spectrum (in d_6-DMSO): 5.6 ppm (1H, d, J = 7 Hz, glucose 1-H). According to the data in [8], this compound had mp 120-121°C.

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SYNTHESIS OF PYRIDINE AND QUINOLINE DERIVATIVES OF FERROCENE FROM β-CHLORO-β-FERROCENYLACROLEIN

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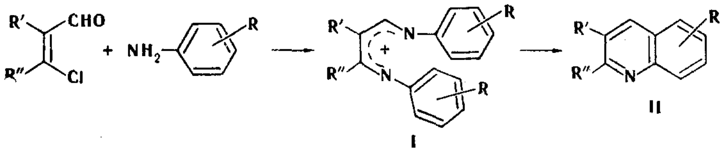
2-Ferrocenylquinolines that contain a hydroxy or methoxy group in the 7 position were obtained by the reaction of β-chloro-β-ferrocenylacrolein with m-anisidine and with m-aminophenol. The introduction of aniline in this reaction leads to the formation of β-ferrocenyl-β-phenylaminoacrolein anil hydrochloride, which cannot be converted to 2-ferrocenylquinoline. 2,3,6-Trisubstituted pyridines that contain a ferrocenyl substituent in the 6 position were obtained by condensation of β-chloro-β-ferrocenylacrolein with β-dicarbonyl compounds.

It is known [1] that β-chloroacroleins are convenient starting compounds for the synthesis of a number of five-, six-, and seven-membered heterocycles. In particular, β-chloro-β-ferrocenylacrolein was previously used for the synthesis of ferrocene-containing pyrazoles [2], pyrimidines [2], pyrylium salts, and the corresponding pyridines [3].

It has been shown [4] that quinoline derivatives II are readily formed via the following scheme in the reaction of β-chloroacroleins with aromatic amines:



However, in an attempt to synthesize 2-ferrocenylquinoline by the reaction of β-chloro-β-ferrocenylacrolein with aniline we isolated only intermediately formed immonium salt Ia (R, R' = H, R'' = ferrocenyl), which is not converted to the corresponding quinoline even when it is refluxed in acetic acid. The introduction in the meta position of the aniline ring of electron-donor substituents facilitates intramolecular electrophilic attack in immonium salt I, which leads to the formation of quinolines II with splitting out of an aniline fragment. In fact, brief refluxing of β-chloro-β-ferrocenylacrolein with m-anisidine or m-aminophenol in benzene leads to the formation of the corresponding quinoline derivatives IIb (R = 7-OCH_3, R' = H, R'' = ferrocenyl) and IIc (R = 7-OH, R' = H, R'' = ferrocenyl). It is apparent that intermediately formed immonium salt I can be converted to a quinoline via two pathways; α-

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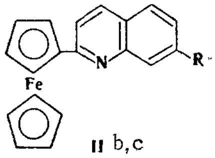
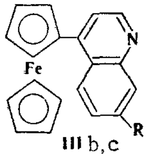
TABLE 1. Pyridines IV

Compound	R_1	R_2	mp, °C	Yield, %
IVa	C_6H_5	C_6H_5	143	34 (25)
IVb	CH_3	CH_3	116	27 (10)
IVc	CH_3	C_2H_5O	82	43 (43)
IVd	$—CH_2C(CH_3)_2CH_2—$		117	45 (21)

or γ-unsubstituted quinolines can be formed, depending on which of the phenyl rings of the immonium salt undergoes electrophilic attack:



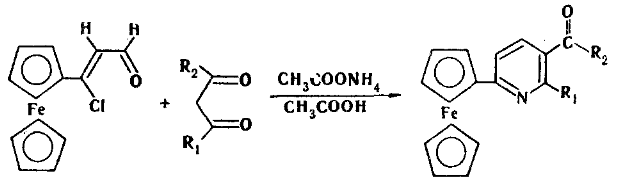
II b,c



III b,c

Signals with the following chemical shifts are observed in the PMR spectrum of quinoline IIb: 3.90 (s, 5H, $C_5H_5^+$ 3H, CH_3O); 4.28, 4.94 (t, 4H, C_5H_4); 6.89-7.80 ppm (m, 5H, quinoline). Two doublet signals at 6.95 and 7.73 ppm (J = 8.22 Hz), which, according to the literature data (α-H signal at 8.81, β-H signal at 7.26, and γ-H signal at 8.00 ppm; $J_{\alpha\beta}$ = 4-5.7 Hz, $J_{\beta\gamma}$ = 6.8-9.1 Hz) [5], can be assigned to the β-H and γ-H signals of the quinoline system, can be isolated in the multiplet signal of the aromatic protons. We were unable to record the PMR spectrum for quinoline IIc in connection with the low solubility of the compound. Thus the chemical shifts of the protons and the spin-spin coupling constant indicate that the compounds obtained are γ-unsubstituted quinlines IIb, c. The compositions and structures of the compounds are also confirmed by the results of elementary analysis and the IR spectra.

We have previously reported [3] the synthesis of pyridine derivatives of ferrocene from γ-unsubstituted ferrocenylpyrylium salts obtained from β-chloro-β-ferrocenylacrolein; however, the explosiveness of the perchlorates of pyrylium derivatives of ferrocene is a significant disadvantage of this method. We attempted to synthesize pyridines directly from β-chloro-β-ferrocenylacrolein by by-passing the step involving the pyrylium salt by condensation with various methyl and methylene ketones in acetic acid in the presence of excess ammonium acetate, which is a convenient condensing and cyclizing agent [6, 7]. We found that the introduction of acetophenones and aliphatic and alicyclic ketones in this reaction does not lead to the desired result. We were able to synthesize pyridine derivatives of ferrocene IV only by condensation of β-chloro-β-ferrocenylacrolein with β-dicarbonyl compounds:



IVa-d

In this case the yields of pyridines IVa-d exceed the yields of the corresponding pyridines synthesized from pyrylium derivatives [3] (Table 1; the yields of pyridines from the corresponding pyrylium salts are presented in parentheses).

The IR and PMR spectra and melting points of IVa-d are identical to the IR and PMR spectra and melting points of the corresponding pyridines that we described in [3].

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord-71IR spectrometer. The PMR spectra of solutions of the compounds in CCl_4 were recorded with a Tesla spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard.

β-Ferrocenyl-β-phenylaminoacrolein Anil Hydrochloride (Ia). A mixture of 0.55 g (0.002 mole) of β-chloro-β-ferrocenylacrolein and 0.4 g (0.004 mole) of aniline was refluxed in 10 ml of benzene for 1.5 h, after which the precipitated dark-red crystals were removed by filtration to give 0.75 g (85%) of a product with mp 236-238°C (dec.). IR spectrum: 3200, 1635, 1589, 1568, 1554, 1250, 1232, 1213, 1030, 980, 834, 760, 748, and 712 cm^{-1}. Found: C 68.3; H 5.4; Cl 7.5; Fe 12.3; N 5.9%. $C_{25}H_{23}ClFeN_2$. Calculated: C 67.8; H 5.2; Cl 8.0; Fe 12.7; N 6.3%.

2-Ferrocenyl-7-methoxyquinoline (IIb). A mixture of 0.55 g (0.002 mole) of β-chloro-β-ferrocenylacrolein and 0.25 g (0.002 mole) of m-anisidine in 10 ml of benzene was refluxed for 1.5 h, after which 0.2 ml (0.002 mole) of 70% $HClO_4$ was added, and the resulting precipitate was removed by filtration and washed with ether. It was then drenched with NH_4OH and allowed to stand for 12 h. The mixture was extracted with benzene, and the extract was chromatographed with a column filled with Al_2O_3 (activity II) (elution with benzene). The orange band (R_f 0.8; benzene) was isolated, the solvent was evaporated to dryness, and the residue was crystallized from isooctane to give 0.3 g (44%) of orange crystals with mp 137-138°C. IR spectrum: 1610, 1590, 1510, 1328, 1222, 1201, 1170, 1027, 854, 840, and 814 cm^{-1}. Found: C 69.4; H 5.0; Fe 16.4; N 3.7%. $C_{20}H_{17}FeNO$. Calculated: C 70.0; H 5.0; Fe 16.3; N 4.1%.

2-Ferrocenyl-7-hydroxyquinoline (IIc). A mixture of 0.55 g (0.002 mole) of β-chloro-β-ferrocenylacrolein and 0.22 g (0.002 mole) of m-aminophenol in 10 ml of benzene was refluxed for 1 h, 0.4 ml (0.004 mole) of 70% $HClO_4$ was added, and the resulting oily precipitate was separated by decantation, washed with ether, and drenched with NH_4OH. The mixture was allowed to stand for 12 h, after which it was extracted with benzene and chromatographed with a column filled with Al_2O_3 (activity II) (elution with ether). The substance that remained at the start was leached out with acetone, the solvent was evaporated to dryness, and the residue was reprecipitated from solution in benzene by the addition of petroleum ether to give 0.1 g (15%) of light-brown crystals with mp 186-188°C (dec.). IR spectrum: 3150, 3000, 1605, 1590, 1520, 1323, 1225, 998, and 827 cm^{-1}. Found: C 68.7; H 4.5; Fe 16.5; N 3.9%. $C_{19}H_{15}FeNO$. Calculated: C 69.2; H 4.6; Fe 17.0; N 4.3%.

General Method for the Synthesis of Pyridines IV. A mixture of 0.55 g (0.003 mole) of β-chloro-β-ferrocenylacrolein and 0.002 mole of the β-dicarbonyl compound was heated in glacial acetic acid until the solid material dissolved completely, after which a tenfold excess of ammonium acetate was added, and the mixture was refluxed for 40-60 min. It was then diluted with water, made alkaline with NH_4OH, extracted with benzene, and chromatographed with a column filled with Al_2O_3 (activity II) in benzene. The solvent was evaporated to dryness, and the residue was recrystallized. Data on IVa-d are presented in Table 1; the IR and PMR spectra were identical to those presented in [3].

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