

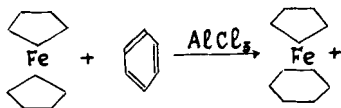
## RECENT ADVANCES IN FERROCENE CHEMISTRY IN THE U.S.S.R.

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The present review deals with the results of investigations on the chemistry of ferrocene made in the Soviet Union. For lack of space we are not able to discuss these results in detail and to compare them with the investigations made in other countries.

### *Exchange of Ligands*

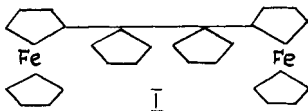
The five-membered ring of ferrocene is exchanged for a six-membered aromatic ring when ferrocene is heated with aromatic hydrocarbons in the presence of aluminum chloride.<sup>1,2</sup> In this case, a singly charged cation of arene-cyclopentadienyliron is formed.



The reaction was carried out with benzene, toluene, p-xylene, mesitylene, diphenyl, chlorobenzene and naphthalene. The cations were isolated as the iodide and tetraphenylborate.

Substituted ferrocenes also interact with aromatic hydrocarbons. Upon heating with mesitylene in the presence of aluminum chloride, the heteroannular diacetyl- and diethylferrocene are converted to the cations of mesitylene-acetylcyclopentadienyliron and mesitylene-ethylcyclopentadienyliron, respectively. The reaction with diethylferrocene occurs more readily than with diacetylferrocene. Accordingly, in a monoacetylferrocene, it is the free five-membered ring which is mainly exchanged for mesitylene to produce the cation of mesitylene-acetylcyclopentadienyliron, whereas in ethylferrocene both the substituted and the free rings are exchanged to form a mixture of cations, in which the amount of mesitylene-cyclopentadienyliron is approximately half as much again as that of mesitylene-ethylcyclopentadienyliron.

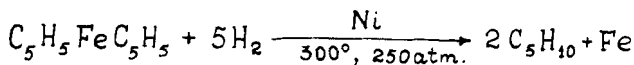
The eliminated cyclopentadiene appears to react with ferrocene. A prolonged heating of ferrocene with  $AlCl_3$  in benzene results in a compound with two ferrocenyl and two cyclopentane groups, for which a structure of bis-I,I' -diferrrocenyl di-I,I' -dicyclopentyl (I) was suggested on the basis of



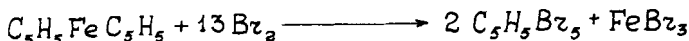
the data of the proton magnetic resonance spectrum<sup>6</sup> (originally this compound was assigned an incorrect structure of pentaethanodiferrocene.<sup>7</sup>

### *Decomposition of Ferrocene System*

Ferrocene decomposes to form cyclopentane and iron under the action of hydrogen under pressure at a high temperature in the presence of Raney nickel.<sup>3</sup>

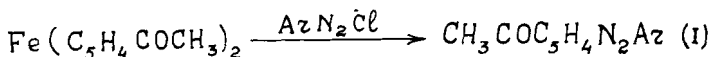


Chlorine decomposes ferrocene (in solution in  $\text{CCl}_4$ ) already at  $0^\circ\text{C}.$ , bromine —upon heating for a short time to form pentahalocyclopentane:<sup>3,4</sup>

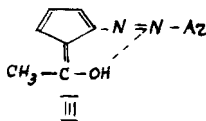
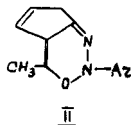


The derivatives of ferrocene (I,I' -ferrocenedicarboxylic acid, I,I' -di(p-nitrophenyl) ferrocene, I,I' -diacetylferrocene,<sup>3</sup> a mixture of acetylated I,I' -dimethylferrocenes)<sup>5</sup> upon hydrogenation are converted to corresponding derivatives of cyclopentane. The monosubstituted ferrocenes (ferrocenecarboxylic acid, ethylferrocene)<sup>3</sup> o-carboxybenzoylferrocene)<sup>8</sup> are decomposed by bromine to form pentabromocyclopentane and its corresponding derivatives (the latter were not isolated).

The ferrocene derivatives with electron withdrawing substituents are readily decomposed when acted upon by the salts of aryldiazoniums and by acids or when their solutions are irradiated. The interaction of p-nitrodiphenyldiazonium chloride with heteroannular diacylferrocenes (diacetyl-, dipropionyl-, dibutyryl-, and dibenzoylferrocene) gives the derivatives of cyclopentadiene containing no iron.<sup>10,11</sup> The reaction of phenyl- and p-tolyldiazonium chloride with I,I' -diacetylferrocene proceeds in a similar manner.<sup>10</sup>



Neither a carbonyl nor a hydroxyl group is found in the derivatives of cyclopentadiene (I) formed, the qualitative reactions for enols are negative, no absorption bands corresponding to the  $\text{C}=\text{O}$ ,  $\text{C}-\text{OH}$  and  $\text{N}-\text{H}$  bonds are present in their infrared spectra. Like isoxazole, these compounds form a complex with cadmium chloride. On the basis of the properties considered, we assigned to them the structure of 1, 2, 3-oxiadiazines (formula II or an analogous one with a different arrangement of double bonds.<sup>12</sup> On the basis of the proton nuclear magnetic resonance spectra, Bozak and Reinhart.<sup>13</sup> Consider, however, these compounds to have structure III.



In acid aqueous solutions acyl- and diacylferrocenes, ferrocene aldehyde, phenylferrocene,  $\alpha$ -pyridyl- and  $\alpha$ -quinolylferrocene, ferrocenylamine and N-alkylferrocenylamines are decomposed to form the derivatives of cyclopentadiene containing no iron.

When heated with a 10 per cent hydrochloric acid in a sealed tube for seven hours, phenylferrocene, benzoylferrocene, I,I' -ferrocenedicarboxylic acid, I,I' -dibenzoylferrocene, acetylferrocene, ferrocene aldehyde and I,I' -diacetylferrocene are decomposed by 8 per cent, 11 per cent, 14 per cent, 21 per cent, 24 per cent, 31 per cent and 62 per cent, respectively. The extent of decomposition was determined from the amount of the iron salt formed. Under these conditions, alkylferrocenes are decomposed by five-six per cent.<sup>14</sup>

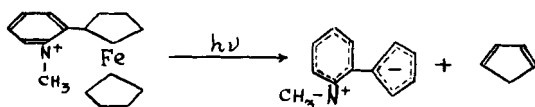
Of especial interest is the quantitative photochemical decomposition of ferro-

enes which have in the  $\alpha$ -position relative to the nucleus an atom carrying a positive or a  $\delta^+$  charge. Thus, in acid aqueous solutions acetyl- and benzoylferrocene, ferrocenylamine, N-ethylferrocenylamine and especially N, N-diethylferrocenylamine,<sup>15</sup>  $\alpha$ -pyridyl-<sup>17</sup> and  $\alpha$ -quinolylferrocene are easily decomposed under the action of light Triethylferrocenylammonium hydroxide is readily decomposed upon illumination.<sup>15</sup>

Upon illumination in aqueous solutions for several hours I,I'-ferrocenedisulfonic acid is converted to an iron salt of a dimer of cyclopentadienesulfonic acid.

In acid medium diphenylferrocenylcarbinol and bis (diphenylhydroxymethyl) ferrocene are decomposed to form diphenylfulvene.<sup>16</sup>

Methiodide of  $\alpha$ -pyridylferrocene is decomposed in an alkaline solution under the action of light to form N-methyl-2-cyclopentadienylidene-1,2-dihydropyridine (N-methyl-2-cyclopentadienylidene-pyridinium) and cyclopentadiene which is isolated as a thallium derivative.<sup>17</sup>



The oxidation of I,I'-dihydroxyferrocene by atmospheric oxygen gives a dimer of cyclopentadienone.<sup>57</sup>

### *Electronic Effects in the Ferrocene Series*

By determining the formal redox potentials of a large series of ferrocene derivatives,<sup>21-23\*</sup> measuring the dissociation constants of acids and phenols and basicity constants of some amines of the ferrocene series,<sup>24</sup> studying the infrared and ultraviolet spectra of substituted ferrocenes<sup>9</sup> and by the subsequent analysis of the data obtained by means of correlation equations we were able to establish the difference in the interaction of the substituents with phenyl nuclei on one hand and with ferrocenyl nuclei, on the other<sup>25-27</sup> and to characterize ferrocenyl as a substituent.<sup>24,26</sup>

The kinetics of ferrocene oxidation with iodine<sup>18</sup> and the solvation of ferri-cinium<sup>19</sup> were investigated.

The change in the redox potentials of ferrocene derivatives depending on the substituent goes parallel with that in the activity of the ferrocene nucleus in the reactions of electrophilic substitution. Ferrocene derivatives, which are not so readily oxidized as ferrocene, are less active than ferrocene in the reactions of electrophilic substitution. Thus, the electron attracting substituents in the ferrocene series are halogens and the  $\text{OCOCH}_3$ ,  $\text{NHCOCH}_3$ ,  $\text{HgCl}$ ,  $\text{CH}_2\text{OH}$ ,  $\text{C}_6\text{H}_5$  groups. Alkylferrocenes are oxidized more readily than ferrocene and they are more active than ferrocene in the reactions of electrophilic substitution of the hydrogens in the rings.

From the values of the redox potentials the equilibrium constants were calculated and the Hammett's equation was applied. Thus, the effect of substituent on the dissociation of benzoic acids was compared with that of the same substituents on the oxidation of iron in the ferrocene derivatives. If the values of  $\epsilon_m$  are used, no linear relationship results, but with the values of  $\epsilon_p$  we obtain a linear relation-

\* Oxidation was effected by potentiometric titration with potassium dichromate in a mixture of  $\text{CH}_3\text{COOH}$  and  $\text{HClO}_4$ . With changing concentration of  $\text{HClO}_4$  in the solvent from 0 to 0.066 mole the absolute values of potentials regularly decrease. For most of monosubstituted ferrocenes these values over the given concentration range change by 25-30 mv.<sup>28</sup>

ship, though not a quite satisfactory one ( $r=0.942$ ), which points to a marked difference in the overall polar influence of the substituents in the ferrocene and benzene series. By using the Taft's suggestion to study separately the interaction between the reaction center and the aromatic ring and that between the substituent and the aromatic ring, it was possible to determine this difference.

The reactivity of mono- and heteroannular disubstituted ferrocenes in the oxidation reaction is well described by the equation  $\log K_{x,y}/K_{11} = P_o \Sigma \rho_p^o$  ( $r=0.993$ ;  $P_o = -8.43$ ) (TABLE 1). Consequently, there is no substantial direct interaction between the substituents in different rings. A correlation analysis points to the existence of an interaction between the substituted five-membered aromatic ring ( $-C_5H_4X$ ) and the reaction center (iron) similar to that between the para-substituted phenyl ring ( $-C_6H_4X$ ) and the reaction center carboxyl), separated from the nucleus by a  $CH_2$ -group, which prevents conjugation. Hence it may be supposed that the reactivity of iron in the oxidation reaction of substituted ferrocenes is not influenced by the effects similar to that of conjugation between the substituted aromatic nucleus and the reaction center in other reaction series. The interaction of the 2p  $\pi$ -orbitals of the rings with each other and with the 4s and 3d orbitals of the metal is of a 6-nature. Therefore, the aromatic five-membered ring does not transfer effects similar to that of conjugation to iron and to another ring. The correlation analysis of the dissociation constants (in 50 per cent ethanol) of ferrocenecarboxylic acids  $X-C_5H_4FeC_5H_4-COOH$  ( $X = \text{alk, H, OCH}_3, \text{Cl, Br, COR, COOCH}_3, \text{CN}$ ), the analysis the infrared spectra of a series of

TABLE 1  
FORMAL OXIDATION POTENTIALS OF SUBSTITUTED FERROCENES  
(v. vs. SCE)

$C_5H_5FeC_5H_4-X$		$FeC_{10}H_8(X)Y$		
X	$E_{r,o}$	(X)	Y	$E_{r,o}$
OCH <sub>3</sub>	-0,166	1,2-(CH <sub>3</sub> ) CONH <sub>2</sub>		-0,399
CH <sub>3</sub>	-0,198	1,3-(CH <sub>3</sub> ) CONH <sub>2</sub>		-0,430
C <sub>3</sub> H <sub>7</sub> -iso	-0,198	1,1'-(CH <sub>3</sub> ) CONH <sub>2</sub>		-0,421
C <sub>2</sub> H <sub>5</sub>	-0,199	1,2-(C <sub>2</sub> H <sub>5</sub> ) CONH <sub>2</sub>		-0,406
CH <sub>2</sub> CH <sub>2</sub> CH = CH <sub>2</sub>	-0,211	1,3-(C <sub>2</sub> H <sub>5</sub> ) CONH <sub>2</sub>		-0,430
H	-0,245	1,1'-(C <sub>2</sub> H <sub>5</sub> ) CONH <sub>2</sub>		-0,419
C <sub>6</sub> H <sub>5</sub>	-0,284	1,2-(C <sub>6</sub> H <sub>5</sub> ) CONH <sub>2</sub>		-0,504
OCOCH <sub>3</sub>	-0,324	1,1'-(C <sub>6</sub> H <sub>5</sub> ) CONH <sub>2</sub>		-0,513
OCOC <sub>6</sub> H <sub>5</sub>	-0,336	1,2-(CH <sub>3</sub> ) C <sub>6</sub> H <sub>5</sub>		-0,144
J	-0,384	1,3-(CH <sub>3</sub> ) C <sub>2</sub> H <sub>5</sub>		-0,145
C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> -p	-0,390	1,2-(C <sub>2</sub> H <sub>5</sub> ) CH <sub>2</sub> OH		-0,262
Cl	-0,408	1,1'-(CH <sub>2</sub> OH) CH <sub>2</sub> OH		-0,386
Br	-0,410	1,1'-(OCH <sub>3</sub> ) COOH		-0,410
COOH	-0,499	1,1'-(J) Cl		-0,529
COOCH <sub>3</sub>	-0,511	1,1'-(Cl) Cl		-0,554
HgCl	-0,278			
CH = CH <sub>2</sub>	-0,280	$C_5H_5FeC_5H_4-Y-C_5H_4FeC_5H_5$		
CH(OH)CH <sub>3</sub>	-0,283	Y	$E'_{r,o}$	$E''_{r,o}$
CH <sub>2</sub> NHCOC <sub>6</sub> H <sub>5</sub>	-0,302	-Hg-	-0,283	-0,655
CH <sub>2</sub> OH	-0,309	-CH <sub>2</sub> -	-0,189	-0,308
CH <sub>2</sub> OCH <sub>3</sub>	-0,302	-CH <sub>2</sub> CH <sub>2</sub> -	-0,214	-0,282
CH <sub>2</sub> COOH	-0,272	-CH <sub>2</sub> OCH <sub>2</sub> -	-0,266	-0,325
C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> -m	-0,358	+		
CONH <sub>2</sub>	-0,484	-		
C <sub>6</sub> H <sub>4</sub> FeC <sub>5</sub> H <sub>5</sub>	-0,189	-CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub>	-0,447	-0,511

monosubstituted ferrocenes as well as the analysis of the electronic absorption spectra of a series of heteroannular disubstituted ferrocenes proved conclusively that the ferrocenyl nucleus hinders conjugation between the substituents attached to different rings. At the same time, the inductive conductivities of the ferrocenyl ( $\rho_i = 1.385$ ) and phenyl ( $\rho_i = 1.464$ ) nuclei are very similar in their values.<sup>9</sup>

On the other hand, good correlation between  $\log K_x/K_H$  and Taft's  $6_p$  constants indicates that the interaction between the substituent and the ring is identical both in the benzene and in the ferrocene series. In accordance with this, the constants  $6_i$  do not describe the reactivity of all substituted ferrocenes investigated in the oxidation reaction. There are such substituents, however, whose interactions with the aromatic ring are known to be predominantly inductive (alkyl and carboxyl groups). For these compounds the reactivity is described by the equation  $\log K_x/K_H = \rho_i 6_i$ ; ( $r = 0.999$ ,  $\rho_i = -14.53$ ). From the deviation of the points for the substituents  $OCH_3$ ,  $Cl$ ,  $Br$ ,  $T$  and  $C_6H_5$  from this straight line, the proneness

of the above substituents to conjugation with the ferrocene nucleus ( $6_c$  ferr.) was estimated. To the first approximation, the conjugation of substituents with a phenyl- and with a ferrocene ring is identical. Marked deviations in the value of  $6_c$  ferr. from the corresponding values in the phenyl nucleus are observed only in the case halogens, particularly for iodine. These differences are still greater when the carboxyl group acts as a reaction center. A diminishment the electron withdrawing properties of halogens are due to some peculiarities in their interaction with the ferrocenyl nucleus. A considerable hypsochromic shift in the maxima is observed in the absorption spectra of chloro- and bromoferrocenes at  $325m\mu$  and  $440m\mu$ , and in that of iodoferrocene—a still greater hypsochromic shift at  $325n\mu$  and a bathochromic one at  $440m\mu$ .<sup>9</sup> Probably, in haloferrocenes of a dative bonding between the d-electrons of halogens and the nonbonding d-orbit of the iron atom, may be formed which results in an essential increase in the +C — effect of halogens. The characteristics of the reactivity of halogens in haloferrocenes are considered below.

We failed to determine the redox potentials of ferrocene derivatives with strong electron withdrawing substituents nitroferrocene, acylferrocenes, ferrocene aldehyde). By the oxidation in an acidic medium, these compounds do not give characteristic reversible potentiometric curves. A sharp passivation of the ferrocene nucleus in the reactions of electrophilic substitution under the influence of one nitrogroup, a jumpwise decrease in the strength of the metal-ring bond upon transition from weak to strong electron withdrawing substituents point to the existence of such effects for these compounds which have no analogies in the benzene series. The structures of the quinoid type are not realized in the ferrocenyl nucleus.\* A realization of such structures would lead to an essential change in the nature of the bond between the cyclopentadienyl rings and the metal atom. We suppose a bond in the nature of a dative one to be realized. In the excited state between the metal atom and the adjacent strong electron withdrawing substituent at the expense of the electrons of the iron atom, which do not participate appreciably in the formation of the bonds with the rings, and of the free orbitals of the substituent. A most convincing proof of this is the shift of the absorption maximum to longer wavelengths observed at  $440m\mu$  in the case of strong electron withdrawing substituents. The fact is that this maximum is attributed to the d-d

\* This is also conclusively proved by the impossibility of rearrangement into the nucleus in the ferrocene series similar to the Claisen rearrangement of allyl phenyl ether and to the benzidine one.<sup>132</sup>

transition between the levels localized mainly on the iron atom and thus not affected by the substituents in the ring. In fact, for most substituents the shifts do not exceed  $3\text{--}4\text{m}\mu$ . For strong electron withdrawing substituents the shifts reach several tens of  $\text{m}\mu$ . Moreover, a considerable increase in intensity is observed at all wave lengths, probably as a result of diminishing differences between the excited and the fundamental states and an increasing transition probability.<sup>9</sup> An increase in the positive charge on the metal atom results in a decrease in the strength of the metal-ring bond. This effect is most pronounced in the case of compounds in which the substituent carrying a single positive charge bound with the ferrocenyl nucleus (see *Decomposition of the Ferrocene System*).

As a substituent in the ferrocene nucleus and in the benzene ring, ferrocenyl displays pronounced electron donating properties.<sup>24</sup> A comparison of the values of redox potentials of ferrocene, methylferrocene, diferrocenyl and methoxyferrocene shows the ferrocenyl to be a stronger electron donating substituent than the methyl group.

As a substituent in the benzene ring, ferrocenyl displays even more pronounced electron donating properties.<sup>24,33</sup> This is evident from the consideration of the dissociation constants of ferrocenylbenzoic acids, p-ferrocenylphenol and ferrocenylanilines.

From the dissociation constants of substituted benzoic acids the values of Hammett's  $\sigma$  were calculated for ferrocenyl;<sup>24</sup>  $\sigma_p = -0.18$ ;  $\sigma_m = -0.15$ . Thus, unlike phenyl, ferrocenyl remains a relatively strong electron donating substituent also in meta-position. As a substituent in the benzene ring, ferrocenyl possesses a positive inductive effect (since from metaposition the influence of the substituent is mainly inductive).

The conjugation of ferrocenyl with the benzene ring and the carboxyl group as the reaction center is but weakly displayed  $\sigma_c = -0.05 \pm 0.01$ ; i.e. it is half as large as for phenyl as a substituent in the benzene ring (for phenyl  $\sigma_c = -0.10 \pm 0.02$ ).\*

Thus, the influence of ferrocenyl as a substituent is determined by the combination of a strong positive inductive effect and a rather weak positive effect of conjugation. This influence of ferrocenyl as a substituent is reflected also in the properties of compounds with two ferrocenyl nuclei. The first redox potentials  $E_{\text{Fe}}$  of diferrocenyl and compounds with two ferrocenyl nuclei separated by groups differing in their conductivity ( $-\text{CH}_2-$ ,  $-\text{Hg}-$ ,  $-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CH}_2\text{OCH}_2-$ ,  $-\text{CH}_2-\overset{+}{\text{N}}(\text{CH}_3)_2\text{CH}_2-$ ) practically coincide. Thus, there is no appreciable conjugation whatever in differrocenyl. It should be noted that the mercury atom interacts with the ferrocenyl nuclei in such a way as to reduce the electronic density on the iron atoms at the moment of reaction. There appears to be an essential difference in the interaction with the mercury atom of the two phenyl nuclei, on one hand, and of the two ferrocenyl nuclei, on the other.

A comparison of the value of  $E_{\text{Fe}}$  with that of  $E_{\text{Fe}}$  of the corresponding mono-substituted ferrocenes shows that the electron donating influence of the second ferrocenyl nucleus is hardly displayed. From the comparison of the values of  $E_{\text{Fe}}$  and of  $E_{\text{Fe}}$ , it follows that the electron withdrawing influence of the ferricinium

\* The values of  $\sigma_c$  were calculated from the equations<sup>29,30</sup> and  $\sigma_c = \sigma_p - 1.13 \sigma_i$ ; and  $\sigma_c = 2 \sigma_m - 2 \sigma_i$ . The values of  $\sigma_p$  and  $\sigma_m$  for phenyl were taken from the work,<sup>31</sup> of  $\sigma_i$  — from survey.<sup>32</sup> The value of  $\sigma_i = -0.12$  for ferrocenyl was calculated on the basis of redox potentials of ferrocene derivatives, in which the substituent is separated from the nucleus by a methylene group and from the potential of diferrocenylmethane.<sup>24</sup>

cation on the other ferrocenyl nucleus is very great, especially so in the case of diferrocenylmercury.<sup>22</sup>

### *Electrophilic Substitution*

#### *Substitution of Hydrogen*

Ferrocene undergoes sulphonation<sup>34,35</sup> Friedel-Crafts, alkylation,<sup>37</sup> acylation,<sup>34,36,38\*</sup> and phosphorylation<sup>39</sup> as well as mercuration<sup>34</sup> and metalation with organolithium<sup>34</sup> and organosodium<sup>5,42</sup> compounds more readily than benzene. Depending on the conditions of the reaction, either mono- or disubstituted ferrocene derivatives or their mixture is obtained. Alkylation of ferrocene gives a mixture of mono- and polyalkylferrocenes.<sup>37</sup>

Ferrocene interacts with aldehydes (formaldehyde, benzaldehyde, p-dimethylaminobenzaldehyde) in the presence of conc. sulfuric acid to form 1, 2-diferrocenylethane and its derivatives.<sup>†</sup>

An elementary reaction of electrophilic substitution—deuterium exchange occurs in an acidic medium.<sup>43</sup> By studying the kinetics of the isotopic hydrogen exchange in ferrocene and its derivatives, it is possible to estimate quantitatively the change in the reactivity under the influence of substituents in electrophilic substitution as well as to compare it quantitatively with benzene and its corresponding derivatives and with other aromatic systems.<sup>20</sup>

The most convenient donor of deuterium is trifluoroacetic acid. The rate constant of the hydrogen exchange of ferrocene is equal to  $1.6 \times 10^{-4} \text{ sec}^{-1}$  at  $25^\circ\text{C}$ . in a benzene solution (the ratio of ferrocene, deuteriotrifluoroacetic acid and benzene being 1:3:20). Under these conditions, benzene is not exchanged. The rate constant of the hydrogen exchange for toluene under the same conditions is equal to  $3 \times 10^{-8} \text{ sec}^{-1}$ , i.e. the rate of hydrogen exchange for ferrocene is by more than three orders of magnitude higher than that for toluene. The electron withdrawing substituents sharply decrease the rate of hydrogen exchange. In acetylferrocene the hydrogens of the five-membered rings are exchanged 1000 times as slow as in ferrocene.<sup>43</sup> The hydrogen exchange rate for phenyl- and 1,1'-diphenylferrocene is somewhat less than for ferrocene.<sup>44</sup> The electron donating substituents enhance the exchange rate. Alkylferrocenes are exchanged about 10 times as fast as ferrocene (rate constants,  $\text{sec}^{-1}$ : methylferrocene —  $8.8 \times 10^{-6}$ ; ethylferrocene —  $8.8 \times 10^{-6}$ ; 1, 1'-diethylferrocene —  $3.7 \times 10^{-5}$ ; ferrocene —  $9.1 \times 10^{-7}$ ).

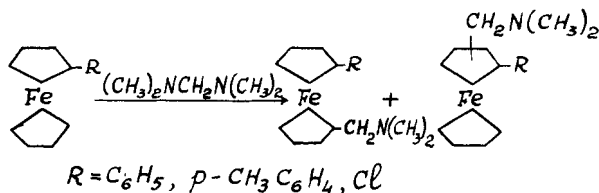
Hydrogens of iodoferrocene are not exchanged for deuterium, but iodine is. A deuterioferrocene is obtained as a ferricinium cation and a complex of iodoferrocene with iodine is formed in addition (it contains no deuterium). An isotopic hydrogen exchange occurs in bromo- and chloroferrocenes along with a dehalogenation.<sup>44</sup>

A decrease in the reactivity in the electrophilic substitution of hydrogens in five-membered rings due to the influence of electron withdrawing substituents is observed not only in deuterium exchange, but also in other electrophilic reactions. Thus, acylation and sulfonation of ferrocene derivatives with electron withdrawing substituents ( $\text{CH}_3\text{CH}_2$  — <sup>45,48</sup>  $\text{CH}_3\text{COO}$ , <sup>63-65</sup>  $\text{Br}$ , <sup>50</sup>  $\text{C}_6\text{H}_5$ , <sup>47</sup>) occurs not so readily as in the case of ferrocene and predominantly into the free five-membered ring. N-acetylaminoferrocene and ferrocenylamine are acetylated with acetic an-

\* The acylation of ferrocene with propionic anhydride in the presence of  $\text{H}_3\text{PO}_4$  gives homoannular dipropionylferrocene (m.p.  $43.5$ – $44.5^\circ$ ), along with propionylferrocene.<sup>33</sup>

† 1,2-diphenyl-1,2-diferrocenylethane upon chromatography on  $\text{Al}_2\text{O}_3$  is partly converted to benzoylferrocene.<sup>113</sup> For the use of adsorption chromatography when working with ferrocene derivatives, see.<sup>113</sup>

hydride in the presence of phosphoric acid also mainly into the unsubstituted five-membered ring.<sup>52</sup> Aminomethylation of phenyl-, p-tolyl- and chloroferrocene also occurs mainly into the free ring.<sup>49</sup> The ratio of hetero and homoannular

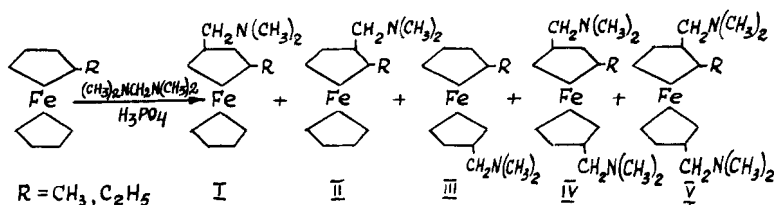


isomers is approximately 5:1. In the case of phenylferrocene, two homoannular isomers were isolated.<sup>49\*</sup>

Ferrocene derivatives with two electron withdrawing substituents (1, 1'-diacylferrocenes and 1, 1'-ferrocenedisulfonic acid 1, 1'-di (p-nitrophenyl) ferrocene) display inertness in reactions of electrophilic substitution.<sup>5,10,46</sup> Only the sulfonation of 1, 1' - di(carbomethoxy) ferrocene was effected.<sup>46</sup> Under the action of sulfur trioxide the acetyl groups in 1, 1'-diacetylferrocene are replaced by sulfonic acid groups.<sup>46</sup>

The electron donating substituents favor the electrophilic substitution of the hydrogens of the ferrocene nucleus. Thus, alkylferrocenes undergo the aminomethylation<sup>51</sup> Friedel-Crafts alkylation<sup>37</sup> and acylation<sup>5,48</sup> more readily than ferrocenes, homoannular isomers being predominantly formed in the case of mono-alkylferrocenes.

Dimethylaminomethylation of methyl- and ethylferrocenes produces a mixture of isomeric mono- (I-III) and di (N, N-dimethylaminomethyl) alkylferrocenes (IV, V).<sup>51</sup>



The yield of di (N, N-dimethylaminomethyl) alkylferrocenes (IV, V) is 7-10 per cent. Under the same conditions, ferrocene gives only mono-(dimethylaminomethyl) ferrocene. Monoaminomethylated alkylferrocenes (I-III) are obtained with a yield of 70-80 per cent. The yield of homoannular isomers (I, II) is five-six times as large that of heteroannular ones (III) and that of the 1, 3-isomer (I) two-three times as large as the yield of the 1, 2-isomer (II). The conclusion concerning the structure was drawn on the basis of the infrared spectra and adsorption capacity.\*

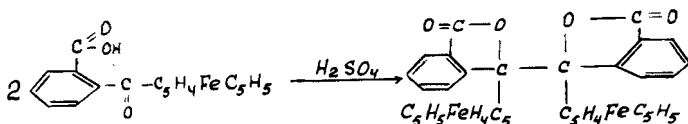
The intramolecular acylation was effected in the instance of  $\omega$ -carboxypropyl-

\* From methiodide of 1, 1' -(N, N-dimethylaminomethyl) phenylferrocene and 1, 1' -(N, N-dimethylaminomethyl)-p-tolylferrocene were obtained 1, 1'-methylphenylferrocene and 1, 1'-methyl-p-tolylferrocene.<sup>47</sup>

\* Methiodide of mono(N, N-dimethylaminomethyl) ethylferrocenes and di(N, N-dimethylaminomethyl) ethylferrocenes were reduced to corresponding di- and trialkylferrocenes and hydrolyzed to carbinols.<sup>51</sup> From methiodide of (N, N, -dimethylaminomethyl)-methylferrocene were obtained 1, 2 and 1,3-dimethylferrocene and, 1, 3, 1'-trimethylferrocene.<sup>51</sup>

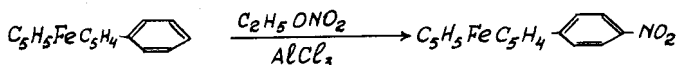


ferrocene<sup>8</sup> and di( $\omega$ -carboxypropylferrocene.<sup>8</sup> o-Carboxybenzoylferrocene, under the conditions of cyclization is converted to 3, 3'-diferricenyl-3, 3'-diphtalide.<sup>55,96</sup>



Alkylferrocenes are metalated with n-butyllithium in tetrahydrofuran<sup>53</sup> and with n-amylsodium<sup>5</sup> into a free five-membered ring. The reaction occurs less readily than in the case of ferrocene.<sup>53</sup>

It is impossible to effect nitration and halogenation of ferrocene since these reactions involve the oxidation of ferrocene to ferricinium, which does not enter into the reaction of electrophilic substitution,<sup>47,92,93</sup> including the reaction of the isotopic hydrogen exchange.<sup>43</sup> It should be noted that ferricinium is rather stable under the conditions of nitration. Thus, the treatment of phenylferrocene with ethylnitrate in the presence of  $\text{AlCl}_3$  produced p-nitrophenylferrocene.<sup>47</sup>



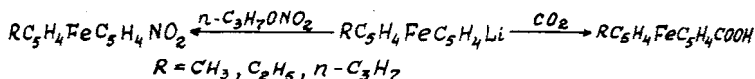
The formation of p-isomer is rather unexpected since, being a substitute in the benzene ring, ferricinium might have been supposed to act as an electron acceptor. In this connection it should be noted the Friedel-Crafts acetylation of diferrocenyl involves the substitution (at least predominantly) into the free five-membered ring and bis-1, (1'-acetylferrocenyl) is formed as a basic product.<sup>74</sup> The electron withdrawing influence of ferrocenyl in this reaction is probably due to the formation of a complex with  $\text{AlCl}_3$ .

### Substitution of Lithium

On account of their availability, the lithioferrocenes play a most important part in the synthesis of its derivatives. From lithioferrocene were obtained ferrocenecarboxylic<sup>34</sup> and ferrocene-boric<sup>56,57</sup> acids, ferrocenylamine,<sup>61</sup> azoferrocene,<sup>58,59</sup>  $\alpha$ -pyridylferrocene,<sup>60</sup> ferrocenylazide,<sup>62\*</sup> diazoaminoferrrocene<sup>62</sup> and benzenediazoaminoferrrocene,<sup>62</sup> dimethylallylferrocenylsilane.<sup>109†</sup>

From 1, 1'-dilithioferrocene were obtained ferrocenedicarboxylic<sup>34</sup> and -diboric acids,<sup>56,57</sup> di-( $\alpha$ -pyridyl) ferrocene<sup>60</sup> and ferrocenylendiazide.<sup>62</sup>

From lithio(alkyl)ferrocenes were synthesized alkylcarboxyferrocene and nitro(alkyl)ferrocenes.<sup>53</sup>



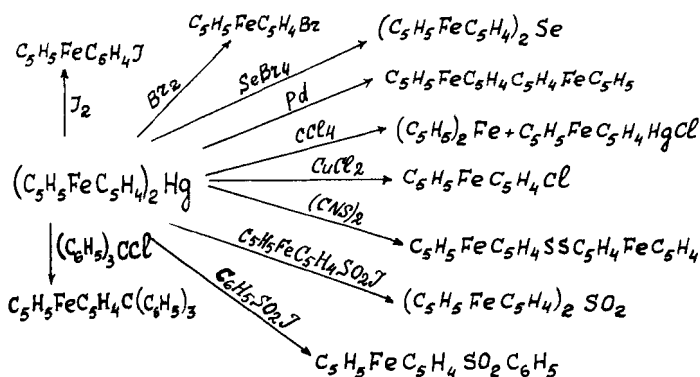
Dilithio(alkyl)ferrocenes were converted to alkyl dicarboxyferrocene and their methyl ethers.<sup>53</sup>

\* Ferrocenylazide reacts with the dimethyl ether of exo-cis-3, 6- $\Delta^4$ -tetrahydrophtalic acid to form the corresponding triazoline and with phenylmagnesium bromide to form benzenediazoaminoferrrocene.<sup>62</sup>

† The addition of silicon-hydrides to dimethylallylferrocenylsilane was described in.<sup>109</sup>

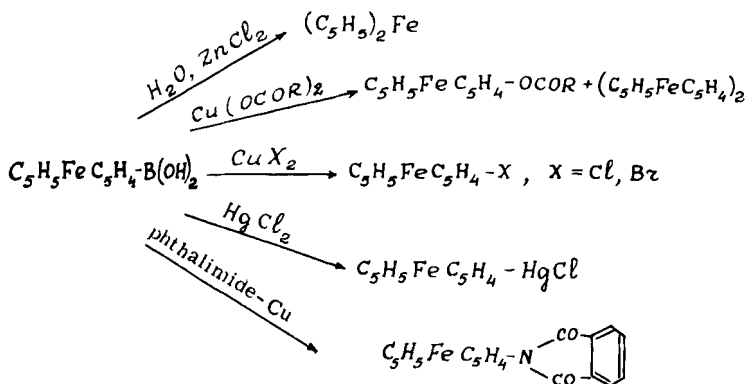
## Substitution of Mercury

The high nucleophilic activity of carbon atoms of ferrocene, which is responsible for the ready electrophilic substitution of the hydrogens in the five-membered rings, can be found also in the properties of mercury derivatives of ferrocene. The exchange of mercury for other groups occurs quite readily. In this way, a large series of ferrocene derivatives was obtained.<sup>69-71</sup> In particular, thus were obtained for the first time the haloferrocenes.<sup>4,76</sup>

Substitution of B(OH)<sub>2</sub>-Group

In their properties ferrocenemono- and diboric acids are similar to arylboric acids.

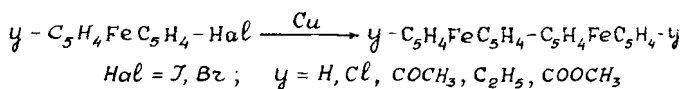
The substitution of B(OH)<sub>2</sub>-group occurs very readily both in mono- and diboric acids.<sup>56,57,72-75</sup> By this method one of the authors together with Sazonova and Drozd obtained mono- and diacetoxoferrocene<sup>57,75</sup> and mono- and 1,1'-dichloroferrocene. Below a scheme of transformations of ferroceneboric acid is given.



1,1'-disubstituted ferrocenes were obtained from ferrocenediboric acid in a similar manner.

By treating 1,1'-ferrocenediboric acid with copper salts it is possible to replace





Heating bromo- and 1,1'-dibromoferrocene with copper produced 1,1'-polyferrocenylenes<sup>74</sup> (which are diamagnetic)<sup>79</sup>

### Homolytic Reactions

Ferrocene reacts with aromatic diazocompounds to form mono- and diarylferrocenes with high yields.<sup>34,61,91</sup> The interaction of ferrocene with heterocyclic diazocompounds obtained from 2-methyl-6-aminobenzothiazole and 2-methyl-5-aminobenzothiazole gave 2-methyl-6- and 2-methyl-ferrocenybenzothiazoles from which thiocyanines were synthesized.<sup>105</sup> Bisdiazocompounds form polymers with ferrocene.<sup>106,108</sup>

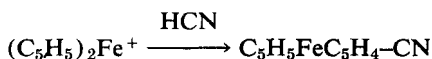
The action of diazocompounds upon p-tolyl-, methyl-, ethyl-, acetyl- and carbo-methoxyferrocene produced a mixture of arylation products (with low yields).<sup>11</sup> 1,1'-Diacylferrocenes react with diazocompounds decomposing the ferrocene nucleus (see above).

The interaction of ferrocene with trichloromethyl radical, which is obtained upon thermal decomposition of trichloroacetic acid in the presence of copper chloride after hydrolysis leads to the formation of carboxyferrocene.<sup>104</sup>

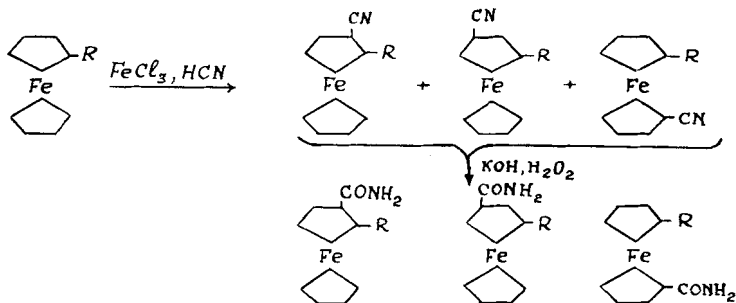
The action of tert-butyl peroxide upon ferrocene and its homologues produced polyferrocenylenes.<sup>102,103,79</sup>

### Ricochet Substitution

Ferricinium salts (or ferrocene in the presence of ferric chloride are cyanated with hydrocyanic acid in tetrahydrofurane<sup>92,93</sup> to form a cyanoferrocene (80-85 per cent yield).



The effect of substituents in the ferrocene nucleus upon the reaction of cyanation is the same as in electrophilic substitution. The electron withdrawing substituents (p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, Cl, Br, CN and especially C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>, CH<sub>3</sub>CO, NO<sub>2</sub>) hinder cyanation and favor the formation of predominantly, or exclusively, heteroannular isomers.<sup>92,94</sup> Cyanation of ferrocene derivatives with electron donating substituents (CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub>) gives predominantly homoannular isomers (a mixture of nitriles of isomeric alkylcarboxyferrocene was converted to a mixture of amides and separated by chromatography). The structure of the isomers was determined on the basis of the infrared and ultraviolet spectra, from the values of redox potentials and by comparing their adsorption on alumina.



m.p., R = CH <sub>3</sub> ,	119–120°,	146–147°,	145–146°,
C <sub>2</sub> H <sub>5</sub> ,	95–96°,	161–162°,	141–142°,

The reaction of cyanation of ferricinium salts cannot be considered to be a reaction of bimolecular nucleophilic substitution for the carbon atom in the five-membered ring. The reaction begins with the cyan attacking the iron atom of the ferricinium cation, which involves the elimination of a proton from the molecule of hydrocyanic acid. This is evidenced by the change in pH of the reaction mixture (pH decreases by 0.5–0.8). Then, the cyan group shifts from the iron atom to the carbon atom of the five-membered ring, which is accompanied by a simultaneous reduction of iron (ricochet substitution).

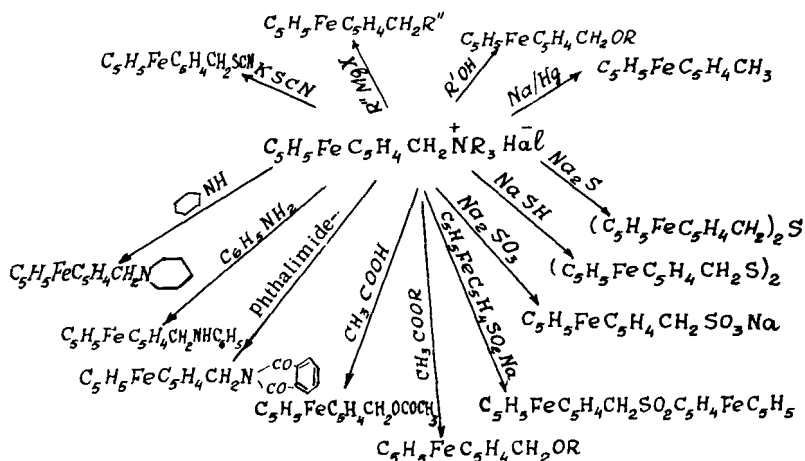
Ferricinium salts also react with acetic anhydride and acetylacetone to form mono- and diacetylferrocenes and tetraferrocenylpentane, respectively. But the mechanism of these reactions is not yet clear. It is possible that in the case of reaction with acetic anhydride we have to deal with a ricochet substitution.

### Properties of Compounds Containing a Ferrocenylmethyl Group

The availability and high reactivity of trialkyl (ferrocenylmethyl) ammonium salts permitted to obtain a number of compounds containing a ferrocenylmethyl group, to study their properties and to determine the effect of ferrocenyl on the stability of the adjacent cationic, radical and anionic centres.

### Substitution of N<sup>+</sup>R<sub>3</sub>-Group in trialkyl(ferrocenylmethyl)ammonium Chloride

Ferrocenylmethylation with trialkyl(ferrocenylmethyl)ammonium salts is an important method of preparing ferrocene derivatives. This method was used to synthesize a large series of substituted ferrocenes.<sup>80–88</sup>



The rate of hydrolysis\* ( $C_5H_5FeC_5H_4CH_2N(CH_3)_2CH_2R$ ) (1) ( $R = H$ ,  $CH = CH_2$ ,  $C_6H_5$ ,  $COONa$ ,  $C_5H_4FeC_5H_5$ ) practically does not depend on the

\* The rate of hydrolysis was estimated from the yield of ferrocenylcarbonyl after the first ten minutes of reaction at 100° in an alkaline aqueous and a 50 per cent aqueous-dioxane solution, as well as in neutral and acid aqueous solutions. For the purposes of synthesis it was expedient to use salt 1, in which  $CH_2R = CH_2C_6H_5$ .<sup>84,85</sup>

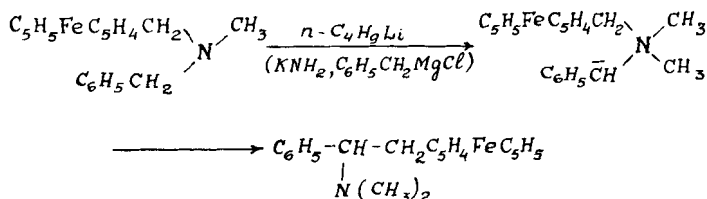
anion of the salt and on the alkali concentration, but rapidly rises with increasing electron withdrawing properties of the radical  $\text{CH}_2\text{R}$ .† Some increase in the rate is observed also with increasing chain length for salts (I) with normal alkyl radicals  $\text{CH}_2\text{R}$  ( $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, n\text{-C}_8\text{H}_{17}$ ), evidently due to rising Brown's B-strain. The hydrolytic decomposition of salts (I) is accelerated by mineral acids in small concentrations. On the basis of all these facts, we may consider the hydrolysis of salts (I) to follow the mechanism  $\text{SN}_1$  via an intermediate formation of the ferrocenylmethyl cation.<sup>84,85</sup>

Salt I,  $\text{CH}_2\text{R} = \text{CH}_2\text{C}_6\text{H}_5$ , smoothly decomposes to form ferrocenylcarbonyl. Thus, the ferrocenylmethyl cation is much more stable than the benzyl cation<sup>84,88</sup> (this was noted earlier by other investigators).

The attempts to obtain salts (I), which have a branching in  $\text{CH}_2$ -group of radical  $\text{CH}_2\text{R}$  or in  $\alpha$ -carbon atom of ferrocenylalkyl group failed. When N-(ferrocenylmethyl)aniline, N-methyl-N-(ferrocenylmethyl)aniline and ( $\beta$ -phenyl- $\alpha$ -ferrocenylethyl)dimethylamine are treated with methyl iodide no quaternary ammonium salts are isolated, but some substances are obtained whose formation can be well accounted for, if it is assumed that the ammonium salts are decomposed at once with the elimination of ferrocenylalkyl cations.<sup>85</sup>

*Rearrangement of Dimethyl(benzyl)ferrocenylmethyl-ammonium Chloride  
under the Action of Nucleophilic Reagents*

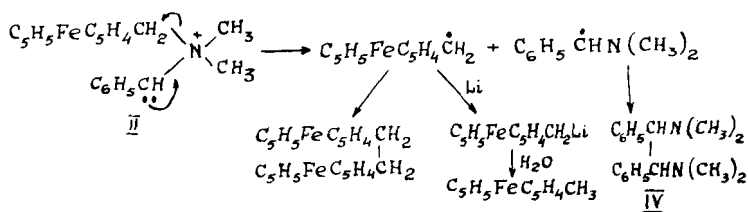
Under the action of butyllithium, potassium amide and even benzylmagnesium chloride, dimethylbenzyl (ferrocenylmethyl) ammonium chloride (I) is rearranged to ( $\alpha$ -phenyl- $\beta$ -ferrocenylethyl) dimethylamine (III).



Thus, metalation goes into methylene of the benzyl group and, consequently, phenyl stabilized the adjacent anionic center to a greater extent than ferrocenyl.<sup>88</sup>

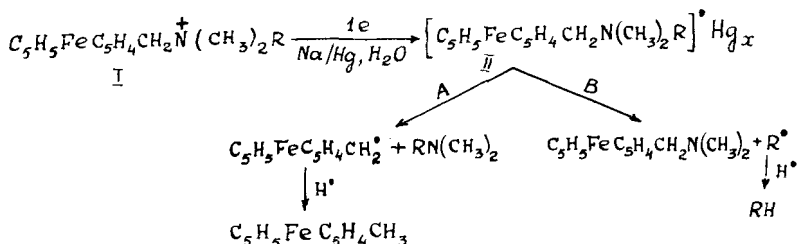
The rearrangement of salt (I) under the action of butyllithium, in addition to amine III, gives methylferrocene, N,N, N,N-tetramethyl- $\alpha, \beta$ -diphenylethylenediamine (IV) and small amounts of 1,2-diferrocenylethane. The formation of these compounds cannot be accounted for on the basis of the reactions of ylides, described earlier. Evidently, a new type of ylide isomerization is observed in this case, which consists in the intramolecular one-electron reduction of nitrogen in ammonium at the expense of the electron pair of the anionic center in ylide (II), resulting in a homolytic decomposition. This is followed by the dimerization of the radicals and the formation of ferrocenylmethyl lithium.<sup>88</sup>

† Dimethyl-bis-(ferrocenylmethyl)ammonium bromide is hydrolyzed approximately as fast as dimethylallyl(ferrocenylmethyl)ammonium bromide. This gives ground to believe that ferrocenylmethyl and allyl are similar in their electron withdrawing properties, or that, possibly, the former is a weaker electron acceptor than the latter, if the F-strain is taken into consideration.



### Homolytic Reactions of Quaternary Ammonium Salts Containing a Ferrocenylmethyl Group

The reduction of quaternary ammonium salts (I) with sodium amalgam appears to proceed in a manner similar to that of the electrochemical reduction of ammonium salts. The first reaction step is the formation of ammonium amalgam. The intermediate product—the ammonium radical (II) is unstable and decomposes homolytically along two directions (A and B).

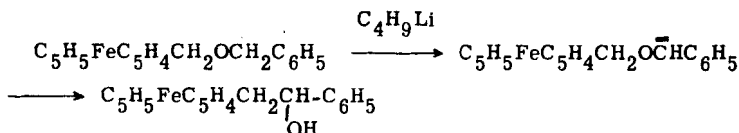


The direction of decomposition of radical (II) is determined mainly by a relative stability of the groups eliminated from nitrogen as a radical and permits to evaluate approximately the stability of these radicals.

The investigation<sup>86</sup> of the reduction of salts (I),  $R = CH_3$ ,  $CH_2 = CHCH_2$  and  $C_6H_5CH_2$ , with sodium amalgam shows that the yields of methylferrocene (direction A) decrease sharply in this series of salts (89, 30 and 1 per cent, respectively), while those of N,N-dimethylaminomethylferrocene (direction B) greatly increase (1, 26 and 64 per cent, respectively). This indicates that the ferrocenylmethyl group is eliminated from the nitrogen of quaternary ammonium salt much more readily than the methyl group, about as readily as the allyl group and much less readily than the benzyl group. Consequently, the ferrocene nucleus stabilizes the adjacent radical center to a lesser degree than the benzene on.<sup>86</sup> The study<sup>87</sup> of the interaction of salts (I),  $R = n-C_3H_7$ ,  $CH_2 = CHCH_2$ ,  $C_6H_5CH_2$  and  $C_5H_5FeC_5H_4CH_2$ , with organomagnesium compounds in the presence of  $CoCl_2$  leads to the same conclusion.

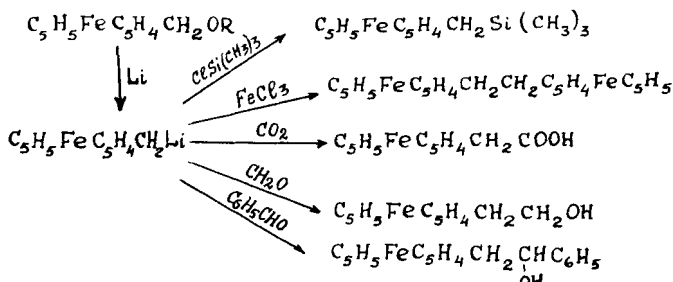
### Ethers of Ferrocenylcarbinol, Ferrocenylmethyllithium

Ethers of ferrocenylcarbinol can be readily obtained by the interaction of corresponding alcohols with ferrocenyl carbinol in the presence of acids,<sup>65,113</sup> or with trialkyl(ferrocenylmethyl)ammonium salts.<sup>67</sup> The rearrangement of the benzylferrocenylmethyl ether under the action of butyllithium leads to the formation of 1-phenyl-2-ferrocenylethanol-1.<sup>89</sup>



This confirms the above conclusion that ferrocenyl stabilizes the adjacent carbanionic center to a lesser extent than phenyl.

Ethers of ferrocenylcarbinol react with lithium in tetrahydrofuran like benzyl ethers to form ferrocenylmethylolithium with a good yield.<sup>65,66,68</sup> The latter is a convenient reagent to be used to introduce the ferrocenylmethyl group.



No reactions involving the transfer of the reaction center are present in the case of ferrocenylmethylolithium<sup>66</sup> in contrast to benzylolithium.

Like ferrocenylcarbinol ethers, the methyl ethers of methyl- and phenyl(ferrocenyl)carbinol react with lithium to form corresponding organolithium compounds.<sup>68</sup>

#### *Reactions of Some Functional Derivatives of Ferrocene. Amino- and Oxyferrocenes*

In most cases, the functional groups in the ferrocene nucleus show a reactivity typical of aromatic compounds. Thus, the interaction of organomagnesium compounds with ferrocene aldehyde, acetyl- and benzoylferrocene produced a number of alcohols of the ferrocene series.<sup>66,113,115,116</sup> The condensation of ferrocene aldehyde with 2-methylbenzothiazole iodoethylate was described in,<sup>105</sup> that with 1,3,3-trimethyl-2-methylenindoline and aromatic amines in.<sup>114</sup>

3(5)-Methyl-5(3)-ferrocenylpyrazole was prepared from acetylacetoferrocene and the interaction of ferrocene and pyrazole systems was considered.<sup>118</sup>

Carbomethoxy- and 1,1'-dicarbomethoxyferrocene were reduced to hydroxymethyl- and 1,1'-di(hydroxymethyl) ferrocene and to methyl- and 1,1'-dimethylferrocene.<sup>42,80</sup> 1,1'-Acylcarboxyferrocene were reduced<sup>63</sup> by the Clemmensen method to alkylcarboxyferrocene and then to alkylferrocenylcarbinols  $\text{HOCH}_2\text{-C}_5\text{H}_4\text{FeC}_5\text{H}_4\text{R}$ ,  $\text{R} = \text{C}_2\text{H}_5$ ,<sup>20</sup> 1.6079;  $\text{n-C}_3\text{H}_7$ ,<sup>20</sup> 1.5932;  $\text{n-C}_4\text{H}_9$ , m.p. 42–43°;  $\text{C}_6\text{H}_5\text{CH}_2$ , m.p. 54.5–55.5°. By the interaction of carbomethoxy- and 1,1'-dicarbomethoxyferrocene with organomagnesium compounds containing silicon, alcohols and ketones of the ferrocene series containing silicon were prepared.<sup>117</sup>

Cyanoferrocene displays reactions typical of nitriles, but these occur under more rigorous conditions than the corresponding reactions of nitriles of the benzene series.<sup>97</sup> The interaction of cyanoferrocene with lithioferrocene produces diferocenylketone, from which triferocenylcarbinol is obtained and then—triferocenylmethane.<sup>98</sup>

In contrast to the compounds of the benzene series, the sulfonic acid group in ferrocenesulfonic acids does not enter into exchange reactions,<sup>40</sup> but preparation

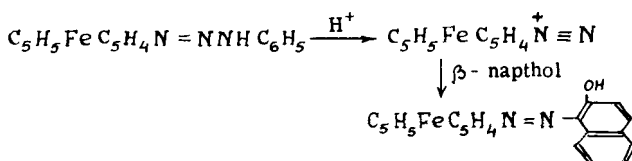


of the derivatives of ferrocenesulfonic acids<sup>35,40,46</sup> and the reduction of the sulfo group to  $\text{SO}_2\text{H}$ - and to  $\text{SH}$  groups<sup>40,41</sup> can be effected in about the same manner as in arylsulfonic acids. Like benzenesulfinic acid, ferrocenesulfinic acids react with mercuric chloride and halides to form mercury derivatives and ferrocenylsulfones, respectively.<sup>41</sup>

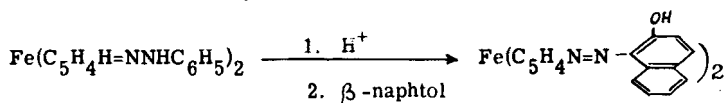
Ferrocenylamine was prepared by the interaction of lithioferrocene with *O*-bezyhydroxylamine,<sup>61</sup> by the catalytic reduction of azoferrocene,<sup>59,120</sup> by the substitution of halogen in haloferrocene by the phthalimide group with a subsequent hydrolysis<sup>77</sup> and by the reduction of ferrocenylazide.<sup>62</sup>

1,1'-Aminoethylferrocene was obtained from 1, 1'-phthalimidoethylferrocene<sup>50</sup> as well as from 1,1'-nitroethylferrocenylamine, and identified as 1,1'-acetaminoethylferrocene. Ferrocenylamine is a 42 times stronger base than aniline, but its basicity is by far nearer to aromatic amines than to aliphatic ones ( $K_b = 4.69 \times 10^{-11}$  in 80 per cent ethanol at  $25^\circ\text{C}$ .). The acetyl,<sup>61,77</sup> benzoyl,<sup>61</sup> mono- and dialkyl (by alkylation with triethyloxonium) derivatives<sup>15</sup> of ferrocenylamine were also obtained. The condensation of ferrocenylamine with nitrosobenzene gives benzeneazoferrocene (basic product) and benzeneazoxyferrocene.<sup>120</sup>

The attempts to diazotize ferrocenylamine failed. Ferrocenyldiazonium salts were prepared via benzenediazoaminoferrrocene.<sup>62,119</sup> Like aromatic diazocompounds, they couple with  $\beta$ -naphthol.<sup>119</sup>



1,1'-Diaminoferrrocene was prepared by the reduction of 1,1'-ferrocenylazide. It is rapidly oxidized in the air and was identified as dimethyl 1,1'-ferrocenylene-bis-carbaminat.<sup>62</sup> The bis-diazocompound obtained from 1,1'-bisbenzenediazoaminoferrrocene couples with  $\beta$ -naphthol to give the bis-azocompound.<sup>119</sup>



Azoferrrocene was obtained by treating lithioferrocene with nitrous oxide. The study of its interaction with reagents which convert azobenzene to benzidine as well as the investigation of the behavior of azoferrrocene under the conditions of preparation of hydrazo compounds and of their subsequent rearrangement to benzidine showed that the rearrangement of the benzidine type is not realized in the ferrocene series.<sup>58,59</sup> Being a substituent in the benzene ring, ferrocenyl hinders the benzidine rearrangement;<sup>99,100</sup> under the conditions of a benzidine rearrangement, *m*- and *p*-ferrocenylhydrazobenzenes are predominantly disproportionated rather than rearranged.

Hydroxyferrocene was prepared by the hydrolysis of acetoxyferrocene.<sup>57,75</sup> Like phenol, it has weak acid properties, decomposes when kept in the air.  $K_a = 6.9 \times 10^{-11}$  in five per cent  $\text{C}_2\text{H}_5\text{OH}$  at  $17^\circ\text{C}$ . (under the same conditions for phenol  $K_a = 1, 2 \times 10^{-10}$ ). Hydroxyferrocene readily undergoes Schotten-Bauman benzoylation and gives methoxyferrocene with dimethylsulfate. Some other ethers and esters of hydroxyferrocene were also obtained.<sup>57,75,101</sup> Claisen rearrangement does not occur in the case of allyl ether of hydroxyferrocene.<sup>101,132</sup>

1,1'-hydroxyacetylferrocene was obtained in a manner similar to that for hydroxyferrocene, it is somewhat more stable in air than hydroxyferrocene, but is readily oxidized in solutions.<sup>50</sup>

1,1'-Dihydroxyferrocene was obtained by the hydrolysis of 1,1'-diacetoxyferrocene; it is unstable in air; its ethers and esters are quite stable.<sup>57,101</sup> The oxidation of dihydroxyferrocene by atmospheric oxygen produces a dimer of cyclopentadienone.<sup>57,101</sup>

#### *X-ray Analysis, Spectroscopy and Other Investigations*

An X-ray analysis was made of 1,1'-diacylferrocenes,<sup>128</sup> ferrocenedisulfonyl chloride,<sup>122</sup> differocenylium, its derivatives and terferrocenylium.<sup>74,121</sup>

The spectra of acyl- and 1,1'-diacylferrocenes were studied in ultraviolet and visible regions;<sup>96,124</sup> the infrared spectra of various ferrocene derivatives were obtained;<sup>96,112,123,126</sup> the integral intensities of the infrared absorption bands of some characteristic vibrations of cyclopentadienyl ring<sup>126</sup> and of some functional groups<sup>127,128</sup> in the ferrocene derivatives were determined.

The X-ray spectra of ferrocene and polyferrocenes were studied.<sup>130</sup>

An electronographic investigation of a ferrocene molecule was made.<sup>129</sup>

Some calculations of the electronic structure of the ferrocene molecule were carried out.<sup>131</sup>

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