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Abstract

Full Text

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ACETYL DERIVATIVES OF PENTAETHANODIFERROCENE

We have obtained mono- and diacetylpentaethanodiferrocene—products of the acylation of the new aromatic compound pentaethanodiferrocene (2), which is formed in the reaction of ferrocene with 1,2-dichloroethane in the presence of anhydrous aluminum chloride; moreover, it turned out that the substance previously obtained by us in this reaction, with m.p. 135° and called "diferrocenylethane" (1), is a mixture of isomers of diferrocenylethane-1,1 and a small amount of diferrocenylethane-1,2.

Fig. 1. IR spectra:
a—monoacetylpentaethanodiferrocene (0.0101 g in 0.8997 g KBr);
b—diacetylpentaethanodiferrocene (0.0061 g in 0.7990 g KBr).

Later we succeeded in isolating both isomers in the individual state, having somewhat modified the procedure for working up the reaction products (details in the experimental section). After purification by chromatography on alumina in a benzene-*n*-heptane 1:1 mixture, the following were obtained: diferrocenylethane-1,1 with m.p. 147-149° (6) and diferrocenylethane-1,2 with m.p. 192-192.5°; the latter is identical with samples obtained by one of us and Kritskaya (4,5)*, and also by one of us, E. G. Perevalova and Yu. T. Ustynyuk (6).

Acylation of pentaethanodiferrocene with acetic anhydride in the presence of 85% phosphoric acid gives the monoacetyl derivative; acylation with acetyl chloride in the presence of anhydrous aluminum chloride in methylene chloride (solvent) gives diacetylpentaethanodiferrocene and other polyacetylpentaethanodiferrocenes.

Monoacetylpentaethanodiferrocene is a yellowish powder, readily soluble in alcohol, acetone, and benzene, less so in water and ether. It was recrystallized from absolute alcohol. Diacetylpentaethanodiferrocene is an orange-yellow powder, recrystallized from *n*-heptane. The acylation confirms the previously proposed structure of pentaethanodiferrocene.

The IR spectra of the acetyl derivatives contain a characteristic frequency in the region of 1670 cm^{-1} (carbonyl group); in addition, monoacetylpentaethanodiferrocene contains frequencies in the regions of 1000 and 1100 cm^{-1} (the free ferrocene ring); diacetylpentaethanodiferrocene contains no bands in the regions of 1000 and 1100 cm^{-1}; consequently, both acetyl groups enter different rings of pentaethanodiferrocene (see Fig. 1b). The presence of two unsubstituted rings in pentaethanodiferrocene may thus be considered proven.

In addition, new physicochemical data have been obtained that confirm the structure of pentaethanodiferrocene. The nuclear magnetic resonance spectra (see Table 1) show the absence of methyl groups in pentaethanodiferrocene, while they are present in the reference compounds—ethylferrocene (^{3}) and diferrocenylethane-1,1 (cf. (^{9})).

Table 1

Table of relative chemical shifts according to NMR spectra

Compound	H_{benzol}	$H_{\square}$	H_{CH}	H_{CH_2}	H_{CH_3}	$H_{\text{CH}} - H_{\square}$	$H_{\text{CH}_2} - H_{\square}$	$H_{\text{CH}_3} - H_{\square}$
Ferrocene	0	3.22	—	—	—	—	—	—
Ethylferrocene	0	3.34	—	5.35	6.56	—	2.02	3.22
Tributylferrocene	0	3.29	—	—	5.86	—	—	2.59
Pentaethanodiferrocene	0	3.29	—	5.35	—	—	2.16	—
Diisopropylferrocene (^{7})	2.72	5.97	7.36	—	8.86	1.39	—	2.89
Diferrocenylethane-1,1 (^{8})	—	5.86	6.58	—	8.86	0.72	—	3.00
Diferrocenylethane-1,2	—	—	—	—	—	—	—	—

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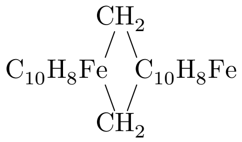
* In these works (^{4},^{5}), and also in works by foreign authors (^{9},^{10}), 1,2-diferrocenylethane was obtained by condensation of formaldehyde with ferrocene and was erroneously taken to be a substance of the structure (cf. (^{11})):



Pentaethanodiferrocene and its acetyl derivatives are amorphous, have no sharp melting points, and gradually darken and soften at about 100°. However, thermograms obtained on a Kurnakov PK-55 pyrometer show that on the heating curve recorded up to 200° no exo- or endothermic effects are observed.

The nuclear magnetic resonance spectra were kindly determined by Yu. Yu. Samitov; the IR spectra were determined by N. A. Chumaevskii. Thermographic measurements were carried out by V. M. Kozhin and E. I. Yarembash, to whom the authors express their deep gratitude.

Separation of the products of the reaction of ferrocene with dichloroethane. The reaction of ferrocene (40 g, 0.21 mole) with dichloroethane (200 ml, 2.5 moles) in the presence of anhydrous aluminum chloride was described by us earlier.

After decomposition of the reaction mixture in the usual way and removal of the solvent, the reaction products were extracted with methanol in a Soxhlet apparatus. The solid residue from the thimble of the Soxhlet apparatus was treated with ether (50 ml per 1 g of substance) and reprecipitated into methanol (10-fold excess). Pentaethanodiferrocene, 1-2 g, was obtained.

The residue insoluble in this amount of ether was reprecipitated from benzene with a 10-fold amount of methanol. 1-2 g of polymer was obtained, mol. wt. 2300. All mother liquors from the Soxhlet apparatus, as well as the solutions after reprecipitation of the samples from ether and benzene, were evaporated to dryness without heating. The residue was subjected to chromatography on Al_2O_3 from a benzene : heptane 1 : 1 mixture on a column 1 m high and 29 mm in diameter, in 1-g portions, at a rate of 5 ml/min. In all, the following were obtained: I—oil, n_D^{20} 1.6056 (3.17 g); II—ferrocene, m.p. 172° (5 g); III—diferrocenylethane-1,1, m.p. 147-149° (1.05 g); IV—intermediate fractions oil + diferrocenylethane-1,1 (2.25 g); V—oil, n_D^{20} 1.6530 (1.8 g); VI—diferrocenylethane-1,2, m.p. 192-192.5° (0.1 g). Weight 0.6 g.

Acetylpentaethanodiferrocene $C_{30}H_{29}Fe_2$—$COCH_3$. A mixture of 2.5 g of pentaethanodiferrocene, 5 g of acetic anhydride, and 0.5 ml of 85% phosphoric acid was heated to 100-105° for 15 min. The mixture was then ···

poured onto ice, washed with a solution of 4 g of sodium bicarbonate in 5 ml of water and then with water. The dark powder (2.6 g) was soluble in *n*-heptane, ether, acetone, and alcohol, and less soluble in water. After recrystallization from absolute alcohol, a yellowish powder was obtained; melting point in a sealed capillary 105-110° (with decomposition).

Found, %:	C 70.87; 70.99;	H 6.25; 6.23;	Fe 20.51; 20.35
$C_{32}H_{32}Fe_2O$. Calculated, %:	C 70.60;	H 5.80;	Fe 20.15

Mol. wt. (benzene, cryoscopy): found 539, $C_{32}H_{32}Fe_2O$. Calculated 544.28.

Diacetylpentaethanodiferrocene. To a solution of 2 g of pentaethanodiferrocene in 20 ml of methylene chloride was gradually added a solution of 0.65 ml of acetyl chloride and 1.04 g of anhydrous aluminum chloride in 20 ml of methylene chloride. Slight heating was observed. The mixture was stirred at room temperature for 5 hr. After standing overnight, the reaction mass was poured into a mixture of ice and HCl (1:1) and extracted with ether and benzene. All solutions were combined, washed with 5% soda solution and with water, and dried over anhydrous sodium sulfate. After removal of the solvent in vacuum (20 mm), 1.62 g of a dark-red precipitate was obtained; after chromatography on silica gel from benzene, 0.3 g of an orange powder was obtained. It was recrystallized from *n*-heptane. It darkens above 80°C.

Found, %:	C 69.55;	H 5.64;	Fe 17.04
$C_{34}H_{34}Fe_2O_2$. Calculated, %:	C 69.60;	H 5.85;	Fe 19.10 (as Fe_2O_3)

Mol. wt. (benzene, cryoscopy): found 583, calculated for $C_{34}H_{34}Fe_2O$ 586.31. In addition, a mixture of isomers of triacetylpentaethanodiferrocene and tetraacetylpentaethanodiferrocene was isolated.

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