CCA-711 547.559.07
Original Scientific Paper

Ferrocene Compounds. III*. On the Tautomerism and Reactions of Some Derivatives of β-Ferrocenoylacrylic acid

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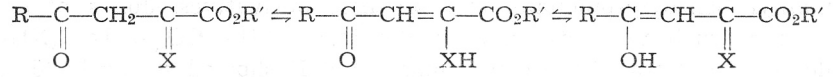
Received January 24, 1972

The tautomerism of Fc—CO—CH_2—CO—CO_2R (Fc = ferrocenyl) (I, R = H; II, R = C_2H_5) and Fc—CO—CH_2—C(= NR)—$CO_2C_2H_5$ (III, R = H; IV—VI, R = alkyl; VII—IX, R = aryl) has been investigated on the basis of their IR, UV and NMR spectra. Reactions of ester II with ammonia and primary aliphatic and aromatic amines, as well as of the compounds I—IX with hydroxylamine hydrochloride and hydrazine hydrate have been studied.

INTRODUCTION

Enolisation of compounds of type A (R = alkyl, aryl; R′ = H, alkyl; X = O) has been explored analytically and by studying the products obtained with typical reagents. Bromination studies[1] showed that alkyl aroylpyruvates



A B C

exist preponderantly in their enolic forms. The forms B (R = aryl; R′ = alkyl; X = O) were indicated by their UV spectra[2]; their reactions with ammonia[3] or hydroxylamine hydrochloride[4] were consistent with the presence of the same forms. These reactions took place through nucleophylic attack of the reagents mentioned on the α-carbon of the diketo ester, and products like methyl α-amino-β-benzoylacrylate or methyl 5-phenyl-3-isoxazolecarboxylate were isolated.[5] Bromination studies[1] showed that acylpyruvates contain a lower proportion of enolised carbonyl than aroylpyruvates.

In view of the electron-donating properties of ferrocene and of its aromatic character, we considered it worthwhile to investigate the influence of the incorporation of ferrocenyl residues into dicarbonyl compounds of this type [Fc—CO—CH_2—CO—CO_2R (I, R = H; II, R = C_2H_5)] on their enolisation. The acid I and ester II have been described in Part I[6] of this series. In the present paper the study was extended to the tautomerism of compounds Fc—CO—CH_2—C(=NR)—$CO_2C_2H_5$ [III, R = H; IV, R = CH_3; V, R = C_2H_5; VI, R = *iso*—C_3H_7; VII, R = C_6H_5; VIII, R = *m*—ClC_6H_4; IX, R = *o*—$(CH_3O)C_6H_4$],

* Part II: M. Laćan and R. Šarac-Arneri, *Croat. Chem. Acta* **43** (1971) 215.

which were synthetised by action of ammonia or primary aliphatic and aromatic amines on ester II. In this connection it seemed of special interest to establish optimal conditions for these reactions and to get insight into their mechanism, as studies of this kind have not been done in detail with β-diketones. Moreover, the action of hydroxylamine or hydrazine on compounds analogous to III—IX has not been studied so far. The structures of compounds I—IX were explored on the basis of spectral data and supported by reactions with the reagents mentioned.

The compounds I—IX as well as some isoxasole and pyrazole derivatives which were prepared in the course of this work can be of interest because of their potential biological activity.[4,7] The compounds I—IX are also interesting as possible polymer precursors.[8]

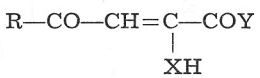
RESULTS AND DISCUSSION

The electron-withdrawing carboxyl or carbethoxyl groups, with the participation of the electron-donating ferrocene nucleus, caused enolisation of the keto group in the α-position of the molecule of acid I or ester II and the structures B (R = ferrocenyl; R′ = H, C_2H_5; X = O) rather than C could be expected. In this connection, and bearing in mind that the β-vinylamino form is preferred in compounds containing the —CO—CH_2—C(=NH)-- arrangement[5a], it seems reasonable to presume for the amino esters III—IX analogous structures B (R = ferrocenyl; R′ = C_2H_5; X = NH, *N*-alkyl, *N*-aryl).

Spectroscopic evidence supports these structures, and therefore the compounds I—IX could be named as derivatives of the α-hydroxy (or α-amino)-β-ferrocenoylacrylic acid. UV absorption data of these compounds resemble closely those of the adducts obtained by action of water, ammonia or amines on methyl benzoylpropionate, and of their derivatives. Jones *et al.*[2] have shown that such products exist in the form C_6H_5—CO—CH=C(XH)—COY (Table I). IR spectra of the compounds I and II showed strong bands at 1620 and 1610 cm^{-1}, respectively, assigned to the enolised β-diketo structure. IR absorption bands of compounds III—IX between 1585—1625 cm^{-1} correspond to $\nu_{C=O}$ of the β-aminovinyl ketones. The bands in the region between 3330 and 3500 cm^{-1} are assigned to ν_{NH} of the same structure. Measured chemical shifts for olefinic protons in the NMR spectra of compounds IV—IX are in agreement with calculated values[9] for the *trans* position of amino groups in the form B (R = ferrocenyl; R′ = C_2H_5; X = *N*-alkyl, *N*-aryl), while in the case of compound III the *cis* configuration [B(X = NH)] seems to be favored (Table II). The amino group proton resonance signals in the region (τ) between — 0.03 and — 1.58 are consistent with the presence of the β-aminovinyl keto structure in compounds III—IX.

In the presence of anions of lower aliphatic acids reactions of ester II with ammonia or amines proceeded at a higher rate and better yields were obtained in shorter reaction times. The compounds III—IX were unstable in acid ethanolic solution and were immediately hydrolyzed to the parent ester II. In alkaline ethanolic solutions cleavage to the corresponding salt of ester II occurred: compounds III—VI hydrolyzed immediately and aryl derivatives VII—IX with delay.

UV Absorption Data[a] of Derivatives of β-Aroylacrylic acid

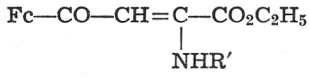


R	X	Y	λ_{max}, μm (ε_{max})[b]	R	X	Y	λ_{max}, μm (ε_{max})
C_6H_5	O	OH	312 (12500)	Fc	O	OH	312 (29000)
C_6H_5	O	OCH_3	311 (15000)	Fc	O	OC_2H_5	310 (11500)
C_6H_5	NH	OCH_3	256 (4500) 352 (17000)	Fc	NH	OC_2H_5	238[c] (7900) 347 (15700)
C_6H_5	NC_6H_5	OCH_3	240 (13000) 373 (19000)	Fc	NC_6H_5	OC_2H_5	329 (13600) 374 (18700)
C_6H_5	NH	NH_2	246 (7000) 256 (7000) 343 (17500)	Fc	NH	N_2H_3	233[c] (11600) 334 (14800)[d]

[a] measured in ethanol solutions, unless otherwise stated; [b] according to reference[2]; [c] inflexion; [d] in dioxane.

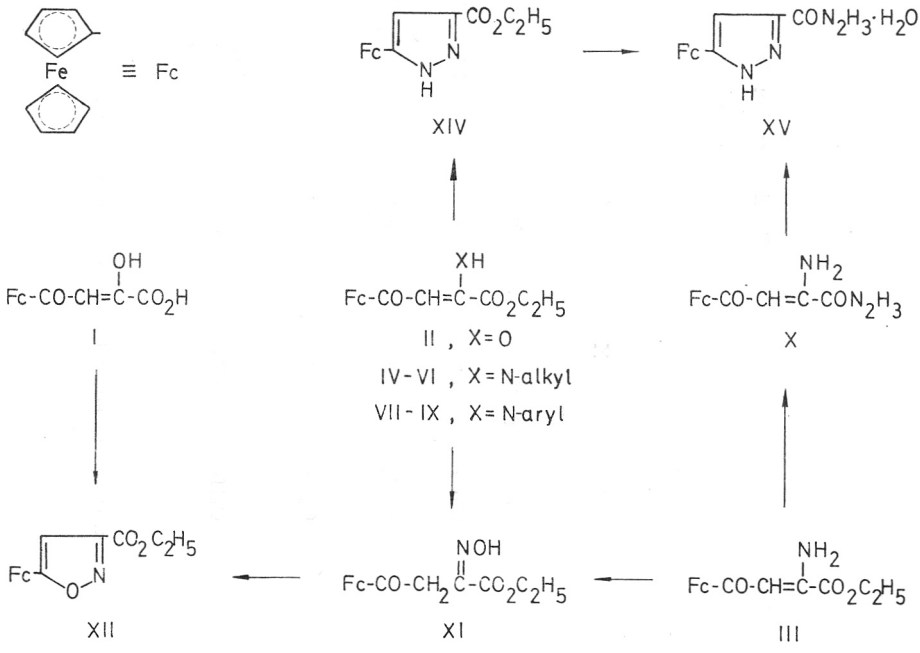
TABLE II

Chemical Shifts[a] of Olefinic Protons in Ethyl α-amino-β-ferrocenoylacrylate and its N-Substituted Derivatives



Compound	R′	Measured shift	Calc'd. shift[b]
III	H	3.74	3.82
IV	CH_3	4.21	4.29
V	C_2H_5	4.25	4.29
VI	iso-C_3H_7	4.32	4.29
VII	C_6H_5	4.00	3.83
VIII	m-ClC_6H_4	3.97	3.83
IX	o-$(CH_3O)C_6H_4$	3.97	3.83

[a] chemical shifts in deuteriochloroform relative to TMS (10.0 τ); [b] according to reference[9].



In the reaction with hydroxylamine hydrochloride, compounds III—IX were converted to the ethyl 5-ferrocenyl-3-isoxazolecarboxylate (XII). The same isoxazole compound XII was prepared by the action of hydrazine hydrochloride on the ester II and acid I, respectively. In the last mentioned reaction (carried out in boiling ethanol during 3/4 hour) the esterification of the carboxyl group and cyclization occurred and ester XII was isolated. The intermediate product in reactions of the compounds II—IX with hydroxylamine was α-oximino-γ'-oxo-γ-ferrocenylbutyrate (XI). It can be isolated in reaction of II with hydroxylamine at *p*H 6—7 or by short action of hydroxylamine hydrochloride on III—IX. Oxime XI can be readily transformed to isoxasole XII by heating its acid ethanolic solution. The structure of the intermediate oxime XI and consequently of the ester XII was deduced from elemental analysis and spectral data. The UV spectrum of compound XI [λ_{max} 222 (ε 22900), λ_{max} 266 (ε 6900), λ_{max} 336 (ε 1300), λ_{max} 455 mμ (ε 510)] was analogous to that of acetylferrocene[10] [λ_{max} 225 (ε 14600), λ_{max} 268 (ε 5400), λ_{max} 335 (ε 1120), λ_{max} 455 mμ (ε 420)] indicating the presence of a free carbonyl group attached to a ferrocenyl residue. The IR spectrum showed bands characteristic for a ferrocenyl ketone[11] (1660 and 1295 cm^{-1}) as well as for an oxime (3260, 1600—1640 and 934 cm^{-1}) indicating the structure XI. The singlet at $\tau = 5.81$ in the NMR spectrum corresponds to the isolated methylene group, thus supporting the same structure. An additional proof of the structure of the ester XII was its saponification to 5-ferrocenyl-3-isoxazolecarboxylic acid (XIII). This hydrolysis was carried out by ethanolic NaOH at 50°. At the boiling point extensive decomposition of the molecule took place.

Ethyl 3(5)-ferrocenyl-5(3)-pyrazolecarboxylate (XIV) was prepared by the action of hydrazine hydrate on the esters III—IX, in the presence of acetic acid as catalyst. In the reaction with excess of free hydrazine hydrate the compounds IV—IX were converted *via* the intermediate ester XIV into 3(5)-ferrocenyl-5(3)-pyrazolecarboxyhydrazide monohydrate (XV). The reaction of the unsubstituted compound III with hydrazine hydrate took a different course. In the first step the carbethoxyl group of the compound III was converted to a carboxyhydrazido group, and α-amino-β-ferrocenoylacrylic acid hydrazide (X) was isolated. In the second step compound X was converted to the pyrazole XV. The IR spectrum of hydrazide X showed amide I [1670 w(?)], amide II (1505 m) and amide III (1270 w cm^{-1}) bands, respectively, (characteristic for the hydrazido group too[12]). The strong band at 1610 cm^{-1} corresponds to the carbonyl group of the β-aminovinyl ketone, indicating a structure analogous to that of the starting material III. The UV spectrum (in dioxane) of the compound X exhibited absorption bands corresponding to those of α-amino-β-benzoylacrylic acid amide (Table I). A broad multiplet centered at $\tau = 7.15$ in the NMR spectrum (in hexadeuterioacetone) of X seems to contain the signals of two amino protons and three carboxyhydrazido protons. The olefinic proton signal at $\tau = 3.95$ corresponds to chemical shifts of those in compounds III—IX (*cf.* Table II). The structures of compounds XIV and XV were supported by preparing the same compounds in a different way, *i. e.* from the ester II and hydrazine acetate and free hydrazine hydrate, respectively. The possible open chain structure of ethyl α,γ-dioxo-γ-ferrocenylbutyric acid monohydrazone was excluded and its cyclic structure XV was demonstrated by dehydration at 180—185° [to anhydrous 3(5)-ferrocenyl-5(3)-pyrazolecarboxyhydrazide (XVI)], and more firmly by its saponification

to the corresponding 3(5)-ferrocenyl-5(3)-pyrazolecarboxylic acid (XVIII). The acid XVIII can be prepared also as its hydrazine salt XVII by the action of hydrazine hydrate in excess on the free acid I. The same acid XVIII was obtained as the reaction product of acid I with semicarbazide hydrochloride under conditions for semicarbazone formation[13]. This leads to the conclusion that due to the presence of the ferrocenyl residue in the molecule an easily occurring hydrolytical cleavage of the carboxamido group in the intermediate semicarbazone or *N*-carboxamido pyrazole took place.

Concluding it can be stated that the reactions of ester II with ammonia or amines, and of compounds I—IX with hydroxylamine or hydrazine, are in agreement with indications of the preponderant presence of the enolic and β-aminovinyl keto forms in these compounds, which are given by their spectral data.

EXPERIMENTAL

The melting points were determined on a Kofler heating microscope and are uncorrected. The IR spectra were recorded as KBr pellets with a Perkin-Elmer Infracord Model 137 spectrometer. The UV spectra were measured on a Perkin-Elmer UV/VIS Model 124 spectrophotometer. The NMR spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane as internal standard. Spectral data of compounds III—XI are presented in the theoretical part of this paper. Thin-layer chromatography (TLC) was done on chromatoplates of silicagel G (Merck) in benzene : ethanol (30 : 1 and 15 : 1)[14].

α-Hydroxy-β-ferrocenoylacrylic acid (α,γ-dioxo-γ-ferrocenylbutyric acid) (I) and its ethyl ester (II) were prepared from acetylferrocene and diethyloxalate according to the procedures described in Part I[6] of this series.

Ethyl α-amino-β-ferrocenoylacrylate (III)

a) Into a solution of 2 g. (6.1 Mmoles) of ethyl α-hydroxy-β-ferrocenoylacrylate (II) in 25 ml. of 96% ethanol 15 Mmoles of 25% aqueous ammonia and several drops of acetic acid were added. During short reflux an additional 10 Mmoles of ammonia were added dropwise. The reaction mixture was cooled to room temperature and the product was precipitated by addition of water. After several hours red crystals were filtered off and washed with water until neutral (melting points, yields and analyses are recorded in Table III).

b) The same product III was obtained in 86.5% yield by action of an excess of ammonium acetate on 0.2 g. (0.6 Mmole) of ester II under similar conditions as described above.

Mixed melting points of samples described under *a*) and *b*) showed no depression and their IR spectra and R_f values (TLC) were identical.

Ethyl α-(N-alkylamino)-β-ferrocenoylacrylate (IV—VI)

To prepare compounds IV—VI 9 Mmoles of aqueous alkylamine and several drops of acetic acid were added to a solution of 3 Mmoles of II in 20 ml. of 96% ethanol. The reaction mixture was refluxed for 1/2—3/4 hour and evaporated *in vacuo* almost to dryness. After standing for 2—3 days at room temperature the resinous solid was filtered off by suction, washed with a small quantity of ethanol and dried. The pulverized raw product was then washed with water, 10% $NaHCO_3$ and water until the filtrate was neutral and colourless (Table III).

Ethyl α-(N-arylamino)-β-ferrocenoylacrylate (VII—IX)

Compounds VII—IX of Table III were obtained by the following general procedure:

Into a solution of 3 Mmoles of ester II in 20 ml. of abs. ethanol 5 Mmoles of arylamine were added. The reaction mixture was refluxed for 1/2—6 hours, reduced *in vacuo* to a small volume, and, after cooling to room temperature, left to stand for several days. Precipitated crystals were filtered off, washed with diluted hydrochloric acid, water, 10% $NaHCO_3$ and water until neutral (Table III).

TABLE III

Ethyl α-amino-β-ferrocenoylacrylate and its N-Substituted Derivatives

$$Fc—CO—CH=C(NHR')—CO_2C_2H_5$$

Compound	R′	Yield of crude prod. %	M. p. °C	Formula	Calc'd. (%) C	H	N	Found (%) C	H	N
III	H	80.0	103—104[a]	$C_{16}H_{17}FeNO_3$	58.74	5.24	4.28	58.84	5.54	4.51
IV	CH_3	84.0	87—88[b]	$C_{17}H_{19}FeNO_3$	59.84	5.61	4.11	59.77	5.74	4.19
V	C_2H_5	85.0	75—76[b]	$C_{18}H_{21}FeNO_3$	60.86	5.95	3.94	60.71	6.04	4.08
VI	*iso*-C_3H_7	87.6	51—52[c]	$C_{19}H_{23}FeNO_3$	61.80	6.28	3.79	61.77	6.22	3.66
VII	C_6H_5	85.7	92—93[d]	$C_{22}H_{21}FeNO_3$	65.52	5.25	3.74	65.53	4.95	3.69
VIII	*m*-ClC_6H_4	94.5	106—108[b]	$C_{22}H_{20}ClFeNO_3$[e]	60.37	4.61	8.10	60.12	4.70	8.19
IX	*o*-$(CH_3O)C_6H_4$	84.5	122—123[b]	$C_{23}H_{23}FeNO_4$	63.76	5.35	3.23	63.42	5.47	3.23

[a] from 55% ethanol; [b] from benzene; [c] from benzene-ether; [d] from abs. ethanol; [e] calc'd. 3.20% Cl, found 3.26% Cl.

α-Amino-β-ferrocenoylacrylic acid hydrazide (X)

To a solution of 0.4 g. (1.2 Mmoles) of ethyl α-amino-β-ferrocenoylacrylate (III) in 7 ml. of abs. ethanol an excess of 90% hydrazine hydrate was added. Shortly afterwards a red crystalline product began to precipitate and after standing for 12 hours at room temperature this was filtered off with suction, and washed with diluted ethanol. 0.35 g. (90.0%) Hydrazide X was obtained; red-orange crystals (from abs. ethanol) m. p. 184—185° (with carbonization).

Anal. $C_{14}H_{15}FeN_3O_2$ (468.14) calc'd.: C 53.70; H 4.83; N 13.42%
found: C 53.76; H 5.05; N 13.07%

Ethyl α-oximino-γ-oxo-γ-ferrocenylbutyrate (XI)

a) To a boiling solution of 0.1 g. (0.3 Mmole) of ester III 0.07 g. (1 Mmole) of hydroxylamine hydrochloride in 2 drops of water was added. After short reflux the reaction mixture was diluted with water to precipitate 0.7 g. (66.6%) of XI; orange-brownish crystals (from 50% ethanol) m. p. 155—156°.

Anal. $C_{16}H_{17}FeNO_4$ (343.16) calc'd.: C 55.99; H 5.00; N 4.08%
found: C 56.06; H 5.07; N 4.05%

Using the same procedure the same oxime XI was obtained from IV—IX. The aliphatic derivatives IV—VI were converted to XI at room temperature in several minutes. The compounds VII—IX had to be kept at short reflux to give oxime XI.

b) A concentrated aqueous solution of hydroxylamine hydrochloride was adjusted to *p*H 6—7 by addition of aqueous Na_2CO_3. To a solution of 0.2 g. (0.6 Mmole) of ester II in 7 ml. of abs. ethanol a quantity of this hydroxylamine hydrochloride solution equivalent to 2 Mmoles was added. The precipitate of sodium salt of II was dissolved by addition of several drops of water. After keeping overnight at room temperature some precipitated tan material was removed by filtration. Addition of water to the filtrate with simultaneous stirring with a glass rod precipitated 0.18 g. (85.6%) of XI.

The compound is identical to the products as prepared under *a*).

Ethyl 5-ferrocenyl-3-isoxazolecarboxylate (XII)

a) To a boiling solution of 0.35 g. (1 Mmole) of ethyl α-amino-β-ferrocenoylacrylate (III) in 5 ml. of abs. ethanol a solution of 0.2 g. (3 Mmoles) of hydroxylamine hydrochloride in a few drops of water was added. The reaction mixture was refluxed for 1/4 hour, cooled to room temperature and diluted with water to precipitate 0.3 g. (85.7%) of ester XII; brownish-orange crystals (from ethanol) m. p. 89—90°. IR spectrum: 1730 s (carbethoxyl C=O), 1615 s, 1500 m and 1425 m (isoxazole ring), 1265 s (carbethoxyl C—O) cm^{-1}.

Anal. $C_{16}H_{15}FeNO_3$ (325.14) calc'd.: C 59.10; H 4.65; N 4.31%
found: C 59.41; H 5.01; N 4.17%

b) Using the same method as described under a), from 1.8 g (6 Mmoles) of I or 0.82 g. (2.5 Mmoles) of II and equimolar quantity of hydroxylamine hydrochloride the same product XII was obtained in a yield of 50.5 and 61.5%.

c) Oxime XI can be converted into isoxazole XII by short reflux of its ethanolic hydrochloric acid solution.

The compounds described under *a*), *b*) and *c*) were identical [mixed m. p., IR spectra, R_f values (TLC)].

5-Ferrocenyl-3-isoxazolecarboxylic acid (XIII)

To a solution of 0.4 g. (1.2 Mmoles) of ester XII in 10 ml. of 66% ethanol heated to 50°, 3 ml. of saturated aqueous NaOH was added. Some dark precipitate was filtered off and the filtrate diluted with water. Sodium salt of acid XIII was decomposed by successive addition of 20% hydrochloric acid. The acidified mixture was allowed to stand overnight at room temperature; 0.2 g. (54.7%) of acid XIII was separated by filtration; yellow crystals (from 80% ethanol or benzene) m. p. 141—

142°. IR spectrum: 3150—2500 w (dimeric carboxyl OH), 1720 s (carboxyl C=O), 1620 m, 1510 m and 1430 m (isoxazole ring), 1265 m (carboxyl C—O), 936 (carboxyl OH) cm^{-1}.

Anal. $C_{14}H_{11}FeNO_3$ (297.09) calc'd.: C 56.59; H 3.79; N 4.72%
found: C 56.63; H 3.93; N 4.45%

Ethyl 3(5)-ferrocenyl-5(3)-pyrazolecarboxylate (XIV)

a) Into a solution of 0.5 g. (1.5 Mmole) of III in 10 ml. of abs. ethanol 4 Mmoles of 90% hydrazine hydrate and 3 drops of glacial acetic acid were added. The reaction mixture was refluxed for 1 hour, then evaporated *in vacuo* to a small volume, upon cooling orange crystallinic material precipitated. It was purified for elemental analysis by filtration and washing with several small portions of ethanol [0.4 g. (90.0%)]. The sample changed crystalline form at 160—170°, sublimed at 184° and melted between 187—194°. IR spectrum: 3600—2900 m (pyrazolic NH), 1720 s (carbethoxyl C=O), 1608 w (pyrazolic C=N), 1450 w (unassigned pyrazolic band), 1242 s (carbethoxyl C—O) cm^{-1}.

Anal. $C_{16}H_{16}FeN_2O_2$ (324.15) calc'd.: C 59.28; H 4.98; N 8.64%
found: C 59.55; H 5.17; N 8.84%

b) The same ester XIV was obtained from II and IV—IX resp. using the same procedure as described above. The aliphatic derivatives IV—VI were converted in several minutes to XIV. Reactions of VII—IX with hydrazine acetate needed longer time.

Mixed m. p. of samples described under *a*) and *b*) exhibited no depression and their IR spectra and R_f values (TLC) were identical.

3(5)-Ferrocenyl-5(3)-pyrazolecarboxylic acid hydrazide monohydrate (XV)

a) 0.9 g. (2.8 Mmoles) of ethyl α-amino-β-ferrocenoylacrylate (III) was dissolved in 20 ml. of abs. ethanol. 5 Mmoles of hydrazine hydrate was added and this reaction mixture left overnight at room temperature. The precipitated product X was dissolved by adding 25 ml. of ethanol to reaction mixture. After the solution had stood for 12 hours the hydrazide XV began to crystallize. After evaporation *in vacuo* to a small volume 0.75 g. (69.5%) of XV was obtained; glittering gold-yellow flakes (from 66% ethanol) which lost water at 180° and then melted with carbonization between 192 and 195°. IR spectrum: 3440—3030 (center at 3260) s (carboxyhydrazido NH and hydrate OH), 1643 s (amide I), 1620 s (pyrazolic C=N), 1565 m (amide II), 1450 w (unassigned pyrazolic band), 1290 m (amide III) cm^{-1}.

Anal. $C_{14}H_{16}FeN_4O_2$ (328.17) calc'd.: C 51.23; H 4.92; N 17.07%
found: C 51.31; H 4.79; N 17.17%

b) Compounds II and III—IX resp. were made to react with excess of hydrazine hydrate as described under *a*), and in all cases the same product XV was isolated in a good yield. IR spectra of all samples were identical and their mixed m. p. showed no depression.

3(5)-Ferrocenyl-5(3)-pyrazolecarboxyhydrazide (XVI)

The title compound was obtained by heating the hydrate XV at 180—185° in a high vacuum for 2—3 hours. Brownish substance, m. p. (carboniz.) 197—198°. IR spectrum: 3450—3020 m (carboxyhydrazido NH), 1635 s (amide I), 1540 m (amide II), 1450 w (unassigned pyrazolic band) 1280 m (amide III) cm^{-1}.

Anal. $C_{14}H_{14}FeN_4O$ (310.10) calc'd.: C 54.22; H 4.55; N 18.07%
found: C 54.27; H 4.59; N 18.04%

Hydrazinic salt of 3(5)-ferrocenyl-5(3)-pyrazolecarboxylic acid (XVII)

To a solution of 2 g. (6.7 Mmoles) of acid I in 100 ml. of abs. ethanol a solution of 20 Mmoles of hydrazine hydrate in 8 ml. of abs. ethanol was added. After half

an hour a small quantity of impurities was removed by filtration. The filtrate was evaporated *in vacuo* to a very small volume yielding 1.5 g. (68.4%) of the hydrazinic salt XVII. An analytical sample was prepared by washing the raw material with hot ethanol; m.p. 150—153°. IR spectrum: 3360—2360 s (associated hydrazinium and pyrazolic NH), 1565 s (carboxylate C=O), 1450 w (pyrazole), 1325 m (carboxylate C—O) cm^{-1}.

Anal. $C_{14}H_{16}FeN_4O_2$ (328.15) calc'd.: C 51.23; H 4.92; N 17.07%
found: C 50.92; H 5.16; N 16.96%

3(5)-Ferrocenyl-5(3)-pyrazolecarboxylic acid (XVIII)

a) An aqueous solution of 3 g. (9.1 Mmoles) of the hydrazinic salt XVII was acidified to *p*H 4—5 by addition of diluted hydrochloric acid whilst stirring to precipitate the dark by-products present. Addition of further quantities of hydrochloric acid to the filtrate until *p*H 2 precipitated 1.4 g. (51.6%) of raw acid XVIII; yellow amorphous material (from 55% ethonol); carbonized at 245—250°. IR spectrum: 3450—2440 m (dimeric carboxyl OH and pyrazolic NH), 1710 s (carboxyl CO), 1615 m (pyrazolic C=N), 1450 m (pyrazole) cm^{-1}.

Anal. $C_{14}H_{12}FeN_2O_2$ (296.10) calc'd.: C 56.78; H 4.09; N 9.46%
found: C 56.60; H 4.23; N 9.63%

b) 3(5)-Ferrocenyl-5(3)-pyrazolecarboxyhydrazide hydrate (XV) can be hydrolyzed into the acid XVIII in 80% yield by refluxing it in 5% aqueous NaOH solution during 3/4 hour and acidification with diluted hydrochloric acid.

Hydrolysis of XV in hydrochloric acid ethanolic solution needed several hours and the material thereby partly decomposed.

c) 1.5 g. (5 Mmoles) of acid I was suspended in 90 ml. of 10% $NaHCO_3$ and filtered from the insoluble part. The filtrate was treated with 1.4 g. (12 Mmoles) of aqueous semicarbazide hydrochloride solution and left to stand overnight. A small quantity of precipitate was removed by filtration and the filtrate added dropwise, with stirring and cooling with ice, to 200 ml. of 25% hydrochloric acid to precipitate 0.8 g. (54.1%) of the acid XVIII.

d) Into an aqueous suspension of 1.5 g. (5 Mmoles) of the acid I, 5.5 ml. of 1*N*—Na_2CO_3 was added. Some insoluble material was filtered off and the filtrate was treated with an aqueous solution of 0.75 g. (6.7 Mmoles) of semicarbazide hydrochloride and 3 ml. of 33% sodium acetate. After standing for several days the precipitated crystals were filtered off, dried, finely pulverized and suspended in an excess of 10% $NaHCO_3$. Insoluble material was removed by filtration and this filtrate together with the above filtrate, after removal of crystals poured into an excess of 25% hydrochloric acid to precipitate 1 g. (67.6%) of the acid XVIII.

Mixed melting points of all substances described under *a*), *b*), *c*) and *d*) exhibited no depression and their IR spectra were identical.

Acknowledgment. We wish to express our thankfulness to Ing. E. Guštak and Dr. I. Butula for helpful discussions and their interest. We are greatly indebted to Professor Z. Štefanac for help in interpretation of spectral data and to Dr. J. Jerkunica for critical examination of the manuscript.

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IZVOD

Studij tautomerije i reakcija nekih derivata β-ferocenoilakrilne kiseline

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Izučavana je tautomerija spojeva s ferocenom — Fc—CO—CH_2—CO—CO_2R (Fc = ferocenil) (I, R = H; II, R = C_2H_5) i Fc—CO—CH_2—C(=NR)—$CO_2C_2H_5$ (III, R = H; IV—VI, R = alkil; VII—IX, R = aril) na temelju njihovih IR, UV i NMR spektara. Ispitani su uvjeti reakcija estera II s amonijakom i primarnim aminima pri čemu su pripravljeni etil α-amino-β-ferocenoilakrilat (III) i njegovi *N*-supstituirani derivati (IV—IX) u 80—95%-tnim prinosima. Ovi esteri izolirani su u obliku stabilnih kristaliziranih spojeva. Djelovanjem hidroksilamin hidroklorida, odnosno hidrazin hidrata na spojeve I—IX dobiveni su pripadni derivati 5-ferocenil-3-izoksazolkarbonske kiseline (XIII), odnosno 3(5)-ferocenil-5(3)-pirazolkarbonske kiseline (XVIII).

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Primljeno 24. siječnja 1972.