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FUNCTIONAL DERIVATIVES OF FERROCENE-1,1$'$-DICARBOXYLIC ACID

(Presented by Academician A. N. Nesmeyanov, February 11, 1958)

Ferrocene-1,1′-dicarboxylic acid was obtained by Woodward and co-workers in 1952 (^{1}); however, until recently its derivatives had not been known, with the exception of the dimethyl ester (II) (see Table 1) (^{1}) and the monomethyl ester (III) (^{2}). In the present work we have obtained a series of new derivatives of this acid.

Table 1

	X	Y
I	$-\mathrm{COOH}$	COOH
II	$-\mathrm{COOCH_3}$	$-\mathrm{COOCH_3}$
III	$-\mathrm{COOH}$	$-\mathrm{COOCH_3}$
IV	$-\mathrm{COCl}$	$-\mathrm{COCl}$
V	$-\mathrm{CONH_2}$	$-\mathrm{CONH_2}$
VI	$-\mathrm{COOCH_3}$	$-\mathrm{CONH_2}$
VII	$-\mathrm{COOH}$	$-\mathrm{CONH_2}$
VIII	$-\mathrm{COOH}$	$-\mathrm{CN}$
IX	$-\mathrm{CN}$	$-\mathrm{CN}$
X	$-\mathrm{H}$	$-\mathrm{CN}$

The acid chloride of ferrocene-1,1′-dicarboxylic acid (IV) was obtained in 30% yield by 3-hour interaction of 0.025 mole of this acid with 0.05 mole of phosphorus trichloride in the cold in 40 ml of benzene, followed by heating of the reaction mixture at 50–60° for 2 hours. It is a red substance, readily soluble in organic solvents, crystallizing from petroleum ether. M.p. 92–93°.

$C_{12}H_8FeO_2Cl_2$.	Found, %:	C 46.83; 46.87; H 2.68; 2.65; Fe 18.07; 17.94
	Calculated, %:	C 46.35; H 2.59; Fe 17.96.

Hydrolysis of the pure acid chloride (IV) proceeds comparatively slowly. Thus, it is hydrolyzed by a 20% soda solution only on heating or upon prolonged standing in the cold, and in this respect it resembles acid chlorides of aromatic acids.

From the acid chloride of ferrocene-1,1′-dicarboxylic acid, with a yield close to quantitative, the amide of this acid (V) was obtained; it is a yellow compound, insoluble in nonpolar and poorly soluble in polar organic solvents. It can be recrystallized from water. It decomposes in the range 270–275°.

$C_{12}H_{12}FeO_2N_2$. Found, %: C 53.02; 53.10; H 4.25; 4.31; F 20.33; 20.42; N 13.11; 12.91
Calculated, %: C 52.98; H 4.44; F 20.53; N 13.21.

On heating the acid methyl ester of ferrocene-1,1′-dicarboxylic acid (III) for 2 hours in phosphorus trichloride, the corresponding acid chloride is obtained; it was not isolated, but after removal of the solvent was treated in the cold with a 25% ammonia solution. The resulting yellow powder of methyl 1-carbamidoferrocene-1′-carboxylate was recrystallized from toluene and from methanol. Yield 60%. The substance is readily soluble in acetone, alcohol, chloroform, and hydrochloric acid. M.p. 143.5–145°.

Found %: C 54.85; 54.94; H 4.50; 4.60; Fe 19.51; 19.29; N 5.09; 5.12
$C_{13}H_{13}FeO_3N$. Calculated %: C 54.40; H 4.56; Fe 19.45; N 4.88.

This ester was hydrolyzed with an excess of 10% NaOH while heating on a water bath for 15 min. 1-Carbamidoferrocene-1′-carboxylic acid (VII) resembles, in solubility, the above-described amide of ferrocene-1,1′-dicarboxylic acid (V). On heating above 200° it gradually decomposes. It can be recrystallized from acetic acid and from methanol.

Found %: C 52.97; 53.08; H 3.94; 4.00; Fe 20.56; 20.83; N 5.37; 5.27
$C_{12}H_{11}FeO_3N$. Calculated %: C 52.78; H 4.05; Fe 20.45; N 5.13.

It was found that the amides described above, (V) and (VII), as well as the amide of ferrocenecarboxylic acid* can be converted into the corresponding nitriles by heating in acetic anhydride.

On heating 1-carbamidoferrocene-1′-carboxylic acid (VII) for 20 min in acetic anhydride at 140°, 1-cyanoferrocene-1′-carboxylic acid (VIII) was obtained in 55% yield; it is a yellow substance with m.p. 179–180° (with decomposition), more readily soluble in polar solvents than in nonpolar ones. It can be recrystallized from toluene and from methanol.

Found %: C 56.56; 56.64; H 3.65; 3.76; Fe 21.88; 21.86; N 5.86; 6.07
$C_{12}H_9FeO_2N$. Calculated %: C 56.52; H 3.56; Fe 21.90; N 5.49.

The nitrile of ferrocene-1,1′-dicarboxylic acid (IX) was obtained by heating the amide of this acid (V) for 6 hours in acetic anhydride (10 ml of acetic anhydride per 1 g of amide) at 100° and subsequently heating the reaction mixture in an ampoule at 170°. Yield 30%. M.p. 166-167.5° (with decomposition) in a sealed capillary. The substance can be recrystallized from methanol and toluene.

Found %:	C 61.17; 60.96; H 3.55; 3.49; Fe 23.73; 23.56; N 11.80; 11.73
$C_{12}H_8FeN_2$. Calculated %:	C 61.06; H 3.37; Fe 23.66; N 11.87.

On heating the amide of ferrocenecarboxylic acid for 40 min at 140° in acetic anhydride, the nitrile of this acid (X) was obtained, and 20% of the starting material was recovered. M.p. (X) 106.5-107.5°; according to the literature, 103-104°.**

Found %:	C 62.74; 62.87; H 4.10; 4.25; Fe 26.21; 26.07; N 6.60; 6.77
$C_{11}H_9FeN$. Calculated %:	C 62.61; H 4.29; Fe 26.47; N 6.64.

When pyridine is allowed to act on acid chloride (IV) in chloroform in the presence of water, elimination of the elements of HCl from two molecules of acid chlo– hydride and two molecules of water, with formation of ferrocene-1,1′-dicarboxylic anhydride (XI)*.

[[chemical structure of (XI), with two Φ groups linked through a cyclic anhydride framework]]

$$\text{where } \Phi = -C_5H_4 - Fe - C_5H_4-$$

(XI)

The yield reached 65% if the reaction was carried out as follows. To a solution of 0.01 mole of the acid chloride (IV) in 15 ml of chloroform, 0.05 mole of pyridine in chloroform was added dropwise with shaking; 1.2 ml of water was then poured in at once, and the mixture was shaken and left for 12 hours. The chloroform solution was then washed with 2% hydrochloric acid, sodium carbonate solution, and water, and dried over calcium chloride. The residue after removal of the solvent in vacuo and washing with ether is a yellow powder, poorly soluble in most organic solvents except chloroform, and decomposing in the range 230-240° (after recrystallization from nitromethane).

$C_{12}H_8FeO_3$.	Found, %:	C 55.92; 55.75; H 3.25; 3.37; Fe 21.60; 21.30
	Calculated, %:	C 56.28; H 3.15; Fe 21.80.

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* Described by Arimoto and Haven (³).

** This nitrile was obtained by American authors by dehydration of the oxime of the corresponding aldehyde (⁴).

Molecular weight (cryoscopy in dioxane) found 556, 528; calculated 512.

Another proof of the above dimeric formula of the anhydride is its reaction with aqueous ammonia. In this case three products are formed: the amide of ferrocene-1,1′-dicarboxylic acid (V), and the ammonium salts of this acid and of 1-carbamidoferrocene-1′-carboxylic acid (VII) (approximately in the ratio 1 : 1 : 2, respectively). In the case of a monomeric anhydride, one would have expected only formation of the last product. The acids isolated from this reaction were separated and identified in the form of their methyl esters. Anhydride (XI) is hydrolyzed by dilute alkali on heating; on prolonged heating with methanol in the presence of hydrochloric acid it gives the methyl ester of ferrocene-1,1′-dicarboxylic acid (II).

We shall also characterize incidentally some salts of ferrocene-1,1′-dicarboxylic acid. The sodium, potassium, and lithium salts of this acid are readily soluble in water but poorly soluble in concentrated alkalis, and owing to this can be isolated in solid form by treating the dry acid with concentrated alkalis. The salt crystals can be washed on the filter with a small amount of methanol to remove alkali.

The yellow-green cupric salt of acid (I) is practically insoluble in water. When 0.01 M aqueous solutions of lead acetate and the sodium salt of acid (I) are mixed, a precipitate of the lead salt of this acid separates. The barium and magnesium salts of this acid are more readily soluble in water. Precipitates of these salts separate when cold-saturated solutions of the chlorides of these metals are mixed with a 0.05 M solution of the sodium salt of acid (I).

In accordance with the aromatic character of ferrocene, it turned out that the radical $-CCl_3$, formed during the thermal decomposition of trichloroacetic acid in the presence of cupric chloride, is capable of replacing one of the hydrogens of ferrocene. Previously this reaction had been known only for such compounds as naphthalene or xylene (^{5}). The decomposition of trichloroacetic acid was carried out in a saturated solution of an equimolar amount of ferrocene in nitrobenzene at 120-130°. Trichloroacetic acid was added in portions together with catalytic amounts of anhydrous cupric chloride and pyridine. After the reaction was complete, the reaction mass was pro— with 10% NaOH, and ferrocenecarboxylic acid was isolated from the alkaline extract. After recrystallization from toluene and methanol, the yield of the acid was 6%, melting point 220-222° (with decomposition) in a sealed capillary. According to the literature, this acid decomposes above 200° (^{6}, ^{7}).

Found, %:	C 57.74; 57.62;	H 4.50; 4.41;	Fe 24.08; 24.12
$C_{11}H_{10}O_2Fe$. Calculated, %:	C 57.43;	H 4.39;	Fe 24.28.

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* Anhydride (XI) was obtained by us jointly with V. K. Plakundov.

After treatment with diazomethane, the methyl ester of this acid was obtained, m.p. 68–69°, which agrees with the literature data (6).

Despite variation of the conditions for decomposition of trichloroacetic acid in a mixture with ferrocene, no products of double trichloromethylation of ferrocene were detected.

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