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Abstract

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DIRECT CYANATION OF FERRICINIUM SALTS

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Ferrocene is readily oxidized in acidic medium, forming ferricinium salts $(C_5H_5)_2\overset{+}{F}eX^-$. The properties of ferricinium salts, in contrast to ferrocene itself ([1,2]), have been little studied. Thus, the reduction ([3–5]) of ferrocene, arylation with diazonium salts ([6]), and the formation of pentahalocyclopentane under the action of halides ([7]) have been described.

In the present work we studied reactions involving replacement of hydrogens in ferricinium salts. We used ferricinium ferrichloride $(C_5H_5)_2\overset{+}{F}eFeCl_4^-$ and ferricinium ferribromide $(C_5H_5)_2\overset{+}{F}eFeBr_4^-$.

In attempts to carry out electrophilic substitution reactions that proceed readily with ferrocene itself—acylation, sulfonation, and mercuration—we were unable to obtain substitution products under those (and even more vigorous) conditions in which ferrocene reacts. Usually 60–85% of ferrocene was recovered, calculated on the ferricinium salt taken into the reaction. The passivity of the ferricinium cation in electrophilic substitution reactions is not unexpected, since the positive charge, irrespective of whether it is localized on the iron atom or delocalized over the entire molecule*, will hinder electrophilic attacks.

It was natural to try to carry out nucleophilic substitution reactions with the ferricinium cation. However, it turned out that very many nucleophilic reagents cannot be used, since these substances, being reducing agents or bases, convert the ferricinium cation into ferrocene. Thus, ethylmagnesium and phenylmagnesium bromides reduce ferricinium ferrichloride to ferrocene in 85–90% yield. In the case of phenylmagnesium bromide, diphenyl was isolated as the second reaction product:

$$2C_6H_5MgBr+(C_5H_5)_2Fe^+FeCl_4^- \rightarrow (C_5H_5)_2Fe+C_6H_5-C_6H_5+FeCl_2+MgCl_2+MgBr_2.$$

When ferricinium ferrichloride is treated with diethylamine in absolute ether, ferrocene is likewise obtained in 88% yield.

The only substitution reaction that we have so far succeeded in carrying out by the action of a nucleophilic reagent on the ferricinium cation is cyanation. When potassium cyanide is allowed to act on aqueous solutions of ferricinium ferribromide, ferrocenecarboxylic acid nitrile is formed in low yield (3%). Such a low yield of the nitrile could be explained by the alkaline reaction of the aqueous solution of potassium cyanide (as already indicated, in alkaline medium the ferricinium cation is converted into ferrocene ([5])). Indeed, when the reaction was carried out in acidic medium, the yield of nitrile increased somewhat (to 6%), but was still too low for the reaction to be of preparative interest.

* According to calculations by E. M. Shustorovich and M. E. Dyatkina ([8]), the positive charge in the ferricinium cation is delocalized: charges of +0.2 are present on the cyclopentadienyl rings, and a charge of +0.6 is present on iron.

The yield of ferrocenecarboxylic acid nitrile increased sharply and amounted to more than 50% when a solution of liquid hydrocyanic acid in dry tetrahydrofuran was used:

$$(C_5H_5)_2Fe^+\ FeCl_4^- \xrightarrow[THF]{\text{liq. HCN}} C_5H_5FeC_5H_4CN.$$

It should be noted that the nitrile is isolated from the reaction mixture in the reduced state, and not as a cation. When the reaction was carried out in liquid hydrocyanic acid without tetrahydrofuran, the yield of nitrile was less than 5%.

We further established that ferrocenecarboxylic acid nitrile is obtained in a yield of more than 80% if the ferricinium salt is replaced by a mixture of ferrocene and anhydrous $FeCl_3$.

We applied the reaction we found to the cyanation of ferrocene derivatives and established that cyanation by the action of liquid HCN in tetrahydrofuran in the presence of $FeCl_3$ is a good preparative method for the synthesis not only of ferrocenecarboxylic acid nitrile*, but also of previously undescribed nitriles of substituted ferrocenecarboxylic acids.

Thus, from methyl- and ethylferrocene we obtained the nitriles of methyl- and ethylferrocenecarboxylic acids in yields of 36 and 53%, respectively:

$$C_5H_5FeC_5H_4R \xrightarrow[THF]{FeCl_3,\ \text{liq. HCN}} C_5H_5FeC_5H_3(R)CN,$$

$$R = CH_3 \text{ or } C_2H_5.$$

In the IR spectra of these nitriles** there are intense absorption bands in the regions 1000 and 1100 cm^{-1}, indicating the presence of an unsubstituted cyclopentadienyl ring ([14]). Consequently, the nitrile group enters (at least predominantly) the cyclopentadienyl ring bearing an electron-donating substituent. The relative positions of the cyano and alkyl groups have not been established.

Ethylferrocenecarboxylic acid nitrile was hydrolyzed to the corresponding homoannular ethylferrocenecarboxylic acid.

On cyanation by the method described above of chloroferrocene and ferrocenecarboxylic acid nitrile, we obtained heteroannular chloroferrocenecarboxylic acid nitrile and heteroannular ferrocenedicarboxylic acid dinitrile in yields of 75 and 23%, respectively:

$$XC_5H_4FeC_5H_5 \xrightarrow[THF]{FeCl_3,\ \text{liq. HCN}} XC_5H_4FeC_5H_4CN,$$

$$X = Cl \text{ or } CN.$$

The absence of an unsubstituted cyclopentadienyl ring in the compounds obtained was proved spectroscopically ([14]). It follows from this that electron-acceptor substituents (Cl, CN) hinder cyanation of the cyclopentadienyl ring to which they are attached, and the CN group enters the free ring.

As already stated, in attempting to cyanate the ferricinium cation we proceeded from the assumption that the latter is capable of nucleophilic substitution reactions. However, the influence of electron-donating and electron-accepting substituents proved to be the same as in electrophilic substitution. This fact is hardly compatible with our initial assumption. The experiments we carried out do not provide sufficient material for establishing the reaction mechanism. It is evident only that the reaction does not begin with attack by the CN anion on one of the carbon atoms of the cyclopentadienyl rings.

* The methods described in the literature for the synthesis of ferrocenecarboxylic acid nitrile are multistage ([9–12]), or give very low yields, as in the case of the action of cyanogen bromide on ferrocene ([13]).

** We express our gratitude to L. A. Kazitsyna for recording the IR spectra.

Regarding the mechanism of the reaction, two assumptions may be put forward. It is possible that a bond is first formed between the CN anion and the iron atom of the ferricinium cation; then a proton attacks one of the hydrogens of the cyclopentadienyl rings, which is split off in the form of hydridic hydrogen and may go toward reduction of the ferricinium cation, while CN combines with a carbon of the cyclopentadienyl ring. It is possible that all stages occur simultaneously within a single reaction complex (or cyclic transition state).

The second assumption is that, in the present case, a specific electrophilic (or homolytic) substitution takes place, and the reaction occurs between ferrocene and the cation CN^+ (or the radical $CN\cdot$). The role of the ferricinium cation (or ferric chloride) would then consist in converting the CN anion into a cation (or radical).

Experimental Part

Preparation of ferricinium ferrichloride. To a solution of 37.2 g (0.2 mole) of ferrocene in 600 ml of dry ether was added a suspension of 65 g (0.4 mole) of anhydrous ferric chloride in 300 ml of ether. The blue-green precipitate of ferricinium ferrichloride that separated was filtered off and washed several times with ether, then with a small amount of absolute alcohol, and again with ether.

$C_{10}H_{10}Cl_4Fe_2$.	Found %:	C 30.67; 30.55; H 2.70; 2.63
	Calculated %:	C 31.29; H 2.63

The ferricinium ferrichloride obtained in this way was used for syntheses without further purification. A purer preparation was obtained after recrystallization from absolute alcohol.

$C_{10}H_{10}Cl_4Fe_2$	Found %:	C 31.03; 30.88; H 2.68; 2.68
	Calculated %:	C 31.29; H 2.63

Ferricinium ferrichloride is stable in air, does not melt, and dissolves in water, alcohol, acetic acid, tetrahydrofuran, and ethyl acetate.

Action of liquid hydrocyanic acid on ferricinium ferrichloride. To a solution of 7.7 g (0.02 mole) of ferricinium ferrichloride in 50 ml of dry tetrahydrofuran was added 30 ml of liquid hydrocyanic acid. The reaction mixture was heated for 3 hours under reflux, connected to an absorption bottle filled with permanganate solution, and was left for 24 hours. Then 10% sodium hydroxide solution was added until the dichroic ferricinium coloration disappeared, and the mixture was extracted with ether. The ether was distilled off; the residue was dissolved in petroleum ether and chromatographed on alumina. Ferrocene was eluted with petroleum ether, and ferrocenecarboxylic acid nitrile with a mixture of petroleum ether and benzene (1:1). There were isolated 0.12 g (3.1%) of ferrocene, melting point and mixed-sample melting point 170–171°, and 2.2 g (52% of theory) of ferrocenecarboxylic acid nitrile, m.p. 107–108° (from petroleum ether); a mixed sample with authentic nitrile melted without depression. Literature data: m.p. 106.5–107.5° [11]; 107–108° [9].

Cyanation of ferrocene in tetrahydrofuran in the presence of $FeCl_3$. To a solution of 3.72 g (0.02 mole) of ferrocene in 50 ml of tetrahydrofuran was gradually added 13 g (0.08 mole) of anhydrous $FeCl_3$, after which 25 ml of liquid HCN was added. The mixture was heated to boiling for 3–4 hours and left overnight. The subsequent work-up was carried out as described above. A total of 3.6 g (86% of theory) of ferrocenecarboxylic acid nitrile was obtained.

Cyanation of methylferrocene [15]. The reaction was carried out as described for ferrocene. The methylferrocenecarboxylic acid nitrile was separated chromatographically from the unreacted methylferrocene. From 5 g of methylferrocene, 1.2 g (24%) was recovered unchanged.

Methylferrocenecarboxylic acid nitrile is a viscous reddish-brown liquid, distills in vacuo in a stream of nitrogen. B.p. 143–143.5°/2 mm, n_D^{18} 1.6215. Yield 2 g (36% of theory).

Found, %: C 64.27; 64.14; H 5.15; 5.06; N 6.49; 6.35; Fe 24.65; 24.53
$C_{12}H_{11}NFe$. Calculated, %: C 64.03; H 4.92; N 6.23; Fe 24.81

Cyanation of ethylferrocene[16] was carried out as described for methylferrocene. From 4 g of ethylferrocene, 2.3 g was obtained (yield 53% of theory) of ethylferrocenecarboxylic acid nitrile. B.p. 152–156°/5 mm; n_D^{20} 1.6090.

Found, %: C 65.58; 65.35; H 5.86; 5.72; N 6.19; 6.08; Fe 22.84; 23.07
$C_{13}H_{13}NFe$. Calculated, %: C 65.30; H 5.47; N 5.86; Fe 23.36

Hydrolysis of $C_5H_5FeC_5H_3(C_2H_5)CN$. A mixture of 0.6 g of the nitrile, 45 ml of alcohol, 35 ml of water, and 5 g of NaOH was heated to boiling for 7 h. 0.4 g of $C_5H_5FeC_5H_3(C_2H_5)COOH$ was obtained. Yield 61% of theory. M.p. 113–114°. Heteronuclear ethylferrocenecarboxylic acid[17] has m.p. 75.5–77.5°.

Found, %: C 60.28; 60.38; H 5.95; 5.73; Fe 22.34; 22.05
$C_{13}H_{14}O_2Fe$. Calculated, %: C 60.49; H 5.46; Fe 21.64

Cyanation of ferrocenecarboxylic acid nitrile was carried out as described for ferrocene. The dinitrile was eluted from the chromatographic column with benzene. From 2.11 g of ferrocenecarboxylic acid nitrile, 1.05 g (50%) of the starting nitrile was recovered; the yield of 1,1′-ferrocenedicarboxylic acid dinitrile was 0.55 g (23% of theory). Melting point in a sealed capillary 165.5–166° (recrystallized from benzene). Literature data[11]: m.p. 166–167.5°.

Found, %: C 61.05; 61.19; H 3.47; 3.44; N 12.31; 12.32; Fe 23.52; 23.50
$C_{12}H_8N_2Fe$. Calculated, %: C 61.05; H 3.42; N 11.87; Fe 23.67

Ferrocenecarboxylic acid dinitrile was also obtained by us from ferrocene without isolation of the mononitrile. Ferrocene was cyanated as described above, and then 20 g of $FeCl_3$ and 18 ml of liquid HCN were added to the reaction mixture. The subsequent operations were carried out in the same way as in the isolation of the mononitrile. 1.29 g was obtained (yield 27% of theory) of the dinitrile and 1.1 g (yield 26%) of the mononitrile.

Cyanation of chloroferrocene was carried out as described above for ferrocene. From 0.11 g of chloroferrocene, 0.09 g was obtained (yield 73% of theory) of chloroferrocenecarboxylic acid nitrile. M.p. 84.5–86° (recrystallized from petroleum ether).

Found, %: C 54.35; 54.28; H 3.81; 3.56; Cl 14.18; Fe 22.71; 22.57
$C_{11}H_8ClNFe$. Calculated, %: C 53.78; H 3.29; Cl 14.45; Fe 22.75

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Note: Figure translations are in progress. See original paper for figures.