β-CHLORO-β-FERROCENYLACRYLALDEHYDE AND ITS APPLICATION IN THE SYNTHESIS OF PYRYLIUM AND PYRIDINE DERIVATIVES OF FERROCENE

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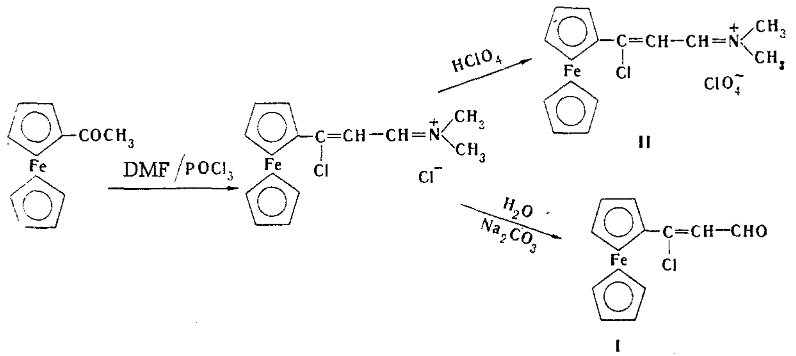
β-Chloro-β-ferrocenylacrylaldehyde, to which an s-cis configuration was assigned on the basis of the PMR spectral data, was synthesized from acetylferrocene by the Vilsmeier–Haack reaction. 2,3,6-Trisubstituted pyrylium salts with a ferrocenyl substituent in the 6 position were obtained by condensation of this aldehyde with β-dicarbonyl compounds. The pyrylium salts were converted to the corresponding pyridines by the action of ammonium acetate in acetic acid. On the basis of the structures of the pyridines it was established that the aldehyde carbon atom initially attacks the β-dicarbonyl compound with subsequent closing of the γ-unsubstituted pyrylium ring.

It is known [1] that β-chloroacrylaldehydes are convenient reagents for the synthesis of diverse heterocycles and, as two of us have previously demonstrated [2], for the synthesis of pyrylium salts. Since pyrylium salts that contain a ferrocenyl substituent were unknown [3] up until now, it seemed of interest to us to synthesize β-chloro-β-ferrocenylacrylaldehyde (I) and use it for the preparation of these compounds.

We obtained aldehyde I by the Vilsmeier–Haack reaction from acetylferrocene:



The intermediate immonium salt was isolated and characterized in the form of the perchlorate (II).

The spin–spin coupling constant (SSCC) of the vinyl and formyl protons (J = 7 Hz) in the PMR spectrum of aldehyde I indicates the s-cis configuration of aldehyde I. According to the data in [1], the chlorine in β-chlorocinnamaldehydes is trans-oriented with respect to the formyl group. Thus the following structure can be proposed for I (see below).

The IR spectrum of aldehyde I contains an intense absorption band of a carbonyl group at 1659 cm^{-1}.

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TABLE 1. Pyridines V

Compound	R′	R″	mp, °C (crystallization solvent)	Found, %			Empirical formula	Calc., %			IR spectrum, cm^{-1}	PMR spectrum							Yield, %
				C	H	N		C	H	N		R′	R″	C_5H_5	C_5H_4	C_5H_2N β-H	γ-H	$J_{\beta,\gamma}$, Hz	
Va	C_6H_5	C_6H_5	143 (isooctane)	75,5	5,2	3,2	$C_{28}H_{21}FeNO$	75,8	4,8	3,2	1650, 1585, 1570, 1292, 927								25
Vb	CH_3	CH_3	116 (isooctane)	67,8	5,8	4,8	$C_{18}H_{17}FeNO$	67,7	5,4	4,4	1680, 1585, 1265, 1150, 830	s 2,36	s 2,64	s 3,86	t 4,24 t 4,80	d 7,03	d 7,66	8,3	10
Vc	C_2H_5O	CH_3	81—82 (alcohol)	65,8	5,9	3,8	$C_{19}H_{17}FeNO$	65,4	5,5	4,0	1720, 1585, 1265, 1150, 1075	t 1,32 q 4,28	s 2,78	s 3,93	t 4,34 t 4,88	d 7,14	d 8,03	8,4	43
Vd	—$CH_2C(CH_3)_2CH_2$—		117 (isooctane)	70,7	6,1	4,4	$C_{21}H_{21}FeNO$	70,2	5,9	3,9	1673, 1575, 1410, 1304, 820	s 2,37	s 1,06, s 2,91	s 3,91	t 4,33 t 4,86	d 7,24	d 7,97	8,15	21

TABLE 2. Pyrylium Salts III

Compound	R′	R″	mp, °C*	IR spectrum, cm^{-1}	Yield, %
IIIa	C_6H_5	C_6H_5	140—160	1675, 1615, 1095	100
IIIb	CH_3	CH_3	130—150	1710, 1620, 1105	100
IIIc	C_2H_5O	CH_3	130—150	1725, 1620, 1098	68
IIId	—$CH_2C(CH_3)_2CH_2$—		140—160	1700, 1620, 1090	72

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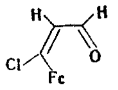
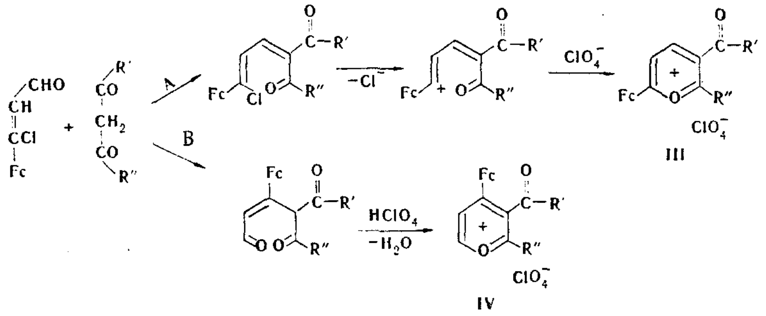
*The pyrylium salts do not have distinct melting points but decompose explosively over the indicated temperature range.



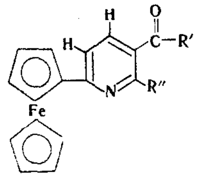
Here and subsequently, Fc is ferrocenyl

We used aldehyde I for the synthesis of pyrylium derivatives of ferrocene. Various pyrylium salts containing a ferrocenyl substituent were obtained in the condensation of aldehyde I with β-dicarbonyl compounds. In this case one might have expected the formation of pyrylium salts via one of the following schemes:

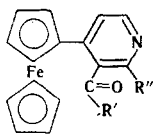


Scheme A could have been realized by electrophilic attack of the enol form of the β-dicarbonyl compound by the carbon atom of the aldehyde group with subsequent formation of γ-unsubstituted pyrylium salt III, and scheme B, in analogy with the condensation of β-chlorovinyl ketones [4], should lead to α-unsubstituted pyrylium salts IV.

To prove the structures of the pyrylium salts we converted them to pyridines by refluxing with ammonium acetate in glacial acetic acid. As a result, pyridines with the following structures could have been formed:



V



VI

Two doublets of the protons of the pyridine ring at 7.03-7.24 and 7.66-7.93 ppm (J = 8.15-8.4 Hz), which, according to the literature data (β-H signals at 7.2, α-H at 8.5, and γ-H at 7.6 ppm; $J_{\alpha,\beta}$ = 4-5 Hz, $J_{\beta,\gamma}$ = 7-9 Hz [5]), can be assigned to the β-H and γ-H signals of the pyridine ring, respectively, are observed in the PMR spectra of the resulting pyridines (Table 1).

Thus the position of the proton signals and the SSCC indicate that the pyridines have structure V and that the reaction of I with β-dicarbonyl compounds consequently proceeds via pathway A to give γ-unsubstituted pyrylium salts III (Table 2).

The IR spectra of the pyrylium salts contain absorption bands of a carbonyl group (1675-1720 cm^{-1}), a pyrylium cation (1610-1620 cm^{-1}), and a ClO_4^- ion (1090-1105 cm^{-1}).

The IR spectra of pyridines V (Table 1) contain absorption bands at 1650-1720 cm^{-1}, which are related to the vibrations of a carbonyl group.

EXPERIMENTAL

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

β-Chloro-β-ferrocenylacrylaldehyde (I). A 2.37-g (0.01 mole) sample of acetylferrocene was added in small portions with stirring and ice-water cooling to a mixture of 1.3 ml (0.014

mole) of $POCl_3$ and 2.5 ml (0.033 mole) of dimethylformamide (DMF), after which the mixture was cooled for 30 min. It was then stirred at room temperature for another 4 h, after which it was poured into ice water, and the aqueous solution was extracted with ether (three 50-ml portions). The ether extracts were discarded, and the aqueous solution was neutralized with sodium carbonate, during which the bright-blue solution turned crimson, and a precipitate formed. The solution and the precipitate were extracted with benzene, and the extracts were dried over Na_2SO_4 and evaporated to a small volume. The concentrated solution was chromatographed with a column filled with activity II Al_2O_3 with elution with benzene. After chromatography, the solution was evaporated to dryness, and the residual oil was crystallized by the addition of petroleum ether. The dark-red crystals were washed with pentane to give 1.5 g (55%) of a product with mp 72-74°. Found, %: C 57.0; H 4.2; Cl 12.6. $C_{13}H_{11}ClFeO$. Calculated, %: C 56.9; H 4.0; Cl 12.9. IR spectrum: 1659, 1595, 1256, 1132, 1101, 1000, 940, 820, and 790 cm^{-1}. PMR spectrum: s, 4.05 (C_5H_5); t, 4.45, t, 4.70 (C_5H_4); d, 6.31 (CCl=CH); d, 10.08 ppm (CHO).

N,N-Dimethyl(β-chloro-β-ferrocenylvinyl)methyleneimmonium Perchlorate (II). The reaction was carried out as described above. The reaction mixture was treated with 70% $HClO_4$ (a twofold excess), 8-10 ml of acetic acid was added, and the mixture was allowed to stand for 3-4 h. The resulting precipitate was removed by filtration, and an additional amount of immonium salt II was precipitated from the mother liquor by the addition of ether; salt II did not have a distinct melting point but decomposed explosively at 150-180°. We were unable to perform the elementary analysis of the immonium salt because of its extreme explosiveness. IR spectrum: 1640, 1560, 1285, 1270, 1247, 1189, 1090, 835, and 793 cm^{-1}. To prove the structure of the immonium salt we converted it to aldehyde I by the action of aqueous Na_2CO_3 on an acetone solution of salt II. The yield of aldehyde I, with mp 72-74°, was 80%.

General Method for the Synthesis of Pyrylium Salts III by Condensation of β-Chloro-β-ferrocenylacrolein with β-Dicarbonyl Compounds. A separately prepared mixture of 0.2 ml (0.002 mole) of 70% $HClO_4$ and 0.6 ml (0.006 mole) of acetic anhydride was added to a solution of 0.55 g (0.002 mole) of β-chloro-β-ferrocenylacrylaldehyde and 0.002 mole of β-dicarbonyl compound in 10 ml of glacial acetic acid, and the mixture was heated for 5-8 min. The course of the reaction was monitored from the change in color. As soon as the crimson color of the β-chloro-β-ferrocenylacrylaldehyde gave way to the blue-green color of the pyrylium salt, heating was discontinued, and the mixture was allowed to stand at room temperature for 4-5 h. The resulting precipitate was removed by filtration and washed with ether. An additional amount of the salt was precipitated from the mother liquor by the addition of ether. The yields of salts III are presented in Table 2. We were unable to perform the elementary analysis of salts III because of their pronounced explosiveness.

Synthesis of Pyridines V from Pyrylium Salts III. Pyrylium salts III were suspended in 10-15 ml of glacial acetic acid, and a tenfold excess of anhydrous ammonium acetate was added. The mixture was refluxed for 1 h, after which it was diluted with water and neutralized with concentrated NH_4OH. The resulting precipitate was removed by filtration, extracted with ether, and chromatographed with a column filled with activity II Al_2O_3 (elution with benzene). The solvent was evaporated to dryness, and the residue was recrystallized. The yields, melting points, and results of elementary analysis are presented in Table 1.

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