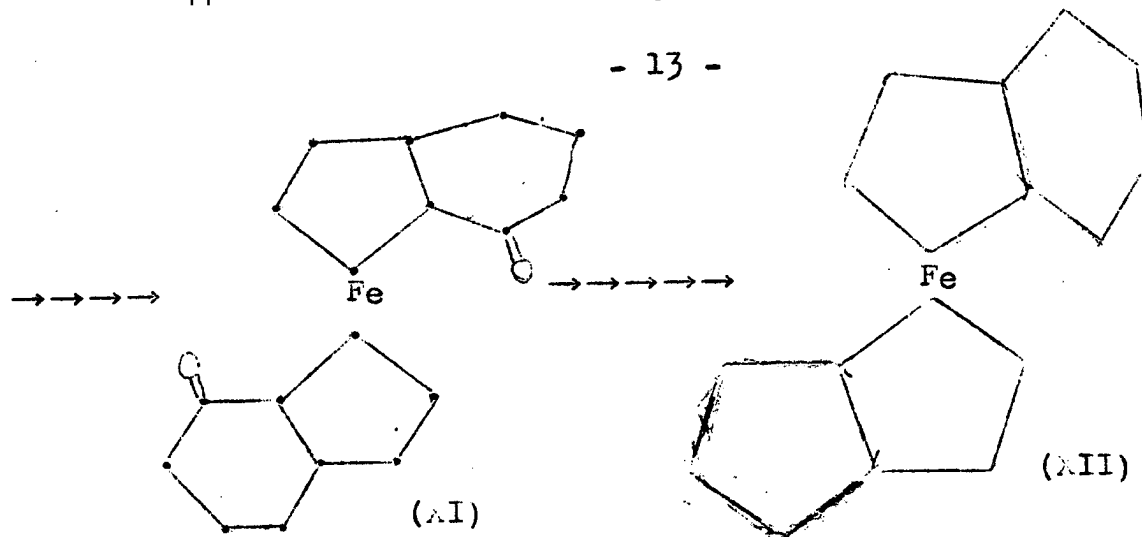
The reactions of intramolecular acylation of ferrocene have
been accomplished by Nesmeyanov, Volkenau, and Vilchevskaya¹¹²;
113. In the reaction of ferrocene with succinic anhydride, they
obtained 1,1'-di-(ω -carboxypropionyl)-ferrocene (XI) (yield 18%),
which was reduced by the Clemmensen method to yield di-(ω -carbox-
ypropyl)ferrocene (λ) in 77% yield, which was then cyclized by
heating with polyphosphoric acid with the formation of di-(ketote-
trahydroindenyl)-iron (XI) (yield, 46%):



* For a discussion of the work of Richmond and Freiser¹¹⁰ see the
review of Dyatkina⁸¹. Also see the work of Semenov and Roberts
111 on the dipole moment of di-(p-chlorophenyl)-ferrocene.

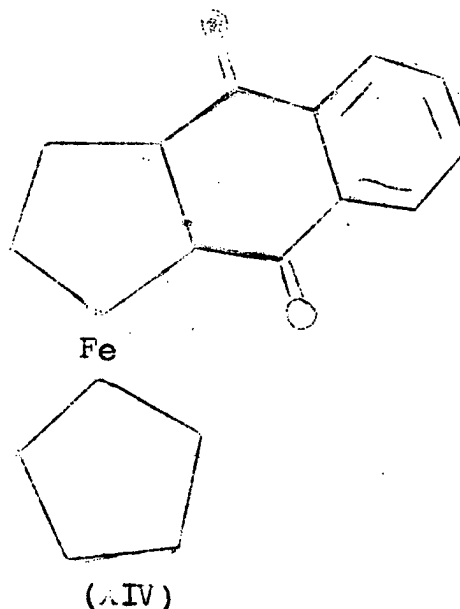
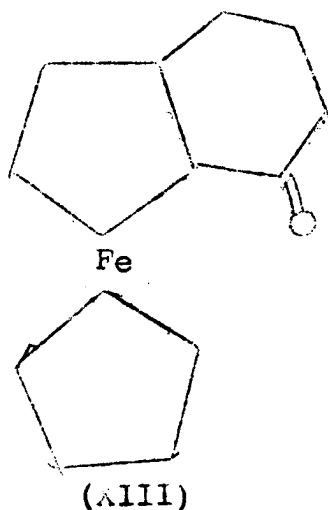
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The structure of di-(detotetrahydroindenyl)-iron (XI) was proved by converting it by Clemmensen reduction to di-(tetrahydroindenyl)-iron (XII), identical with the compound obtained by Fischer and Reus¹¹⁴ via hydrogenation of diindenyliron (see the section "Diindenyl compounds of metals").

By analogous methods Nesmeyanov, Volkenau, and Vilchevshaya¹¹³ obtained cyclopentadienylketo tetrahydroindenyliron (XIII) and the ferrocene analog of anthroquinone (XIV).



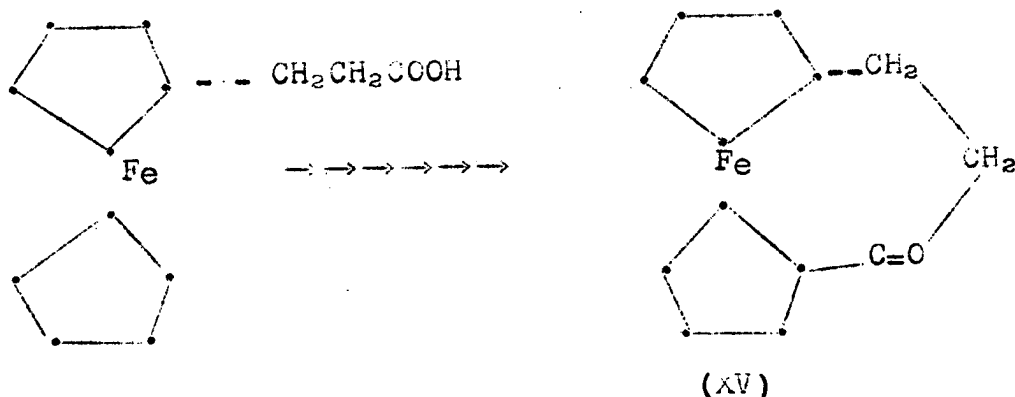
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It must be noted that it is not possible to cyclize ω -carboxypropionylferrocene while *o*-carboxybenzoylferrocene is easily cyclized giving compound XIV¹¹³. Thus a complete analogy to benzene derivatives is observed. It is known that benzoylpropionic acid does not cyclize while *o*-benzoylbenzoic acid readily forms anthraquinone upon heating.

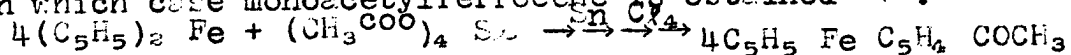
Somewhat later the intramolecular acylation of ferrocene was carried out as well by Rinehart and coworkers^{115, 116}. The substances obtained by them are listed in table 2.

Ferrocenepropionic acid, in contrast to its higher homologues, cyclizes with the formation of a bridge between the two cyclopentadiene rings¹¹⁵. The structure of 1,1'-2-(ketotrimethyleneferrocene) (XV) was proved spectroscopically.



Pauson¹³ showed that ferrocene is acylated in the presence of $AlCl_3$ more rapidly than anisole: upon competitive acetylation, by means of the complex $CH_3COCl \cdot AlCl_3$, of a mixture of ferrocene and anisole taken in the ratio 1:10, acetylferrocene is formed, not methoxyacetophenone.

The ease of substitution of the hydrogens in ferrocene is evident in the fact that in contrast to benzene, ferrocene is acylated not only in the presence of $AlCl_3$, but also in the presence of $SnCl_4$, in which case monoacetylferrocene is obtained¹¹⁷.



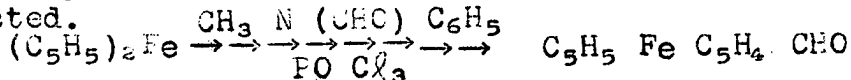
Monoacetylferrocene is formed in good yield in the acylation of ferrocene with acetic anhydride in the presence of BF_3 ¹¹⁸ or of phosphoric acid¹¹⁹. Monopropionyl¹¹⁸ and monobenzoylferrocene^{120, 121} have been described.

Formylation^{119, 122, 123} of ferrocene is accomplished by the action of *N*-methylformanilide and $POCl_3$ on ferrocene; in this case

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ferrocenylaldehyde is formed in 70% yield; the dialdehyde was not detected.



The mild conditions required for formylation again indicate the increased reactivity of ferrocene in comparisons to benzene.

b) Alkylation

Alkylferrocenes were first obtained by Nesmeyanov and Volkenau¹⁸⁷ by Clemmensen reduction of acylferrocenes. By this means, ethyl-, 1,1'-diethyl-, 1,1'-dipropyl-, 1,1'-dibutyl-, and 1,1'-dibenzylferrocene (yields 50-70%) were synthesized. Methyl-¹²⁴ and 1,1'-dimethylferrocene¹²⁵ were obtained by lithium aluminum hydride reduction of the corresponding ferrocenecarboxylic acids. Methylferrocene¹²⁴ was also prepared by sodium amalgam reduction of the methiodide of N,N-dimethylaminomethylferrocene (see the section "reactions of condensation and other reactions").

In one of the patents, the catalytic reduction of ferrocenyl ketones¹²⁶, $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{COCCnH}_{2n+1}$ (where $n = 1$ to 15), to alkylferrocenes is described.

Attempts by Biemschneider and Helm¹⁷ to alkylate ferrocene by the Friedel-Crafts method were unseccessful.

Direct alkylation of ferrocene in the presence of aluminum chloride was described by Nesmeyanov and Kochetkova in 1956¹²⁷⁻¹³⁰. As alkylating agents alkyl halides were used (methyl bromide and iodide, ethyl bromide, isopropyl, t-butyl, and t-amyl chlorides), and also benzyl chloride, dichloroethane, and olefins (ethylene, propylene, and isobutylene). The reaction was carried out in an excess of alkyl halide, in n-heptane, or in petroleum ether.

In the alkylation of ferrocene, a mixture of mono-, di-, and polyalkylferrocenes is obtained.

By means of infrared spectra (in individual cases by bromination) it was established that the dialkylferrocenes formed by direct alkylation (even di-tert-butylferrocene and di-tert-amylferrocene) contain an unsubstituted cyclopentadiene ring¹²⁹.

Thus, the introduction of an alkyl group into the ferrocene nucleus facilitates subsequent alkylation, just as is the case in the benzene series, in which process a mixture of dialkylferrocenes is obtained with substituents in a single cyclopentadiene ring. Such dialkylferrocenes we shall subsequently refer to as homoannular.

Homoannular isomeric dialkylferrocenes were separated chroma-

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tographically on alumina. It was found that a characteristic difference exists in the infrared spectra of isomeric dialkylferrocenes^{74, 128}.

Alkylation of ferrocene by isobutylene at 50-60° leads chiefly to mono- and to homoannular di-t-butylferrocene. At higher temperatures (100-150°) a crystalline tri-t-butylferrocene and a liquid tetra-t-butylferrocene are formed. In the infrared spectra of these substances there are no characteristic frequencies in the region 1003 and 1107 cm⁻¹, and consequently the t-butyl groups are situated in different cyclopentadiene rings¹³⁰.

In the reaction of ferrocene with dichloroethane in the presence of anhydrous aluminum chloride, along with diferrocenylethane and other products, under specific conditions¹²⁷ a powdery high polymer can be obtained.

It possesses the characteristics of an ion exchange resin. The capacity upon oxidation with a 0.1N solution of potassium dichromate in sulfuric acid under static conditions is 2.8 - 3.5 milliequivalents per gram of air-dried resin.

c) Sulfonation

Attempts to sulfonate ferrocene by means of concentrated sulfuric acid did not yield positive results: upon solution of ferrocene in concentrated sulfuric acid, it is converted into the ferricinium cation¹⁰⁰ and the obtaining of ferrocenesulfonic acid is unsuccessful⁹⁹.

Nesmeyanov, Perevalova, and Churanov^{131, 132} showed that ferrocene is sulfonated by pyridinesulfur trioxide in a manner analogous to that of five-membered heterocycles²¹⁹. Upon heating ferrocene for four hours with pyridine-sulfur trioxide in dichloroethane, ferrocenemonosulfonic acid is obtained in 80% yield, calculating from the ferrocene which reacted. Upon more prolonged heating of ferrocene with an excess of pyridine-sulfur trioxide, ferrocene disulfonic acid is obtained in a 41% yield. The monodisulfonic acids were isolated in this case in the form of their barium or lead salts.

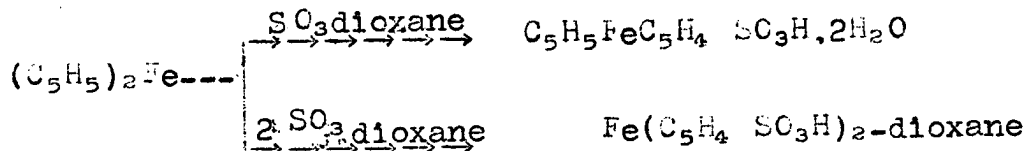
Weinmayr⁹⁹ sulfonated ferrocene with a mixture of sulfuric acid and acetic anhydride* and obtained ferrocenemono- and disulfonic acids which were isolated as the ammonium salts. Oxidation of ferrocene to the cation does not take place under the conditions of the reaction.

The monosulfonic acid of ferrocene in the form of its crystalline dihydrate was obtained by Nesmeyanov, Perevalova, and Churanov¹³² in quantitative yield upon treatment of its lead salt with

*The sulfonating agent in this case is probably acetyl sulfate.

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hydrogen sulfide, and also upon sulfonation of ferrocene with dioxanesulfotrioxide in equimolecular amount at room temperature (yield 62% based on reacted ferrocene):

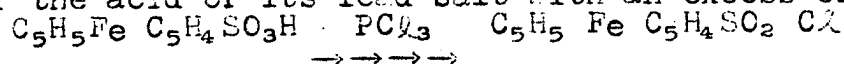


If dioxanesulfotrioxide is taken with ferrocene in the ratio of 3.1, then the disulfonic acid is obtained in good yield (in the form of a complex ¹³² with dioxane) virtually without admixture of the mono-acid.

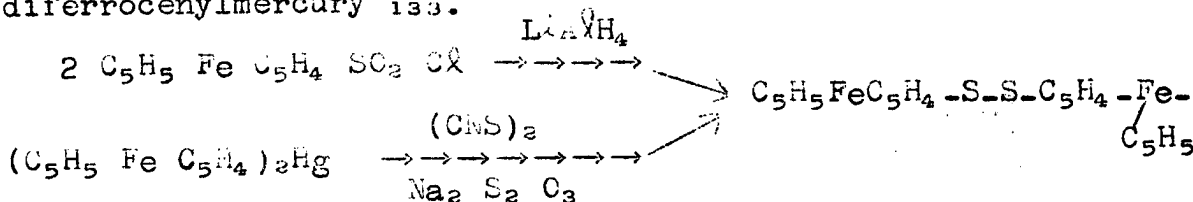
Potentiometric titration of the ferrocenedisulfonic acid thus obtained gives a curve typical of a monobasic acid, which indicates the closeness of the first and second ionization constants, and hence the slight influence of the sulfonic acid groups on each other. This is supporting evidence for the location of the sulfonic acid groups in different cyclopentadienyl rings ¹³², which is also confirmed spectroscopically ¹³³.

For both sulfonic acids, S-benzylthiuronium salts and salts with several amines have been obtained ¹³².

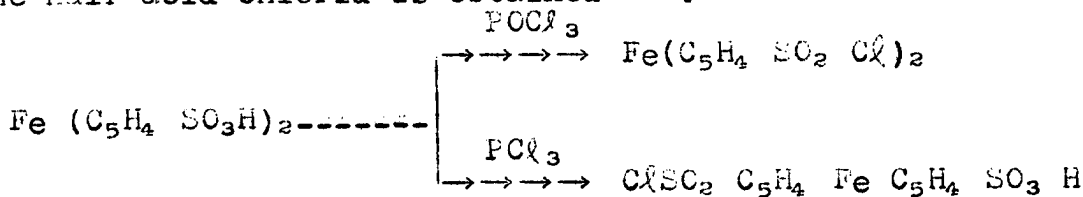
By the action of diazomethane, the methyl esters of the ferrocenesulfonic acids have been synthesized. The acid chloride of the monosulfonic acid is easily formed in good yield upon unprolonged heating of the acid or its lead salt with an excess of PCl_3 ¹³².



Upon reduction of the acid chloride with lithium aluminum hydride, ferrocenyldisulfide is obtained, identical with that obtained from diferrocenylmercury ¹³³.



The diacid chloride of the disulfonic acid is obtained upon heating the disulfonic acid with POCl_3 ; by the action of an excess of PCl_3 , the half acid chloride is obtained ¹³³.



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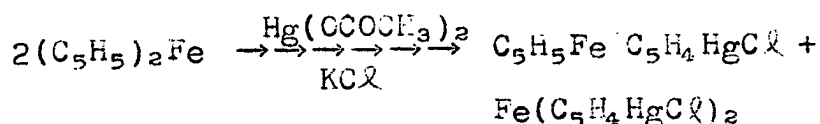
d) Metallation

Ferrocene metallates extraordinarily easily under conditions under which benzene does not react. The mercuration of ferrocene by mercuric acetate¹¹⁷ and the obtaining of the lithium and sodium derivatives by means of n-butyllithium and phenylsodium, respectively, was described by Nesmeyanov and co-workers in 1954*. The metallation of ferrocene by n-butyllithium was also published somewhat later by Benkeser, Coggin, and Schroll¹³⁵. The metallated ferrocenes thus formed can be used for a whole series of syntheses.

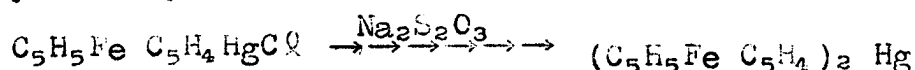
Mercury Derivatives of Ferrocene

Haloferrocenes

The mercuration of ferrocene, in contrast to benzene, is easily accomplished by means of mercuric acetate at room temperature in ether-alcohol or benzene-alcohol solution. In this process there is formed a mixture of acetates of mono- and di-mercurated ferrocene which is converted into the chlorides by potassium chloride (overall yield 65%)¹¹⁷:

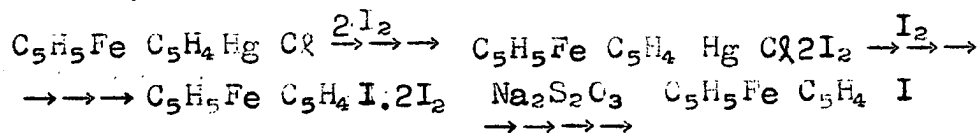


Ferrocenylmercuric chloride readily symmetrizes in the presence of a saturated aqueous solution of thiosulfate, giving diferrocenylmercury:¹¹⁷



By means of the mercury derivatives of ferrocene, Nesmeyanov, Perevalova, and Nesmeyanova¹⁰⁶ obtained halogen derivatives of ferrocene, which cannot be obtained by direct halogenation.

By the action of an excess of iodine on ferrocenylmercuric chloride, there first forms a complex with iodine; upon further reaction with iodine, a replacement of mercury by iodine takes place and iodoferrocene is formed in the form of a complex with iodine, which then is decomposed by means of thiosulfate; yield of iodoferrocene, 64%.

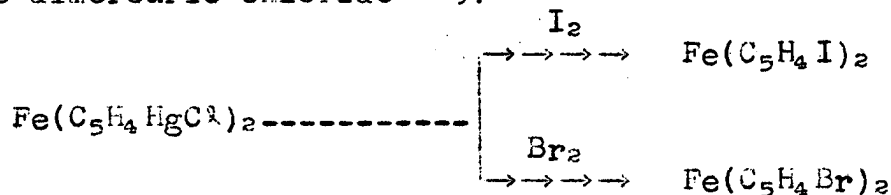


* In 1957, Hausch, Vogel and Rosenberg repeated this work.

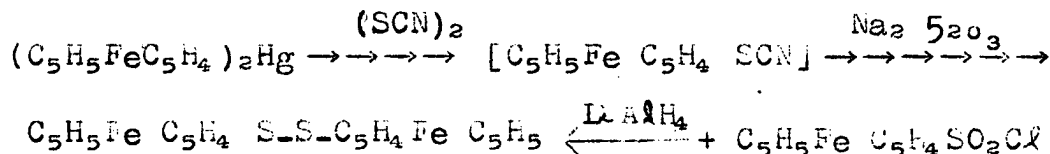
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Iodine in iodoferrocene is inert to nucleophilic substitution and in this respect surpasses the iodine of iodobenzene. Thus, it does not react with solutions of potassium acetate and potassium hydroxide in methanol upon heating to 100°. Attempts to use copper as a catalyst did not yield positive results. Ferrocenylmagnesium iodide could not be obtained by heating iodoferrocene with magnesium in ether.

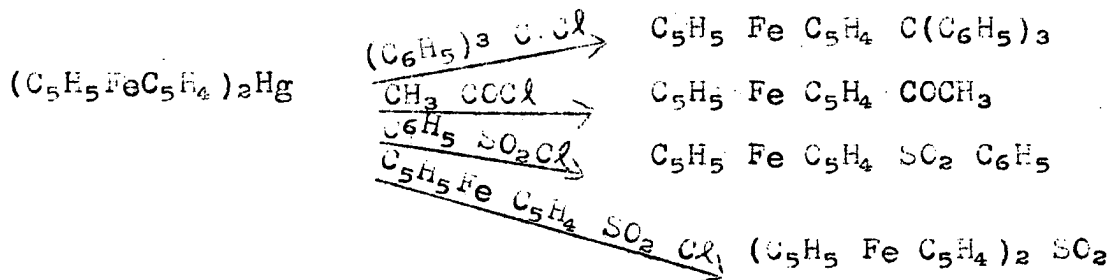
Bromoferrocene is obtained by the action of bromine on diferrocenylmercury. Diiodoferrocene and dibromoferrocene were synthesized analogously by the action of the corresponding halogens on ferrocene dimercuric chloride 106:



With thiocyanogen, diferrocenylmercury also reacts and forms a complex in which mercury is probably replaced by--SCN upon further reaction with thiocyanogen, but thiocyanatoferrocene cannot be isolated because upon subsequent treatment of the reaction mixture with sodium thiosulfate, (to remove excess thiocyanogen) it is converted into ferrocenyl disulfide, identical with that obtained by reduction of ferrocenesulfonyl chloride 133, 136.



The synthetic possibilities of mercurated ferrocene are not limited to using it for obtaining halogen derivatives and ferrocenyl-disulfide. It was found that ferrocenylmercuric chloride and especially diferrocenylmercury are extraordinarily reactive in reactions of electrophilic substitution as is ferrocene itself. Thus, diferrocenylmercury reacts with triphenylmethyl chloride yielding triphenylmethylferrocene; with acetyl chloride it forms acetylferrocene, and upon reaction with benzene--and ferrocenesulfonyl chlorides there is obtained phenylferrocenylsulfone and diferrocenyl sulfone respectively 136:



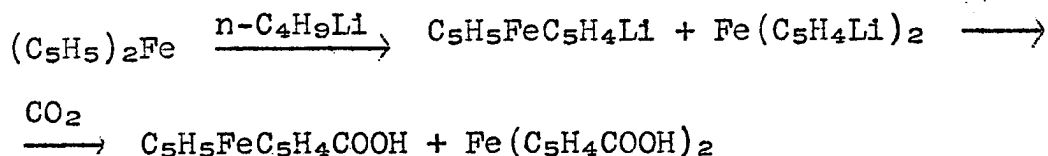
Upon reaction of Se Br₄ with diferrocenylmercury, selenium is reduced and diferrocenylselenium is formed 136.

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LITHIUM AND SODIUM DERIVATIVES OF FERROCENE

Ferrocenylamine

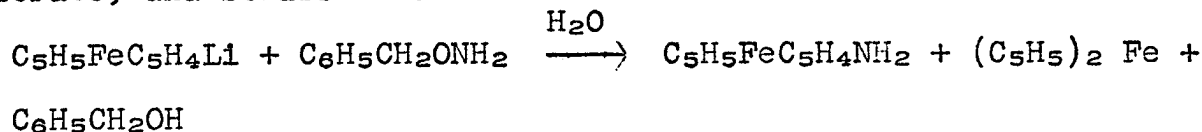
Ferrocene is metalated by n-butyllithium in ether solution^{117,135}. Upon heating for 12 hours with an excess of butyllithium, an equimolecular mixture of ferrocenylmono- and dilithium is formed which yields a mixture of ferrocenecarboxylic and ferrocenedicarboxylic acids¹¹⁷ upon carbonation with an average yield of ~30%:



The ferrocenedicarboxylic acid obtained in this way is identical with the acid obtained by Woodward and coworkers¹² by oxidation of 1,1'-diacetylferrocene (see the section "Properties of acylferrocenes")

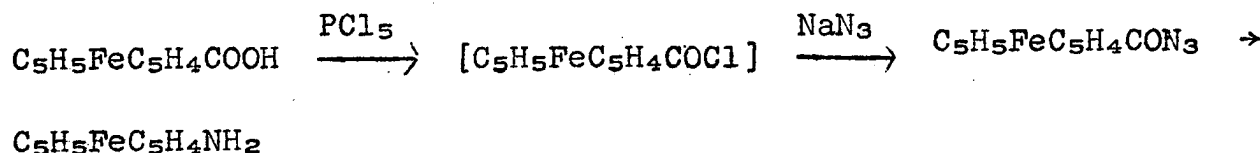
The lithium derivatives of ferrocene have been used to obtain mono- and di(triphenylsilyl)-ferrocene¹³⁵, and also mono- and di(trimethylsilyl)-ferrocene¹³⁴.

The use of ferrocenyllithium to obtain aminoferrocene¹³⁷ by the method described by Sheverdina and Kocheshkov¹³⁸ affords great interest. Thus, Nesmeyanov, Perevalova, and Shilovtseva¹³⁷, by the action of O-benzylhydroxylamine on ferrocenyllithium, obtained ferrocenylamine characterized by its acetyl and benzoyl derivatives, picrate, and Schiff's base^{131,137}:



Ferrocenylamine is rapidly oxidized in air; under the action of nitrous acid under usual diazotization conditions it undergoes drastic changes, and the formation of a diazonium salt could not be detected. The basicity constant of ferrocenylamine in 80% alcohol is 1.55×10^{-9} and surpasses by 20-fold the constant for aniline under the same conditions, which indicates the more powerful electron-donating properties of ferrocenyl radical as compared with phenyl¹³⁹.

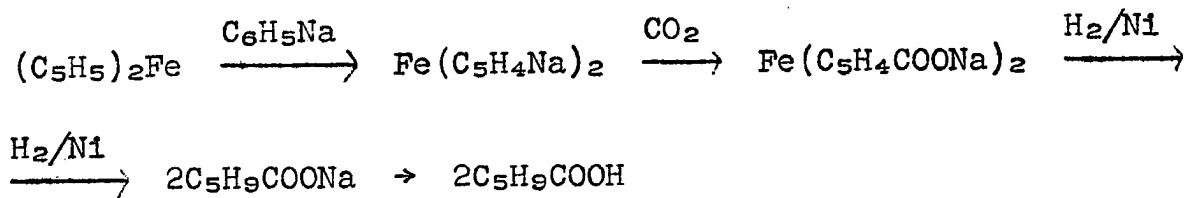
Later Arimoto and Haven¹⁴⁰ synthesized ferrocenylamine from the azide of ferrocenecarboxylic acid by means of the Curtius rearrangement:



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The acid chloride was not isolated. It was not possible to obtain ferrocenylamine from the oxime of acetylferrocene or from the amide of ferrocenecarboxylic acid¹⁴⁰.

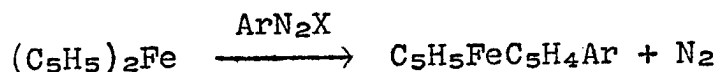
By the action of phenylsodium¹²⁵ on ferrocene, the disodium derivative is formed which upon reaction with CO₂ is converted into ferrocenedicarboxylic acid (yield 42%) identical with that obtained by other methods. The carboxyl groups in the ferrocenedicarboxylic acid thus obtained are located in different cyclopentadiene rings which is rigorously proved by the isolation upon hydrogenation of cyclopentanecarboxylic acid¹⁰⁴:



e) Arylation

The conditions under which the above observed reactions of substitution of the hydrogens of ferrocene take place allow one to compare this organo-iron compound in reactivity with such benzene derivatives as phenol and aniline. Therefore one might expect that ferrocene would undergo the azo coupling reaction. However, it was found that the reaction proceeds in a different direction.

In 1954 Nesmeyanov, Perevalova, and Golovnya^{117,114} first showed that upon reaction of ferrocene with diazo compounds nitrogen is evolved and arylferrocenes are formed. Thus, the reaction of arylation of ferrocene proceeds similarly to the reaction of obtaining the unsymmetrical biaryls¹⁴²:



The arylation of ferrocene is carried out in water-ether medium at 20-35°; under these conditions monoarylferrrocenes are preferentially formed (yields 40-64%), in some cases along with a small quantity of diarylferrrocenes¹⁴¹. Thus p-tolyl-, p-nitrophenyl-, p-hydroxyphenyl-, p-anisylferrrocene, and others were obtained (see table 6). In the case of benzenediazonium salts, polyphenylferrrocenes are obtained.

The reaction mechanism is probably free radical.

Later (1955) Broadhead and Pauson¹⁰³ accomplished the arylation of ferrocene by means of diazonium salts in acetic acid solution; yields in this process are usually lower than in carrying out the reaction in ether. They also showed that phenylation of ferrocene can be carried out by means of benzenediazonium sulfate or the double salt of benzenediazonium chloride with ZnCl₂ as well as with N-nitrosoacetanilide, which confirms the free radical nature of the reaction mechanism. The reaction with N-nitrosoacetanilide and with the

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double diazonium salt was carried out in cyclohexane and in acetic acid; the yield and ratio of phenyl- and diphenylferrocene are close in both cases. Ferrocene cannot be arylated by phenyl radicals which are formed in the decomposition of phenylazotriphenylmethane or benzoyl peroxide, or by the reaction of phenylmagnesium bromide with bromobenzene in the presence of CoCl_2^{103} .

Broadhead and Pauson¹⁰³ suggest that ferrocene forms an intermediate complex with the diazonium salt which rearranges with the formation of the arylferrocene or arylferricinium salt.

Weinmayr¹⁰⁰ showed that ferrocene can be arylated as well in the form of the ferricinium cation in strongly acidic medium, the yields being of the same order as are obtained when carrying out the reaction with ferrocene itself in ether or acetic acid medium, but the quantity of di- and polyarylferrrocenes is usually greater.

It must be noted that in both cases (with ferrocene and with the ferricinium salt) the reaction products contain ferrocene and the arylferrocenes formed both in the free state as well as in the form of the ferricinium salts, which indicates that the arylation of ferrocene is accompanied by oxidation-reduction processes.

Pauson¹³ suggests that the mechanism of arylation of the ferricinium cation differs from the mechanism of arylation of free ferrocene.

Further arylation of arylferrocenes always takes place in a different cyclopentadiene ring, which indicates the deactivating influence of the aryl group on ferrocene. Only in the reaction of p-methoxybenzenediazonium salts did Broadhead and Pauson¹⁰³ isolate in small amount (0.7%) a homoannular dianisylferrocene in which the presence of an unsubstituted cyclopentadiene ring was proved by them by means of infrared spectra; the relative positions of the anisyl groups was not established.

The position of the aryl groups in 1,1'-diphenylferrocene was proved by an independent synthesis from phenylcyclopentadiene³⁰, and in 1,1'-di-(p-nitrophenyl)-ferrocene by hydrogenation under pressure in the presence of nickel sponge (cyclopentylcyclohexane was obtained)¹⁰⁴.

The reaction of diazonium compounds with ferrocene is a convenient method for the synthesis of arylferrocenes. This method allows one to obtain arylferrocenes having various substituents in the benzene rings, and is more widely applicable and much less beset with difficulties than the obtaining of arylferrocenes by means of arylcyclopentadienes³⁰. However, the latter means is used with success for the synthesis of polyphenylated ferrocenes with known relative positions of the phenyl groups^{30,100} (see table 6).

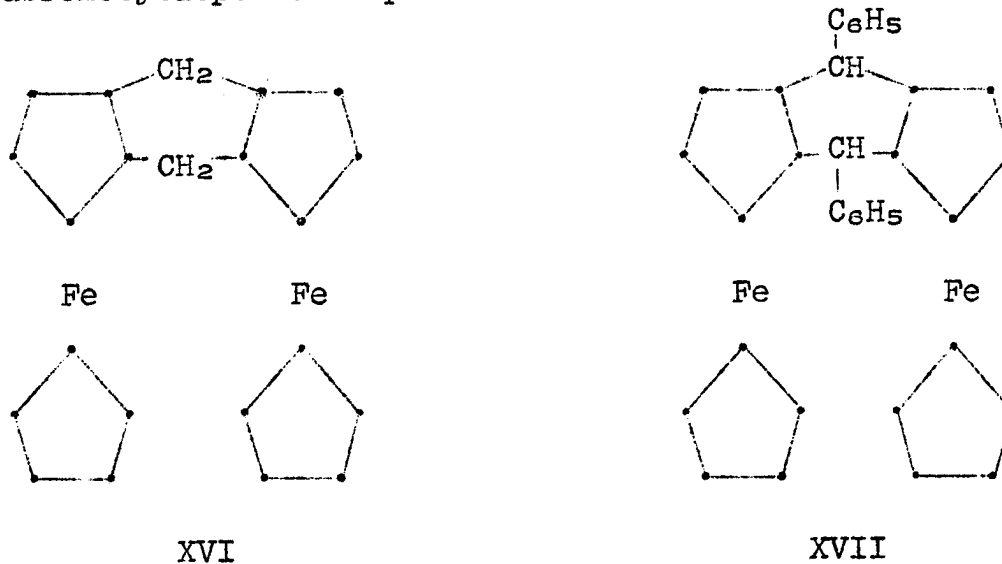
The great reactivity of ferrocene in reactions of homolytic substitution is indicated as well by the reaction with trichloromethyl radical, formed in the thermal decomposition of trichloroacetic acid in the presence of cupric chloride; after the hydrolysis of tri-

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chloromethylferrocene, ferrocenecarboxylic acid is isolated (yield 5.7%)¹⁴³. In this way, from the data presented it is quite apparent that ferrocene is very active both in reactions of electrophilic and free radical substitution. The substitution reactions proceed with ferrocene much more easily than with benzene.

f) Condensation Reactions and Other Reactions

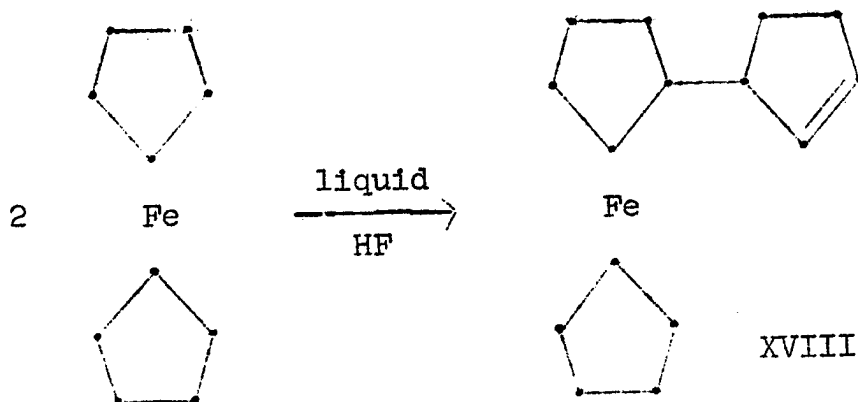
Ferrocene, like aromatic hydrocarbons condenses with formaldehyde and benzaldehyde^{17,99,121,144}. Nesmeyanov and Kritskaya¹⁴⁴ showed that the reaction proceeds in the presence of concentrated sulfuric acid upon unprolonged heating. With formaldehyde there forms first a derivative of the ferricinium cation, which after reduction in acid medium yields a substance which probably has structure (XVI); the presence in this compound of an unsubstituted cyclopentadiene ring was proved spectroscopically and by the isolation of pentabromocyclopentane upon bromination⁷⁴:



With benzaldehyde, ferrocene forms two substances^{17,99,141,145}, one of which has, apparently, structure (XVII)⁷⁴, analogous to that offered for the product of the reaction of ferrocene with formaldehyde. The substance obtained upon condensation of ferrocene with dimethylaminobenzaldehyde contains the hydroxyl group⁷⁴.

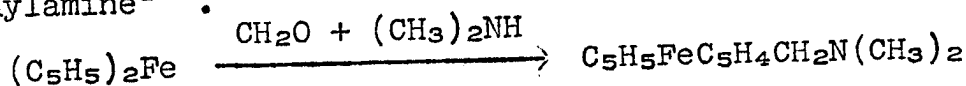
In liquid hydrogen fluoride at 30-100°, ferrocene undergoes a unique transformation to cyclopentenylferrocene (XVIII) in which process a part of the ferrocene decomposes⁹⁹:

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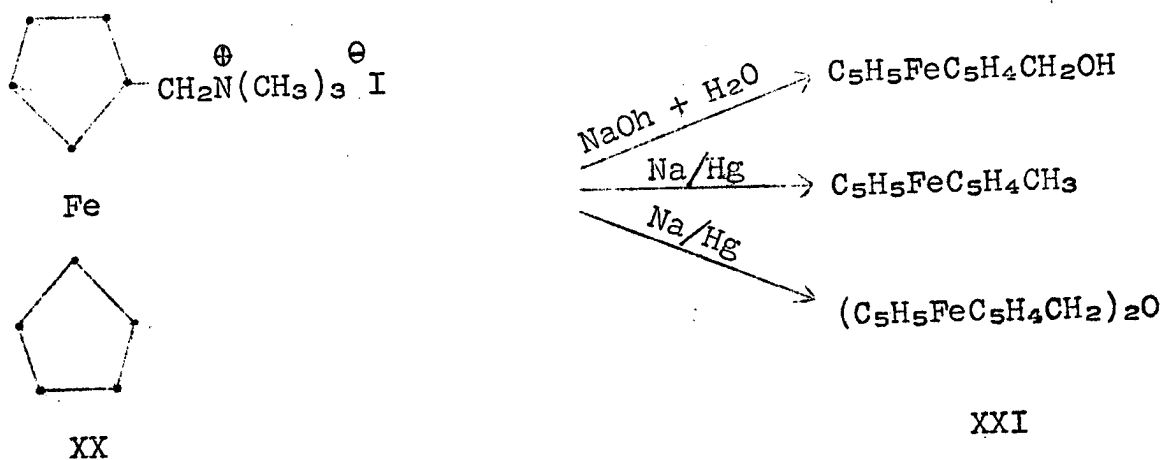
The presence of the double bond in the compound obtained (XVIII) was proved by hydrogenation in the presence of platinum oxide. Cyclopentenylferrocene, in spite of the presence of the double bond, is stable in hydrogen fluoride at 100° and does not undergo polymerization or react with benzene⁹⁹.

The condensation with olefins (propylene or diisobutylene) in liquid hydrogen fluoride, which proceeds easily in the benzene series, does not proceed with ferrocene⁹⁹. The great nucleophilic activity of ferrocene is manifest in the reaction with formaldehyde and dimethylamine¹⁴⁶.

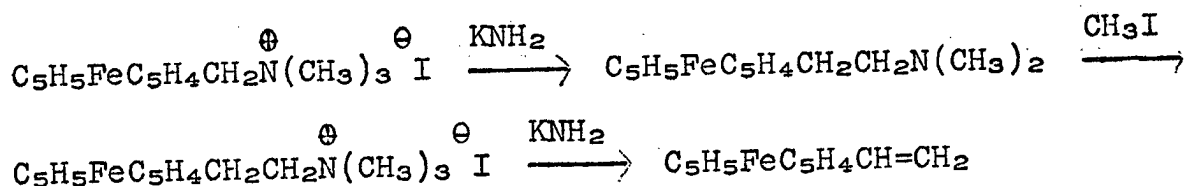


XIX

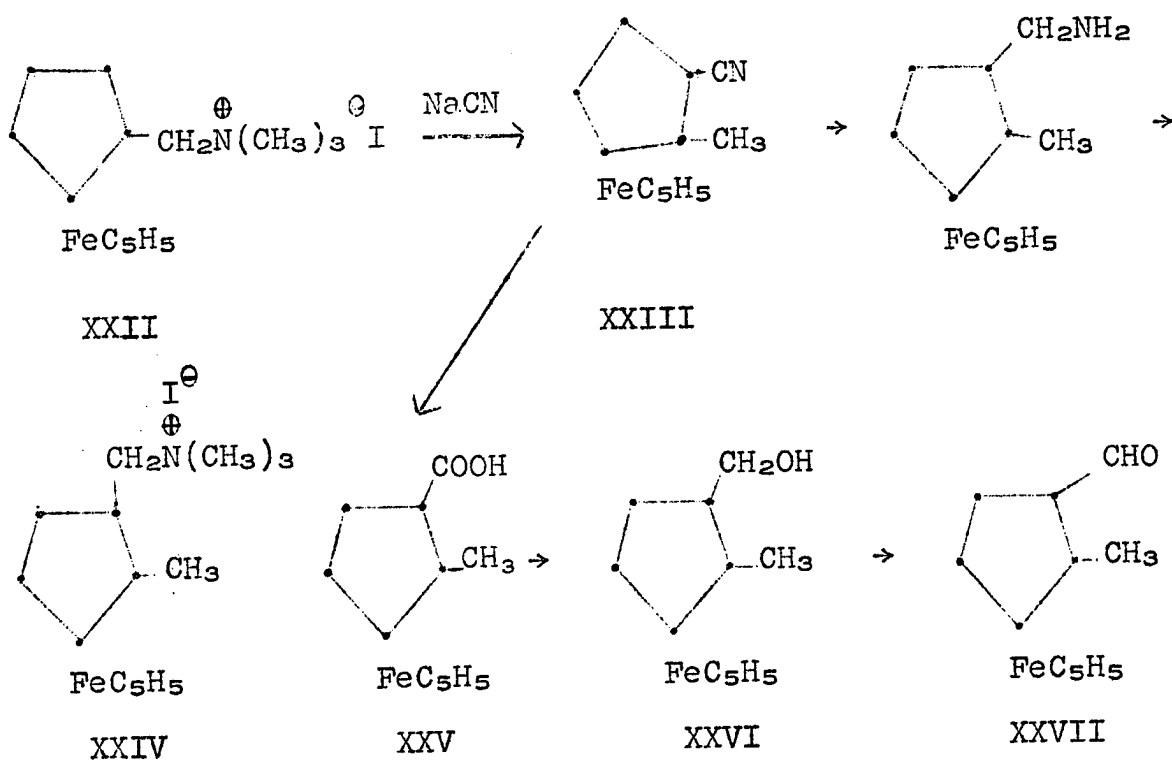
The N,N-dimethylaminomethylferrocene (XIX) thus formed yields a methiodide with methyl iodide (XX) which is used to obtain a series of other ferrocene derivatives (the yields in most cases are good)^{124, 147-149}. Thus, by the action of aqueous alkali, the methiodide (XX) is transformed into ferrocenylcarbinol¹⁴⁷; while upon reduction of XX with sodium amalgam, methylferrocene and a small quantity of the simple ether of ferrocenylcarbinol (XXI) are formed¹²⁴:



Upon treatment of the methiodide (XX) with potassium amide in liquid ammonia N,N-dimethylaminoethylferrocene (XXII) was obtained, the methiodide of which was then converted into vinylferrocene¹⁴⁷.



Upon reaction of the methiodide (XX) with aqueous sodium cyanide, 1-cyano-2-methylferrocene (XXIII) is formed, from which the methiodide of 1-methyl-2-dimethylaminoferrocene (XXIV) is synthesized by reduction and methylation. Hydrolysis of the nitrile (XXIII) yields 2-methylferrocenecarboxylic acid (XXV) which is reduced to 1-hydroxymethyl-2-methylferrocene (XXVI) which upon MnO₂ oxidation yields 1-formyl-2-methylferrocene XXVII¹⁴⁸.



Kursanov and Parness^{150,151} found that the hydrogens of ferrocene do not exchange with D₂O in the presence of an alkaline catalyst (N,N-dimethylpyridonimine).

The absence of exchange indicates the covalent character of the bonds between iron and the cyclopentadiene rings since the cyclopentadienyl anion under these conditions would enter into the reaction of hydrogen exchange.

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REACTIONS OF FERROCENES SUBSTITUTED IN THE NUCLEUS

The introduction of substituents into the cyclopentadienyl rings exerts a profound influence on the reactivity of the ferrocene nucleus. This influence manifests itself not only in the ease of further substitution of the cyclopentadienyl hydrogens and the stability of the bonds between the iron and the cyclopentadiene rings, but also in the lability to oxidation to derivatives of ferricinium cation and the stability of the latter. The character of the influence depends on the degree of electrophilicity of the substituent

Particular interest is engendered by the investigation begun recently of the orientative influence of the substituent already present in further substitution within the same cyclopentadiene ring.

The properties of the ferrocenes substituted in the nucleus which have been most thoroughly studied - acyl-, aryl-, alkyl-, and carboxy-ferrocenes - are discussed below.

PROPERTIES OF ACYLFERROCENES

For acylferrocenes, two types of reactions are of primary interest - the substitution of the hydrogens of the cyclopentadiene rings, which affords great interest from the point of view of influence of the acyl group on the reactivity of the ferrocene nucleus, and reactions of the keto-group which do not involve the ferrocene nucleus.

It has been found that the introduction of an acetyl group sharply lowers the lability toward further substitution within the same cyclopentadiene ring and noticeably lowers the tendency toward substitution in the second cyclopentadiene ring. Thus, further acylation of acetylferrocene goes preferentially, as has already been indicated, in the second cyclopentadiene ring, and furthermore forms only a very small quantity of 1,2-diacetylferrocene; hence the second acetyl group goes to the carbon neighboring the one which already bears an acetyl group¹⁰⁸.

Triacetylferrocene can not be obtained¹⁵². The two acetyl groups in 1,1'-diacetylferrocene greatly deactivate both rings (each deactivates its own as well as the other ring).

1,1'-Diacetylferrocene does not react with mercuric acetate, either at room temperature (under conditions for mercurating ferrocene) or upon heating¹⁵².

The deactivating influence of an acetyl group on the second cyclopentadiene ring is evident in the fact that in the presence of SnCl_4 - a catalyst whose action is milder than that of AlCl_3 , only monoacetylferrocene is formed¹¹⁷.

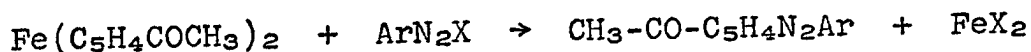
In ferrocenemonoaldehyde, a second formyl group can not be introduced by the action of N-methylformanilide in the presence of

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POCl_3 , which also indicates the deactivation of both cyclopentadiene rings by the aldehyde group^{119,123}.

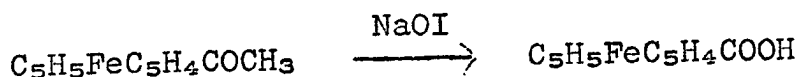
Acetyl-, 1,1'-diacetyl- and 1,1'-dipropionylferrocene dissolve in concentrated hydrochloric acid to produce a deep violet-red color^{12,107}. Upon dilution of the hydrochloric acid solutions with water right after solution, the ketones are isolated without change and in this way can be purified of ferrocene. Upon standing for several hours in hydrochloric acid solution, the acylferrocenes decompose with formation of ferrous ions¹⁷, which indicates the sharp decrease in stability to hydrolysis of the bonds between iron and the substituted cyclopentadiene rings as compared with the corresponding bonds in ferrocene itself.

Upon reaction with diazonium salts, 1,1'-diacetylferrocene behaves quite differently from ferrocene. Upon carrying out the reaction under conditions analogous to the conditions for arylation of ferrocene^{103,117,141}, the ferrocene nucleus is cleaved and products are formed which do not contain iron and corresponding in elemental analysis to arylazoacetocyclopentadiene, but their structures are not as yet proved¹⁵²:

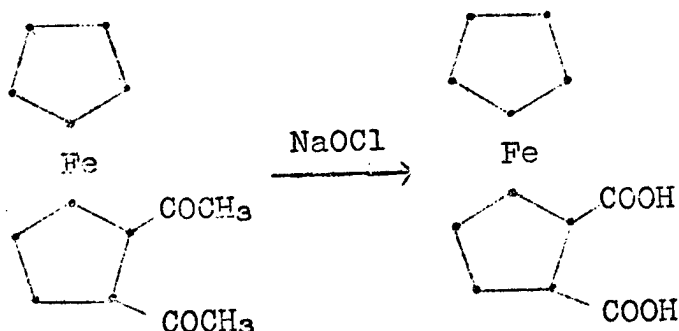


The reaction was carried out with p-nitrobenzene-, p-toluene-, and benzenedi-azonium salts¹⁵².

It must be noted that acetylferrocenes upon oxidation are not transformed into derivatives of ferricinium cation, but yield ferrocenecarboxylic acids; hence in acylferrocenes the iron is not oxidized to the trivalent state. Thus, Weinmayr^{99,153}, by hypiodite oxidation of acetylferrocene obtained ferrocenecarboxylic acid which was earlier synthesized by A. N. Nesmeyanov and coworkers¹¹⁷ by means of ferrocenyllithium



Upon oxidation with hypochlorite or hypiodite of 1,1'- and 1,2-diacetylferrocene, 1,1'- and 1,2-ferrocenedicarboxylic acid were obtained^{12,103}:

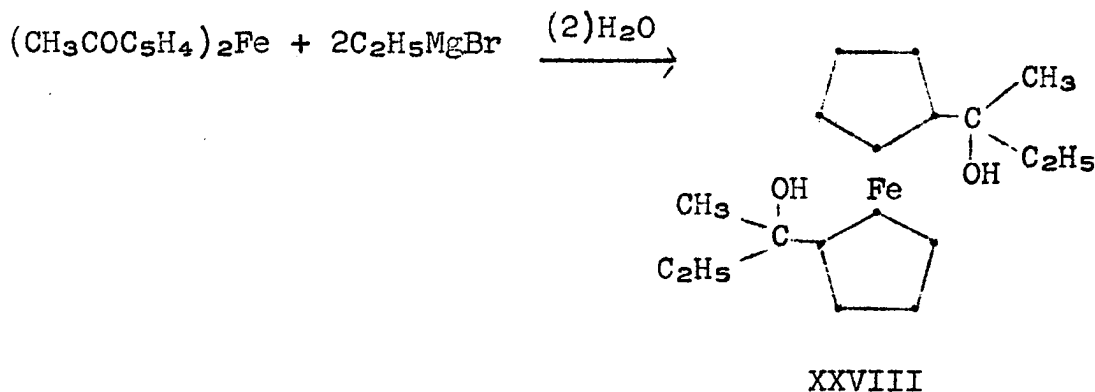


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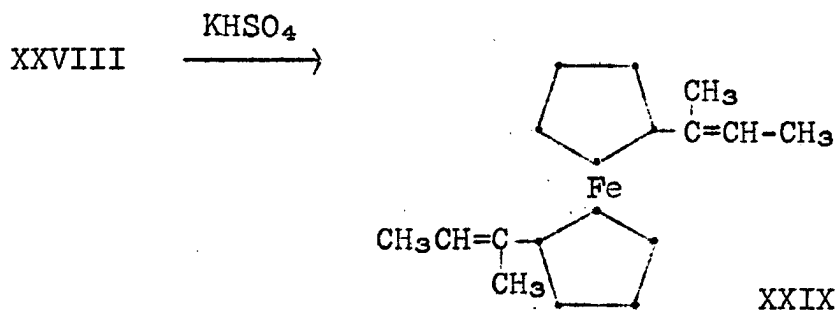
Thus, the acetyl group in acetylferrocene sharply lowers the tendency toward further substitution in the same ring, and more weakly, but nevertheless noticeably lowers the reactivity toward substitution in the second ring; on the other hand - in acetylferrocene (and especially in diacetylferrocene) the stability of the iron toward oxidation increases, and the stability of the bonds of the cyclopentadiene rings with iron decreases.

The carbonyl group in acylferrocenes gives reactions characteristic of ketones^{117-119, 121, 154}, among which it reacts with organomagnesium compounds with the formation of the corresponding tertiary alcohols containing the ferrocenyl group^{17, 125}.

Riemschneider and Helm¹⁷, by the reaction of 1,1'-diacetylferrocene with ethylmagnesium bromide, obtained 1,1'-bis(α -hydroxy-sec.-butyl)-ferrocene (XXVIII) having two asymmetric carbon atoms:



and isolated two stereoisomers, probably the meso form and racemate. Upon dehydration of these carbinols by KHSO_4 , Riemschneider and Helm¹⁷ obtained a mixture of isomeric 1,1'-bis-(α,β -dimethylvinyl)-ferrocenes (XXIX).



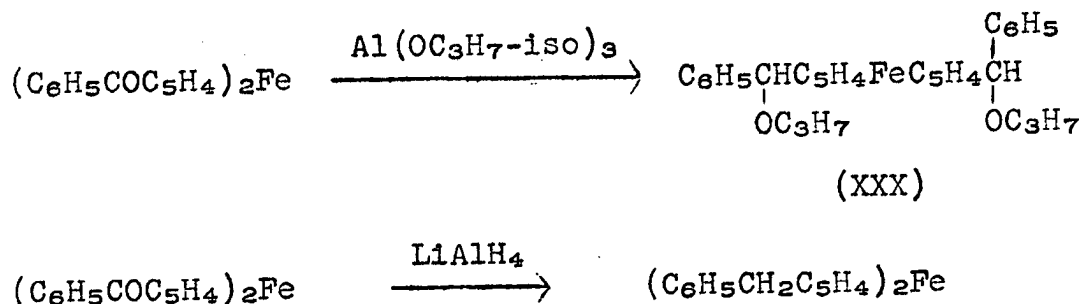
Upon dehydration of 1,1'-bis-(α -hydroxyisopropyl)-ferrocene, only polymer forms - $(\text{C}_{15}\text{H}_{18}\text{O}_{15}\text{Fe})_x$ ¹⁷.
(sic)

Clemmensen reduction of acylferrocenes, as has already been mentioned, is a method of obtaining individual alkylferrocenes¹⁰⁷. 1,1'-Diacetylferrocene is readily reduced catalytically in the presence of Raney nickel¹⁰⁷.

CONTINUED

By reduction of acetylferrocene with lithium aluminum hydride, Arimoto and Haven¹⁴⁰ obtained methylferrocenylcarbinol, upon dehydration of which, and also upon pyrolysis of its acetate, vinylferrocene was isolated. They prepared polymers of vinylferrocene and also its copolymers with methyl methacrylate, styrene, and chloroprene.

Upon reduction of 1,1'-dibenzoylferrocene with aluminum isopropoxide, 1,1'-bis-(phenylisopropoxymethyl)-ferrocene is obtained (XXX)¹⁷ and upon reduction with LiAlH₄, 1,1'-dibenzylferrocene¹²⁵ is formed in almost quantitative yield.



Very recently, various other transformations of the carbonyl group have been accomplished with acetyl-^{118,119}, benzoyl-^{120,121}, and formylferrocenes^{119,147}, and for acetylferrocene, condensations involving the α -hydrogen atom have also been carried out^{116,118,119}, leading to various ferrocenyl-substituted alcohols, acids, unsaturated ketones and other derivatives which are presented in the corresponding tables.

Formylferrocene enters into virtually all the reactions typical of the aldehyde group. However, oxidation to the acid was not successful¹¹⁹. Ferrocenecarboxylic acid is obtained from the aldehyde only by means of the Cannizzaro reaction¹⁴⁷.

It must be noted that in the infrared spectrum of formylferrocene taken above 45°, bands characteristic of the hydroxyl group were unexpectedly found¹¹⁹.

PROPERTIES OF ARYL- AND ALKYLFERROCENES

In the study of the properties of arylferrocenes, interest is afforded by the elucidation of the mutual influence of the aryl and ferrocenyl groups. On the basis of the extant experimental data, one may say that arylferrocenes show a somewhat decreased reactivity, in comparison with ferrocene, toward further substitution of the hydrogens of the cyclopentadiene rings. Thus, in the further phenylation of phenylferrocene, the unsubstituted ring is attacked preferentially¹⁰³, and in arylation of ferrocene with an excess of arenediazonium salt, 1,1'-diarylferrocenes are obtained. Only in the case of *p*-methoxybenzenediazonium salts did Broadhead and Pauson¹⁰³ isolate a small quantity of homoannular di-(*p*-anisyl)-ferrocene with the relative positions of the *p*-anisyl groups undetermined.

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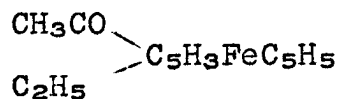
A sharp decrease in reactivity toward electrophilic substitution is observed with *p*-nitrophenyl- and especially with 1,1'-di(*p*-nitrophenyl)-ferrocene¹⁵². Neither of these compounds is acylated or sulfonated under those conditions under which these reactions proceed for ferrocene. 1,1'-Di(*p*-nitrophenyl)ferrocene is not mercurated, while mono-*p*-nitrophenylferrocene yields di-(chloro-mercury)-*p*-nitrophenylferrocene only in 15% yield while 72% of the original *p*-nitrophenylferrocene is recovered unchanged¹⁵².

By the reduction of *p*- and *m*-nitrophenylferrocene, *p*- and *m*-ferrocenylaniline are obtained and a series of their derivatives¹³⁷ (acetyl, benzoyl, and others). The basicity constants of these amines, and also the dissociation constants of *p*-ferrocenylphenol¹³⁹, *p*- and *o*-ferrocenylbenzoic acids¹³¹, and for comparison some aromatic derivatives are presented in table 10.

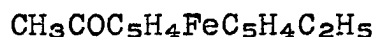
The basicity constant of *p*-ferrocenylaniline is three times as great than the constant of aniline and 17 times as great as the constant of *p*-aminobiphenyl. Similar comparisons are observed for phenols: *p*-ferrocenylphenol is significantly less acidic than phenol and *p*-hydroxybiphenyl. From comparison of the data given, it follows that ferrocenyl is a considerably more powerful electron-donating group than phenyl, and when introduced into the benzene ring behaves as a sharply defined orth-para director.

Thus, with respect to ferrocenyl, the aryl group is an electron acceptor. Indeed as has already been mentioned, not only *p*-nitrophenyl, but also the unsubstituted phenyl group somewhat lowers the reactivity of the ferrocene nucleus.

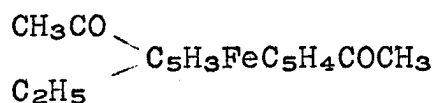
As has already been said above, alkyl groups, in contrast to aryl, increase the tendency toward further substitution of the hydrogens of the ferrocene nucleus. Thus, Nesmeyanov and Volkenau¹⁵⁴ did not succeed in obtaining monoacetylethylferrocene from ethylferrocene in the presence of AlCl₃ under the conditions for obtaining monoacetylferrocene. Monoacetylethylferrocene was synthesized by them by the action of acetyl silicate on ethylferrocene in the presence of SnCl₄. The products isolated were homoannular ethylacetylferrocene (XXXI), 1,1'-ethylacetylferrocene (XXXII), and ethyl-diacetylferrocene (XXXIII) in the ratio 3.5 : 1 : 1.



XXXI



XXXII



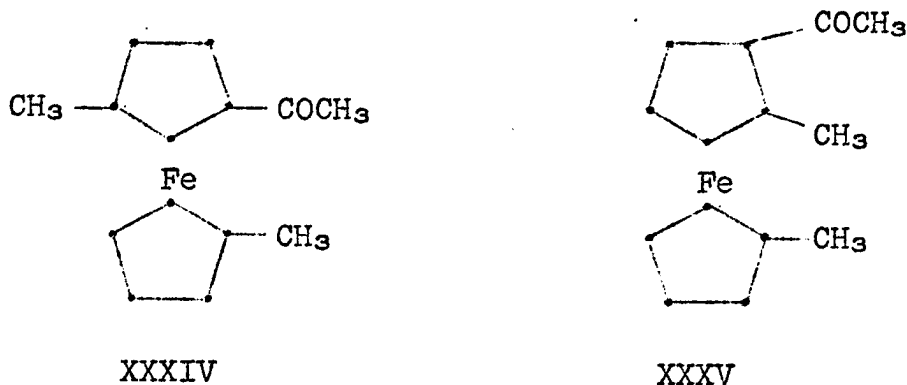
XXXIII

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Upon reduction, (XXXI) yields homoannular diethylferrocene (the relative positions of the ethyl groups is not established; the presence of an unsubstituted ring was proved by bromination); (XXXII) is transformed into 1,1'-diethylferrocene, and (XXXIII) forms triethylferrocene, the structure of which is not established.

Thus the ethyl group orients the acetyl group in subsequent substitution chiefly in the same cyclopentadiene ring and principally in one specific position (it is not established in which).

Upon acylation with acetic anhydride in the presence of $AlCl_3$ of 1,1'-dimethylferrocene, 1,1'-dimethyl-3-acetylferrocene (XXXIV) and 1,1'-dimethyl-2-acetylferrocene (XXXV)¹⁵⁵, are formed in the ratio of 7 : 3. The ratio of the corresponding isomers obtained upon acylation of 1,1'-diisopropylferrocene¹⁵⁵ is equal to 9 : 2. Thus in this case as well, the formation of one of the isomers in greater quantity is observed.

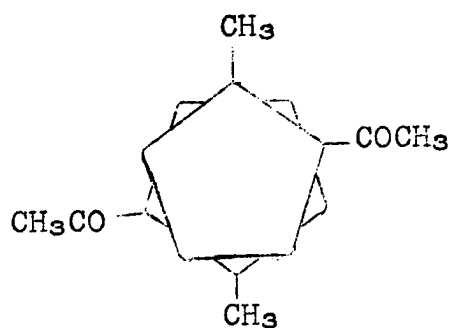


Acetyldialkylferrocenes are oxidized to the corresponding dialkylferrocenecarboxylic acids and reduced to trialkylferrocenes. The relative positions of the groups within one ring is established spectroscopically¹⁵⁵.

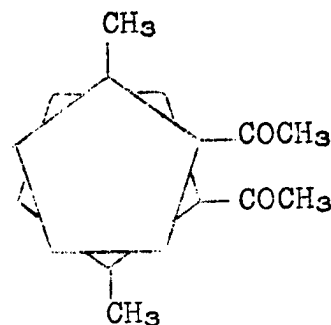
Nesmeyanov and coworkers¹⁵⁶ showed that in acylation of 1,1'-dimethylferrocene with acetyl chloride in the presence of $AlCl_3$, triacetyldimethylferrocene is formed along with diacylated products. This fact indicates that the methyl groups which are present in the ferrocene nucleus significantly facilitate subsequent acylation. As has already been mentioned, attempts to obtain triacetylferrocene by means of the Friedel-Crafts reaction are not successful.

Rinehart and Motz¹⁵⁷ isolated stereoisomers for 1,1'-dimethyl-2,2'-diacetylferrocene, XXXVI and XXXVII, and for 1,1'-dimethyl-3,3'-diacetylferrocene, XXXVIII and XXXIX, and reduced them to the corresponding dimethyldiethylferrocenes.

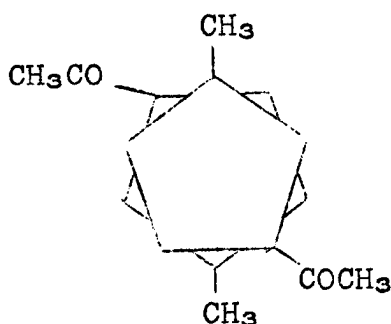
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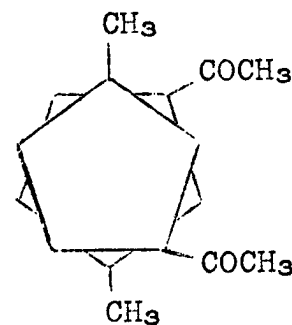
XXXVI



XXXVII



XXXVIII



XXXIX

As has already been noted in the section "Alkylation", in the alkylation of ferrocene homoannular dialkylferrocenes are formed. This indicates the activating influence of the alkyl group especially on that cyclopentadiene ring to which it is attached.

Aryl- and alkylferrocenes are easily oxidized to derivatives of the ferricinium cation^{107,141}. Upon standing, liquid alkylferrocenes gradually decompose with formation of a precipitate¹⁰⁷.

Piper and Wilkinson⁷⁰ took the nuclear magnetic resonance spectrum of 1,1'-dimethylferrocene.

PROPERTIES OF FERROCENECARBOXYLIC ACIDS

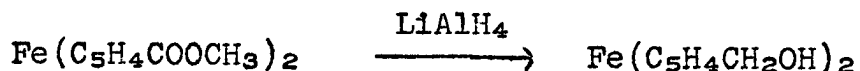
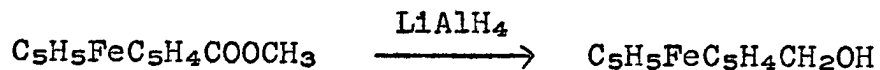
Ferrocenecarboxylic acids (monoferrocenecarboxylic acid and two diacids - 1,1'- and 1,2-ferrocenedicarboxylic acids have been obtained*) are quite stable substances, yielding water-soluble salts with alkalis and forming methyl esters under ordinary conditions^{12,108,117,135}. The nitrile of ferrocenecarboxylic acid has been synthesized via the oxime of formylferrocene¹²² and from the amide¹⁴³. Derivatives of 1,2-ferrocenedicarboxylic acid have already been described in the section "Acylation and alkylation of ferrocene".

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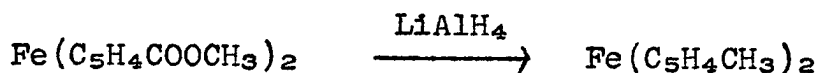
*The method of obtaining them is described in the sections "Metalation" and "Properties of Acylferrocenes".

The monoamide and mononitrile of 1,1'-ferrocenedicarboxylic acid have been obtained by Nesmeyanov and Reutov¹⁴³.

By the reduction of the dimethyl esters of ferrocenecarboxylic acids, Nesmeyanov, Perevalova and Beinoravichute¹²⁵ obtained ferrocenylcarbinol and 1,1'-di(hydroxymethyl)-ferrocene in good yield.



The dimethyl ester of ferrocenedicarboxylic acid also is easily reduced by lithium aluminum hydride to 1,1'-dimethylferrocene (yield 89%)¹²⁵:



In the work of Wilkinson, Cotton and Birmingham²⁶ the synthesis of 1,1'-dimethylferrocene by means of methylcyclopentadienylsodium is mentioned (reference to unpublished data).

The carboxylic acid group exerts a deactivating influence on further substitution of the hydrogens of the ferrocene nucleus. Thus, Nesmeyanov and Reutov¹⁵⁸ showed that in the reaction of dioxanesulfotrioxide with a mixture of ferrocene and ferrocenecarboxylic acid (competitive sulfonation) ferrocene is sulfonated while the acid is unchanged. Acylation of the methyl ester of ferrocenecarboxylic acid proceeds in the unsubstituted cyclopentadiene ring. In the reaction of this ester in the presence of aluminum chloride with the acid chlorides of acetic and butyric acids, acetyl- and butyrylferrocenecarboxylic acids are obtained after subsequent saponification. The location of the substituents in different cyclopentadiene rings was established spectroscopically and also by oxidation of acetylferrocenecarboxylic acid to the known 1,1'-ferrocenedicarboxylic acid¹⁵⁸. Ethyl- and butylferrocenecarboxylic acids were obtained by reduction of these keto acids.

An interesting study of the influence of substituents on the dissociation constants of ferrocenecarboxylic acids was carried out by these same authors¹⁵⁸. They found that the alkyl or acetyl group located in one cyclopentadiene ring influences the dissociation constant of a carboxyl group located in the other ring. Alkyl groups lower, while acyl groups augment the dissociation constant of the corresponding acid.

The order of influence was compared with the influence of the same substituents on the dissociation constant in p-substituted benzoic acids.

Ferrocene and compounds similar to it constitute the first example of a conjugated system (see ¹⁵⁹) which includes a metal atom.

CONTINUED

Generalizing the properties of ferrocene discussed above, one can note the following particulars:

1. Unusual stability for an organometallic compound.
2. Complete absence of the addition reactions characteristic of unsaturated compounds.
3. Ease of electrophilic substitution reactions which take place under milder conditions than are necessary for benzene.
4. Ease of oxidation of the iron to the trivalent (formal) state and at the same time complete stability to oxidation of the internal bonds of the cyclopentadiene rings.
5. Strong influence of substituents on the reactivity of the ferrocene nucleus, especially evident within one cyclopentadiene ring, but very significantly transmitted from one ring to the other as well.

It is evident that ferrocene is a new aromatic system of the non-benzenoid type.

POSSIBILITIES FOR TECHNOLOGICAL APPLICATION OF FERROCENE

In the patent literature ferrocene has been suggested for use as an additive in mineral oils as an antidetonator^{143,153}, and as a thermally stable heat transfer agent¹⁶. Ferrocene is also useful for accomplishing the smokeless combustion of oils¹⁶⁰.

III. PROPERTIES OF DICYCLOPENTADIENYL COMPOUNDS OF METALS

At the present time dicyclopentadienyl compounds of the majority of metals have been obtained. The methods for obtaining them were discussed above. The physical and especially the chemical properties have not been studied in as much detail as those of ferrocene itself. The magnetic properties of all the compounds obtained have been investigated and spectra have been taken (usually infrared); for some of them X-ray crystallographic analysis has been carried out and polarographic measurements have been made. Of the chemical properties which are usually investigated there is the reaction with maleic anhydride and the ease of hydrolysis of the bond between the cyclopentadiene rings and the metal, and oxidation to the cation is described or conversely reduction of the cation. The character of the spectrum and its agreement with the spectrum of ferrocene usually serve as a basis (sometimes not completely adequate) for judgement as to the three-dimensional structure of the given dicyclopentadienylmetal. The ease of hydrolysis, and the reaction with FeCl_2^{28} to form ferrocene serve as criteria of the ionic nature of the bond between metal and cyclopentadiene ring, while the absence of reaction with maleic anhydride

CONTINUED

of the Diels-Alder type serves as an indication of the aromaticity of the rings and the presence of "sandwich" bonds between the metal and the cyclopentadiene ring.

The reactions of aromatic substitution have been studied in detail only for ferrocene. Attempts were made to accomplish these reactions with nickelocene, cobalticinium salts, and dicyclopentadienyl compounds of titanium. Negative results were obtained in all cases.

It is possible that this is due to the decreased stability, in comparison with ferrocene, of dicyclopentadienyl derivatives of nickel and titanium, which is confirmed for nickelocene by mass-spectral investigations⁸² and theoretical calculations. The question as to the possibility of electrophilic substitution reactions for the cation has not been studied even for ferricinium ion. Dunitz and Orgel⁸¹ calculate that in the cations of dicyclopentadienyl compounds, the d-orbitals of the central atoms are significantly more stable than the π -orbitals of the C_5H_5 rings, and therefore in compounds of tetravalent titanium and trivalent iron, cobalt, and nickel, the character of the bonds is shifted in the direction of more ionic character. This must lead to a decrease in the stability and to diminishing of the reactivity toward aromatic substitution.

The behavior of ruthenocene (the closest dicyclopentadienylmetal in all properties and stability to ferrocene) in reactions of aromatic electrophilic substitution has not been studied, possibly because of the difficult accessibility of the metal itself.

Below, the physical and chemical properties of dicyclopentadienyl compounds, grouped according to their group in the periodic system of elements, are discussed.

DICYCLOPENTADIENYL COMPOUNDS OF ELEMENTS OF GROUP VII IN THE PERIODIC SYSTEM

Dicyclopentadienyl compounds have been obtained for all elements of the eighth group except palladium (see table 1). The physical and chemical properties of ferrocene were discussed above.

All dicyclopentadienyl compounds of elements of group VIII have the centrally symmetrical antiprismatic structure, the cyclopentadiene ring bound to the metal just as in ferrocene^{18,19,31,72,98}.

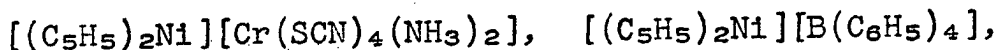
Spectroscopic^{18,19,21-24,161} and mass-spectroscopic⁸² investigations and polarographic^{19,21,24,84} and magnetic measurements^{18,19,21,11,17,31,32,89,98} are in complete agreement with the "sandwich" structure of dicyclopentadienyl compounds of metals of group VIII.

For the ortho-para interconversion of hydrogen in the presence of nickelocene and cobalticene see⁸⁸.

CONTINUED

The densities of nickelocene and cobalticene⁷² are equal to d^{18} 1.47 g./cm³ and d^{18} 1.49 g./cm³ respectively.

The green nickelocene, $(C_5H_5)_2Ni$, is paramagnetic, sublimes in vacuum, dissolves readily in non-polar solvents, gradually is oxidized in air, especially in solutions³¹, does not dissolve in water and is not decomposed by water, and does not form ferrocene with ferrous chloride²⁸. Nickelecinium cation, $(C_5H_5)_2Ni^+$, yields water-insoluble salts only with complex ions such as are shown below:



and is unstable in water, decomposing in several minutes^{19,31}. Comparison of mass-spectra shows that the bond between the nickel and the cyclopentadienyl rings in nickelocene is much weaker than in ferrocene²⁸. For the heat of formation of nickelocene from cyclopentadiene radicals and the gaseous metal, see²¹.

Reactions of aromatic substitution are not known for nickelocene. Wilkinson, Pauson, and Cotton²¹ unsuccessfully tried to acylate nickelocene by the Friedel-Craft reaction. Our attempts to accomplish acylation by acetylborontrifluoride, arylation, and metalation of nickelocene under conditions analogous to those under which these reactions were carried out for ferrocene, also gave negative results. In the process, a significant part of the nickelocene decomposed even when the reaction was carried out under nitrogen.

In the patent literature there is an indication that nickelocene may be used as an antidetonator and as a catalyst in some organic reactions⁴⁴.

Cobalticene $(C_5H_5)_2Co$ is extremely easily oxidized³² to the very stable diamagnetic cation $(C_5H_5)_2Co^+$, which is isoelectronic with ferrocene and yields water-insoluble salts, similarly to ferricinium and nickelecinium, only with large anions³⁸. Cobalticinium salts are not decomposed by concentrated sulfuric and nitric acids, but in their presence, substitution in the nucleus does not take place^{18,22}. Cobalticinium nitrate is not ozonized, even upon prolonged passage of ozone into a solution of the salt in acetic acid for many hours³⁶. Our attempts to acylate by the Friedel-Crafts method, arylate, sulfonate and nitrate cobalticinium picrate were also unsuccessful. In all cases the cobalticinium salt was recovered unchanged.

In anhydrous solvents $(C_5H_5)_2Co^+Br^-$ is reduced by lithium aluminum hydride to $(C_5H_5)_2Co$ in good yield⁴³.

The action of water does not cleave the bonds between the metal and the rings in cobalticene; only slow oxidation to the cation takes place²⁸; with $FeCl_2$ ferrocene is not formed²⁶.

By the action of an alkali metal cyclopentadienyl compound on $(C_5H_5)_2Co^+$, Fischer¹⁶² obtained a substance stable to hydrolysis with the composition $Co_2(C_5H_5)_5$ to which he assigned structure (XL). The

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dipole moment of this compound is zero⁵⁹.

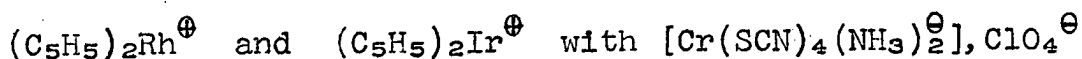


XL

Ruthenocene is similar to ferrocene in properties and stability^{23,82,84}. The reactions of substitution of the hydrogens of the cyclopentadiene rings has not been studied. For the nuclear magnetic resonance spectrum of ruthenocene see⁷⁰.

Wilkinson, Cotton, and Birmingham²⁶ studied the reaction of dicyclopentadienyl compounds of iron, ruthenium, cobalt, and nickel with benzophenone, m-nitrobenzaldehyde, maleic anhydride, and methyl maleate and found that only ferrocene and ruthenocene are inert to all these reagents. Cobalticene forms colored products with benzophenone; nickelocene does not react. Cobalticene and nickelocene react with maleic anhydride; however the character of the reaction has not been studied, and therefore it is impossible to draw any conclusions.

Dicyclopentadienyl compounds of rhodium and iridium²⁴ have been obtained only in the form of salts of the cations



and others and the free bases $(\text{C}_5\text{H}_5)_2\text{RhOH}$ and $(\text{C}_5\text{H}_5)_2\text{IrOH}$. The cations of the dicyclopentadienyl compounds of rhodium and iridium are similar in properties and stability to cobalticinium cation.

An attempt to isolate dicyclopentadienylrhodium, $(\text{C}_5\text{H}_5)_2\text{Rh}$, by electrolytic reduction in aqueous solution was not successful²⁴; a hydride of dicyclopentadienylrhodium is described¹⁶³.

In his review Pauson¹³ refers to the private communication of Lippincott concerning the obtaining of a dicyclopentadienyl compound of osmium.

DICYCLOPENTADIENYL COMPOUNDS OF ELEMENTS OF GROUP VII IN THE PERIODIC SYSTEM

Dicyclopentadienyl compounds have been obtained for rhenium⁴⁷ and manganese^{25,26,33,46,164,165}.

Dicyclopentadienylmanganese is paramagnetic^{26,69}, has an arrangement of atoms in space similar to ferrocene, in the form of a pentagonal antiprism, but the bonds between manganese and the

CONTINUED

cyclopentadiene rings is of the ionic type^{26,46,82,164}. In chemical properties, $(C_5H_5)_2Mn$ is similar to $(C_5H_5)_2Mg$, with which it forms mixed crystals. Upon heating, the brown dicyclopentadienylmanganese changes color and is transformed into another modification^{26,46}. $Mn(C_5H_5)_2$ decomposes upon attempts to oxidize it to the cation, reacts with aldehydes, ketones, and maleic anhydride; forming products which have not been investigated²⁶.

Wilkinson, Cotton, and Birmingham²⁶ mention the obtaining of $(CH_3C_5H_4)_2Mn$ by means of methylcyclopentadienylsodium (reference to unpublished work).

A dicyclopentadienyl compound of rhenium is known^{47,166} only in the form of the hydride, $(C_5H_5)_2ReH$. The structure was confirmed by nuclear magnetic resonance study^{47,70,163}. The hydride hydrogen atom is located in the space between the cyclopentadiene rings. $(C_5H_5)_2ReH$ does not react with water or with $6NNaOH$, reacts slowly with the oxygen of the air, dissolves in organic solvents. Solutions in liquid ammonia do not conduct the electric current; upon reaction with $FeCl_2$, ferrocene is not formed. $(C_5H_5)_2ReH$ dissolves in dilute hydrochloric or sulfuric acid with formation of the cation $[(C_5H_5)_2ReH_2]^+$ which is precipitated in the form of the silicotungstate or reineckeate.

Wilkinson and Birmingham⁴⁷ believe that the hydride of dicyclopentadienylrhenium has a structure similar to ferrocene.

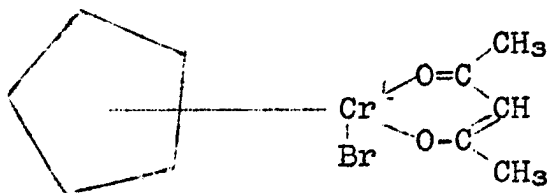
DICYCLOPENTADIENYL COMPOUNDS OF GROUP VI OF THE PERIODIC SYSTEM

Of the elements of group VI, dicyclopentadienyl compounds have been obtained for chromium^{26,27,43,33,70}, molybdenum²⁷ and tungsten²⁷

Dicyclopentadienylchromium, $(C_5H_5)_2Cr$, is paramagnetic^{68,69}, thermally stable to 300° , but is extremely easily oxidized in air, ignites spontaneously in finely pulverized form; is not appreciably decomposed by water^{26,34}; evolves cyclopentadiene on treatment with dilute mineral acids, forming a dark blue solution³⁴ in which neither the chromium ion nor the cation $(C_5H_5)_2Cr^+$ is detected. Dicyclopentadienylchromium reacts with $FeCl_2$ to form ferrocene (yield 70%) and a blue-green substance of undetermined structure²⁶; upon heating under pressure with CO, dicyclopentadienylchromium forms first chromium cyclopentadienylcarbonyls of various compositions and then $Cr(CO)_6$ ³⁵. Dicyclopentadienylchromium reacts with maleic anhydride, aldehydes, and ketones; neither the products so formed nor the nature of the reactions have been investigated²⁶. By the action of iodine dicyclopentadienylchromium is transformed into the iodide of the cation, $(C_5H_5)_2CrI$ ⁴⁹. It was not possible to take the infrared spectrum of dicyclopentadienylchromium³⁴.

Thomas¹⁶⁷ obtained the bromide of the cyclopentadienylacetylacetate of chromium and showed by this means the possibility of the existence of compounds of chromium with one cyclopentadiene ring:

CONTINUED



Dicyclopentadienyl compounds of tetra- and pentavalent molybdenum and pentavalent tungsten have been isolated in the form of salts²⁷.

IV

IV



V

V



Cotton and Birmingham²⁷ calculate on the basis of infrared spectra that these compounds have structures similar to ferrocene.

DICYCLOPENTADIENYL COMPOUNDS OF ELEMENTS OF GROUP V OF THE PERIODIC SYSTEM

Of the elements of group V, dicyclopentadienyl compounds of vanadium^{19,20,26,43,50,68,168}, niobium²⁰, tantalum²⁰, bismuth⁵¹, antimony, and arsenic⁵¹ are described; triphenylphosphonium cyclopentadienylide has also been obtained⁵².

The dicyclopentadienyl compound of tetravalent vanadium has been isolated in the form of the chloride and bromide.

The dichloride of dicyclopentadienylvanadium is paramagnetic, dissolves in polar organic solvents, forms a green solution in water, in which it decomposes rapidly upon addition of alkali; in acid solution it is preserved for several hours. It is reduced by LiAlH_4 to dicyclopentadienylvanadium, $(\text{C}_5\text{H}_5)_2\text{V}^{4+}$.

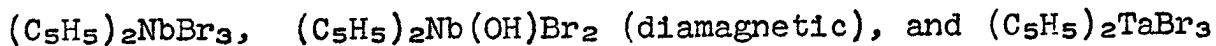
The ion of the trivalent vanadium compound, $(\text{C}_5\text{H}_5)_2\text{V}^{\oplus}$, oxidizes rapidly in air^{20,26}.

Dicyclopentadienylvanadium, $(\text{C}_5\text{H}_5)_2\text{V}$, is paramagnetic, rather stable^{26,82}, is not decomposed by water, is hardly decomposed at all even in acid medium, forms traces of ferrocene with FeCl_2 ²⁶, reacts with aldehydes, ketones, and maleic anhydride forming products which were not investigated²⁶, and with CO yields $\text{C}_5\text{H}_5\text{V}(\text{CO})_4$ ^{50,169}. The

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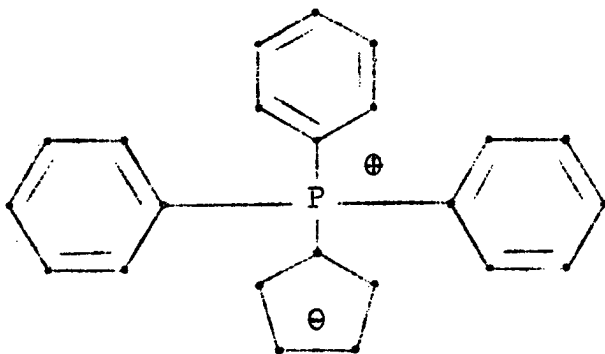
The data of X-ray crystallographic analysis indicate the "sandwich" structure¹⁶⁹.

The dicyclopentadienyl compounds of pentavalent niobium and tantalum²⁰ were isolated in the form of salts:



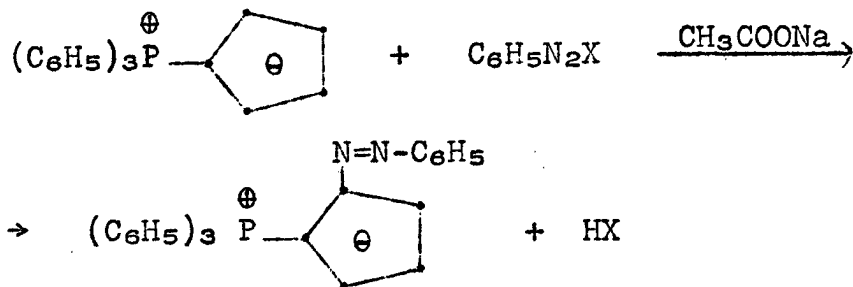
The infrared spectra of the dicyclopentadienyl compounds of V, Nb, and Ta are consistent with each other and have bands characteristic for "sandwich" compounds^{20,28}.

Triphenylphosphonium cyclopentadienylide is obtained⁵² in the reaction of bromocyclopentadiene with triphenylphosphine and subsequent treatment of the reaction product with aqueous sodium hydroxide. Ramirez and Levy⁵² calculate that the substance has the ionic structure (XLI). The cyclopentadiene ring is aromatized.



XLI

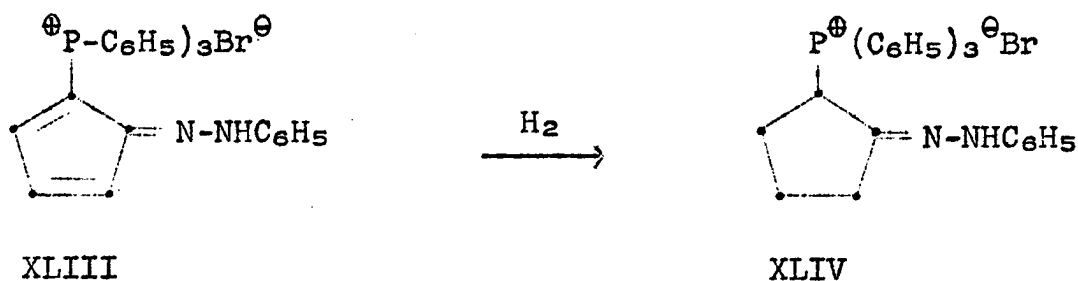
Triphenylphosphonium cyclopentadienylide is stable and almost useless for the synthesis of olefins, in contrast to other phosphine-methylenes, for example, $(\text{C}_6\text{H}_5)_3\text{P}=\text{CH}_2$ and $(\text{C}_6\text{H}_5)_3\text{P}=\text{CHC}_6\text{H}_5$. In the reaction of the cyclopentadienylide with benzenediazonium ion, azo coupling takes place¹⁷⁰.



XLIII

CONTINUED

In acid medium, the azo compound (XLII) forms a salt (XLIII) yielding upon hydrogenation compound XLIV, the structure of which was proved by independent synthesis¹⁷⁰.



DICYCLOPENTADIENYL COMPOUNDS OF ELEMENTS OF GROUP IV OF THE PERIODIC SYSTEM

Dicyclopentadienyl compounds of titanium^{19,20,39,53} zirconium^{19,2} tin⁵⁴, lead^{54,59}, and silicon^{56,57} have been obtained.

The salts of dicyclopentadienyltitanium (IV) cation $(\text{C}_5\text{H}_5)_2\text{TiX}_2$, are diamagnetic^{19,20,68}, stable in air, dissolve in organic solvents and water (hydrolyzes somewhat), and yield precipitates with the same anions^{19,20} as do other cyclopentadienylmetal cations.

Attempts to acylate dicyclopentadienyltitanium bromide by the Friedel-Crafts method gave no positive results²⁰; it was also impossible to isolate an alcoholate in the reaction with butyl alcohol in the presence of pyridine²⁰. With phenyllithium, dicyclopentadienyltitanium chloride forms diphenyldicyclopentadienyltitanium^{171,172}, which gradually decomposes at room temperature.



By analogous means, meta- and para- $(\text{CH}_3\text{C}_6\text{H}_4)_2\text{Ti}(\text{C}_5\text{H}_5)_2$ were obtained. $[\text{p}-(\text{CH}_3)_2\text{NC}_6\text{H}_4]_2\text{Ti}(\text{C}_5\text{H}_5)_2$ ¹⁷² and $(\text{CH}_3)_2\text{Ti}(\text{C}_5\text{H}_5)_2$ ⁷⁰ are very unstable, yield 1%.

Salts of dicyclopentadienyltitanium (III), $(\text{C}_5\text{H}_5)_2\text{TiX}$, are obtained by reduction of $(\text{C}_5\text{H}_5)_2\text{TiX}_2$ electrolytically²⁰ or with LiAlH_4 ⁴⁸. The dicyclopentadienyl compound of divalent titanium⁵³, $(\text{C}_5\text{H}_5)_2\text{Ti}$, is diamagnetic, decomposes in air, but can be preserved well in an atmosphere of inert gas, is thermally unstable, upon heating in an atmosphere of inert gas decomposes below its melting point ($\sim 130^\circ$), reacts very slowly with water which does not contain air, is transformed by dilute hydrochloric or sulfuric acid into compounds of tetravalent titanium, and forms an etherate with tetrahydrofuran. Solutions of dicyclopentadienyltitanium in ammonia virtually do not conduct the electric current. In the reaction of $(\text{C}_5\text{H}_5)_2\text{Ti}$ with FeCl_2 only traces of ferrocene are formed⁵³.

The properties described for dicyclopentadienyltitanium and also the similarity of infrared spectra^{19,20} of $(\text{C}_5\text{H}_5)_2\text{TiBr}_2$ with the spectra of ferrocene and ruthenocene enable one to assert that dicyclopentadienyl compounds of titanium are similar in structure

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to ferrocene⁵³.

Wilkinson and coworkers^{19,20} obtained dicyclopentadienylzirconium (IV) bromide, $(C_5H_5)_2 ZrBr_2$, the properties of which have hardly been studied; there is only the information that this compound is diamagnetic²⁰, the infrared spectrum is given, and mention is made of an attempt at polarographic investigation¹⁹.

Dicyclopentadienyltin, $(C_5H_5)_2 Sn$, and dicyclopentadienyllead, $(C_5H_5)_2 Pb$, are organometallic compounds with an ordinary C-M bond⁵⁴. $(C_5H_5)_2 Sn$ is diamagnetic⁴⁸, has a dipole moment of 1.01 debye⁵⁹, and reacts with maleic anhydride⁴⁵. Cyclopentadienylphenyl compounds of tetravalent tin have been described⁵⁵; it was not possible to isolate tetracyclopentadienyltin in pure form⁵⁵.

Dicyclopentadienyllead is diamagnetic⁴⁸, has a dipole moment of 1.63 debye⁵⁹, is not hydrolyzed by water, but is easily oxidized in air⁴⁵.

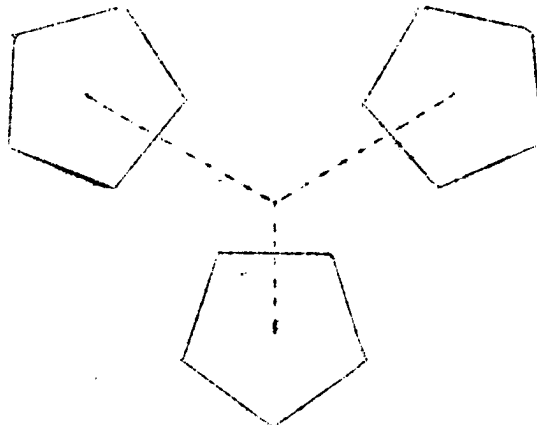
Cyclopentadienyl compounds of silicon have been obtained:



TRICYCLOPENTADIENYL COMPOUNDS OF ELEMENTS OF GROUP III OF THE PERIODIC SYSTEM

Elements of group III of the periodic system in contrast to others yield only tricyclopentadienyl compounds.

Thus tricyclopentadienyl compounds have been obtained for scandium, yttrium, and the lanthanides-- lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, dysprosium, erbium, and ytterbium^{28,29}. A hypothesis has been expounded, that in these tricyclopentadienyl compounds the cyclopentadienyl rings are arranged so that perpendiculars going through the centers of the rings intersect at the site of the metal atom and form angles of 120° with each other⁵⁸.



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