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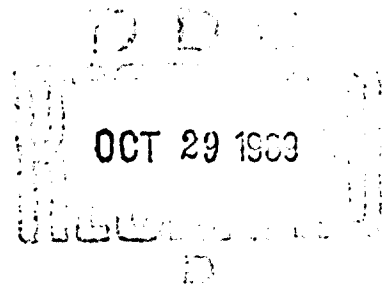
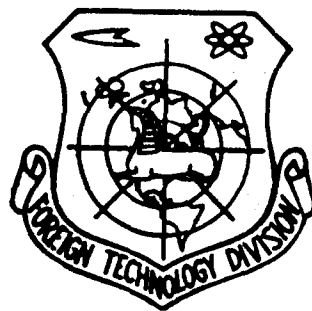
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SYNTHESIS OF FERROCENECARBOXYLIC ACIDS AND THEIR DERIVATIVES

by

I. A. Golubeva, T. P. Vishnyakova, and N. N. Bul'on



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ABSTRACT

(U) Following a tabulation of known methods for synthesis of ferrocenedicarboxylic acids, the paper reports on methods for which increased yields are claimed. Ferrocenedicarboxylic acid was prepared (yield 45.2 percent of theory) by hypochlorite oxidation of acetylferrocene, ferrocene-1,1' -dicarboxylic acid (90-92 percent) by similar oxidation of 1,1' diacetylferrocene, carbamylferrocene (70-72 percent) by direct reaction of ferrocene with carbamyl chloride in the presence of AlCl₃ (subscript 3), and 1,1' -dicarbamylferrocene (almost 100 percent) by passing ammonia through a benzol solution of the diacid chloride. There are 25 literature citations, of which 7 are Russian.

SYNTHESIS OF FERROCENECARBOXYLIC ACIDS AND THEIR DERIVATIVES

I. A. Golubeva, T. P. Vishnyakova,
and N. N. Bul'on

There are a number of known methods for the synthesis of ferrocenecarboxylic acid: carboxylation of lithium ferrocenes [3-7], oxidation of acetylferrocene by sodium hypochlorite [8] and by iodine in pyridine [9-10], hydrolysis of carbamylferrocene and diphenylcarbamylferrocene [11], synthesis of ferrocenecarboxylic acid from ferroceneformaldehyde by the Cannizzaro reaction [12, 13] and reacting ferrocene with trichloroacetic acid [14]; finally, alkaline hydrolysis of the nitrile of ferrocene carboxylic acid [15].

Table 1 presents the basic methods of synthesizing ferrocenecarboxylic acids.

The first method includes a stage in which lithium derivatives of ferrocene are prepared and yields a mixture of mono- and 1,1'-diferrocenecarboxylic acids with a total yield of 30-78%. The content of ferrocene monocarboxylic acid in this mixture varies from 50 to 70% and does not exceed 43% of theory. The ferrocenecarboxylic acid yield was only 14% for oxidation of acetylferrocene by sodium hypochlorite, and 35-50% for oxidation by iodine in pyridine; however, the latter method requires a rather long reaction time, from 26 to 38 h.

Hydrolysis of carbamylferrocene and diphenylcarbamylferrocene gives ferrocenecarboxylic acid yields of 40 and 71.5%,

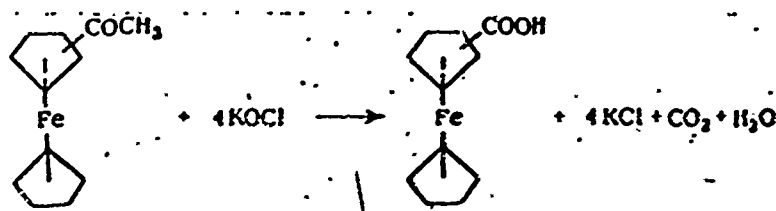
Table 1. Methods of Ferrocenecarboxylic Acid Synthesis

a. Способ получения	b. Общий выход кислот, % от теоретического		c. Содержание кислот в продуктах реакции, вес. %		f. Температура плавления, °C		g. Ссылки на литературу
	d. моль.	e. l, l'-ди.	d. моль.	e. l, l'-ди.	d. моль.	e. l, l'-ди.	
h. По реакции: $\text{Fe}(\text{C}_5\text{H}_5)_2 + \text{C}_6\text{H}_5\text{Li} + \text{CO}_2$ i. a) в эфире.	30-35	—	70	30	Разлагается при 195-205	к Не плавится до 250	[3, 4]
l. b) в среде тетрагидрофурана; эфир	67-78	43-46.5	53.5-57	—	Разлагается при 215-220	Разлагается при 250-260	[5-7]
м. Окисление NaOCl	14	—	100	—	Разлагается при 225-230	—	[8]
a) $\text{C}_5\text{H}_5\text{FeC}_3\text{H}_7\text{COCH}_3$	77	100	—	100	—	Возгоняется при 230	[2, 18, 19]
b) $(\text{C}_6\text{H}_5)_2\text{Fe}(\text{COCH}_3)_2$	35-50	—	100	—	Разлагается при 208.5	—	[9, 10, 16]
о. Окисление I_2 в пиридине	14	—	—	100	—	—	То же p
a) $\text{C}_5\text{H}_5\text{FeC}_3\text{H}_7\text{COCH}_3$	40	—	100	—	225-230	—	[11]
b) $\text{C}_5\text{H}_5\text{FeC}_3\text{H}_7\text{CON}(\text{C}_6\text{H}_5)_2$	71.5	—	100	—	201-204	—	[11, 12]
c) $\text{C}_5\text{H}_5\text{FeC}_3\text{H}_7\text{CN}$	80	—	100	—	196-201	—	[15]
q. Гидролиз	34	100	—	100	η с разложением	—	[15]
d) $(\text{C}_5\text{H}_5)_2\text{Fe}(\text{CN})_2$	10-27	—	100	—	Разлагается при 210	—	[13]
h. По реакции $\text{C}_5\text{H}_5\text{FeC}_3\text{H}_7\text{CHO} + \text{KOH}$	60	—	100	—	219-225	—	[14]
$(\text{C}_5\text{H}_5)_2\text{Fe} + \text{Cl}_3\text{CCOOH}(\text{CuCl}_2)$	42	100	—	100	Разлагается при 220-222	—	[17]
$(\text{C}_5\text{H}_5)_2\text{Fe} + \text{C}_6\text{H}_5\text{Na}, \text{CO}_2$							

KEY: (a) method of preparation; (b) total yield of acids, % of theory; (c) content of acid in reaction products, % by weight; (d) mono-; (e) l, l'-di-; (f) melting point, °C; (g) source; (h) by the reaction; (i) in ether; (j) decomposes at; (k) does not melt below; (l) in tetrahydrofuran: ether mixture; (m) oxidation by NaOCl ; (n) sublimes at; (o) oxidation by I_2 in pyridine; (p) same; (q) hydrolysis of; (r) with decomposition.

respectively, but involves a rather lengthy synthesis (12-18 h) and preparation of the starting compounds is quite complex. The ferrocenecarboxylic acid yield obtained from ferrocenecarboxaldehyde by the Cannizzaro reaction is 10-27%, while that obtained by reacting ferrocene with trichloroacetic acid does not exceed 6%.

In the present study, the simplest (in the authors' opinion) method of synthesizing ferrocenecarboxylic acid was employed: oxidation of acetylferrocene by hypochlorite according to the scheme



The literature does not give a detailed description of this synthesis method; as was indicated above, the yield of ferrocenecarboxylic acid has been only 14% [8].

The acetyl- and 1,1'-diacetylferrocene needed to synthesize the acids were obtained by the known methods: the former from ferrocene and acetic anhydride in the presence of 85% phosphoric acid with a yield of 70-71% of theory [1], and the latter from ferrocene and acetyl chloride in the presence of AlCl_3 , with a yield of about 80% [2].

Table 2. Influence of Reaction Conditions on Ferrocenecarboxylic Acid Yield

a Условия реакции				f
b температура, °C	c продолжительность, ч	d молярное соотношение $\text{C}_{10}\text{H}_8\text{FeC}_4\text{H}_4\text{COCH}_3/\text{KOCl}$	e концентрация раствора KOCl, вес. %	Выход, % от теоретического
70	5	1:10	7.7	28.0
50	5	1:10	7.7	35.0
30	5	1:10	7.7	24.5
50	10	1:10	7.7	31.3
50	3	1:10	7.7	30.0
50	5	1:20	15.4	45.2
50	5	1:40	30.8	42.2

KEY: (a) reaction conditions; (b) temperature, °C; (c) time; hours; (d) molar ratio; (e) concentration of KOCl solution, % by weight; (f) yield, % of theory.

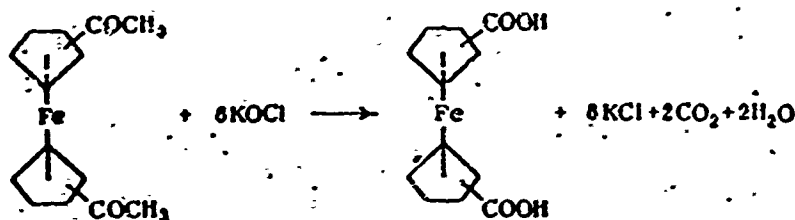
To ascertain the influence of reaction conditions on ferrocenecarboxylic acid yield, the reaction temperature was varied from 30 to 70°C, the reaction time from 3 to 10 h, and the potassium hypochlorite solution concentration from 7.7 to 30.8%. The results of the experiments are shown in Table 2.

As we see from the data presented, the maximum ferrocene-carboxylic acid yield (45.2% of theory) was obtained at 50°C, a reaction time of 5 h, and a potassium hypochlorite solution concentration of 15.4%.

Several methods are known for the synthesis of ferrocene-1,1'-dicarboxylic acid (see Table 1). As we noted, carboxylation of lithium ferrocenes yields a mixture of the acids. The content of ferrocene-1,1'-dicarboxylic acid in this mixture is 30-70% and does not exceed 35% of theory [3-7]. Oxidation of acetylferrocenic acid by iodine in pyridine gives a 14% yield of ferrocene-1,1'-dicarboxylic acid [16].

The yield of ferrocene-1,1'-dicarboxylic acid obtained from ferrocene and phenyl sodium amounts to 42% of theory [17]. It has been possible to obtain a 77% yield of ferrocene-1,1'-dicarboxylic acid by oxidizing 1,1'-diacetylferrocene with sodium hypoiodite and hypochlorite [2, 18, 19].

The latter method was used in the present study to synthesize ferrocene-1,1'-dicarboxylic acid:



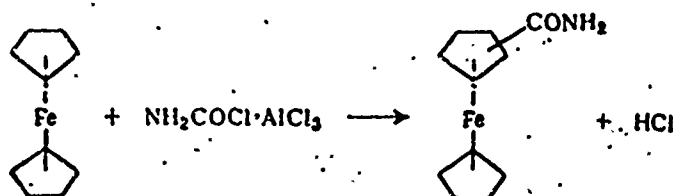
The synthesis conditions were modified slightly from those described in the literature: the reaction was conducted for 5 h at 50°C and a potassium hypochlorite concentration of 27.7%. The yield of ferrocene-1,1'-dicarboxylic acid was then 90-92% of theory.

The literature describes three methods for the synthesis of the amide of ferrocenecarboxylic acid (carbamylderrocene). For example, carbamylderrocene has been obtained from ferrocene carboxylic acid chloride and concentrated ammonium hydroxide [2].

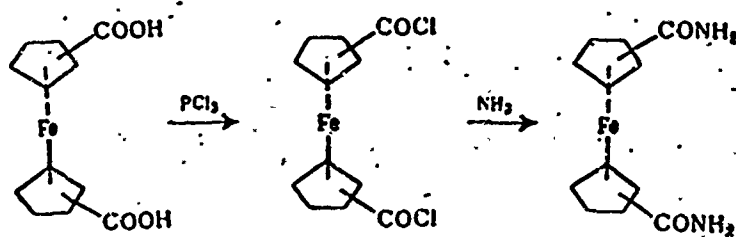
The authors do not indicate the synthesis conditions or the carbamylderrocene yield. A possible way to synthesize carbamylderrocene (yield 93% of theory) by alkaline hydrolysis of the nitrile of ferrocenecarboxylic acid in the presence of hydrogen peroxide has been described [15]. However, this method involves the complicated preparation of ferrocenecarboxylic acid nitrile [21].

Other authors [11] prepared carbamylferrocene with a 70.5% yield by alkylating ferrocene with carbamyl chloride in the presence of aluminum chloride as a catalyst. But carbamyl chloride is a highly unstable substance, which decomposes into cyanuric acid and hydrogen chloride, so that it becomes inconvenient to work with it. The stability of carbamyl chloride can be improved by adding aluminum chloride (molar ration 1:1). This results in formation of a stable compound that melts in the 60-80°C range [23-24].

In the present study, carbamylferrocene was synthesized by direct reaction of ferrocene with carbamyl chloride in the presence of AlCl_3 , and using the complex of carbamyl chloride with aluminum chloride, by the scheme



The yield of carbamylferrocene was about the same in both cases, at 70-72% of theory. The carbamyl chloride needed for this synthesis was obtained by treating ammonium chloride or ammonia with phosgene [23, 24]. The diamide of ferrocene-1,1'-dicarboxylic acid (dicarbamylferrocene) was obtained by the reaction [15]:

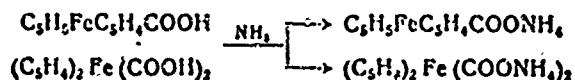


The intermediate product - the diacid chloride of ferrocene-1,1'-dicarboxylic acid - can be obtained by reaction of ferrocene-1,1'-dicarboxylic acid with hydroxyallyl chloride [21], by the reaction between ferrocene-1,1'-dicarboxylic acid and PCl_3 (molar ratio 1:2) in benzol [15] or without a solvent and with a 115-fold excess of PCl_3 [25]. The former method gives a rather high yield of the diacid chloride (~80% before recrystallization), but requires preliminary synthesis of the hydroxyallyl chloride, the yield of which is very small. In the latter method, the diacid chloride of ferrocene-1,1'-dicarboxylic acid was obtained with a 30% yield after agitating for 3 hours at 5-6°C and 5 hours at 50°C. We did not succeed in improving this yield in synthesis of the diacid chloride by this method. An attempt to prepare the diacid chloride by reacting ferrocene-1,1'-dicarboxylic acid with PCl_5 failed. Goldberg [25] did not isolate the diacid chloride prepared by boiling ferrocene-1,1'-

dicarboxylic acid for 24 hours with a 115-fold excess of PCl_3 ; it was converted at once into the dimethyl ester of ferrocene-1,1'-dicarboxylic acid. The authors of this paper obtained the diacid chloride of ferrocene-1,1'-dicarboxylic acid with 46% of the theoretical yield by boiling ferrocene-1,1'-dicarboxylic acid for 12 hours with a 115-fold PCl_3 excess.

1,1'-dicarbamylferrocene was obtained with almost 100% yield by passing ammonia through a benzol solution of the diacid chloride.

The literature does not describe the preparation of ammonium salts of ferrocenecarboxylic acids. The authors prepared these ammonium salts by passing gaseous ammonia through a solution of the ferrocenecarboxylic acids in dimethylformamide at room temperature:



EXPERIMENTAL

1. Synthesis of Ferrocenecarboxylic Acids

Ferrocenecarboxylic acid was synthesized by the following method: 125 ml of a (~15.4% by weight) potassium hypochlorite solution to which 5.7 g (0.025 mole) of acetylferrocene had been added were placed in a triple-neck flask fitted with an agitator, a reflux condenser, and a thermometer. The reaction was carried out in darkness. The mixture was heated to 50°C with vigorous agitation. At 1, 5, 2, and 3 h after the reaction temperature had stabilized, 62.5-ml portions of potassium hypochlorite solution were added and the mixture was then agitated for 2 h at 50°C and immediately filtered off. The filtrate was treated with an aqueous solution of sodium bisulfite and acidified with hydrochloric acid until a yellow precipitate appeared. To make sure that all of the hypochlorite had been decomposed, the reaction mass was tested with potassium iodide solution. The crude acid was reprecipitated with 10% HCl solution from saturated sodium bicarbonate solution. It was then washed with water to remove sodium chloride and dried. The ferrocenecarboxylic acid yield was 2.6 g (45.2% of theory).

The ferrocenecarboxylic acid was a yellow substance, soluble in organic solvents and crystallizing from a toluol-ligroin (1:1) mixture. The literature cites various melting (decomposition) points for ferrocenecarboxylic acid; they vary from 195 to 230°C. The melting range found by the authors was 195-200°C (with decomposition).

Elementary composition, %: C-57.64; 57.50; H-4.65; 4.28; Fe-24.24; 24.10.

Calculated for $\text{C}_{11}\text{H}_{10}\text{C}_2\text{Fe}$, %: C-57.4; H-4.35; Fe-24.3.

Ferrocene-1,1'-dicarboxylic acid was synthesized by the same method with an additional hot-benzol washing to remove any acetylferrocenecarboxylic acid that may have formed during the reaction.

The ferrocene-1,1'-dicarboxylic acid was an orange-yellow substance, insoluble in benzol or ether, and crystallizing from glacial acetic acid and from alcohol. According to some literature sources, the acid does not melt below 250°C [3, 4], while according to others it sublimates at 230°C [2, 18, 19]. The ferrocene-1,1'-dicarboxylic acid obtained by the authors neither melts nor decomposes below 250°C.

Elementary composition, %: C-52.40; 52.35; H-3.82; 3.6; Fe-20.46; 20.38.

Calculated for $C_{12}H_{10}FeO_4$, %: C-52.5; H-3.65; Fe-20.44.

2. Synthesis of Ferrocenecarboxylic Acid Amide (Carbamylferrocene)

Carbamylferrocene was synthesized by the following method: a suspension of the complex of carbamylchloride with aluminum chloride, consisting of 10 g (0.075 mole) of $AlCl_3$ and 6 g (0.075 mole) of NH_2COCl in 150 ml of dichloroethane, was poured into a triple-neck flask fitted with a stirrer, a dropping funnel, and an air condenser at 0°C. During 20 min, a solution of 9.3 g (0.05 mole) of ferrocene in 200 ml of dichloroethane was added to the mixture with cooling. The mixture was brought to room temperature for 1 h and then agitated for 16-20 h in a nitrogen atmosphere. The aluminum chloride was decomposed with 100 ml of water and the organic phase washed with water, dried with sodium sulfate, and evaporated to a residue, which was washed with petroleum ether. The residue was recrystallized from water to obtain 8.2 g of carbamylferrocene (71.2% of theory). According to literature sources, the melting point of carbamylferrocene varies from 168 to 171°C, in agreement with our result (168-170°C).

Elementary composition, %: C-57.82; 57.91; H-4.96; 4.79; Fe-24.11; 24.3; N-6.03; 6.12.

Calculated for $C_{12}H_{10}FeNO$, %: C-57.7; H-4.8; Fe-24.4; N-6.1.

3. Synthesis of Diamide of Ferrocene-1,1'-dicarboxylic Acid (1,1'-dicarbamylferrocene)

The diacid chloride of ferrocene-1,1'-dicarboxylic acid was first synthesized by boiling 5.5 g (0.025 mole) of ferrocene-1,1'-dicarboxylic acid with 200 ml (2.3 moles) of PCl_5 for 12 h in a nitrogen atmosphere. The PCl_5 excess was then driven off under vacuum; the residue was recrystallized from petroleum ether to obtain 3.26 g (46% of theory) of the diacid chloride of ferrocene-1,1'-dicarboxylic acid. At this point, in view of the rapid hydrolysis of the diacid chloride, we did not isolate the latter, but extracted the residue repeatedly with benzol after driving

off the PCl_3 and used the extract to synthesize 1,1'-dicarbamylferrocene.

To prepare 1,1'-dicarbamylferrocene, ammonia was passed through a precooled benzol solution of ferrocene-1,1'-dicarboxylic acid dichloride at a rate such that the reaction temperature did not rise above 15°C and the evolution of white NH_4Cl fumes was not too violent. The mixture was allowed to stand overnight after the reaction. The reaction mass was then filtered off and the residue washed first with benzol and then with water and recrystallized from water. 1,1'-dicarbamylferrocene was obtained with a yield of almost 100%. It takes the form of light-yellow crystals with bronze iridescence, melting at 275°C (according to literature data, $t_{\text{pl}} = 270-275^\circ\text{C}$).

Elementary composition, %: C—52.69; 53.02; H—4.69; 4.32; Fe—20.79; 20.70; N—10.31; 10.40.

Calculated for $\text{C}_{12}\text{H}_{12}\text{FeN}_2\text{O}_2$, %: C—52.94; H—4.44; Fe—20.68; N—10.21.

4. Synthesis of Ammonium Salts of Ferrocenecarboxylic Acids

Ammonium salts of the ferrocenecarboxylic acids were prepared with almost 100% yields by passing ammonia through a solution of the ferrocenecarboxylic acids in dimethylformamide at room temperature (weight ratio of acid:solvent 1:10). The reaction was considered complete when no more ammonia was absorbed. The resulting residue was filtered off, washed with dimethylformamide and then with ether, and dried in a vacuum. The ammonium salts of ferrocenemono- and 1,1'-dicarboxylic acids do not melt, but darken at temperatures of 220 and 230°C , respectively.

Elementary composition for $\text{C}_{11}\text{H}_{13}\text{FeNO}_2$, %: C—53.53; 53.60; H—5.56; 5.45; Fe—22.80; 22.95; N—5.49; 5.73.

Calculated, %: C—53.4; H—5.56; Fe—22.7; N—5.7.

Elementary composition for $\text{C}_{12}\text{H}_{10}\text{FeN}_2\text{O}_4$, %: C—46.48; 46.65; H—5.12; 5.15; Fe—18.25; 18.1; N—9.08; 9.14.

Calculated, %: C—46.7; H—5.18; Fe—18.22; N—9.1.

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Symbol List

Manu- script page	Symbol	English Equivalent
8	пл pl	melting