

SYNTHESIS OF MONOACETYL FERROCENE

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ABSTRACT

In this article the reactivity of ferrocene is thoroughly investigated, the method of synthesis of monoacetylferrocene is improved; the structure of monoacetylferrocene is studied by means of IK spectroscopy, mass spectrometry.

KEYWORDS: *Ferrocene, Electrophonic Substitution, Acylation, Monoacetylferrocene, Catalyst, Reaction Yield, IK Spectroscopy, Mass Spectrometry.*

INTRODUCTION

LITERATURE ANALYSIS AND METHODS

Initially, in the 19th century the first organometallic compounds were synthesized, but by the second half of the 20th century, chemistry of organometallic compounds began to develop rapidly.

The first complex with a variable degree of oxidation of the metal - the olefin complex of platinum was obtained in 1827 by the Danish scientist W. Zeise. In 1890, L. Mond, K. Langer and F. Quincke succeeded in synthesizing nickel tetracarbonyl. In 1919, F. Hein synthesized a benzene chromium π -complex. The growing interest in organic compounds of transition metals is associated with the discovery of the first organo-iron compound, ferrocene. In 1951, with the synthesis of ferrocene, the synthesis of π -complexes, compounds of the "sandwich" type, a special type of organometallic compounds, and the comprehensive study began [1, 2].

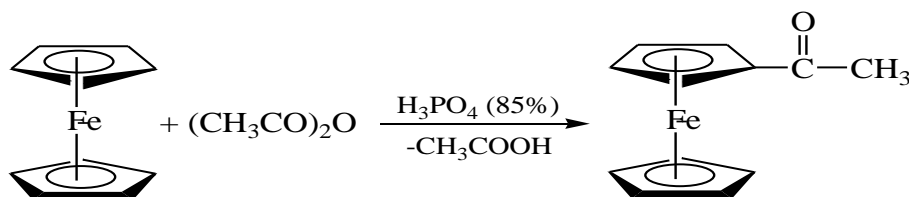
Ferrocene can enter into various reactions. These reactions can be divided into three groups:

1. Reactions going only on cyclopentadienyl rings;
 2. Reactions involving an iron atom;
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3. Reactions with the decay of the IKon-carbon bond.

As mentioned above, since the ferrocene-containing metal-containing nobenzoide is an aromatic system, it can easily enter into exchange reactions on cyclopentadienyl rings. The ferrocene core remains unchanged in almost all reactions. Since there are two rings in the molecule, the chemical changes in ferrocene are also different [3].

Ferrocene is more susceptible to electrophilic substitution reactions than benzene. For example, the acylation reaction of ferrocene proceeds in the presence of phosphoric acid under the action of acetic anhydride [4, 5].

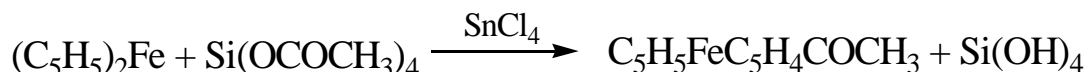


The acetyl group reduces the activity of ferrocene. The addition of the next substituent to the molecule, for example, the acetylation reaction proceeds under more severe conditions in the presence of Lewis acids:

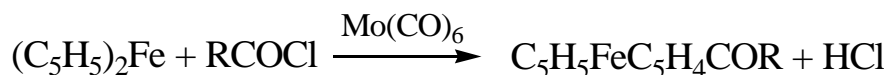


As a result of the reaction, a predominantly heteroannular diacetyl compound is formed - 1,1'-diacetylferrocene and a small amount of its homoannular isomer - 1,2-diacetylferrocene:

Acetylferrocenes are mainly obtained by reacting ferrocene with acid chlorides or anhydrides in the presence of aluminum chloride. Since side reactions are more likely in the presence of aluminum chloride, it is recommended to use less acidic catalysts in the production of acetylferrocenes, such as tin chloride, phosphoric acid. Scientists have reported that acetylferrocene is formed when ferrocene is exposed to acetic acid, silicic anhydride, and tin(IV) chloride.



It has been shown that ferrocene can be acylated with acyl chlorides in the presence of hexacarbonylmolybdenum:



Acetylferrocenes are used to prepare other ferrocene derivatives.

Acetylferrocene is mainly obtained by reacting ferrocene with acid chlorides or anhydrides in the presence of aluminum chloride. Due to the high probability of side reactions in the presence of aluminum chloride, the literature provides information on the formation of acetylferrocene in good yields in the preparation of acetylferrocene under the action of less acidic catalysts, such as tin chloride, phosphoric acid. It is indicated that the reaction is carried out at 100°C for 10 minutes, the yield is 70-75% [4].

RESULTS AND DISCUSSION

Taking into account the above information, we have improved the method for producing ferrocene with acetic anhydride, and, in contrast to the methods given in the literature, we managed to increase the reaction yield by 5% by increasing the temperature by 4-5 ° C, time 5 minutes and catalyst content 1.5 times. The yield of the resulting acetylferrocene was 80%.

The electronic structure of raw materials and compounds used for the synthesis of acetylferrocene and reactions was first determined using quantum chemical calculations. The calculations were performed using the Gaussian-98W DFT/B3LYP method 3-21G program [5].

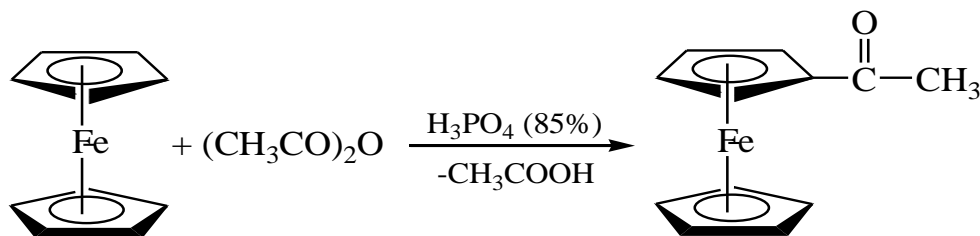
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It is known that column chromatography is widely used in the separation of mixtures of organic substances. This method is preferred over other physicochemical methods because it is accurate and does not require much time. The method of column chromatography makes it possible to isolate the formed acetylferrocene from mixtures [7].

The mixture was separated on a TLC column in acetone:benzene (3:1). According to the results of chromatographic analysis, in our opinion, ferrocene and acetylferrocene precipitate without a mixture. On drying, the precipitate formed a brown substance. The resulting mixture was converted into concentrated hydrochloric acid (ferrocene is insoluble in hydrochloric acid, but passes into the ionic state, acetylferrocene is highly soluble). It was then filtered through a Schott filter under vacuum and the filtrate was poured into ice water to form an orange precipitate.

The reaction was carried out according to the following scheme:



The structure of acetylferrocene was studied by IR spectroscopy. The fact that the absorption lines of the IR spectrum at 1101, 1005 cm^{-1} belong to the unchanged cyclopentadienyl ring in the ferrocene residue, and the absorption lines at 1662, 1652 cm^{-1} belong to the $>\text{C}=\text{O}$ -bond in the acetyl residue group confirms the formation of acetylferrocene [8.9]. Physicochemical parameters of acetylferrocene are given in Table 1.

TABLE 1 PHYSICO-CHEMICAL PROPERTIES OF ACETYLFERROCENE

Compound	Output, %	T.c. °C	R _f (system)	Scalding area in the IR-spectrum, cm ⁻¹		Found o, %	Calculated, %
				Fc	>C=O	Fe	Fe
FcAc	80	86-87	0,57 (A) 0,44 (B)	1101,1005	1662, 1652	24,56	24,49

System: acetone-bensol 3:1 (A), petroleum ether-bensol 1:1 (B).

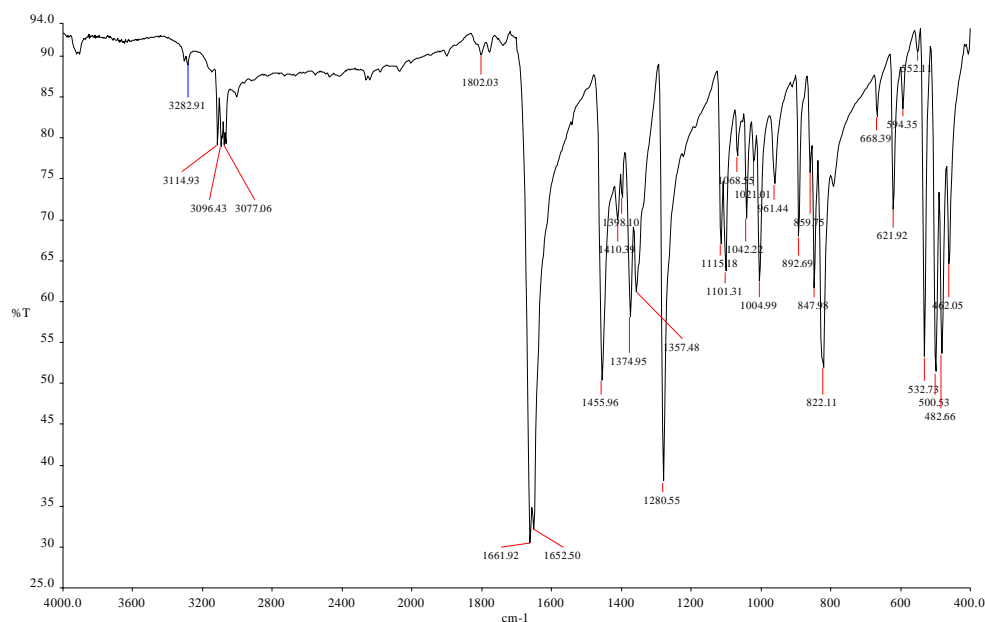


Figure 1. IR spectra of monoacetylferrocene

The IR spectrum data are consistent with the results of mass spectrometric analysis (Fig. 2). The values of the peaks formed in the mass spectrum are given in the following table [10].

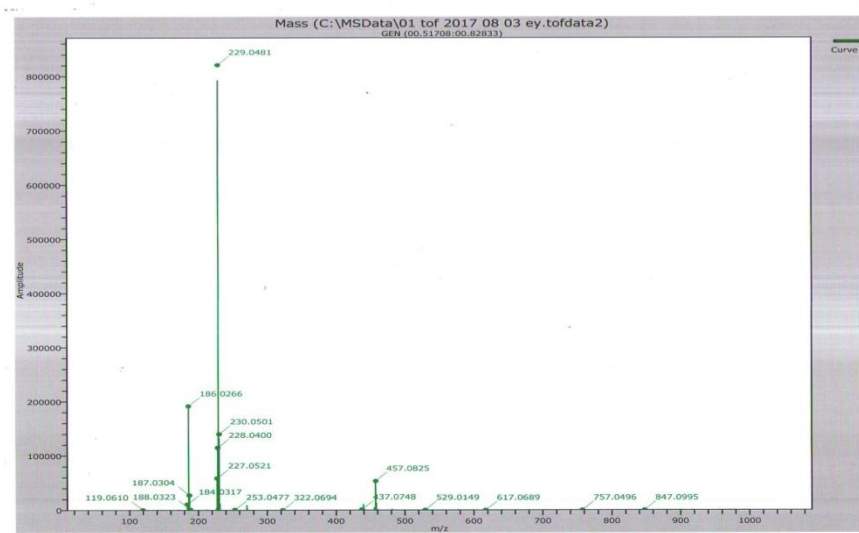


Figure2. Mass spectrum of monoacetylferrocene

TABLE 2 MASS SPECTROMETRIC PARAMETERS OF ACETYLFERROCENE

	Formula	m/z	Relative intensity %
	$(C_5H_5)_2FeCOCH_3 + H^+$		
	$(C_5H_5)_2Fe^+$		
	$(C_5H_5)_2FeCOCH_3^+$		
	$(C_5H_5)_2FeCOCH_3 + H^+$		

Experimental part

25 g (0.134 mol) of ferrocene, 150 ml of acetic anhydride, 10 ml of orthophosphoric acid (85%) were placed in a two-necked flask with a capacity of 500 ml. The mixture was heated on a sand bath for 15 min after rising to 104–105°C and stirred with a screw mixer. Then 100 g of ice was poured into a liter jar, hot ice was poured into the mixture and left for a day.

A day later, a saturated solution of $NaHCO_3$ was neutralized in the mixture and this process was continued until the complete precipitation of the precipitate. The precipitate is separated from the solution by filtration. The separated precipitate is gradually treated with concentrated HCl, placing it in a mortar. This process continued until the precipitate dissolved. The solution is filtered on a Schott filter, the filtrate is poured 2-4 times into ice water, the formation of a precipitate indicates the formation of acetylferrocene. The precipitate was filtered off and washed with water.

The resulting substance was dried in the open air, then dried in a vacuum desiccator over P_2O_5 . The dried substance was recrystallized from n-heptane. Dark red crystalline substance. Output - (80%). $T_{m.p.} = 86-87^\circ C$.

IR (ν ; cm^{-1}): 1101, 1005 (Fc), 1662-1652 ($>C = O$). Found: % Fe, 24,56. Calculated: % Fe, 24,49. General formula: $C_{12}H_{12}FeO$. Mass spectrum: (m/z) 229 $(C_5H_5)_2FeCOCH_3 + H^+$, 186 $(C_5H_5)_2Fe^+$, 228 $(C_5H_5)_2FeCOCH_3^+$. System: acetone-benzol 3:1 (A), petroleum ether-benzol 1:1 (B). $R_f = A-57, B-0,44$

CONCLUSION

Thus, in contrast to the methods presented in the literature, the yield of the reaction increased by 5% as a result of increasing the temperature to 4-5°C, the time to 5 minutes and the amount of catalyst by 1.5 times. Ferrocenecarboxylic acid was synthesized by oxidation of the obtained acetylferrocene. Some water-soluble derivatives of ferrocenecarboxylic acid are approved for practical use as biostimulants that have a positive effect on the germination, growth, development and productivity of cotton.

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