UDC 547.1.13

SYNTHESIS AND RESEARCH INTO FERROCENYL-O-CARBOXYBENZOYL CARBOXYLIC ACID OBTAINED BY THE REACTION OF ADDITION OF FERROCENYLLITHIUM (SODIUM) OF ORGANOMETALLIC COMPOUNDS TO PHTHALANHYDRIDE

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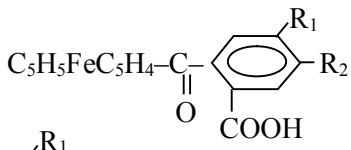
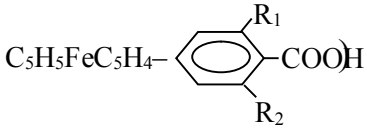
The paper deals with the synthesis of carboxybenzoyl carboxylic acid to synthesize some practically important derivatives of ferrocenyl by using ecologically pure reagents. The structures and some properties of obtained compounds have been studied. With that end in view, we used combination reaction of ferrocenyllithium or sodiumorganometallic compounds to phthalanhydride in stoichiometric composition. An appropriate method for wasteless and highly productive goal-oriented product from reaction mixture has been developed.

Keywords: *ferrocene, ferrocenyl-o-carboxybenzoyl carboxylic acid, phthalanhydride, ferrocenyllithium (sodium) oranometallic compounds.*

INTRODUCTION

We refer to aromatic acid residue containing ferrocene derivative

ferrocenyl-o-carboxybenzoyl (Fc-o-CBCA)  and

ferrocenebenzoic acid (Fc BA 

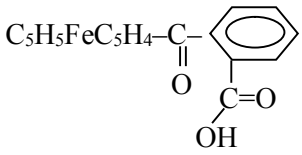
which are widely used as a key compound for the study and application in ferrocene chemistry [1-3]. According to the literature, relevant methods have been developed for synthesis of these two types of compounds. Presently these compounds are widely used in treatment of different diseases, prevention of polymer materials from ageing, ray refraction, preparation of smoke reducing admixture composition materials for diesel fuels [4].

Unlike the existing method in literature for synthesizing this compound based on ferrocenyl-o-carboxybenzoyl carboxylic acid (Fc-o-CBCA), production of the compound through the use of new, more profitable and ecologically pure reagents of great importance. However, this method is notable for some shortcomings. These are multistage synthesis method; in some intermediate stages the synthesis is very harmful for human organism and envronment from ecological standpoint; the process is multistage and prime cost of the end product is high due to great losses; use of special reagents to extract selectively the end product out of reaction mixture.

In considering the above, the development of the new synthesis method by using simple, one-stage non-prohibited reagents is a relevant problem.

EXPERIMENTAL PART

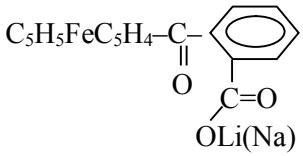
Synthesis of ferrocenyl-o-carboxybenzoyl carboxylic acid



Metallization of feroccene with n-BuLi was conducted according [3] method. Thus, the difference between existing method and the new one is that for increasing thermal stability of ferrocenyllithium (mainly sodium) the process was lapsed by adding 5-10 ml/1l TMDA-tetramethylenediamine stabilizing reagent.

With that end in view, following the blowing N_2 to 4-neck flask which is provided with 0.5 l reflux condenser, mechanical mixer and thermometer 0.1 mol (18.6 g) ferrocene is added, and 220 ml heptane is added and mixed. Then 27 ml (1.25 N) n-BuLi produced on the basis of [5] method at N_2 pressure, is added by mixing within 10 minutes at 20^0C temperature. Temperature of reaction mixture rises up to 40^oC. At this temperture, the reaction mixture is mixed within 2-3 hours. Then mixing is stopped and temperature is decreased to room temperature, 1 mol (14,8 g) phthalanhydride is dissolved in 150 ml heptane, added and mixed for 20 minutes. Colour of the solution changes from light yellow to light blue. Mixing lasts for 1 hour. During mixing the color of the reaction mixture changes.

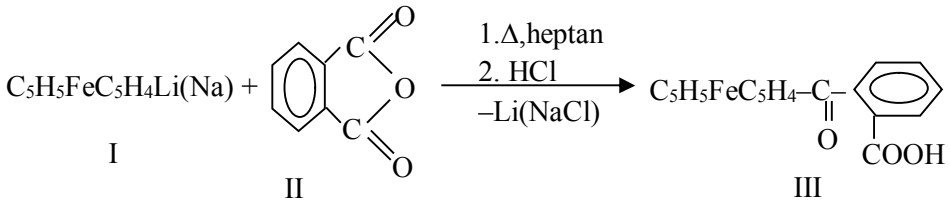
The compound product obtained by this way ferrocenyl-o-carboxybenzoyllithium (sodium) carboxylate salt



is hydrolized with 5% HCl.The solution changes its color into light yellow. Surface organic phase is separated from water phase and vaporized. The end product of Fc-o-CBCA with 26.7 g humidity mass is obtained. It is dehydratized till constant mass in the range of 30-40^{o}C temperature. As a result, we obtained III compound with dry mass 25.14 g or 82% yield. Melting temperture of the compound is T_{rmelt}= 118-119^{o}C, decomposition temperature is $T_{decom.}$=280^{o}C. Element composition of III compound fully corresponds to $C_{18}H_{11}FeO_3$ formula.

DISCUSSION OF RESULTS

To synthesize Fc-o-CBCA compound, we used interaction reaction (1) between highly reactive ferrocenyllthium $C_5H_5FeC_5H_5Li$ [3] or sodium $C_5H_5FeC_5H_5Na$ [4] organometallic compounds with phthalanhydride $C_6H_4[-CO]_2O$.



(1)

(1) When the reaction is conducted in terms of the said medium and the III end product is obtained, just one cyclopentadienyl substituted ferrocene derivative is formed with 40-80% yield.

According to the research, it revealed that at 20-40°C temperature range, intensive mixing within 2-3 hours (1) makes it possible to finish the combination reaction completely. Reaction solutions are Li(Na) carboxylate complexes to contain 4 mol water in their molecules.

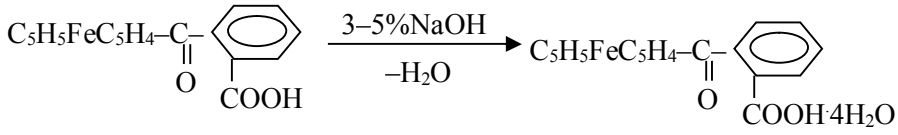
$$Fc–\underset{\underset{O}{\|}}{C}–C_6H_4COOLi(Na)\cdot 4H_2O$$

The compounds which have $T_{decom.}$> 140°C (IV) and $T_{decom.}$> 160°C (V) decomposition temperatures are obtained practically with the same yield by processing both IV and V carboxylate complexes with HCl. Note that IV and V carboxylate complexes are processed with 5% HCl and converted into III Fc-o-CBCA compound with 80-90% yield and melting temperature $T_{melt.}$=160-210°C.

Some structural properties of obtained compounds have been studied by micro-analysis, thermogravimetric, IR-spectra and NMR ^1H spectral methods. For III compound IR spectrum (KBr): $\upsilon_{COOH(OH)}$=3300-3500 sm^{-1}; $\upsilon_{C=O}$=1630 sm^{-1}; $\upsilon_{COOH(C=O)}$=1720 sm^{-1}; for V IR spectrum (KBr): υ_{COO}=1660 sm^{-1}; $\upsilon_{C=O}$=1580 sm^{-1}; for III NMR ^1H spectrum (CCl_4): $\delta_{C5H4(\alpha,\ \beta)}$=3,78-3,91 m.h.; δ_{C5H5}=4,12 m.h.;δ_{C6H4}=6,24-7,18 m.h.;δ_{COOH}=4,25 m.h.

Thermogravimetric studies made it possible to discover that during thermal processing the IV and V carboxylate complexes are exposed to decarboxylation reaction in the range of 180-260°C temperature, and then decomposed. Compositions of decomposed products consist, as a rule, of ferrocene, diphenyl acetone, biphenyl, ferrocenylmethyl carbinol and other compound mixtures identified with the help of liquid phase chromatography.

When studying some chemical properties of III Fc-o-CBCA, it became possible to establish that as a result of processing the compound by (2) reaction with 3-5% $NaHCO_3$ sodium tetrahydrate, derivative of V ferrocenyl-o-carboxybenzoyl carboxylic acid is easily obtained with 90-95% yield.



III V (2)

By using (2) reaction LiOH which was used for obtaining of IV derivative, it revealed relatively low base properties than NaOH and required heating of the reaction to make it more complex and multi-stage. As a result, the yield of greater part of IV compound is found to make up 25-35% due to the decomposition of ferrocene nucleus.

As for the dissolution ability of III, IV and V compounds, III dissolves in 125 mg/l water as an organometallic carboxylic acid while IV and V show highly soluble ability until the solution is saturated. When these compounds were kept for 1-2 days directly on daylight, the solution blushes and then blue deposite is formed to reveal the decomposition of ferrocene nucleus in V compound. Thus, both IV and V compounds can be kept in dark in solid state for a long time.

At present III ferrocenyl-o-carboxybenzoyl carboxylic acid is widely applied for prevention iron deficiency – anaemia disease, and it is a raw material for mass production due to high solubility in water IV Na-o-carboxybenzoylferrocene (ferrocero-num) preparation.

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СИНТЕЗ И ИССЛЕДОВАНИЕ ФЕРРОЦЕНИЛ-О-КАРБОКСИБЕНЗОИЛ КАРБОНОВОЙ КИСЛОТЫ, ПОЛУЧЕННОЙ РЕАКЦИЕЙ ПРИСОЕДИНЕНИЯ ФЕРРОЦЕНИЛЛИТИЙ (НАТРИЙ) МЕТАЛЛООРГАНИЧЕСКИХ СОЕДИНЕНИЙ С ФТАЛЕВЫМ АНГИДРИДОМ

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Статья посвящена синтезу карбоксибензоил карбоновой кислоты с использованием экологически чистых реагентов для получения ряда производных ферроцена, имеющих практическое значение. Были исследованы структуры и некоторые свойства полученных соединений. Для этого использованы реакции присоединения металлоорганических соединений стехиометрического порядка, таких как ферроценниллитий или натрий с фталевым ангидридом. Был разработан соответствующий метод для безотходного и высокопродуктивного получения целевого продукта из реакционной смеси.

***Ключевые слова**: ферроцен, ферроценил-о-карбоксибензоил карбоновая кислота, фталевый ангидрид, ферроценниллитий(натрий) металлоорганические соединения.*

FERROSENİL-O-KARBOKSİBENZOİL KARBON TURŞUSUNUN FERROSENİLLİTİUM (NATRİUM) METALÜZVİ BİRLƏŞMƏLƏRİNİN FTALANHİDRİDƏ BİRLƏŞMƏSİ REAKSİYASI ƏSASINDA SİNTEZİ VƏ TƏDQİQİ

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Məqalə ferrosenin praktiki əhəmiyyət kəsb edən bir sıra törəmələrinin sintezi üçün karboksibenzoil karbon turşusunun ekoloji təmiz reagentlərdən istifadə etməklə sintezinə həsr edilmişdir. Alınan birləşmələrin quruluş və bəzi xassə xüsusiyyətləri tədqiq edilmişdir. Bunun üçün ferrosenillitium və ya natriummetalüzvi birləşmələrinin stexiometrik tərtibdə ftalanhidridə birləşməsi reaksiyasından istifadə edilmişdir. Məqsədli məhsulun reaksiya qarışığından itkisiz və yüksək çıxımla əldə olunması üçün müvafiq metod işlənib hazırlanmışdır.

***Açar sözlər:** ferrosen, ferrosenil-o-karboksibenzoil karbon turşusu, ftal anhidridi, ferrosenillitium (natrium) metalüzvi birləşmələri.*

Redaksiyaya daxil olub 26.09.2015.