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Reaction of Acetylferrocene with Dimethylformamide Dimethyl Acetal and Some Transformations of the Reaction Product

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Abstract—1-Dimethylamino-3-ferrocenyl-3-oxoprop-1-ene was synthesized by the reaction of acetylferrocene with dimethylformamide dimethyl acetal. Its reactivity in the reactions with mononucleophilic (sodium salts of phenol, thiophenol, benzenesulfinate, diethylphosphorous acid) and binucleophilic reagents (hydrazine hydrate, hydroxylamine, amidines, 1,2-diaminobenzene, 2-aminophenol, 2-aminothiophenol) and methyl iodide was studied. As a result, we obtained new ferrocene-containing α-keto-unsaturated compounds and heterocycles of pyrazole, isoxazole, pyrimidine, and benzazepine series. In the reaction with CH_3I formed ferrocenoylacetylene which in the presence of dicarbonyl-bis(triphenylphosphine)nickel catalyst easily trimerized to give a mixture of 1,2,4- and 1,3,5-triferrocenoylbenzene.

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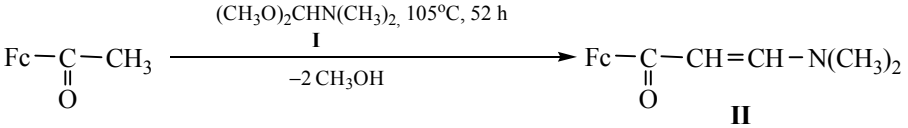
Studies in the chemistry of ferrocene and its derivatives attracted attention in connection with a number of unusual and unique properties of these compounds [1, 2], including a wide range of biological activity. Most interesting with respect to the biological effects are heterocyclic derivatives of ferrocene [3, 4], whose activity depends on the nature of functional groups and the nature of the heterocycle in their molecules. The methods for obtaining these ferrocene derivatives play an important role, for they stimulate the research on new heterocyclic compounds of the ferrocene series with potential practically useful properties.

Here we report on the first examined reaction of acetylferrocene with dimethylformamide dimethyl acetal **I**, which is known [5–9] to be able to react with compounds containing labile hydrogen atoms. In the reaction two moles of methanol were released and the corresponding enamines were formed, the highly reactive reagents in organic synthesis [10–12] of compounds of various types, including heterocycles. Therewith, the greater lability of the substrate hydrogen atoms, the easier proceeds its condensation with acetal **I** [7–9]. In this regard, we can expect a low reactivity of acetylferrocene in the reaction with acetal **I**, since the acidity of the hydrogen atoms of acetyl groups is significantly reduced by the influence of electron-donating ferrocenyl core [1]. Indeed, we found that acetylferrocene poorly reacted with acetal **I**: only on prolonged (52 h) boiling in a large excess of the latter in an inert atmosphere. Even in these conditions, only 26% of acetylferrocene reacted with compound **I** to form enamine **II** in quantitative yield with respect to the converted acetylferrocene. The more prolonged reflux of the reaction mixture led to its darkening due to the decomposition of ferrocene-containing components, and the yield of the desired product **II** decreased.



II

Fc = $C_5H_5FeC_5H_4$.

Table 1. Yields, melting points, TLC, elemental analysis, and chromato-mass-spectral data of compounds **III–XXI**

Comp. no.	Yield, %	mp, °C	R_f (system)	Mass-spectrum, m/z $[M+1]^+$	Found, %				Formula	Calculated, %				M_{calc}
					C	H	Fe	N		C	H	Fe	N	
II	99.2[a]	169–170	0.55 (**B**)	284	63.38	5.89	19.73	4.87	$C_{15}H_{17}FeNO$	63.60	6.01	19.75	4.95	383
III	99.2	151–152[b]	0.65 (**A**)	253	61.64	4.81	21.93	10.94	$C_{13}H_{12}FeN_2$	61.90	4.76	22.22	11.12	252
IV	72.0	110–112[b]	0.72 (**A**)	254	61.40	4.28	22.07	5.54	$C_{13}H_{11}FeNO$	61.66	4.35	22.13	5.53	253
V	52.0	174–175	0.48 (**A**)	280	60.03	4.48	19.89	14.93	$C_{14}H_{13}FeN_3$	60.22	4.66	20.07	15.05	279
VI	64.2	158–159	0.73 (**A**)	350	61.67	5.41	15.93	11.86	$C_{18}H_{19}FeN_3O$	61.89	5.44	16.05	12.03	349
VII	86.5	152–154	0.54 (**A**)	342	66.75	6.33	16.28	12.18	$C_{19}H_{15}FeN_3$	66.86	6.58	16.42	12.32	341
VIII	86.7	181–182	0.59 (**A**)	376	60.64	4.46	14.85	11.17	$C_{19}H_{17}FeN_3O_2$	60.80	4.53	14.93	11.20	375
IX	89.2	208–209	0.51 (**B**)	354	67.81	4.19	15.73	11.74	$C_{20}H_{15}FeN_3$	67.99	4.25	15.86	11.90	353
X	73.0	138–139	0.77 (**C**)	329	69.63	4.55	16.83	8.42	$C_{19}H_{16}FeN_2$	69.51	4.88	17.07	8.54	328
XI	71.4	118–120	0.64 (**C**)	330	69.45	4.31	16.94	4.09	$C_{19}H_{15}FeNO$	69.30	4.56	17.02	4.26	329
XII	84.2	133–134	0.71 (**C**)	346	65.82	4.24	16.18	3.88	$C_{19}H_{15}FeNS$	66.09	4.35	16.23	4.06	345
XIII	59.0	174–175	0.68 (**B**)	324	66.96	6.38	17.27	4.25	$C_{18}H_{21}FeNO$	66.87	6.50	17.34	4.33	323
XIV	67.5	184–186	0.47 (**B**)	346	69.63	5.48	16.19	3.95	$C_{20}H_{19}FeNO$	69.57	5.51	16.23	4.06	345
XV	70.8	128–129	0.38 (**C**)	333	68.79	4.61	16.74		$C_{19}H_{16}FeO_2$	68.67	4.82	16.87		332
XVI	79.5	136–137	0.44 (**C**)	349	65.51	4.47	16.23		$C_{19}H_{16}FeOS$	65.52	4.60	16.09		348
XVII	75.4	184–185	0.36 (**C**)	381	59.84	4.18	14.86		$C_{19}H_{16}FeO_3S$	60.00	4.21	14.74		380
XVIII	70.5	108–109	0.72 (**C**)	377	54.36	5.68	14.73		$C_{17}H_{21}FeO_4P$	54.26	5.59	14.89		376
XIX	81.0	78–80[b]	0.81 (**A**)	239	65.42	4.17	23.38		$C_{13}H_{10}FeO$	65.55	4.20	23.53		238
XX+XXI	84.0	218–220	0.56 (**A**)	715[c]	65.24	4.09	23.61		$C_{39}H_{30}Fe_3O_3$	65.55	4.20	23.53		714

[a] With respect to the converted acetylferrocene. [b] Published data [13] mp: 148–153°C (**III**); 110–112°C (**IV**); 78–80°C (**XIX**). [c] Two peaks with the integral intensities ratio 1:3.

Table 2. IR and ^{1}H NMR spectral data for compounds **III–XXI**

Comp. no.	IR spectrum, ν, cm^{-1}			^{1}H NMR spectrum, δ, ppm
	Ferrocene core	Aromatic system	Functional groups	
II	2997, 1596, 1418, 1101, 1000, 807		1668 (C=O), 1624 (C=C)	2.98 s (6H, $2CH_3$), 4.15 s (5H, C_5H_5), 4.36 m (2H, C_5H_2), 4.76 m (2H, C_5H_2), 5.36 d (1H, C=CH, *J* 16.2 Hz), 7.69 d (1H, C=CH–N, *J* 16.2 Hz)
III	3005, 1563, 1460, 1098, 1002, 812	1605, 1502, 1431	3423 (N–H)	3.98 s (5H, C_5H_5), 4.23 m (2H, C_5H_2), 4.62 m (2H, C_5H_2), 6.48 d (1H, Het), 7.54 d (1H, Het)
IV	3002, 1560, 1462, 1100, 1000, 810	1602, 1501, 1426		4.08 s (5H, C_5H_5), 4.35 m (2H, C_5H_2), 4.78 m (2H, C_5H_2), 6.05 d (1H, Het), 7.97 d (1H, Het)
V	3000, 1564, 1456, 1102, 1005, 816	1608, 1505, 1428	3420, 3392 (NH_2)	4.10 s (5H, C_5H_5), 4.52–4.76 m (6H, C_5H_4, NH_2), 6.08 d (1H, Het), 8.46 d (1H, Het)
VI	3005, 1568, 1448, 1101, 998, 812	1606, 1501, 1430		3.28–3.49 m (4H, $2NCH_2$), 3.76–3.98 m (4H, $2OCH_2$), 4.08 s (5H, C_5H_5), 4.56 m (2H, C_5H_2), 4.81 m (2H, C_5H_2), 6.18 d (1H, Het), 8.44 d (1H, Het)
VII	3000, 1584, 1447, 1107, 1000, 818	1611, 1598, 1523, 1503, 1428		4.12 s (5H, C_5H_5), 4.58 m (2H, C_5H_2), 4.78 m (2H, C_5H_2), 7.53–8.79 m (6H, Het)
VIII	3006, 1584, 1462, 1102, 1001, 821	1604, 1506, 1438	1689 (C=O)	1.24 t (3H, CH_3), 4.12 s (5H, C_5H_5), 4.31 q (2H, OCH_2), 4.50 m (2H, C_5H_2), 4.77 m (2H, C_5H_2), 6.51 d (1H, Het), 7.52 s (1H, Het), 8.55 d (1H, Het)

Table 2. (Contd.)

Comp. no.	IR spectrum, ν, cm^{-1}			^1H NMR spectrum, δ, ppm
	Ferrocene core	Aromatic system	Functional groups	
IX	3000, 1592, 1419, 1102, 998, 819	1603, 1598, 1520, 1500, 1438		4.04 s (5H, C_5H_5), 4.51 m (2H, C_5H_2), 4.73 m (2H, C_5H_2), 6.24 d (1H, Het), 7.03–7.24 m (4H, C_6H_4), 8.07 d (1H, Het)
X	3004, 1582, 1418, 1100, 1003, 819	1602, 1560, 1450, 1436	3428 (NH), 1622 (C=N), 1612 (C=C)	4.07 s (5H, C_5H_5), 4.38 m (2H, C_5H_2), 4.66 m (2H, C_5H_2), 6.72 d (1H, C=CH), 7.00–7.18 m (4H, C_6H_4), 8.12 d (1H, C=CH–N)
XI	3002, 1580, 1418, 1100, 1002, 818	1604, 1563, 1452, 1432	1622 (C=N), 1610 (C=C)	4.11 s (5H, C_5H_5), 4.42 m (2H, C_5H_2), 4.78 m (2H, C_5H_2), 6.83 d (1H, C=CH), 7.03–7.24 m (4H, C_6H_4), 8.26 d (1H, C=CH–O)
XII	3000, 1586, 1420, 1102, 1000, 823	1602, 1568, 1454, 1430	1621 (C=N), 1612 (C=C)	4.10 s (5H, C_5H_5), 4.40 m (2H, C_5H_2), 4.80 m (2H, C_5H_2), 6.72 d (1H, C=CH), 7.01–7.25 m (4H, C_6H_4), 8.18 d (1H, C=CH–S)
XIII	2998, 1592, 1418, 1100, 1003, 810	1608, 1561, 1456, 1430	1669 (C=O), 1624 (C=C)	1.38–1.84 m (6H, 3 CH_2), 3.16–3.42 m (4H, 2 NCH_2), 4.12 s (5H, C_5H_5), 4.38 m (2H, C_5H_2), 4.78 m (2H, C_5H_2), 5.38 d (1H, C=CH, *J* 16.4 Hz), 7.71 d (1H, C=CH–N, *J* 16.4 Hz)
XIV	3000, 1589, 1420, 1104, 1002, 810	1602, 1571, 1453, 1436	3426 (NH), 1668 (C=O), 1624 (C=C)	4.02 s (5H, C_5H_5), 4.36 m (2H, C_5H_2), 4.75–4.98 m (4H, C_5H_2, NCH_2), 5.41 d (1H, C=CH, *J* 16.2 Hz), 6.98–7.11 m (5H, C_6H_5), 7.74 m (1H, C=CH–N)
XV	2998, 1576, 1422, 1100, 1000, 812	1603, 1562, 1452, 1429	1671 (C=O), 1618 (C=C)	4.13 s (5H, C_5H_5), 4.42 m (2H, C_5H_2), 4.78 m (2H, C_5H_2), 5.73 d (1H, C=CH, *J* 15.8 Hz), 7.08–7.38 m (5H, C_6H_5), 8.29 d (1H, C=CH–O, *J* 15.8 Hz)
XVI	2999, 1578, 1426, 1103, 1001, 816	1605, 1560, 1453, 1420	1668 (C=O), 1620 (C=C)	4.12 s (5H, C_5H_5), 4.40 m (2H, C_5H_2), 4.72 m (2H, C_5H_2), 5.64 d (1H, C=CH, *J* 16.1 Hz), 7.06–7.43 m (5H, C_6H_5), 8.16 d (1H, C=CH–S, *J* 16.1 Hz)
XVII	3002, 1569, 1428, 1102, 1000, 817		1681 (C=O), 1628 (C=C), 1332, 1152 (SO_2)	4.10 s (5H, C_5H_5), 4.42 m (2H, C_5H_2), 4.72 m (2H, C_5H_2), 5.83 d (1H, C=CH, *J* 16.2 Hz), 7.28–7.64 m (5H, C_6H_5), 8.54 d (1H, C=CH–SO_2, *J* 16.2 Hz)
XVIII	3000, 1573, 1426, 1100, 1002, 818		1678 (C=O), 1624 (C=C), 1262 (P=O), 1156 (P–O)	1.24 t (3H, CH_3), 4.08 s (5H, C_5H_5), 4.28 q (4H, 2OCH_2), 4.40 m (2H, C_5H_2), 4.71 m (2H, C_5H_2), 5.79 d (1H, C=CH, J_{HH} 16.0 Hz), 7.86–8.03 m (1H, C=CH–P, J_{HH} 16.0 Hz, $^2J_{PH}$ 17.2 Hz)
XIX	3008, 1584, 1418, 1103, 1000, 820		2148 (C≡C), 1665 (C=O)	4.17 s (5H, C_5H_5), 4.36–4.48 m (3H, C_5H_2, ≡CH), 4.69 m (2H, C_5H_2)
XX+XXI	3002, 1582, 1428, 1100, 1000, 816	1608, 1564, 1552, 1438, 1406	1702, 1694 (C=O)	4.18 s (15H, 3 C_5H_5), 4.49 m (6H, 3 C_5H_2), 4.76 m (6H, 3 C_5H_2), 7.65–8.07 m (3H, C_6H_3)

The composition and structure of compound **II** are confirmed by elemental analysis, GC–MS (Table 1), IR and ^1H NMR spectral data (Table 2), as well as by a variety of chemical transformations.

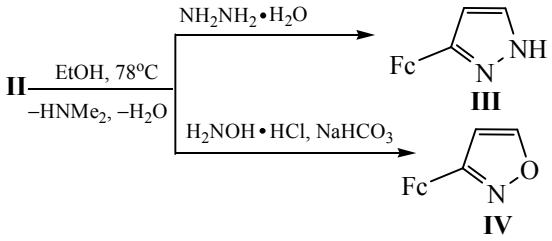
The IR spectrum of ketoenamine **II** contains characteristic absorption bands of stretching vibrations of C–H bond of the cyclopentadienyl rings at 3100–3086 cm^{-1}, carbonyl C=O group at 1668 cm^{-1}, and double C=C bond at 1624 cm^{-1}.

In the ^1H NMR spectrum of compound **II** the signals of HC=CH groups appear as doublets at 5.36 and 7.69 ppm with the coupling constant 16.2 Hz, indicating *trans*-configuration of substituents at the carbon atoms at the double bond. The spectrum also

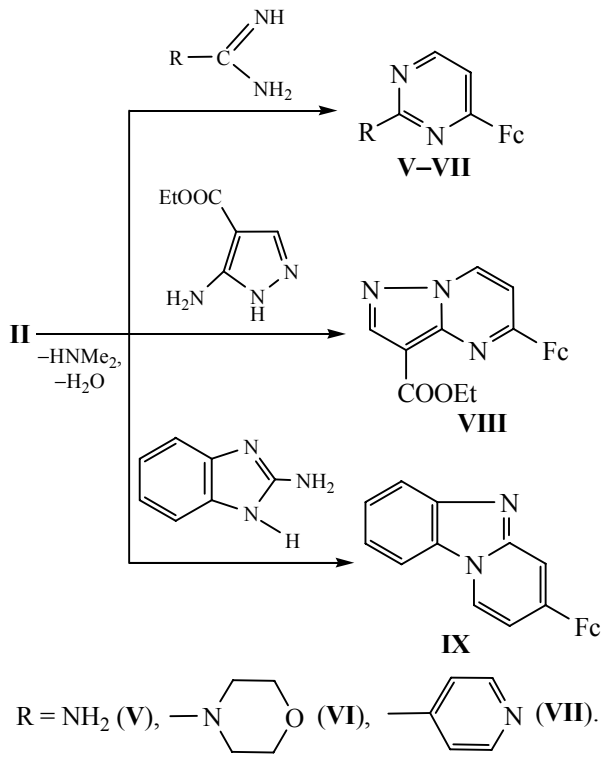
contains singlets at 2.98 and 4.15 ppm, respectively, relating to the six protons of the dimethylamino group and to the five protons of C_5H_5, and multiplets at 4.36 and 4.76 ppm characteristic of the four protons of substituted cyclopentadienyl ring.

The study of enamine **II** reactivity showed that it is a valuable reagent in the synthesis of various ferrocene derivatives. Thus, it reacts readily with binucleophilic reagents to form five-, six- and seven-membered heterocyclic ferrocene-containing compounds **III–XII**.

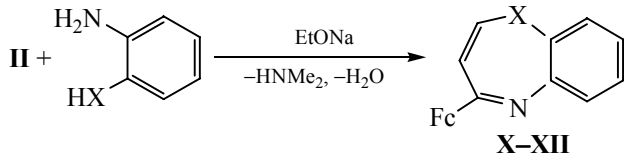
In particular, refluxing enamine **II** with an excess of hydrazine hydrate in ethanol affords 3-ferrocenylpyrazol **III** in nearly quantitative yield, and the reaction with hydroxylamine produces 3-ferrocenyloxazol **IV**, but in lower (72%) yield.



For the synthesis of six-membered heterocycles on the basis of enamine **II**, we used the reagents containing amidine group (NH=C–NH_2): guanidine, morpholino-1-carboxamidine, pyridine-4-carboxamidine, ethyl 5-amino-1*H*-pyrazolo-4-carboxylic acid, and 1*H*-benzimidazole-2-amine. These reagents react with enamine **II** in the suitable reaction conditions to form ferrocene-containing pyrimidine **V–IX** in yields of 72–85%.



The synthesis of the seven-membered heterocyclic compounds was carried out by the condensation of enamine **II** with 1,2-disubstituted aromatic binucleophiles, 1,2-diaminobenzene, 2-aminophenol, and 2-aminothiophenol, at heating the equimolar amounts of reactants in anhydrous ethanol in the presence of sodium ethoxide. As a result, the corresponding 5-ferrocenyl-substituted benzazepines **X–XII** containing two heteroatoms in the ring were obtained in the yield of 68–73%.

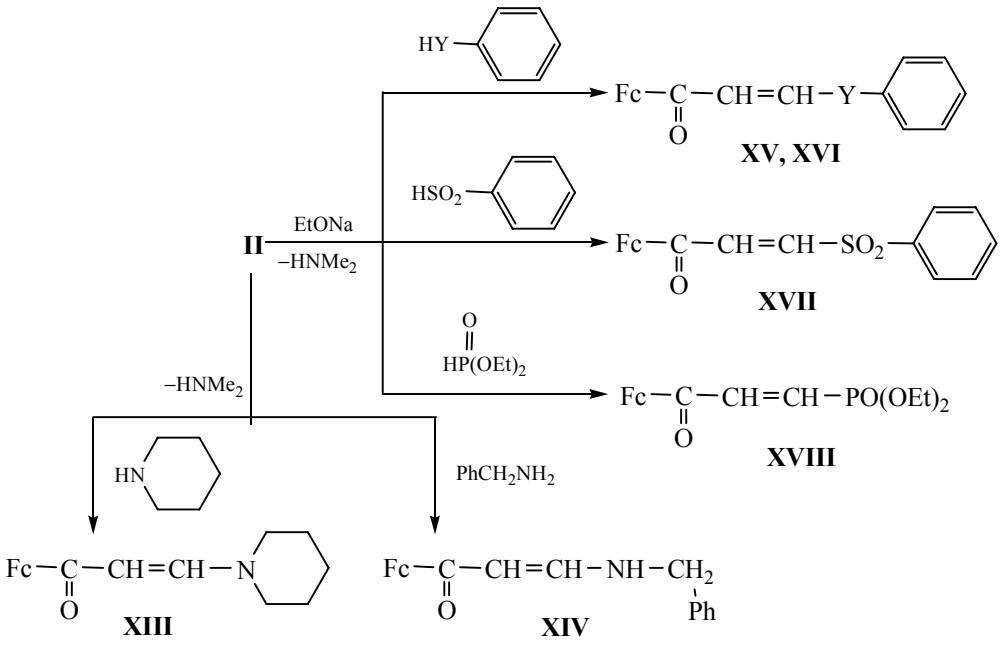


X = HN (**X**), O (**XI**), S (**XII**).

It should be noted the high regioselectivity of the above mentioned heterocyclization reactions involving enamine **II** due to the specificity of the structure of binucleophilic reagents. The latter in the reaction are preferably condensed with carbonyl group of the substrate **II** due to the presence in them of the primary amino groups. Then the subsequent elimination of dimethylamino group of substrate **II** or intermediate formed in the presence of a strong base leads to the closure of the heterocycle to give the end products **III–XII**.

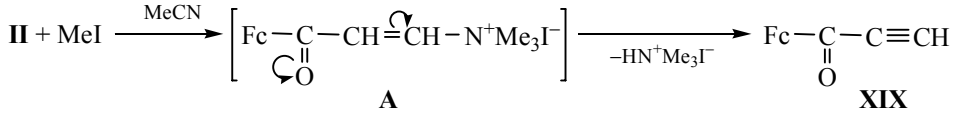
We also investigated the reaction of enamine **II** with some mononucleophilic reagents proceeding through the substitution of dimethylamino group. Thus, reflux in toluene of equimolar amounts of compound **II** with piperidine and benzylamine gives rise to amines **XIII** and **XIV**. On heating with the sodium salts of phenol, thiophenol, and benzenesulfinate, and diethylphosphorous acid in ethanol the nucleophilic substitution proceeds to afford compounds **XV–XVIII** as a result of the formation of new C–O, C–S, and C–P bonds.

It is known [10] that enamines, as the bases, are able to react with electrophilic reagents. In particular, we studied the reaction of enamine **II** with methyl iodide as the electrophilic reagent. It was unexpectedly found that on reflux of reagents in anhydrous



X = O (**XV**), S (**XVI**).

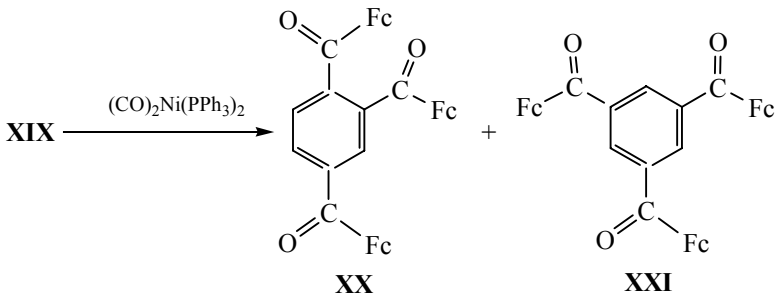
acetonitrile the quaternary trimethylammonium salt **A** is not formed, but formed 3-ferrocenylpropyn-3-one **XIX** previously described in [13]. The formation of this compound in 81% yield can probably be explained by the formation in the first stage of the reaction of easily decomposing iodomethylate **A**:



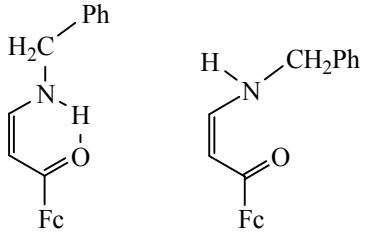
Elimination of the trimethylammonium hydroiodide from the salt **A** is caused of course by the high acidity of the α-hydrogen atom owing to the electron-withdrawing effect of the neighboring carbonyl group as well as trimethylammonium group, whose negative inductive effect is conjugated with the π-electrons of the double bond.

Compound **XIX** synthesized reacted with hydrazine hydrate and hydroxylamine under the reaction conditions [13] affords, respectively, pyrazol **III** and oxazole **IV**, previously obtained from enamine **II**.

Also it was found that under heating in benzene in the presence of a catalytic amount of dicarbonyl-bis (triphenylphosphine)nickel the compound **XIX** undergoes trimerization to form a mixture of 1,2,4- and 1,3,5-triferrocenoylbenzenes **XX** and **XXI**, which is a characteristic transformation for acetylene and its derivatives.



The composition and structure of compounds **III–XXI** are confirmed by analytical and spectroscopic data given in Tables 1 and 2. It should be noted that in the ^{1}H NMR spectrum of compound **XIV** the fragments CH=CH, CH_2 appear as doubled signals with the integral intensity ratio ~3:7, due, as we think, to the existence of two isomers **B** and **C**.



B **C**

Moreover, the signal of the NH proton of isomer **B** is located in the weak field at 8.10 ppm, whereas the same proton in isomer **C** resonates in a strong field at 5.38 ppm with the same ratio of the integral intensities. The formation of such isomers has previously been noted in [9].

By GC–MS and ^{1}H NMR spectral data, the ratio of structural isomers **XX** and **XXI** in a mixture is 1:3.

Thus, based on accessible acetylferrocene we developed a convenient method of obtaining 1-dimethylamino-3-ferrocenyl-3-oxoprop-1-ene **II**, which can be widely used in the synthesis of various ferrocene derivatives of the scientific and practical interest.

EXPERIMENTAL

Commercial reagents (Acros) were used. The IR spectra were recorded on a UR-20 spectrometer from KBr pellets. The ^{1}H NMR spectra were registered on a Varian Mercury Plus-400 spectrometer (400 MHz) in $CDCl_3$ with internal reference HMDS. GC–MS spectra were recorded on a Thermo Finnigan Surveyor MSQ (USA) instrument by chemical ionization at atmospheric pressure. Identity and purity of the compounds obtained was monitored by TLC on Silufol UV-254 plates, eluents ethyl acetate–chloroform, 4:1 (**A**), acetone (**B**), ethyl acetate–hexane, 1:1 (**C**).

1-Dimethylamino-3-ferrocenyl-3-oxoprop-1-ene (II). A mixture of 11.4 g of acetylferrocene and 200 ml of dimethylformamide dimethyl acetal **I** was refluxed under inert atmosphere for 52 h at stirring. Excess of acetal **I** was removed in a vacuum. The residue was subjected to chromatography eluting the starting acetylferrocene with ethylacetate and then the target product **II** with acetone. After the solvent removal the unreacted acetylferrocene (8.39 g, 73.6%) and enamine **II** (3.71 g, 99.2%, with respect to the converted acetylferrocene) were isolated.

3-Ferrocenylpyrazol (III). A mixture of 0.5 g of enamine **II** and 0.5 ml of hydrazine hydrate in 3 ml of ethanol was refluxed with stirring for 2 h, the solvent was removed in a vacuum. The mixture was mixed with 30 ml of water and extracted with ethyl acetate (2×30 ml). The organic layer was washed with water and dried over anhydrous sodium sulfate. After the removal of solvent in a vacuum, 0.45 g (99.2%) of compound **III** was obtained, which was crystallized from benzene.

3-Ferrocenyloxazol (IV). To a solution of 0.5 g of enamine **II** in 5 ml of ethanol was added aqueous solution of hydroxylamine prepared from 0.63 g of $HONH_2$·HCl and 0.84 g of $NaHCO_3$ in 5 ml of water, the mixture was refluxed under stirring for 5 h, cooled, mixed with 50 ml of water, and extracted with ethyl acetate (2×50 ml). The organic layer was dried over anhydrous sodium sulfate. After distilling off the solvent in a vacuum, the residue was purified by chromatography eluting with the ethyl acetate–hexane (4:1) mixture. Yield 0.33 g (72%) of compound **IV**, which was crystallized from aqueous ethanol (1:1).

Compound **XII** was obtained similarly.

2-Amino-4-ferrocenylpyrimidine (V). A mixture of 0.5 g of enamine **II**, 0.52 g of guanidine dihydrochloride, and 1.24 g of K_2CO_3 in 5 ml of DMSO was stirred at 80–90°C under argon for 1.5 h, cooled, diluted with 50 ml of water, and extracted with ethyl acetate (3×70 ml). The organic layer was washed with water and dried over anhydrous sodium sulfate. After distilling off the solvent in a vacuum the residue was purified by chromatography eluting with the ethyl acetate–chloroform mixture (5:1). Yield 0.26 g (52%) of azine **V**, which was crystallized from aqueous methanol (2:1).

Compound **VI** was obtained similarly.

2-(Pyridin-4-yl)-4-ferrocenylpyrimidine (VII). A mixture of 0.57 g of enamine **II**, 0.77 g of pyridine-4-carboxamidine dihydrochloride, and 1.12 g of potassium *tert*-butoxide in 10 ml of anhydrous ethanol was refluxed with stirring under argon for 2 h, cooled, diluted with 100 ml of water, and extracted with ethyl acetate (3×80 ml). The organic layer was washed with

water and dried over anhydrous sodium sulfate. After distilling off the solvent in a vacuum the residue was purified by chromatography eluting with the ethyl acetate–chloroform mixture (5:1). Yield 0.59 g (86.5%) of compound **VII**, which was crystallized from aqueous methanol (2:1).

Compounds **VIII–IX** were obtained similarly.

5-Ferrocenyl-1*H*-benzo[*a*]-1,4-diazepine (X). To a solution of 2 mmol of sodium ethoxide in 5 ml of anhydrous ethanol was added 2 mmol of 1,2-diaminobenzene. The mixture was stirred under argon for 30 minutes. Then 2 mmol of enamine **II** was added, and the mixture was refluxed for 3 h, cooled, diluted with 50 ml of water and extracted with ethyl acetate (3×60 ml). The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated. The residue was purified by chromatography eluting with the ethyl acetate–hexane mixture (2:1). Yield 0.48 g (73%) of compound **X**, which was crystallized from ethyl acetate–hexane mixture (1:1).

Compounds **XI** and **XII** were synthesized similarly.

1-Piperidino-3-ferrocenyl-3-oxoprop-1-ene (XIII). A mixture of 0.57 g of enamine **II** and 0.2 ml of piperidine in 3 ml of anhydrous toluene was refluxed with stirring for 5 h. Then the solvent was removed on a rotary evaporator and the residue was crystallized from ethyl acetate–hexane, 1:1. Yield 0.38 g (59%).

Compound **XIV** was obtained similarly.

1-(*o*-Phenoxy)-3-ferrocenyl-3-oxoprop-1-ene (XV). To a solution of 2 mmol of EtONa in 5 ml of anhydrous ethanol under an argon atmosphere was added 2 mmol of phenol. The mixture was stirred for 30 min, then 2 mmol of enamine **II** was added and the mixture was refluxed under stirring for 3 h to complete consumption of the starting compounds (TLC monitoring). After the removal of solvent, the residue was dissolved in 100 ml of ethyl acetate, washed with water, dried over anhydrous sodium sulfate, the solvent was removed on a rotary evaporator, and the residue was crystallized from aqueous ethanol (1:1). Yield 0.47 g (70.8%).

Compounds **XVI–XVIII** were synthesized similarly.

3-Ferrocenylpropyn-3-one (XIX). A mixture of 1.13 g of enamine **II** and 3 ml of CH_3I in 10 ml of anhydrous acetonitrile was refluxed with stirring for 8 h. Then 50 ml of water and 100 ml of ethyl acetate were added. The organic layer was separated and the aqueous solution was extracted with 60 ml of ethyl acetate. The combined organic solutions were washed with water, dried over anhydrous sodium sulfate, and concentrated. The residue was purified by chromatography eluting with the ethyl acetate–hexane mixture (5:1). Yield 0.77 g (81%) of compound **XIX**, which was crystallized from a mixture of benzene and hexane (1:3).

Trimerization of compound (XIX). To a solution of 0.5 g of compound **XIX** in 5 ml of anhydrous benzene was added 0.05 g of dicarbonyl-bis(triphenylphosphine)nickel [15], and the mixture was stirred at 70–75ºC in an argon atmosphere for 5 h to complete consumption of the starting compounds (TLC monitoring), was filtered and concentrated. The residue was crystallized from the hexane–methylene chloride mixture (2:1). Yield 0.42 g (84%) of a mixture of compounds **XX** and **XXI**.

REFERENCES

1. Perevalova, E.G., Reshetova, M.D., and Grandberg, K.I., *Metody elementoorganicheskoi khimii. Zhelezoorganicheskie soedineniya. Ferrotsen* (Methods of Organoelemental Chemistry. Organoiron Compounds. Ferrocene), Moscow: Khimiya, 1983.
2. Staveren, D.R., and Metzler-Nolte, N., *Chem. Rev*., 2004, vol. 104, no. 12, p. 5931.
3. Zora, M. and Gormen, M., *J. Organomet. Chem*., 2007, vol. 692, no. 22, p. 5026.
4. Snegur, L.V., Nekrasov, Yu.S., Sergeeva, N.S., Zhilina, Zh.V., Gumenyuk, V.V., Starikova, Z.A., Simenel, A.A., Morozova, N.V., Sviridova, I.R., and Babin, V.N., *Appl. Organometal. Chem*., 2008, vol. 22, p. 139.
5. Effenberger, F. and Simchen, G., *Chem. Ber.,* 1963, vol. 96, no. 4, p. 1350.
6. Bredereck, H., *Chem. Ber.,* 1968, vol. 101, no. 1, p. 41.
7. Hengartner, V., Batcho, A.D., Blount, J.F., Leimgruber, W., Larscheid, M.E., and Scott, J.W., *J. Org. Chem.,* 1979, vol. 44, no. 12, p. 3748.
8. Ponticello, G.S. and Baldwin, J.J., *J. Org. Chem.*, 1979, vol. 44, no. 14, p. 4003.
9. Golyanskaya, O.M., Voloshin, N.A., Chernyshev, A.V., Dubonosov, A.D., Metelitsa, A.V., Mezheritskii, V.V., and Bren', V.A., *Zh. Org. Khim.,* 2008, vol. 44, no. 4, p. 608.
10. Shmushkovich, J., *Enaminy* (Enamines), in *Uspekhi organicheskoi khimii* (Advances of Organic Chemistry), Knunyants, I.L., Ed., Moscow: Mir, 1966, vol. 4, pp. 5–123.
11. Bredereck, H., Sell, R., and Effenberger, F., *Chem. Ber.*, 1964, vol. 97, no. 11, p. 3407.

12. Dominquez, E., Ibeas, E., Martinez de Marigorta, E., Palacios, J.K., and Saumartin, R., *J. Org. Chem.*, 1996, vol. 61, no. 15, p. 5435.
13. Schlögl, K. and Monar, A., *Monatsh. Chem.,* 1962, vol. 93, no. 4, p. 861.
14. Reutov, O.A., Kurts, A.L., and Butin, K.P., *Organicheskaya khimiya* (Organic Chemistry), Moscow: Mosk. Gos. Univ., 1999, pt. 1, pp. 492–496.
15. Dzhemilev, U.M., Popod'ko, N.R., and Kozlova, E.V., *Metallokompleksnyi kataliz v organicheskom sinteze* (Metal Complex Catalysis in Organic Synthesis), Moscow: Khimiya, 1999, pp. 60–61.