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Synthesis of 1,1'-Diacetylferrocene Dioxime Esters

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Abstract—1,1'-Diacetylferrocene dioxime was synthesized by the reaction of 1,1'-diacetylferrocene with hydroxylamine. The dioxime reacts readily with carboxylic acids chlorides in the presence of pyridine with the formation of 1,1'-diacetylferrocene dioxime esters.

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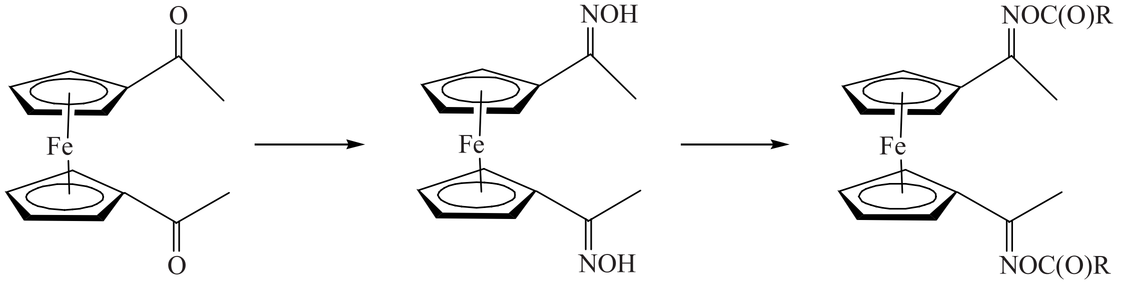
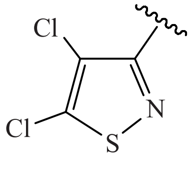
Ferrocene and its derivatives possess uncommon electronic and magnetic properties and exhibit a wide spectrum of biological activity [1, 2]. The biological effect of a substituted ferrocene significantly depends on the number and nature of the functional groups in its molecule, which stimulates the work on the synthesis of new compounds of ferrocene series [2–4].

The purpose of this work is development of preparative method for the synthesis of the previously unknown esters of 1,1'-diacetylferrocene dioxime **III–XXXIV**. Esters **III–XXXIV** were obtained by the reaction of 1,1'-diacetylferrocene dioxime **II** with carboxylic acid chlorides in the presence of pyridine (ratio of reagents 1:2:2) in the medium of anhydrous diethyl ether. As a result the ferrocene-containing esters of aliphatic **III–XVIII**, cycloaliphatic and polycyclic **XIX, XX**, aromatic and alkylaromatic **XXI–XXIII**, **XXVI–XXXI,** and functionally substituted carboxylic acids **XXIV–XXXIV** were synthesized. The yield of compounds **III–XXXIV** is 78–85%. The initial 1,1'-diacetylferrocene dioxime **II** was

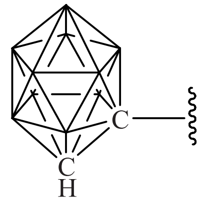


I **II** **III–XXXIV**

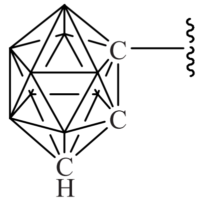
R = Me (**III**), Et (**IV**), Pr (**V**), Me_2CH (**VI**), Bu (**VII**), Me_2CHCH_2 (**VIII**), Me_3C (**IX**), $Me(CH_2)_4$ (**X**), $Me(CH_2)_5$ (**XI**), $Me(CH_2)_6$ (**XII**), EtBuCH (**XIII**), $Me(CH_2)_7$ (**XIV**), $Me(CH_2)_8$ (**XV**), $Me(CH_2)_{11}$ (**XVI**), MeO (**XVII**), EtO (**XVIII**), *cyclo*-C_6H_{11} (**XIX**), 1-Ad (**XX**), C_6H_5 (**XXI**), $C_6H_5(CH_2)_2$ (**XXII**), $C_6H_5MeCHCH_2$ (**XXIII**), $Cl_2C{=}CCl$ (**XXIV**), $Cl_2C{=}CClCH_2$ (**XXV**), 2,4-$Cl_2C_6H_3$ (**XXVI**), $C_6H_5(CHBr)_2$ (**XXVII**), $C_6H_5C(H){=}C(C^oN)$ (**XXVIII**), 3-$O_2NC_6H_4$ (**XXIX**), 4-$O_2NC_6H_4$ (**XXX**), 3,5-$(O_2N)_2C_6H_3$ (**XXXI**),



(**XXXII**),



(**XXXIII**),



(**XXXIV**).

synthe-sized by the reaction of 1,1'-diacetylferrocene **I** with hydroxylamine in ethanol [1].

The 1,1'-diacetylferrocene dioxime esters **III–XXXIV** are intensively colored orange or brown crystalline compounds or viscous oily liquids. Structures of the synthesized 1,1'-diacetylferrocene dioxime esters **III–XXXIV** are confirmed by the data of elemental analysis, by cryoscopic determination of the molecular weights of the compounds soluble in the benzene (see the table), and by the IR, UV and ^{1}H NMR spectra. According to the data of ^{1}H NMR spectroscopy, purity of the obtained esters is 95±2%.

In the IR spectra of the 1,1'-diacetylferrocene dioxime esters **III–XXXIV** absorption bands are

Yields, melting points, data of element analysis and molecular weights of compounds **III–XXXIV**

Comp. no.	Yield, %	mp, °C	Found, %				Formula	Calculated, %				*M*	
			C	H	Fe	N		C	H	Fe	N	found	calculated
III	80	106–107	56.41	5.38	14.19	7.06	$C_{18}H_{20}FeN_2O_4$	56.27	5.25	14.54	7.29	368.4	384.2
IV	78	65–66	58.55	6.02	13.28	6.46	$C_{20}H_{24}FeN_2O_4$	58.27	5.87	13.55	6.80	398.5	412.3
V	84	–	60.34	6.53	12.46	6.08	$C_{22}H_{28}FeN_2O_4$	60.01	6.41	12.68	6.36	425.7	440.3
VI	85	70–71	60.28	6.47	12.35	6.17	$C_{22}H_{28}FeN_2O_4$	60.01	6.41	12.68	6.36	428.2	440.3
VII	83	–	61.89	6.98	11.74	5.48	$C_{24}H_{32}FeN_2O_4$	61.55	6.89	11.92	5.98	453.6	468.4
VIII	82	–	61.75	7.02	11.58	5.66	$C_{24}H_{32}FeN_2O_4$	61.55	6.89	11.92	5.98	456.0	468.4
IX	80	156–157	61.82	7.00	11.63	5.68	$C_{24}H_{32}FeN_2O_4$	61.55	6.89	11.92	5.98	458.4	468.4
X	84	41–42	63.20	7.52	11.03	5.41	$C_{26}H_{36}FeN_2O_4$	62.91	7.31	11.25	5.64	483.1	496.4
XI	82	–	64.38	7.83	10.37	5.15	$C_{28}H_{40}FeN_2O_4$	64.12	7.69	10.65	5.34	508.9	524.5
XII	80	–	65.47	8.14	9.88	4.86	$C_{30}H_{44}FeN_2O_4$	65.21	8.03	10.11	5.07	542.4	552.5
XIII	81	–	65.68	8.20	9.92	4.76	$C_{30}H_{44}FeN_2O_4$	65.21	8.03	10.11	5.07	540.5	552.5
XIV	78	–	66.39	8.45	9.37	4.60	$C_{32}H_{48}FeN_2O_4$	66.20	8.33	9.62	4.83	568.3	580.6
XV	78	–	67.45	8.82	8.84	4.33	$C_{34}H_{52}FeN_2O_4$	67.10	8.61	9.18	4.60	597.2	608.6
XVI	80	61–62	69.83	9.54	7.82	3.76	$C_{40}H_{64}FeN_2O_4$	69.35	9.31	8.06	4.04	681.7	692.8
XVII	81	89–90	52.24	4.94	13.08	6.48	$C_{18}H_{20}FeN_2O_6$	51.94	4.84	13.42	6.73	404.6	416.2
XVIII	80	75–76	54.29	5.53	12.27	6.05	$C_{20}H_{24}FeN_2O_6$	54.07	5.45	12.57	6.31	431.8	444.3
XIX	82	116–117	64.92	7.12	10.45	5.13	$C_{28}H_{36}FeN_2O_4$	64.62	6.97	10.73	5.38	517.1	520.4
XX	84	170–171	69.56	7.19	8.72	4.18	$C_{36}H_{44}FeN_2O_4$	69.23	7.10	8.94	4.49	606.0	624.6
XXI	84	139–140	66.43	4.93	10.68	5.24	$C_{28}H_{24}FeN_2O_4$	66.16	4.76	10.99	5.51	492.4	508.3
XXII	80	119–120	68.34	5.82	9.65	4.76	$C_{32}H_{32}FeN_2O_4$	69.08	5.71	9.89	4.96	548.3	564.5
XXIII	81	–	69.23	6.18	9.14	4.50	$C_{34}H_{36}FeN_2O_4$	69.92	6.12	9.43	4.73	578.2	592.5
XXIV[a]	82	135, decomp.	39.28	2.35	8.76	4.30	$C_{20}H_{14}Cl_6FeN_2O_4$	39.07	2.29	9.08	4.56	601.4	614.9
XXV[b]	80	120–121	41.34	2.97	8.40	4.04	$C_{22}H_{18}Cl_6FeN_2O_4$	41.10	2.82	8.69	4.36	628.8	643.0
XXVI[c]	80	121–122	52.27	3.20	8.19	4.08	$C_{28}H_{20}Cl_4FeN_2O_4$	52.05	3.12	8.64	4.34	–	646.1
XXVII[d]	78	109–110	43.70	3.36	6.17	3.01	$C_{32}H_{28}Br_4FeN_2O_4$	43.67	3.21	6.35	3.18	–	880.0
XXVIII	79	149–150	67.18	4.38	8.86	8.76	$C_{34}H_{26}FeN_4O_4$	66.90	4.29	9.15	9.18	–	610.4
XXIX	81	180–181	56.22	3.90	9.03	9.12	$C_{28}H_{22}FeN_4O_8$	56.21	3.71	9.33	9.36	–	598.3
XXX	80	143–144	56.54	3.85	9.10	9.05	$C_{28}H_{22}FeN_4O_8$	56.21	3.71	9.33	9.36	–	598.3
XXXI	83	147–148	49.28	3.16	7.86	11.79	$C_{28}H_{20}FeN_6O_{12}$	48.86	2.93	8.11	12.21	–	688.3
XXXII[e]	80	167, decomp.	40.37	2.19	8.06	8.04	$C_{22}H_{14}Cl_4FeN_4O_4S_2$	40.03	2.14	8.46	8.49	–	660.2
XXXIII[f]	78	>320	37.84	5.70	8.73	4.05	$C_{20}H_{36}B_{20}FeN_2O_4$	37.50	5.66	8.72	4.37	–	640.6
XXXIV[g]	78	>320	37.88	5.72	8.19	3.91	$C_{20}H_{36}B_{20}FeN_2O_4$	37.50	5.66	8.72	4.37	–	640.6

[a] Found Cl, %: 34.18. Calculated Cl, %: 34.59. [b] Found Cl, %: 32.76. Calculated Cl, %: 33.08. [c] Found Cl, %: 21.63. Calculated Cl, %: 21.95. [d] Found Br, %: 35.97. Calculated Br, %: 36.32. [e] Found: Cl, %: 21.19; S 9.20. Calculated: Cl, %: 21.48; S 9.71. [f] Found B, %: 33.21. Calculated B, %: 33.75. [g] Found B, %: 33.47. Calculated B, %: 33.75.

present of the bonds C–H(cyclopentadienyl) 3100±10; S–H(aliph.) 2955±5, 2925±10, 2855±5; C=O 1755±20; C=C(cyclopentadienyl) 1600±5, 1460±10, 1330±10, 1303±5; CO 1170±25, 1065±25 cm^{-1}. In the IR spectrum of nitrile **XXVIII** an absorption band of C≡N is observed at 2223 cm^{-1}. In the IR spectra of nitrobenzoates (**XXIX–XXXI**) there are two characteristic absorption bands of NO_2 group at 1535±10 and 1345±3 cm^{-1}. In the IR spectra of carboranes **XXXIII** and **XXXIV** there are absorption bands C–H(carb) 3071 (**XXXIII**) and 3032 (**XXXIV**); B–H 2680±25 cm^{-1}.

In the UV spectra of the 1,1'-diacetylferrocene dioxime esters **III–XXXIV** there are absorption bands with the following maxima [$\lambda_{max,}$ nm (ε)]: 223 (18000), 282 (9000), 334 (3000), 453 (300), caused by the presence in the molecules of 1,1'-diacetylferrocene di-*O*-acyloxime fragments. In the ^1H NMR spectra of the 1,1'-diacetylferrocene dioxime esters **III–XXXIV** the signals of the protons of methyl group are singlets in the region of 2.19–2.32 ppm, the signals of C_5H_4 protons of cyclopentadienyl groups are two broad singlets in the region of 4.40–4.95 ppm.

In the IR, UV and ^1H NMR spectra of the 1,1'-diacetylferrocene dioxime esters **III–XXXIV** there are also the absorption bands and the proton signals which confirm the presence of the corresponding structural fragments of ester groups.

EXPERIMENTAL

The IR spectra of compounds were registered on a Protege-460 Nicolet IR Fourier spectrophotometer from KBr pellets, the UV spectra, on the Specord UV-Vis instrument from 1×10^{-4} M solutions of compounds in methanol, the ^1H NMR spectra, on the spectrometer Tesla BS-587A (100 MHz) from 5% solutions in chloroform-*d* or DMSO-d_6, chemical shifts were determined relative to internal reference TMS. The elemental analysis was carried out on a Vario EL-III Elementar C,H,N,O,S-analyzer, an error in the determination was 0.1%. The molecular weight (*M*) of the compounds soluble in benzene was determined by cryoscopy. 1,1'-Diacetylferrocene (**I**) was used of “analytically pure” grade, of 99% purity, with mp 126–127°C, 1,1'-diacetylferrocene dioxime **II** was synthesized by the reaction of 1,1'-diacetylferrocene **I** with hydroxylamine in ethanol, mp 141–142°C [1].

1,1'-Diacetylferrocene dioxime esters III–XXXIV *(general procedure).* 0.01 mol of oxime **II** was dissolved in 50 ml of anhydrous ether, and 0.02 mole of anhydrous pyridine was added to the solution. To the obtained solution at cooling to 15°C and stirring with a magnetic stirrer was added 0.02 mole of the respective carboxylic acid chloride. The mixture was stirred for 8 h and then left at the temperature 20–23°C for 24– 36 h. The liquid 1,1'-diacetylferrocene dioxime esters **V**, **VII**, **VIII**, **X**–**XV**, **XXIII** were separated as follows: the reaction mixture was diluted with water and the product was extracted with ether. Organic layer was separated, washed with water and 5% solution of $NaHCO_3$ and dried over $CaCl_2$ The solvent was then removed at a reduced pressure (10–15 mm Hg) avoiding heating above 25–30°C. The final purification was carried out by column chromatography on the silica gel L 5/40 μm, the products were eluted with ether–hexane 1:1 mixture. Crystalline esters **III**, **IV**, **VI**, **IX**, **XVI–XXII**, **XXIV–XXXIV** were isolated by filtration of the reaction mixture through the porous glass filter, the precipitate was washed on the filter with a small amount of ether and then washed with water for removing pyridine hydrochloride. The products were dried in air, final purification was carried out by recrystallization from methanol.

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