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м-ФЕРРОЦЕНИЛБЕНЗОЙ КИСЛОТАСИНИНГ МЕТИЛОЛДИТИОМОЧЕВИНА БИЛАН РЕАКЦИЯСИНИ ЎРГАНИШ

ИЗУЧЕНИЕ РЕАКЦИИ *м*-ФЕРРОЦЕНИЛБЕНЗОЙНОЙ КИСЛОТЫ С МЕТИЛОЛДИТИОМОЧЕВИНОЙ

STUDY OF THE REACTION OF *м*-FERROCENYL BENZOIC ACID WITH METHYLOLDITHIOUREA

I.Askarov[1], M.Khojimatov[1], F.Abdugapparov[1]

[1] I.Askarov — *Doctor of Chemistry, Professor of Andijan State University.*
[2] M.Khojimatov — *Andijan State University.*
[3] F.Abdugapparov — *Andijan State University.*

Аннотация

Мақолада м-ферроценилбензой кислотасининг метилолдитиомочевина билан синтези, олинган янги бирикманинг тузилишини исботловчи ИҚ-спектроскопия ва масс-спектрометриктаҳлил натижалари келтирилган.

Аннотация

В статье приведены результаты синтеза м-ферроценилбензойной кислоты с метилолдитиомочевиной и ИК-спектроскопическогои масс-спектрометрического анализа, доказывающих структуру полученного нового соединения.

Annotation

This article presents the method of synthesis of m-ferrocenyl benzoic acid with methyloldithiourea and the results of IR spectroscopy and mass spectrometry analysis proving the structure of the new substance obtained.

Таянч сўз ва иборалар: *ферроцен, ферроцерон,метилолдитиомочевина, м-ферроценилбензой кислота, ферроценли электродлар, ИК-спектроскопия.*

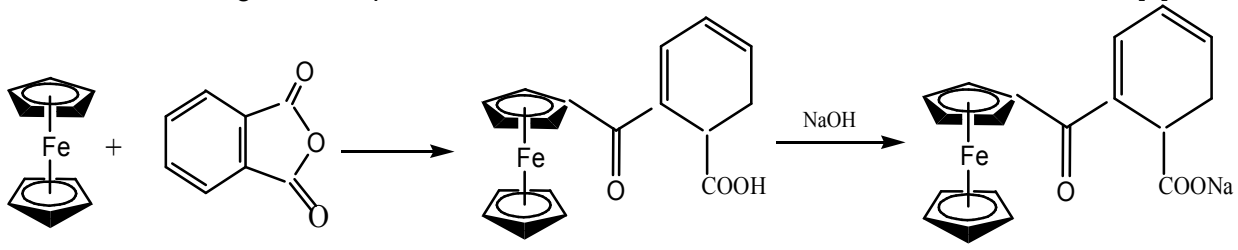
Ключевые слова и выражения: *ферроцен, ферроцерон, метилолдитиомочевина, м-ферроценилбензойная кислота, ферроценовые электроды, ИК-спектроскопия.*

Keywords and expressions: *ferrocene, ferroceron, methyloldithiourea, m-ferrocenyl benzoic acid, ferrocene electrodes, IR spectroscopy.*

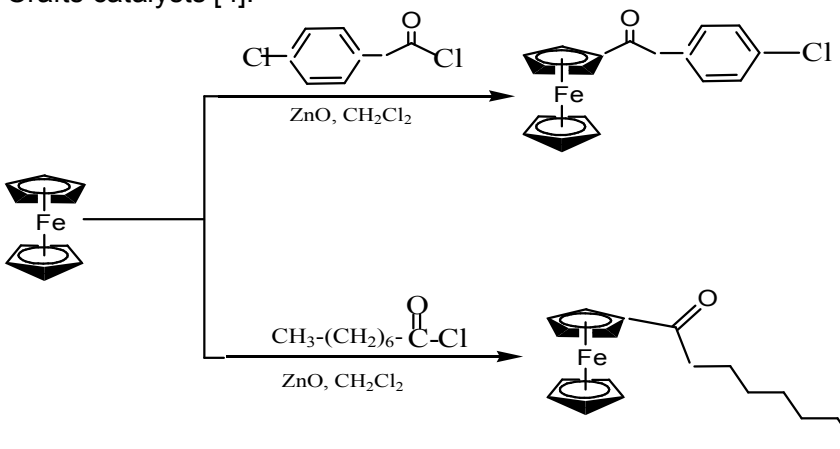
Introduction. The possibility of synthesizing biologically active substances based on ferrocene has been thoroughly analyzed in the scientific literature. They note that due to the peculiar molecular structure of the ferrocenyl ring in ferrocenyl-containing compounds, they exhibit biological activity [1]. Numerous facts about the successful use of ferrocene derivatives in medicine also show their biological activity. The lipophilicity of ferrocene fragments, as well as its ability to pass into solution in the form of an easily soluble salt, prove the high stability and safety of ferrocene compounds [2].

One of the reasons for using ferrocene derivatives in medicine is their ability to stimulate the process of hematopoiesis, so they can be used as a means to treat iron deficiency in the body (anemia).

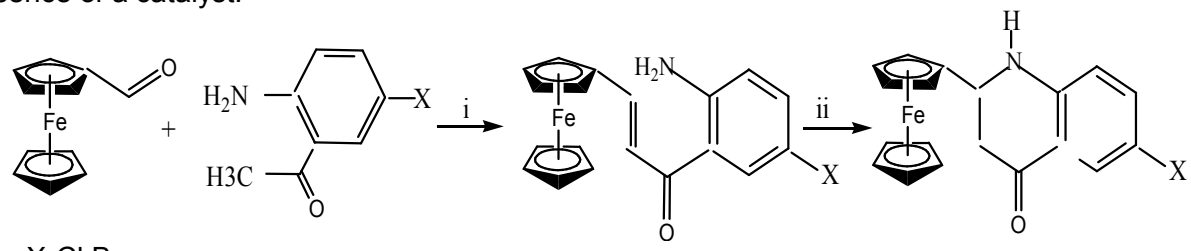
Ferroceron (o-carboxybenzoylferrocene) – synthesized from ferrocene and phthalic anhydride, is the first ferrocene drug that has positive results in the treatment of various forms of anemia [3].



Ferrocene derivatives with acetyl chloride and octanoyl chloride were synthesized in the presence of Friedel-Crafts catalysts [4]:



Some researchers have synthesized ferrocene derivatives with antimicrobial properties [5]. In this case, ferrocenecarboaldehyde and o-aminoacetophenone enter into aldol condensation in the presence of a catalyst:

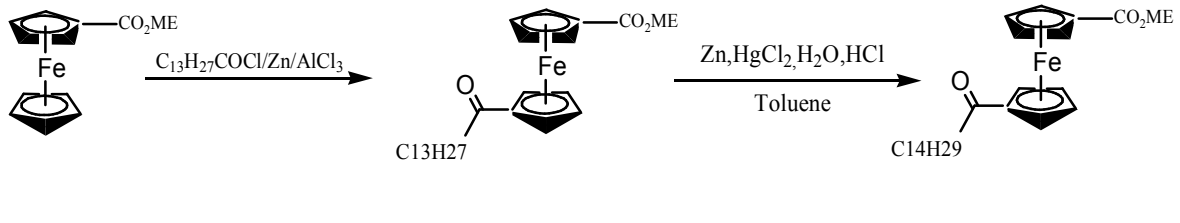


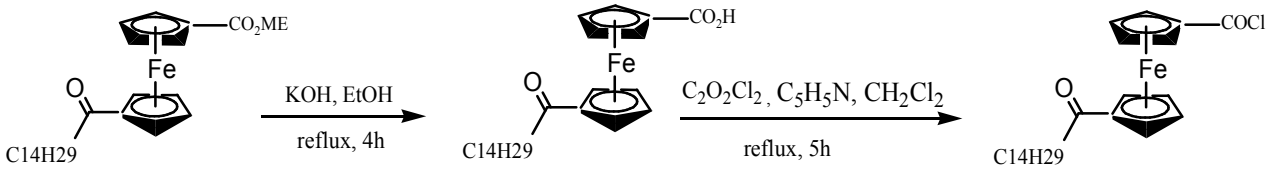
X-Cl,Br

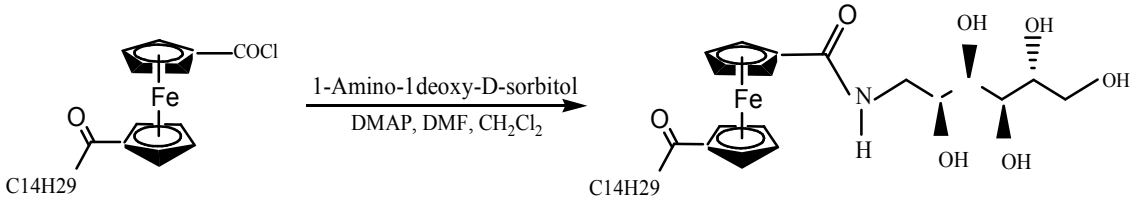
i-NaOH, C_2H_5OH

ii-CH_3COOH/H_3PO_4

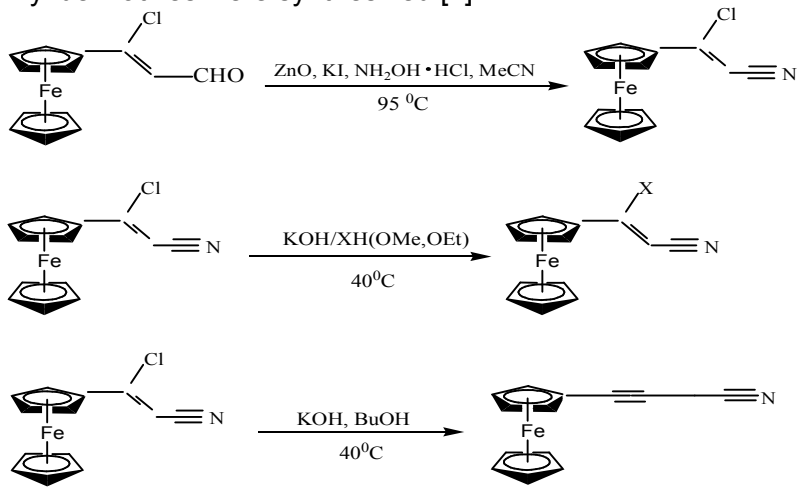
Using the redox properties of ferrocene under suitable conditions, it is possible to create iron-organic resins, redox polymers, ferrocene electrodes, antistatic substances and redox-active liquid crystal materials [6]:







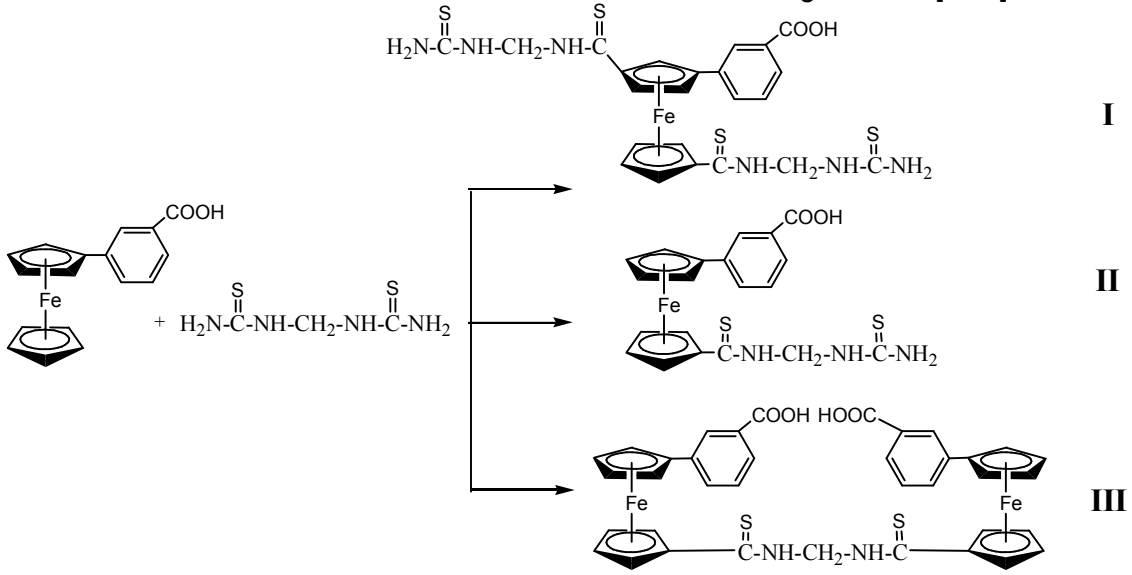
In order to obtain an expansion of the arsenal of biologically active substances based on ferrocene, its cyanvinyl derivatives were synthesized [7].



Thanks to the research of such foreign scholars as H. Slegel, R. B. Woodward, A. N. Nesmeyanov, L. P. Asatiani, E. A. Kollenikova and uzbek scientists Makhsumova A. G., Y. T. Nasriddinov, S. K. Karimov, Sh. M. Kirgizova, A. M. Jurayev, N. T.Tulakov, K. K. Otakhonov, O. S. Abdullayev and including our research the opportunity to obtain a variety of new compounds based on ferrocene [8].

In this paper, the reaction of m-ferrocenyl benzoic acid with methyloldithiourea is studied. When acting on m-ferrocenyl benzoic acid, mainly three compounds were obtained based on the diazotization reaction with methyloldithiourea.

The reaction was carried out on the basis of the following scheme [9.10]:



The reaction yield was for (I)-1%, (II)-45%, and (III) 2 %. These compounds are separated by column chromatography.

Experimental part. For column chromatography, a column with a height of 30 cm and a diameter of 3 cm (silica gel of the LS 5/40 μ brand) was used. The solvent system is diethyl ether-hexane (2:1). IR spectra were taken on the Perkin Spectrum spectrophotometer (version 10.4.2, Germany), mass spectra on the Perkin Elmer AxION 2TOF MS (Germany).

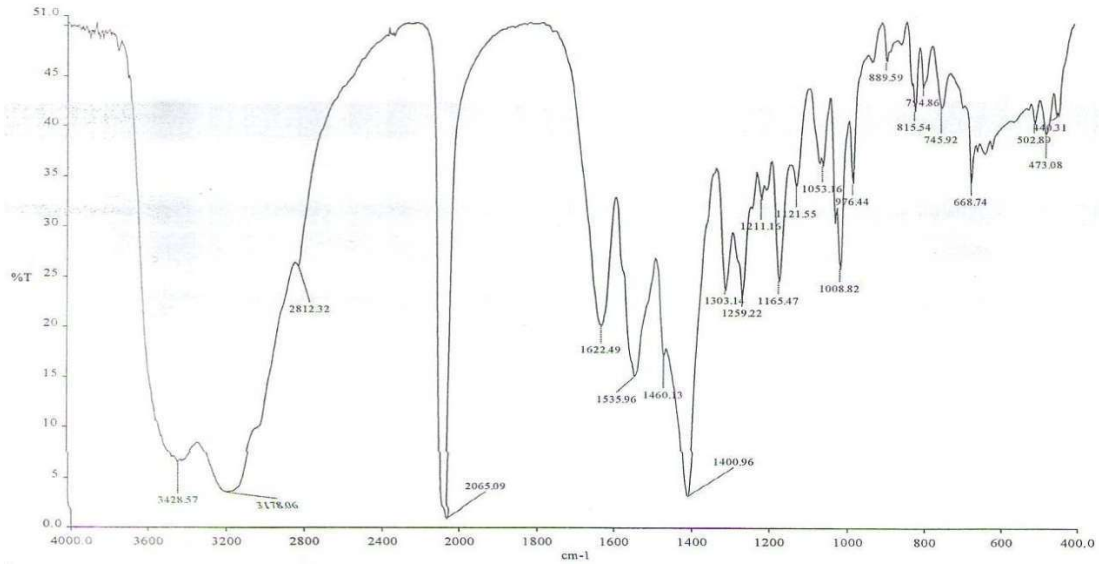
150 ml of water, 100 g of ice, 5 g of methyloldithiourea and 8.5 ml of concentrated hydrochloric acid were placed in a 3-neck 500 ml flask equipped with an auto-mixer, a drop funnel and a thermometer. The mixture was strongly mixed at a temperature of -2 oC. Through a drop funnel, a solution of 15 g of sodium nitrite in 40 ml of water was added to the mixture for 1

hour.Then, the ice bath was replaced with water. 1.0 g of m-ferrocenyl benzoic acid dissolved in 200 ml of diethyl ether was added to the reaction mixture. The drip funnel was replaced with a return refrigerator. The mixture was heated by stirring at 34-36 oC for 2.5 hours. After the reaction, the ether and water layers were separated using a dividing funnel. The water layer was extracted 3 times with diethyl ether. Mixed the essential layers and 2 times washed with water. Then the essential layers were extracted several times with a 2% solution of sodium hydroxide. The resulting aqueous extract was neutralized with a 5% solution of hydrochloric acid. The resulting red-brown sediment was filtered and dried at room temperature.

Separation of substances. Chromatography on the column was performed at room temperature. Elution time is 1 hour. Output of compound I 0.015 g (1 %), compound II 0.67 g (45%), compound III 0.03 g (2%). T.PL.=107-108 ^{0} C.

Analysis of the results obtained.

As indicated above, 1'-(3-carboxyphenyl)-1-N- ferrocenylthioamidomethan- tiocarboxamide (compound II) was obtained with the highest yield. The structure of the obtained compounds was studied using IR spectroscopy and mass spectrometry. Thus, in the IR spectrum of compound II, the absorption band at 1008 cm^{-1} shows the presence of a substituted cyclopentadienyl ring in the ferrocene residue. The absorption band at 1400 cm^{-1} is characterized by deformation vibrations of the-OH group, the valence vibrations of the-OH and - NH groups correspond to intense bands at 3428 and 3178 cm^{-1}, and the absorption band at 815 cm^{-1} indicates the presence of a substituted benzene ring.



In the mass spectrum of 1'-(3-carboxyphenyl)-1-N-ferrocenylthioamido-methantiocarboxamide, intense peaks of functional groups can be observed at 419 m/ z, 393 m/z, 378 m/z.

When studying the solubility of the studied compounds in various solvents, the following results were obtained: acetone > diethyl ether > DMFA > chloroform > dioxane > diethylene glycol-diethyl ether > hexane > heptane > octane.

Conclusion. As a result of this work, the reaction of m-ferrocenyl benzoic acid with methyloldithiourea was performed. The structure of the obtained compounds was studied by IR spectroscopy and mass spectrometry. Taking into account the fact that many ferrocene derivatives have biological activity, we study the biological activity of the synthesized new substance.

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