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Some Acyl Ferrocenes and their Reactions

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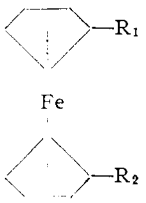
Formylcyclopentadienyl-(cyclopentadienyl)-iron, the first ferrocene derivative bearing an aldehyde function, has been synthesized by reaction of ferrocene with N-methylformanilide. A number of new diacylferrocenes have also been prepared by the Friedel–Crafts reaction. These new acyl derivatives, as well as the known acetylferrocene and diacetylferrocene, undergo many reactions characteristic of the carbonyl group.

Acyl derivatives of dicyclopentadienyliron were first reported by Woodward[1] who prepared bis-(acetylcyclopentadienyl)-iron by a Friedel–Crafts reaction of dicyclopentadienyliron with acetyl chloride in the presence of aluminum chloride. This synthesis has been viewed by some as important evidence of aromatic character for dicyclopentadienyliron, though others have pointed out that acylation with Friedel–Crafts catalysts occurs with simple alicyclic compounds.[2]

DERIVATIVES OF DICYCLOPENTADIENYLIRON



R_1	R_2	
CHO	H	I
$\mathrm{COCH_3}$	H	II
$\mathrm{CH{=}NOH}$	H	III
$\mathrm{CH_2OH}$	H	IV
$\mathrm{CH_2N(CH_3)_3I}$	H	V
CN	H	VI
$\mathrm{CH(OH)CN}$	H	VII
$\mathrm{CH{=}C(CN)CO_2H}$	H	VIII
$\mathrm{CH(NH_2)CH_3}$	H	IX
$\mathrm{CH_2\overset{S}{\overset{\|}{C}}—[N(CH_2CH_2)_2O]}$	H	X
$\mathrm{CH_2CO_2H}$	H	XI
$\mathrm{CH_2CON(CH_2CH_2)_2O}$	H	XII
$\mathrm{COCH_2CH_2CO_2H}$	$\mathrm{COCH_2CH_2CO_2H}$	XIII
$\underbrace{\mathrm{CHCH_2CH_2CO}}_{\mathrm{O}}$	$\underbrace{\mathrm{CHCH_2CH_2CO}}_{\mathrm{O}}$	XIV
$\mathrm{COCH_2CH_2CN}$	$\mathrm{COCH_2CH_2CN}$	XV
$\mathrm{(CH_2)_4NH_2}$	$\mathrm{(CH_2)_4NH_2}$	XVI
$\mathrm{CHOHCH_3}$	$\mathrm{CHOHCH_3}$	XVII
$\mathrm{COCH_2CH_2CO_2C_2H_5}$	$\mathrm{COCH_2CH_2CO_2C_2H_5}$	XVIII

Acetylcyclopentadienyl-(cyclopentadienyl)-iron (II) has been prepared by reaction of dicyclopentadienyliron with acetic anhydride in anhydrous hydrogen fluoride,[3] and in the presence of stannic chloride.[4] Pauson[5] interprets these results and his unpublished synthesis of the monoacetyl derivative with a boron trifluoride catalyst as evidence that dicyclopentadienyliron is more reactive than benzene. Some support is given this conclusion by our synthesis of formylcyclopentadienyl-(cyclopentadienyl)-iron from N-methylformanilide, dicyclopentadienyliron and phosphorus oxychloride, and by our preparation of acetylcyclopentadienyl-(cyclopentadienyl)-iron from dicyclopentadienyliron and acetic anhydride with phosphoric acid catalyst.

Diacyl derivatives of dicyclopentadienyliron reported herein were prepared by the Friedel–Crafts method. The acyl derivatives have been studied to determine effects of the dicyclopentadienyliron ring system on some reactions of the carbonyl group. In most cases, normal functionality was observed.

Formylcyclopentadienyl-(cyclopentadienyl)-iron; Dicyclopentadienylironcarboxaldehyde.—This aldehyde I was synthesized in 55% yield by the reaction of N-methylformanilide with dicyclopentadienyliron in phosphorus oxychloride at 50–55°.[5a] The new aldehyde formed such typical derivatives as a bisulfite addition product, a cyanohydrin, an oxime, an azine, a rhodanone and an acetal. It could be reduced to an alcohol and a hydrocarbon, and it underwent reductive amination. In other respects the aldehyde I displayed unexpected properties.

Under a polarizing microscope, formylcyclopentadienyl-(cyclopentadienyl)-iron was observed to undergo a sharp transition at 45° after which it was isotropic up to a temperature of 124.5°. Between these two temperatures, a liquid crystal region was observed and at 124.5° a sharp change in viscosity indicated the final melting point. Above the transition temperature of 45°, a sharp absorption peak characteristic of hydroxyl groups was observed in the infrared spectrum (Fig. 1). This unexplained hydroxyl absorption did not appear at the expense of carbonyl absorption and was observed only at temperatures above 45°. Chemically, the aldehyde was sensitive to oxidation either in dilute aqueous solutions or in concentrated anhydrous hydrocarbon solutions. The oxidation product, however, was not the carboxylic acid, since no acidic materials could be isolated from the typical amorphous brown oxidation product. When the aldehyde I was treated with Raney nickel and hydrogen at 50°, another unusual reaction was observed in its unexpected conversion to oxydimethylenebis-(dicyclopentadienyliron), $(C_5H_5FeC_5H_4CH_2)_2O$, instead of the expected alcohol, $C_5H_5FeC_5H_4CH_2OH$ (IV).

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[1] R. B. Woodward, M. Rosenblum and M. Whiting, THIS JOURNAL, **74**, 3458 (1952).

[2] E. O. Fischer and R. Jira, *Z. Naturforsch.*, **8b**, 1 (1953).

[3] V. Weinmayr, THIS JOURNAL, **77**, 3009 (1955).

[4] A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. A. Nesmeyanova, *Doklady Akad. Nauk. S.S.S.R.*, **97**, 459 (1954).

[5] P. L. Pauson, *Quart. Revs.*, **9**, No. 4, 391 (1955).

(5a) M. Rosenblum, *Chem. & Ind.*, No. 3, 72 (1957), disclosed the synthesis of formylferrocene by this route after this paper had been submitted for publication.

Acetylcyclopentadienyl-(cyclopentadienyl)-iron.—A new method for the synthesis of acetylcyclopentadienyl-(cyclopentadienyl)-iron (II) has been discovered in which acetylation is accomplished with acetic anhydride at 90° with phosphoric acid catalyst. This suggests that dicyclopentadienyliron is more reactive toward electrophilic substitution than realized heretofore. Some reactions of the monoacetyl derivative II have already been described. These include oxidation to a monocarboxylic acid, conversion to an oxime and reduction to a monoethyl derivative.[6] Acetylcyclopentadienyl-(cyclopentadienyl)-iron has now been found to undergo reductive amination and the Willgerodt reaction. The Willgerodt reaction proceeded smoothly in morpholine to give a stable crystalline thiomorpholide (X) which could be hydrolyzed in methanolic potassium hydroxide to the carboxymethyl derivative XI, and the carboxamide XII. Both the amide and free acid were stable in crystalline form, but aqueous solutions of the acid rapidly turned blue on exposure to air.

Bis-[(3-carboxypropionyl)-cyclopentadienyl]-iron.—Dicyclopentadienyliron reacted with succinic anhydride in the presence of aluminum chloride catalyst to give a bis-(carboxyacyl) derivative (XIII). Attempts to perform a Wolff–Kishner or Clemmensen reduction on this diacyl derivative were unsuccessful. Catalytic reduction apparently stopped at the hydroxyl stage as evidenced by isolation of the corresponding dilactone XIV. The dilactone also was obtained by catalytic reduction of the diethyl ester of bis-[(3-carboxypropionyl)-cyclopentadienyl]-iron (XVIII).

Bis-[(4-aminobutyl)-cyclopentadienyl]-iron.—This new diamine XVI was prepared readily by catalytic reduction of bis-[(3-cyanopropionyl)-cyclopentadienyl]-iron (XV), obtained by reaction of bis-[(3-chloropropionyl)-cyclopentadienyl]-iron with potassium cyanide. The bis-(chloroacyl) derivative was obtained by the method of Woodward[1] from ferrocene and β-chloropropionyl chloride with aluminum chloride catalyst. Bis-[(4-aminobutyl)-cyclopentadienyl]-iron underwent the reactions characteristic of an aliphatic diamine.

Experimental

Formylcyclopentadienyl-(cyclopentadienyl)-iron (I).—A mixture of 112 g. (0.6 mole) of finely ground dicyclopentadienyliron and 107 g. (0.7 mole) of phosphorus oxychloride was heated to 50°, and 81 g. (0.6 mole) of N-methylformanilide was added dropwise with stirring in 1.25 hours. The reaction mixture was cooled slowly to room temperature and allowed to stand for three hours. The resulting mixture was poured onto ice (500 g.) and extracted with diethyl ether for 45 hours in a continuous extractor. The extract was washed with water, 5% aqueous sodium carbonate solution, and again with water. The washed extracts were dried with anhydrous magnesium sulfate and the ether removed by distillation. Crude aldehyde was obtained as a black oil that solidified on standing. It was sublimed at 70° (1 mm.) to give 85.4 g. (66% yield) of formylcyclopentadienyl-(cyclopentadienyl)-iron. A recrystallization from a mixture of *n*-heptane and methylene chloride (3 to 1), gave 71 g. (55% yield) of pure aldehyde as a reddish-brown crystalline solid.

Anal. Calcd. for $C_{11}H_{10}FeO$: C, 61.7; H, 4.71; Fe, 26.1; mol. wt., 214. Found: C, 61.9; H, 4.73; Fe, 26.3; mol. wt., 202.

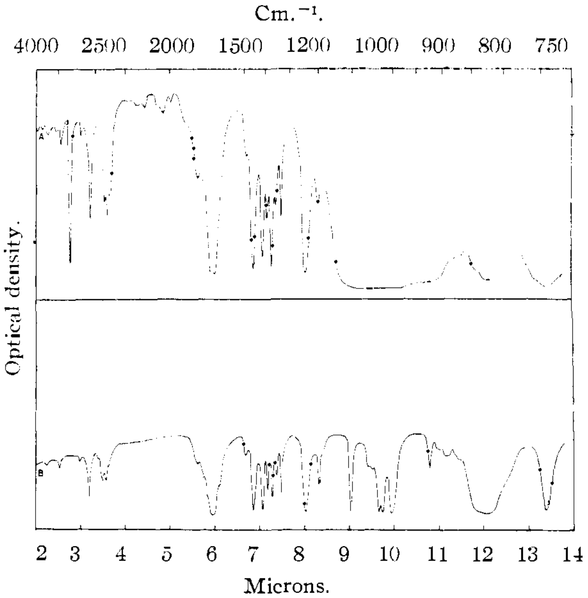

Fig. 1.—Infrared spectrum of formylcyclopentadienyl-(cyclopentadienyl)-iron above (A) and below (B) the transition temperature of 45°.

The aldehyde showed a sharp transition temperature at 45° under polarized light. True melting indicated by a sharp viscosity change occurred at 124.5°. The aldehyde was also prepared with dimethylformamide[7] as the formylating agent. This method required more vigorous conditions (85°, 3.5 hr.), produced considerable tar and gave only 23% yield of aldehyde I in 17% conversion.

Formylcyclopentadienyl-(cyclopentadienyl)-iron (10 g., 0.046 mole) was shaken vigorously with 100 g. of 40% aqueous sodium bisulfite and 15 ml. of ethyl alcohol to obtain 13.3 g. (90% yield) of a yellow bisulfite addition compound. The addition product could not be purified readily by recrystallization and was merely washed with cold water and with chloroform. The analyses indicated some impurities were still present in the product.

Anal. Calcd. for $C_{11}H_{11}FeNaO_4S$: C, 41.5; H, 3.5; Fe, 14.4; S, 10.1. Found: C, 34.7; H, 3.8; Fe, 16.2; S, 10.6.

An oxime III was prepared in 77% yield by reaction of hydroxylamine with I in aqueous methanol at 30°. The oxime was recrystallized from a 2:3 mixture of benzene and heptane, m.p. 133–135°. A transition temperature was noted at 98°.

Anal. Calcd. for $C_{11}H_{11}FeNO$: C, 57.6; H, 4.84; Fe, 24.4; N, 6.11. Found: C, 57.8; H, 5.08; Fe, 24.4; N, 6.37.

A semicarbazone was obtained in 58% yield by reaction of semicarbazide with I in aqueous ethyl alcohol at 60°. The purified semicarbazone, m.p. 203–204° dec., was obtained by recrystallization from a 5:4 mixture of ethyl alcohol and dimethylformamide.

Anal. Calcd. for $C_{12}H_{13}FeN_3O$: Fe, 20.6; N, 15.5. Found: Fe, 20.8; N, 15.5.

An isonicotinylhydrazone, prepared from I according to the method of Fox and Gibas,[8] was obtained in 39% yield after recrystallization from a mixture of isopropyl alcohol and ethyl alcohol (2:1), m.p. 212–213°.

Anal. Calcd. for $C_{17}H_{15}FeN_3O$: Fe, 16.7; N, 12.6. Found: Fe, 17.0; N, 12.5.

An azine, prepared by reaction of I with hydrazine hydrate in methanol at room temperature, was obtained in 47% yield as red-brown crystals after recrystallization from dimethylformamide, m.p. 245°.

Anal. Calcd. for $C_{22}H_{20}N_2Fe_2$: N, 6.61. Found: N, 6.65.

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[6] F. S. Arimoto and A. C. Haven, THIS JOURNAL, **77**, 6295 (1955).

[7] E. Campaigne and W. L. Archer, *ibid.*, **75**, 989 (1953).

[8] H. Fox and J. T. Gibas, *J. Org. Chem.*, **18**, 994 (1953).

A rhodanone, prepared according to the method of Julian and Sturgis,[9] was obtained in 70% yield as a deep blue crystalline compound. This highly insoluble product was purified by extraction with hot xylene after thorough washing with water, m.p. 245° dec.

Anal. Calcd. for $C_{14}H_{11}FeNO_2$: Fe, 17.0; N, 4.25; S, 19.5. Found: Fe, 16.9; N, 4.37; S, 19.2.

Hydroxymethylcyclopentadienyl-(cyclopentadienyl)-iron (IV).—A solution of 10.7 g. (0.05 mole) of I in 250 ml. of anhydrous diethyl ether was reduced with lithium aluminum hydride by the method of Arimoto and Haven[6] to obtain a yellow solid weighing 9.5 g. (88% yield). Recrystallization from a mixture of 60 ml. of Skellysolve B and 10 ml. of chloroform gave 5.4 g. (47% yield) of long yellow needles, m.p. 74–76°. Infrared analysis showed a sharp hydroxyl band and the usual bands for ferrocene.

Anal. Calcd. for $C_{11}H_{12}FeO$: C, 61.1; H, 5.60; Fe, 25.8; mol. wt., 216. Found: C, 60.9; H, 5.69; Fe, 26.0; mol. wt., 225.

Attempts to prepare IV by catalytic reduction of I using the same conditions successful in reducing acetylferrocene to the corresponding alcohol led to a new product believed to be an ether. When 10.0 g. (0.047 mole) of formylferrocene was reduced with Raney nickel catalyst under 135 atm. of hydrogen at 50° for 1.5 hours, 9.0 g. of light yellow product was obtained. After recrystallization from a chloroform–heptane mixture, 5.35 g. of yellow crystals, m.p. 129–130°, was obtained. The infrared spectrum of the product did not show hydroxyl or carbonyl absorption bands. The spectrum did show the presence of ether links, and a molecular weight determination supports the proposed ether structure, $(C_5H_5FeC_5H_4CH_2)_2O$, oxydimethylenebis-(dicyclopentadienyliron).

Anal. Calcd. for $C_{22}H_{22}Fe_2O$: C, 63.8; H, 5.35; Fe, 27.1; mol. wt., 414. Found: C, 63.7; H, 5.49; Fe, 27.4; mol. wt., 465.

Ferrocenylmethyltrimethylammonium Iodide (V).—A solution of 21.4 g. (0.1 mole) of I in 100 ml. of methanol was heated with 25 g. of dimethylamine in the presence of Raney nickel catalyst at 120° for three hours under 165 atm. pressure of hydrogen. The reaction mixture was filtered through charcoal, diluted with water and extracted with four 75-ml. portions of ether. The combined extracts were washed once with water, dried over magnesium sulfate and filtered. The clear filtrate was treated with a solution of 20 g. of methyl iodide in 50 ml. of anhydrous ether. The yellow precipitate that formed almost immediately was washed with dry ether and dried in a vacuum desiccator over phosphorus pentoxide. The finely divided yellow quaternary methiodide, m.p. 218° dec., weighed 29.1 g. (76% yield) and was readily soluble in water.

Anal. Calcd. for $C_{14}H_{20}FeIN$: C, 43.7; H, 5.23; Fe, 14.5; N, 3.63; I, 32.9. Found: C, 43.9; H, 5.30; Fe, 14.7; N, 3.55; I, 32.9.

This quaternary ammonium iodide was reported recently by Hauser and Lindsay[10] who prepared it by quaternization of dimethylaminoferrocene prepared from ferrocene, formaldehyde and dimethylamine.

Cyanocyclopentadienyl-(cyclopentadienyl)-iron (VI).—Acetic anhydride (40 ml.) was added to 20 g. of the oxime III at room temperature to give a deep red-brown solution. After about 30 minutes, the reaction mixture was poured onto 200 g. of ice, 10 g. of sodium carbonate added, and the red-orange oil that separated was extracted with methylene chloride. The combined extracts were washed with 100 ml. of 5% aqueous sodium carbonate followed by three washings with distilled water. The methylene chloride solution was dried over magnesium sulfate, filtered, and the solvent was evaporated at room temperature under a stream of nitrogen. The resulting viscous red oil decomposed slowly at room temperature to give acetic acid. Analysis indicated the oil was an acetate of the oxime III.

Anal. Calcd. for $C_{13}H_{13}FeNO_2$: Fe, 20.6. Found: Fe, 20.7.

The oxime acetate was placed in a vacuum desiccator over phosphorus pentoxide and pumped to remove the acetic acid produced by slow decomposition. After several days, the oil solidified. The solid residue was sublimed at 100° (1 mm.) for several days until no more brown sublimate was obtained. The crude product (10 g.) was recrystallized from 125 ml. of *n*-heptane to obtain 8.5 g. (46% yield) of pure cyanoferrocene, m.p. 103–104°.

Anal. Calcd. for $C_{11}H_9FeN$: C, 62.6; H, 4.30; Fe, 26.3; N, 6.64. Found: C, 62.6; H, 4.61; Fe, 26.7; N, 6.64.

1-Hydroxy-1-cyanomethylcyclopentadienyl-(cyclopentadienyl)-iron (VII).—The bisulfite addition compound of ferrocenecarboxaldehyde (I) was prepared by adding 21.4 g. (0.1 mole) of I in 35 ml. of ethyl alcohol to 20.8 g. (0.2 mole) of sodium bisulfite in 100 ml. of distilled water. To this slurry was added 9.8 g. (0.2 mole) of sodium cyanide in 100 ml. of water. The mixture was stirred for two hours at about 50°, cooled in ice and filtered. Extraction of the moist product (31 g.) with two 175-ml. portions of benzene and concentration of the extracts gave 17 g. of crude cyanohydrin. After recrystallization from benzene containing a trace of alcohol, 12.5 g. (52%) of cyanohydrin VII was obtained, m.p. 104°, slight decomposition, followed by sharp and complete decomposition at 125°.

It was not possible to prepare the cyanohydrin VII directly from ferrocenecarboxaldehyde and sodium cyanide. Successful preparations of VII were achieved only with the bisulfite addition compound as intermediate.

Anal. Calcd. for $C_{12}H_{11}FeNO$: C, 59.8; H, 4.60; Fe, 23.2; N, 5.81. Found: C, 59.6; H, 4.68; Fe, 23.5; N, 6.03.

2-Cyano-2-carboxyvinylcyclopentadienyl-(cyclopentadienyl)-iron (VIII).—A solution of 21.4 g. (0.1 mole) of I in anhydrous pyridine (50 ml.) was mixed at room temperature with a solution of 26 g. of cyanoacetic acid (0.3 mole) in 20 ml. of pyridine. The mixture was heated 2.5 hours on a steam-bath, cooled and allowed to stand for two days at room temperature. The mixture was diluted with 500 ml. of cold water, cooled in an ice-bath, and acidified with 150 ml. of 6 *N* sulfuric acid. The acidified mixture was extracted with four 150-ml. portions of methylene chloride and the combined extracts were washed three times with 200 ml. of water. The methylene chloride solution was dried with magnesium sulfate and evaporated to an oil which was treated with a solution of sodium carbonate monohydrate (20 g. in 200 ml. of water). The pastey mass that resulted was diluted with 100 ml. of water and filtered. The alkaline filtrate was cooled in an ice-bath and acidified with 6 *N* sulfuric acid to give 5.3 g. (19%) of a purple, gummy precipitate that crystallized on standing. Recrystallization from a mixture of chloroform and carbon tetrachloride gave 3.5 g. of pure VIII, m.p. 158.5–160° dec.

Anal. Calcd. for $C_{14}H_{11}FeNO_2$: C, 59.8; H, 3.95; Fe, 19.9; N, 4.98. Found: C, 59.8; H, 3.95; Fe, 19.7; N, 4.90.

The free acid VIII gave deep purple solutions in acetone or alcohol. Ultraviolet and visible spectra taken on the alcohol solution showed strongest absorptions at 2620, 3200 and 8300 Å.

Sodium Salt.—The solid remaining from the sodium carbonate extraction was dried over phosphorus pentoxide and extracted once with 150 ml. of chloroform to remove unreacted aldehyde. The residue was recrystallized from ethyl alcohol to give 9.4 g. (31% yield) of a dark red sodium salt of VIII.

Anal. Calcd. for $C_{14}H_{10}FeNNaO_2$: Fe, 18.4; Na, 7.59. Found: Fe, 17.9; Na, 8.02.

The sodium salt reacted readily with cupric acetate to give a red insoluble copper salt.

Hydantoin from Formylcyclopentadienyl-(cyclopentadienyl)-iron.—Moist bisulfite addition compound, prepared from 21.4 g. (0.1 mole) of ferrocenecarboxaldehyde (I), was slurried in 150 ml. of ethyl alcohol and added rapidly to a stirred mixture of 29.4 g. (0.45 mole) of potassium cyanide, 86.3 g. (0.9 mole) of ammonium carbonate, 150 ml. of distilled water and 50 ml. of ethyl alcohol. The reaction was stirred vigorously at 55° for 1.5 hours and cooled to room temperature. The alcohol was distilled from the mixture, and the residue was cooled and filtered to give 19 g. of an olive-brown hydantoin. The crude hydantoin was washed with hot benzene and hot methanol. The gray residue (11 g.) was purified by solution in 4% aqueous sodium hydroxide solution followed by filtration and acidification to give 9.0 g. (32% yield) of an olive product. One recrys-

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[9] P. L. Julian and B. M. Sturgis, THIS JOURNAL, **57**, 1126 (1935).

[10] C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **21**, 382 (1956).

tallization from 1,2-dimethoxyethane and one from aqueous dimethylformamide afforded a pale yellow-brown crystalline product, m.p. 192–197° dec.

Anal. Calcd. for $C_{13}H_{12}FeN_2O_2$: C, 54.9; H, 4.26; Fe, 19.7; N, 9.86. Found: C, 54.3; H, 4.48; Fe, 19.7; N, 9.64.

5-Ferrocenylmethylenebarbituric Acid.—A solution of 6.4 g. (0.05 mole) of barbituric acid and 3.0 g. of anhydrous potassium acetate in 150 ml. of glacial acetic acid was filtered and heated to 95°. To it was added portionwise in about two minutes 10.7 g. (0.05 mole) of aldehyde I. The reaction mixture, which became deep blue immediately, was allowed to cool slowly to room temperature. The mixture was filtered and the crystalline violet precipitate was washed once with glacial acetic acid and three times with methanol. The washed product weighed 11.1 g. after drying over phosphorus pentoxide. An additional 2.0 g. of product (total yield 80%) was obtained by dilution of the filtrate with water to cause precipitation. After filtration, drying and sublimation of the residue, volatile impurities such as formylferrocene and ferrocene were removed by sublimation. The compound did not melt below 360°.

Anal. Calcd. for $C_{15}H_{12}FeN_2O_3$: C, 55.6; H, 3.73; N, 8.64. Found: C, 55.1; H, 3.76; N, 8.95.

Acetylcyclopentadienyl-(cyclopentadienyl)-iron (II).—A mixture of 93 g. (0.5 mole) of dicyclopentadienyliron, 250 ml. of acetic anhydride and 20 ml. of 85% phosphoric acid was heated at 100° for 10 minutes. The reaction mixture was cooled slightly and poured onto ice. After standing overnight, the mixture was neutralized with 200 g. of sodium carbonate monohydrate in 200 ml. of water. The resulting brown pasty mass was cooled in an ice-bath and filtered. The tan product was washed four times with 100-ml. portions of water and filtered. The granular product was dried in a vacuum desiccator over phosphoric anhydride. Sublimation of the crude product at 100° (1 mm.) gave 81.5 g. (71.4% yield) of an orange crystalline product II, m.p. 85–86° (lit.[3] 85–86°) after recrystallization from *n*-heptane.

1-Aminoethylcyclopentadienyl-(cyclopentadienyl)-iron (IX).—A mixture of 22.8 g. (0.1 mole) of the monoacetyl derivative II, 125 ml. of absolute ethyl alcohol, 30 g. of liquid ammonia and 10 g. of Raney nickel catalyst was heated for 3 hr. at 100° and 135 atm. hydrogen pressure. The red orange solution was mixed with 2 g. of Celite and filtered to remove catalyst. The filtrate was poured into 500 ml. of cold water and extracted with diethyl ether. About 600 ml. of extracts were combined, washed three times with water, and dried with anhydrous magnesium sulfate. The drying agent was removed by filtration, the filtrate was diluted with one liter of anhydrous ether, and the solution was treated with dry hydrogen chloride. After about 15 minutes, the pink amine hydrochloride was collected by filtration, washed with diethyl ether, partially air-dried, slurried with 100 ml. of chloroform at room temperature, and filtered. Further washing with chloroform on the büchner funnel gave a pale yellow solid weighing 5.9 g. after drying in a vacuum desiccator over phosphoric anhydride. Recrystallization from 75 ml. of anhydrous ethyl alcohol gave 3.3 g. of a lemon-yellow hydrochloride, m.p. 163–165° dec.

Anal. Calcd. for $C_{12}H_{16}ClFeN$: C, 54.2; H, 6.07; N, 5.27. Found: C, 54.4; H, 6.19; N, 5.37.

Thiomorphylamidomethylcyclopentadienyl-(cyclopentadienyl)-iron (X).—A mixture of 9.5 g. of the monoacetyl derivative II, 1.9 g. of sulfur and 5.2 ml. of morpholine was heated at 130° for 2.5 hours. The viscous black reaction mixture was extracted with hot methanol, and the extracts were diluted with water to give a dark brown precipitate of thioamide X. Successive recrystallizations from benzene–hexane and water–methanol mixtures gave orange needles, m.p. 128.5–129°, yield 4.5 g. (30%).

Anal. Calcd. for $C_{16}H_{19}FeNOS$: C, 58.3; H, 5.83; N, 4.26; S, 9.74. Found: C, 58.9; H, 6.01; N, 4.48; S, 9.79.

Carboxymethylcyclopentadienyl-(cyclopentadienyl)-iron (XI).—A solution of 5.0 g. of the thioamide X in 50 ml. of 10% methanolic potassium hydroxide was refluxed 17 hours. The reaction mixture was poured into 800 ml. of cold water and was thoroughly extracted with ether. Neutralization of the aqueous layer with concentrated hydrochloric acid gave a fine yellow precipitate. Recrystallization from deoxygenated methanol gave light yellow needles, m.p. 150–152°,[11] yield 2.5 g. (60%).

Anal. Calcd. for $C_{12}H_{12}FeO_2$: C, 59.1; H, 4.96. Found: C, 59.1; H, 5.17.

Carboxymorphilomethylcyclopentadienyl-(cyclopentadienyl)-iron (XII).—The ether extracts from synthesis of XI were combined, washed with water, dried over magnesium sulfate and evaporated to dryness. The residue was recrystallized from a mixture of benzene and hexane. The amide crystallized as fine yellow needles, m.p. 148–149°, yield 0.3 g. (6%).

Anal. Calcd. for $C_{16}H_{19}FeNO_2$: C, 61.3; H, 6.12; N, 4.47. Found: C, 61.1; H, 6.10; N, 4.57.

Bis-[(3-carboxypropionyl)-cyclopentadienyl]-iron (XIII).—A mixture of 96 g. (0.72 mole) of anhydrous aluminum chloride in 200 ml. of methylene chloride was treated with 36 g. (0.36 mole) of succinic anhydride. The mixture was stirred and shaken a few minutes and a solution of 33.3 g. (0.18 mole) of ferrocene in 200 ml. of methylene chloride was added in small portions over a 10-minute period. Hydrogen chloride gas was evolved and the heat of reaction brought the mixture to 35°. The dark violet, viscous solution was allowed to stand 7 hours at room temperature, poured onto ice, and filtered. The air-dried solid (yield 46 g.), was extracted once with 800 ml. of boiling water and twice with 150 ml. of boiling water. The combined extracts were cooled in an ice-bath and filtered to obtain 19.7 g. (38% yield) of crystalline bis-[(3-carboxypropionyl)-cyclopentadienyl]-iron, m.p. 164–166° dec.[11]

Anal. Calcd. for $C_{18}H_{18}FeO_6$: C, 56.0; H, 4.69; Fe, 14.5; neut. equiv., 193. Found: C, 56.3; H, 4.94; Fe, 14.9; neut. equiv., 193.

The acid XIII was converted to the corresponding diethyl ester XVIII by slowly distilling a solution of 21.3 g. of the acid, 1.5 g. of sulfuric acid, 200 ml. of ethyl alcohol and 250 ml. of toluene through a small still. After slow distillation for 4 hours, the remaining solution was cooled to room temperature and washed with 75 ml. of 10% aqueous sodium carbonate solution. The toluene solution was dried over magnesium sulfate, filtered and evaporated at room temperature to obtain 23 g. (94%) of red-brown crystals. Crystallization from ethyl alcohol gave 20.3 g. of shiny orange-brown platelets of bis-[3-carbethoxypropionyl)-cyclopentadienyl]-iron (XVIII), m.p. 134–136°.

Anal. Calcd. for $C_{22}H_{26}O_6Fe$: C, 59.7; H, 5.92; Fe, 12.6. Found: C, 59.8; H, 6.04; Fe, 12.8.

Bis-[(5-oxotetrahydro-2-furyl)-cyclopentadienyl]-iron (XIV).—A mixture of 17.1 g. (0.06 mole) of (XIII), 200 ml. of ethyl alcohol and 1 g. of ruthenium dioxide was heated for 3 hours at 85° under 165 atm. of hydrogen pressure. The reaction mixture was heated on a steam-bath and filtered through charcoal. Evaporation of the alcohol gave a tan, gummy residue that was converted to 7.5 g. of fine yellow powder by extraction with methanol. Recrystallization from 50 ml. of chloroform gave 4.3 g. of a yellow crystalline product. This was dissolved in 30 ml. of boiling chloroform, diluted with 25 ml. of methanol and evaporated until crystallization began. The mixture was cooled slowly to obtain 3.7 g. (17.5%) of golden yellow crystals of pure bis-[(5-oxotetrahydro-2-furyl)-cyclopentadienyl)-iron, m.p. at 165° dec.

Anal. Calcd. for $C_{18}H_{18}FeO_4$: C, 61.0; H, 5.12; Fe, 15.8. Found: C, 61.2; H, 5.12; Fe, 15.9.

The lactone also was obtained by hydrogenation of the ester XVIII with Raney nickel catalyst at 75° and 135 atm. of hydrogen pressure.

Bis-[(3-cyanopropionyl)-cyclopentadienyl]-iron (XV).—A solution of 10 g. of bis-[(3-chloropropionyl)-cyclopentadienyl]-iron (prepared by the method of Woodward[1] in 34% yield) and 4.0 g. of potassium cyanide in 150 ml. of ethyl alcohol was refluxed for 4 hours. The reaction mixture was filtered and the filtrate was cooled in an ice-bath to obtain 5.4 g. of an orange-red crystalline material, m.p. 118–121°. Recrystallization from toluene followed by recrystallization from ethyl alcohol gave orange crystals, m.p. 133–134°.

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[11] Variations in decomposition temperatures have been noted in ferrocene derivatives having carboxyl functions. The decomposition temperature of bis-{(3-carboxypropionyl)cyclopentadienyl}-iron varies with heating rate. This may account for some discrepancy between our melting points and those of Rinehart, Curby and Sokol (p. 3420).

Anal. Calcd. for $C_{18}H_{16}N_2O_2Fe$: C, 62.1; H, 4.63; Fe, 16.0. Found: C, 61.9; H, 4.83; Fe, 16.4.

Bis-[(4-aminobutyl)-cyclopentadienyl]-iron (XVI).—A solution of 8.2 g. (0.023 mole) of XV in 100 ml. of ethyl alcohol was hydrogenated over Raney nickel catalyst at 65° and 135 atm. of hydrogen pressure. The solution was filtered to remove catalyst, dried over magnesium sulfate and diluted with 500 ml. of ether. Dry hydrogen chloride gas was passed in to produce a dark red oil that slowly crystallized. The product was filtered, washed with ethyl alcohol and dissolved in 50 ml. of water. Addition of an aqueous solution of sodium carbonate precipitated 5.3 g. of an orange solid which was recrystallized from heptane to give fine orange crystals, m.p. 137–138°.

Anal. Calcd. for $C_{18}H_{28}N_2Fe$: N, 8.53; Fe, 17.0; neut. equiv., 164. Found: N, 8.87; Fe, 17.8; neut. equiv., 162.

Bis-[(1-hydroxyethyl)-cyclopentadienyl]-iron (XVII).—To a cooled solution of 3 g. of lithium aluminum hydride in 150 ml. of tetrahydrofuran, 30 g. of bis-(acetylcyclopentadienyl)-iron was added slowly. After the reaction was complete, 25 g. of ethyl acetate was added to the yellow solution. A mixture of ether, ethyl alcohol and the calculated quantity of water to destroy the aluminum complexes was added to the mixture. The solution was filtered with aid of Celite, and the filter cake was washed thoroughly with ether. Evaporation of the filtrates gave 27.8 g. (92%) of crude, yellow diol. Recrystallization from hexane gave yellow crystals, m.p. 69–71°.

Anal. Calcd. for $C_{14}H_{18}O_2Fe$: Fe, 20.4. Found: Fe, 20.6.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Organic Chemistry of Ferrocene. II. The Preparation of ω-Ferrocenyl Aliphatic Acids[1]

BY KENNETH L. RINEHART, JR., RONALD J. CURBY, JR., AND PHILLIP E. SOKOL

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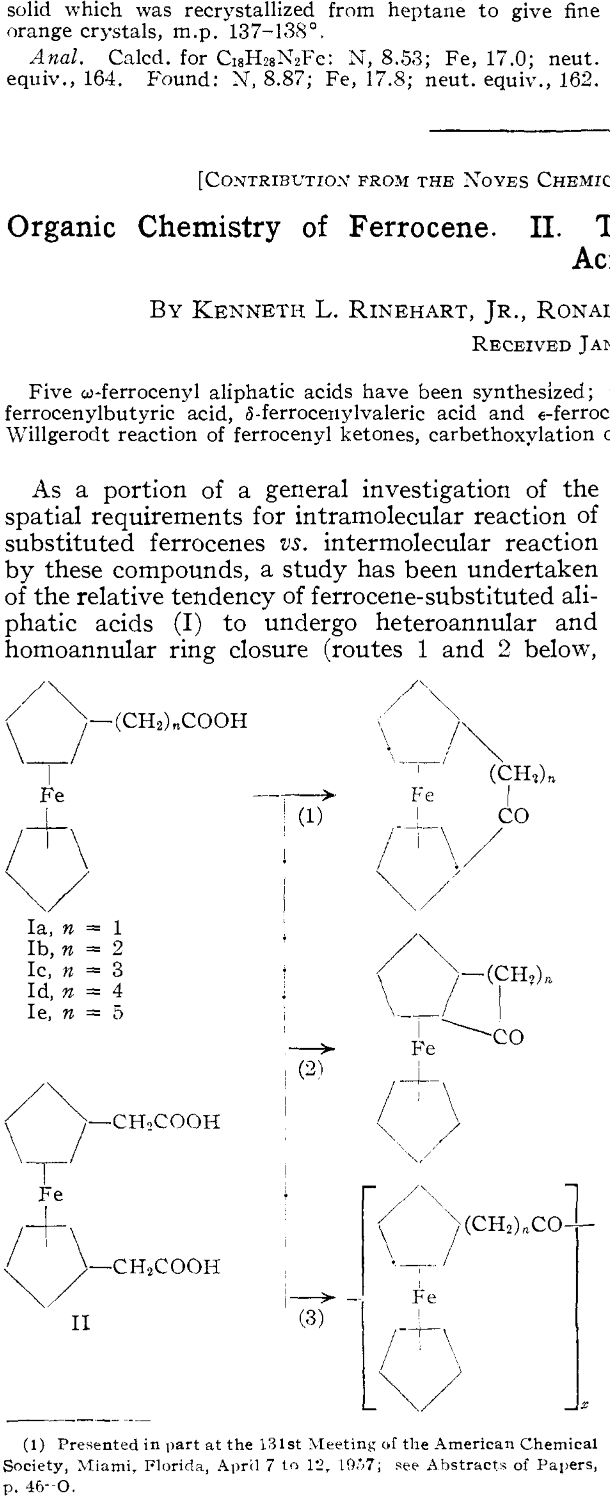
Five ω-ferrocenyl aliphatic acids have been synthesized; these are ferrocenylacetic acid, β-ferrocenylpropionic acid, γ-ferrocenylbutyric acid, δ-ferrocenylvaleric acid and ε-ferrocenylcaproic acid. Synthetic methods employed include the Willgerodt reaction of ferrocenyl ketones, carbethoxylation of acetylferrocene and Friedel–Crafts acylations of ferrocene.

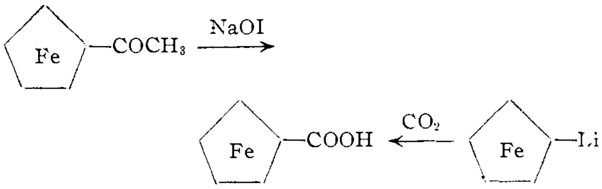
As a portion of a general investigation of the spatial requirements for intramolecular reaction of substituted ferrocenes *vs.* intermolecular reaction by these compounds, a study has been undertaken of the relative tendency of ferrocene-substituted aliphatic acids (I) to undergo heteroannular and homoannular ring closure (routes 1 and 2 below, respectively) and polymer formation (route 3).[1,2] The present paper deals with the synthesis of the ω-ferrocenylmonocarboxylic acids ferrocenylacetic acid (Ia), β-ferrocenylpropionic acid (Ib), γ-ferrocenylbutyric acid (Ic), δ-ferrocenylvaleric acid (Id) and ε-ferrocenylcaproic acid (Ie) and the dicarboxylic acid 1,1′-ferrocenediacetic acid (II).



Ia, $n = 1$
Ib, $n = 2$
Ic, $n = 3$
Id, $n = 4$
Ie, $n = 5$

II

A number of substituted ferrocenecarboxylic acids (I, $n = 0$) have been previously prepared, both by the hypohalite oxidation of the corresponding acetylferrocenes[3–6] and by the carboxylation of ferrocenyllithium compounds.[7,8] As neither of these methods is readily applicable to the synthesis of the present acids, alternative routes have been investigated, adapted to the preparation of the individual compounds.



The higher homologs of the present series (Ic, Id, Ie) were easily prepared in sizable quantities by hydrogenation of the corresponding ω-keto acids (IIIa, IIIb, IIIc). The keto acids, in turn, were prepared by Friedel–Crafts acylation of fer-

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[1] Presented in part at the 131st Meeting of the American Chemical Society, Miami, Florida, April 7 to 12, 1957; see Abstracts of Papers, p. 46-O.

(2) K. L. Rinehart, Jr., R. J. Curby, Jr., and Sung Moon, in preparation.

(3) K. L. Rinehart, Jr., K. L. Motz and S. Moon, THIS JOURNAL, **79**, 2749 (1957).

(4) R. B. Woodward, M. Rosenblum and M. C. Whiting, *ibid.*, **74**, 3458 (1952).

(5) M. Rosenblum, Ph.D. Thesis, Harvard University, August, 1953.

(6) V. Weinmayr, THIS JOURNAL, **77**, 3009 (1955).

(7) R. A. Benkeser, D. Goggin and G. Schroll, *ibid.*, **76**, 4025 (1954).

(8) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. A. Nesmeyanova, *Doklady Akad. Nauk., SSSR*, **97**, 459 (1954).