[CONTRIBUTION FROM THE RESEARCH DIVISION, WYANDOTTE CHEMICALS CORPORATION]

Ferrocenes. IV. Hydroxybenzoylferrocenes and Ethyl Ferrocenecarboxylates[1,2]

ROBERT L. SCHAAF

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2-Methoxy- and 2,4-dimethoxybenzoylferrocene were prepared by Friedel-Crafts reactions on ferrocene and were used to prepare 2-hydroxy-, 2-hydroxy-4-methoxy-, and 2,4-dihydroxybenzoylferrocene. Ethyl ferrocenoate and diethyl 1,1'-ferrocenedicarboxylate were prepared from the crude acids, and basic hydrolyses of these esters furnished pure ferrocenoic acid and 1-carboxy-1'-carbethoxyferrocene, respectively. At 250–345° ferrocenoic acid decomposed to ferrous ferrocenoate. A Friedel-Crafts reaction of ferrocene with ethyl orthoformate gave diferrocenylmethanol.

During an investigation of the effect of ultraviolet absorbers on the stability of certain polymer systems to high intensity ultraviolet radiation,[3] it became desirable to have available ferrocene derivatives related to commercial ultraviolet absorbers as well as derivatives of 1,1'-ferrocenedicarboxylic acid (IX). This paper describes the synthesis of 2-hydroxybenzoylferrocene (III), 2-hydroxy-4-methoxybenzoylferrocene (IV), 2,4-dihydroxybenzoylferrocene (V), and the ethyl esters of IX and of ferrocenoic acid (X).

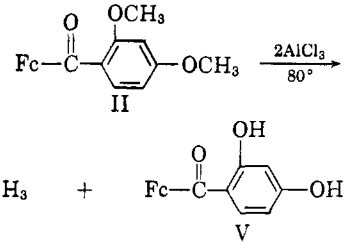
Treatment of ferrocene with equimolar quantities of aluminum chloride and 2-methoxybenzoyl chloride in methylene chloride furnished 2-methoxybenzoylferrocene (I) in 45% yield. The yield was lower than that (70–75%) reported for benzoylferrocene prepared under similar conditions,[4] a fact in agreement with the work of Weliky and Gould, who prepared anisoylferrocene in 26% yield but obtained benzoylferrocene in 67% yield.[5] The lower yield of I was not due to concomitant formation of the bis compound, 1,1'-bis(2-methoxybenzoyl)-ferrocene, but, on the contrary, conditions expected to be favorable for formation of the bis compound yielded I. Thus, when ferrocene was added to two equivalents each of aluminum chloride and 2-methoxybenzoyl chloride, the yield of I was 46%.

Similarly, 2,4-dimethoxybenzoylferrocene (II) was prepared in 41% yield when an excess of ferrocene was used, and the yield was improved to 57% by employing a 100% excess of the acid chloride in dilute solution. When the ratio of ferrocene to acid chloride to aluminum chloride was 1:3:3, aroylation took place on the benzene portion of II as well as on the ferrocene portion. A mixture of products was obtained, and infrared analysis indicated that a major portion of the products consisted of monosubstituted ferrocenes (not identical with II), although disubstituted ferrocenes were also formed.

When an equimolar mixture of I and aluminum chloride in benzene was refluxed for six hours,[6] 2-hydroxybenzoylferrocene (III) was obtained in 26% yield, and 34% of I was recovered. By doubling the quantity of aluminum chloride employed, the yield of III was increased to 43%. The chelated phenol III, unlike phenol itself, could be removed from aqueous sodium hydroxide solution by extraction with chloroform, benzene, or ether.

Treatment of the dimethoxy compound, II, with two equivalents of aluminum chloride in refluxing benzene for ten minutes yielded 26% crude hydroxymethoxy compound, IV, and 35% crude dihydroxy compound, V. Separation of IV from V was not difficult; both dissolved in 5% sodium hydroxide solution, but only IV was removed by extraction of the basic solution with benzene. Attempts to prepare V from II by treatment with 50% hydriodic acid or with hydrogen bromide in hot glacial acetic acid did not yield ferrocenes soluble in base nor was starting material recovered.

Fc = ferrocenyl.



Lithiation and carbonation of ferrocene by known methods[7] and esterification of the resulting mixture of acids with ethanol furnished 21–27% of ethyl ferrocenoate (VI), 18–21% of diethyl 1,1'-ferrocenedicarboxylate (VII), and 10–18% of crude 1-carboxy-1'-carbethoxyferrocene (VIII). Compound VI has been described previously, prepared in 47% yield from the acid.[8] For preparation of the pure

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[2] This investigation was conducted under Air Force Contract AF 33(616)7214, monitored by the Materials Central, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.

[3] R. G. Schmitt and R. C. Hirt, *J. Polym. Sci.*, **45**, 35 (1960).

[4] M. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **22**, 903 (1957).

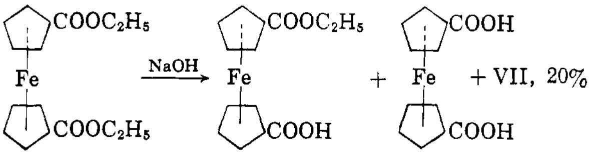
[5] N. Weliky and E. S. Gould, *J. Am. Chem. Soc.*, **79**, 2742 (1957).

[6] F. Ullmann and I. Goldberg, *Ber.*, **35**, 2811 (1902).

[7] D. W. Mayo, P. D. Shaw, and M. Rausch, *Chem. & Ind.*, 1388 (1957).

[8] V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 3009 (1955).

ester-acid, VIII, basic hydrolysis of the diester was employed to give 55% VIII, 16% diacid, and 20% recovery of diester.

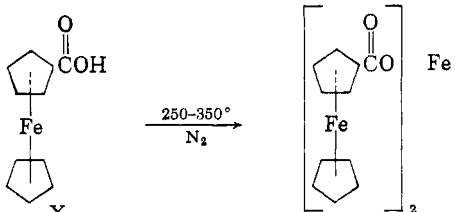


VII VIII, 55% IX, 16%

Pure ferrocenoic acid (X), m.p. 224–225° (slow dec.), was prepared by hydrolysis of pure ester (80% yield) obtained from the crude acid (56% yield). The procedure of Little and Eisenthal was convenient for preparation of crude X, m.p. 210° (dec.),[9] but the product was not readily purified by crystallization. From most preparations, the acid has melted with decomposition near 210°,[9–11] while from oxidation of acetylferrocene, it melted at 225–230°.[8]

Micro boiling points of the above ferrocenes and certain related compounds were determined under nitrogen as an indication of thermal stability as well as volatility. The three hydroxylbenzoylferrocenes decomposed visibly in the range 225–250°. In contrast, the hydroxyl-free ketones I, II, benzoylferrocene,[12] and diferrocenyl ketone[13] (XII) were stable to 345–395°, where they slowly decomposed, in part to ferrocene. A reproducible boiling point (310°) was obtained with the ester VI, but the diester VII decomposed slowly near 345°.

Ferrocenoic acid slowly decomposed at 250° under nitrogen and within two minutes at 345° decomposition was complete to analytically pure ferrous ferrocenoate (XI). This pyrolysis product was identified by analysis, examination of the infrared spectrum, and conversion to the acid, X. The yield in this clean-cut decomposition was 75%, which did not take into account undecomposed acid which distilled from the hot zone. The ester-acid VIII decomposed vigorously near 240°.



X XI, 75%

Two attempts to prepare the diethyl acetal of diformylferrocene were unsuccessful. Thus, cyclopentadienyllithium did not react with ethyl orthoformate in tetrahydrofuran during 72 hours at room temperature; addition of ferrous chloride gave ferrocene in 66% yield. From the reaction of ferrocene with aluminum chloride and excess ethyl orthoformate in refluxing ethylene chloride was obtained 10% diferrocenylmethanol (XIII), along with 58% recovered ferrocene. Recently, alcohol XIII was described prepared in overall 9% yield by reduction of the ketone XII obtained from ferrocene and phosgene.[14]

$$\mathrm{FcH} + 4\mathrm{HC(OC_2H_5)_3} \xrightarrow[\text{(b) OH}^-]{\text{(a) 2AlCl}_3} (\mathrm{Fc})_2\mathrm{CHOH} + \mathrm{FcH}$$

Fc = ferrocenyl. XIII, 10% 58%

All of the monosubstituted ferrocenes showed bands in the infrared near 1100 and 1000 cm.$^{-1}$, while the disubstituted ferrocenes did not.[15] Absorption maxima in the 200 to 500 mμ range for certain of the ferrocenes are given in Table I.

TABLE I

Absorption Maxima of Certain Ferrocenes

Compound	λ, mμ (log ε)			
	200–249	250–299	300–399	400–500
I	204 (4.60)	275 (3.85)	345 (3.09)	458 (2.70)
II	225 (4.35)	271 (4.03)	343 (3.18)	455 (2.69)
III	204 (4.65)	260 (4.08)	339 (3.70)	475 (3.01)
IV	235 (4.17)	286 (4.15)	329 (3.97)	470 (2.98)
V		283 (4.10)	327 (3.89)	468 (2.98)
VI	212 (4.57)	263 (3.67)	303 (2.98)	444 (2.30)
VII	218 (4.59)	256 (3.94)		450 (2.40)
VIII	218 (4.54)	255 (3.98)		448 (2.48)
XII	232 (4.33)	271 (4.08)	347 (3.44)	456 (3.01)

EXPERIMENTAL[16]

2-Methoxybenzoylferrocene (I). *A.* Anhydrous aluminum chloride (39.9 g.; 0.3 mole) was added in one portion to a solution of 51.3 g. (0.3 mole) of 2-methoxybenzoyl chloride in 300 ml. of dry methylene chloride at −40° and stirred for 1.5 hrs. below −30°. The solution was maintained at −30° or below while it was added during a 100-min. period to 55.8 g. (0.3 mole) of ferrocene in 300 ml. of dry methylene chloride at room temperature. The mixture was stirred overnight, added to 500 g. of ice, and stirred for a 1-hr. period. The water layer was extracted twice with chloroform, the organic layers were combined and extracted twice with water, and the organic solution was dried with magnesium sulfate. After removal of solvent *in vacuo*, benzene (175 ml.) was added, and, inasmuch as crystals formed, some of the benzene was removed under vacuum, and the mixture was

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[9] W. F. Little and R. Eisenthal, *J. Am. Chem. Soc.*, **82**, 1577 (1960).

[10] M. Rosenblum, Ph.D. thesis, Harvard University, August, 1953.

[11] K. L. Rinehart, Jr., K. L. Motz, and S. Moon, *J. Am. Chem. Soc.*, **79**, 2749 (1957).

[12] M.p. 108–108.5°; ref. 4.

[13] M.p. 209.5–210°; M. D. Rausch, E. O. Fischer, and H. Grubert, *J. Am. Chem. Soc.*, **82**, 76 (1960).

[14] K. Schlögl and A. Mohar, *Monatsh. Chem.*, **92**, 219 (1961).

[15] M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958).

[16] Melting points were taken in sealed capillaries under nitrogen and are uncorrected. Analysis for iron was performed in this laboratory by Mr. Peter A. Marsh. Other analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

refrigerated. Filtration and washing with a small amount of benzene and excess ether gave 43.0 g. (45%) of I, m.p. 132–134.5°. After recrystallization from toluene and from 2-propanol, the product was chromatographed on alumina in petroleum ether–benzene (1:1) by elution with petroleum ether–benzene (1:1), benzene-ether (1:1), and chloroform. Combination of all fractions and recrystallization from 2-propanol furnished I, m.p. 136–137°.

Anal. Calcd. for $C_{18}H_{16}FeO_2$: C, 67.52; H, 5.04; Fe, 17.44. Found: C, 67.65; H, 5.09; Fe, 17.52, 17.25.

B. 2-Methoxybenzoic acid (15.2 g.; 0.10 mole) and 9.5 ml. (0.13 mole) of thionyl chloride were heated in a hot water bath for 10 min. and the excess thionyl chloride removed *in vacuo.*[17] The resulting acid chloride was added dropwise to 13.3 g. (0.10 mole) of powdered anhydrous aluminum chloride in 65 ml. of dry methylene chloride at −40° under a slow stream of nitrogen, and the mixture stirred 15 min. to dissolve solidified acid chloride. To the mixture was added 9.3 g. (0.05 mole) of ferrocene in six portions during a 5-min. period and the solution stirred at −35 to −30° for 5 hrs. The mixture was poured onto ice, the water layer extracted with methylene chloride, and the combined organic layers extracted twice with water, once with 100 ml. of 5% sodium hydroxide solution, and once more with water. The organic layer was dried, solvent removed *in vacuo,* and the residue dissolved in 50 ml. of benzene. Chromatography of this solution on 320 g. of alumina in petroleum ether–benzene (1:1) by elution with petroleum ether–benzene (1:1) and benzene-ether (1:1) yielded, after ether wash of solid fractions, 7.4 g. (46%) of I, m.p. 135–137°. Subsequent elution with methylene chloride–methanol (3:1) removed 5.4 g. of a mixture of products which could not be readily separated.

2-Hydroxybenzoyl ferrocene (III). *A.* A mixture of 138 g. (0.431 mole) of 2-methoxybenzoylferrocene (I) and 116 g. (0.87 mole) of powdered aluminum chloride in 1300 ml. of benzene was stirred and refluxed under nitrogen for a 1-hr. period. After the mixture was cooled in an ice bath, it was poured onto ice; it was necessary to add benzene and ice and to stir thoroughly in order to complete the transfer. The organic layer was washed with water, most of the benzene was removed *in vacuo,* and a solution of 125 g. of sodium hydroxide in 2300 ml. of water was added. Residual benzene was removed by distillation *in vacuo,* and after the mixture was stirred overnight, it was warmed to dissolve the precipitated sodium salt, filtered through Celite, and the filtrate acidified. The precipitate which formed was dissolved in ether; the ether solution was washed with water and dried with magnesium sulfate. Solvent was removed, and the residue was extracted with 1500 ml. and again with 500 ml. of boiling hexane. By seeding and cooling the extracts to −60° overnight, there was obtained 85 g. of crystals, which upon two recrystallizations from ether yielded 57 g. (43%) of III, m.p. 87.5–88.5°.

Anal. Calcd. for $C_{17}H_{14}FeO_2$: C, 66.69; H, 4.61; Fe, 18.25. Found: C, 66.49; H, 4.42; Fe, 18.12, 18.10.

B. A mixture of 1.6 g. (0.005 mole) of I and 0.67 g. (0.005 mole) of powdered aluminum chloride in 15 ml. of benzene was refluxed for 6 hrs., cooled, and treated with 5 ml. of water. The mixture was stirred overnight; the benzene layer was washed with water and dried with magnesium sulfate. Removal of benzene and washing the residue with ether left 0.55 g. (34%) of recovered I, m.p. 133.5–135.5°. From the ether wash was isolated 0.39 g. (26%) of crude III, m.p. 79–85°, by removal of ether and crystallization of the residue from petroleum ether-benzene.

2,4-Dimethoxybenzoylferrocene (II). *A.* To 122 g. (0.671 mole) of 2,4-dimethoxybenzoic acid in 500 ml. of benzene was added 100 g. (0.84 mole) of thionyl chloride, the mixture stirred and heated for a 10-min. period in a hot water bath, and the benzene removed *in vacuo.* The solid residue was dissolved in 3500 ml. of anhydrous methylene chloride, 156 g. (0.84 mole) of ferrocene was added, and the mixture was stirred in an ice bath under nitrogen while 89.4 g. (0.671 mole) of powdered anhydrous aluminum chloride was added in six portions during a 30-min. period. The mixture was refluxed 1 hr., cooled, and poured onto ice. After the hydrolyzed mixture was stirred for 15 min., the organic layer was washed twice with water, once with 5% sodium hydroxide solution, and again with water. The organic layer was dried with magnesium sulfate, and solvent was removed under vacuum. Crystallization of the residue (194 g.) from 200 ml. of benzene yielded 95.4 g. (40.5%) of II, m.p. 130.5–132°; removal of benzene from the filtrate and fractional crystallization of the residue from ether gave wide-melting fractions, presumably mixtures of the desired product and ferrocene. Three recrystallizations of the crude product from benzene raised the melting point to 133–133.5°. By chromatography of the crude product on alumina, a fraction m.p. 133.5–133.8° was obtained.

Anal. Calcd. for $C_{19}H_{18}FeO_3$: C, 65.16; H, 5.18; Fe, 15.95. Found: C, 65.06; H, 5.22; Fe, 15.95, 15.89.

The yield was not improved by doubling the reaction time.

B. 2,4-Dimethoxybenzoic acid (1.56 moles) was converted to the acid chloride and treated with 0.75 mole of ferrocene and 0.75 mole of aluminum chloride in 8000 ml. of methylene chloride as in the preceding experiment. The mixture was stirred overnight at room temperature, added to ice water, and the aqueous layer discarded. The organic layer was washed with water and twice with 5% sodium hydroxide solution. After the organic layer was dried with magnesium sulfate, the solvent was removed, the residue was recrystallized from 400 ml. of toluene, and the solid was washed with ether. The product, obtained in two crops totaling 207 g., was recrystallized twice from toluene, yielding 151 g. (57%) of II, m.p. 132.5–133.5°, undepressed on admixture with a sample prepared by method A.

2-Hydroxy-4-methoxybenzoylferrocene (IV) *and 2,4-dihydroxybenzoylferrocene* (V). A mixture of 100 g. (0.286 mole) of 2,4-dimethoxybenzoylferrocene (II) and 76 g. (0.570 mole) of powdered anhydrous aluminum chloride in 900 ml. of benzene was stirred and refluxed under nitrogen for a 10-min. period; the effluent gas was acidic.[18] After it was cooled in an ice bath, the mixture was hydrolyzed with ice water, filtered, and the water layer discarded. The benzene layer and filtered solid were combined and extracted with 1000 ml. of 5% sodium hydroxide solution. Subsequent extraction of the basic layer with benzene produced a difficult emulsion and removed only 1.8 g. of material. Evaporation of the benzene solutions *in vacuo* left 43.9 g. of solid, from which 25 g. (26%) of hydroxymethoxy compound (IV), m.p. 121–123°, was obtained by recrystallization from ether; three additional recrystallizations furnished 11.5 g. of purified IV, m.p. 123.5–125.5°. The basic layer was filtered, cooled in an ice bath, and acidified with 15% hydrochloric acid. The resulting precipitate was washed with water, dried, and then extracted with 700 ml. and again with 150 ml. of boiling toluene; insoluble material (16.2 g.) melted above 200°. Cooling the extracts at −60° overnight yielded 32.2 g. (35%) of product, m.p. 168–172°, from which 10.5 g. of dihydroxy compound V, m.p. 175–176° (slow dec.), was obtained by three recrystallizations from chloroform.

A similar, earlier run in which the reaction time was 1 hr. yielded 22% IV, m.p. 121.5–126° and 17% V, m.p. 168.5–172°. In this run, the benzene solution that had been extracted with base was evaporated and the residue extracted with several portions of ether. From the initial extracts was obtained IV (14%) melting from 116°, while the later ex-

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[17] Under these conditions 2-methoxybenzoyl chloride, b.p. 122°/6 mm., was prepared in 94% yield; the method is that of H. R. Eisenhauer and K. P. Link, *J. Am. Chem. Soc.*, **75**, 2046 (1953).

[18] Hydrogen chloride would be evolved if the by-product methyl chloride reacted with the solvent or ferrocene nucleus under these Friedel-Crafts conditions.

tracts yielded IV (11%) melting at 124–126°. The former could not be purified to m.p. 124–126° by recrystallization from ether, ethanol, or 2:1 ether-chloroform, by chromatography on alumina, by fractional extraction with ether, or by crystallization of the sodium salt from water, although minor fractions melting near this range could be obtained by repeated purification. The hydroxymethoxy compound IV from later extracts was recrystallized from ether; m.p. 124.5–126°.

Anal. Calcd. for $C_{18}H_{16}FeO_3$: C, 64.31; H, 4.80; Fe, 16.61. Found: C, 64.41; H, 4.81; Fe, 16.54.

The accompanying dihydroxy compound V, m.p. 168.5–172°, was not readily purified by recrystallization from toluene or methanol-water, but two subsequent recrystallizations from chloroform furnished pure V, m.p. 176–177° (slow dec.).

Anal. Calcd. for $C_{17}H_{14}FeO_3$: C, 63.38; H, 4.38; Fe, 17.34. Found: C, 63.30; H, 4.45; Fe, 17.32.

1,1'-Bis(2,4-dimethoxybenzoyl)ferrocene (*attempted*). A solution of 27.4 g. (0.15 mole) of 2,4-dimethoxybenzoic acid and 14.5 ml. (0.20 mole) of thionyl chloride in 100 ml. of benzene was heated for 15 min. in a hot water bath and the volatile material removed *in vacuo.* Ferrocene (9.3 g.; 0.05 mole) and 200 ml. of dry methylene chloride were added to the residue, and the mixture was stirred in an ice bath under nitrogen while 20.0 g. (0.15 mole) of aluminum chloride was added in 7 portions during a 25-min. period. The mixture was stirred without the bath for 40 hrs. and poured onto ice-water. The water layer was extracted with chloroform and the combined organic layers extracted with water and with 5% sodium hydroxide solution. The organic layer was dried with magnesium sulfate, filtered through Celite, and the filtrate evaporated *in vacuo.* Chromatography of the residue in benzene on alumina in benzene gave a total of 26.4 g. of oils and glasses (calcd. for 100% disubstitution, 25.8 g.). The infrared spectrum of one major fraction (13.8 g.) showed medium bands at 1100 and 1000 cm.$^{-1}$ (monosubstituted ferrocene[15]) but was not identical with that of II; for example, the former showed a strong band at 1130 cm.$^{-1}$ not in the latter, and the latter had strong bands at 1315 and 1045 cm.$^{-1}$ which were medium-weak in the former. The infrared spectrum of a second fraction (9.4 g.) did not show a distinct peak at 1000 cm.$^{-1}$, although a peak was present at 1100 cm.$^{-1}$ (O—CH_3).

Diethyl 1,1'-ferrocenedicarboxylate (VII). A solution of *n*-butyllithium, prepared[19] from 494 g. (3.6 moles) of *n*-butyl bromide in 500 ml. of ether and 61.8 g. of lithium in 1300 ml. of ether, was added to 111 g. (0.6 mole) of ferrocene in 1800 ml. of anhydrous tetrahydrofuran at −20 to −25° under nitrogen. The mixture was stirred 24 hrs., cooled to −55°, and added slowly to a slurry of ether and Dry Ice. The solvent was allowed to evaporate, the residue was extracted with water, and the aqueous extract was filtered and acidified. Filtration, washing with water, and thorough drying over phosphorus pentoxide yielded 118 g. of a mixture of ferrocenoic acid and ferrocenedicarboxylic acid.[7] A portion (67.3 g.) of the mixture, 2000 ml. of absolute ethanol, and 12 ml. of concentrated sulfuric acid was refluxed for 5 hrs., the ethanol removed *in vacuo*, and the residue extracted with ether. The solution was washed with 5% sodium bicarbonate solution and with water, dried with magnesium sulfate, and the ether removed under vacuum. The residue, 61.7 g., was dissolved in benzene and chromatographed on 2 lbs. of alumina in petroleum ether-benzene (1:1), by elution with petroleum ether–benzene (1:1), benzene, and ether. From the initial fractions was obtained 23.6 g. (27%) of ethyl ferrocenoate (VI), m.p. 61–64° (lit., m.p. 61–62° [8]), and from the final fraction was isolated 20.2 g. (18%) of diester VII, m.p. 39–40°. After two recrystallizations from hexane, the diester melted at 41.5–42°.

Anal. Calcd. for $C_{16}H_{18}FeO_4$: C, 58.20; H, 5.49; Fe, 16.92. Found: C, 58.19; H, 5.37; Fe, 16.85, 16.52.

Solid material soluble in bicarbonate solution was extracted with ether and the ether solution dried with magnesium sulfate. Removal of ether and recrystallization of the residue from 50% aqueous ethanol yielded 10.1 g. (10%) of crude VIII, m.p. 136–138°.

In a larger run, distillation of the mixture of esters yielded 14% VI, b.p. 114–129°/0.3–0.45 mm., m.p. 53–55°, and 21% VII, b.p. 158°/0.4 mm., m.p. 38.5–40°. From a middle fraction an additional 7% VI, m.p. 57–59°, was obtained by decantation of oil from solid which formed, and recrystallization of the solid from ethanol. From acidified bicarbonate washes, 18% crude VIII, m.p. 125–130°, was obtained.

An attempt was made to prepare the diester by addition of 0.05 mole of aluminum chloride to a mixture of 0.02 mole of ferrocene and 0.05 mole of ethyl chloroformate in dry methylene chloride at −35°, but no color change occurred, and upon warming the mixture to 20°, a gas began to evolve from the brown solution.[20]

1-Carboxy-1'-carbethoxyferrocene (VIII). A solution of 5.2 g. (0.13 mole) of sodium hydroxide in 260 ml. of water and 260 ml. of ethanol was added to 42.9 g. (0.13 mole) of the diester VII, the mixture refluxed 30 min., and poured into water. Extraction with ether and evaporation of the dried extract left 8.75 g. (20%) of recovered VII, m.p. 38.5–41°. The basic layer was filtered, the filtrate acidified, and the resulting precipitate washed with water and dried; additional solid (1.07 g.) was obtained by extraction of the acidified solution with ether. The mixture of acids was stirred in 3000 ml. of ether for 30 min., again with 2600 ml. of ether, and finally with 500 ml. of ether in order to remove the ester-acid from the diacid. The insoluble diacid, IX, m.p. above 265°, weighed 5.67 g. (16%). Cooling the ether extracts to −60° overnight gave 19.5 g. of ester-acid, VIII, m.p. 144–145°; an additional 2.2 g. of VIII, m.p. 144–145°, was obtained by removal of ether and crystallization of the residue from ether (total yield, 55%). The melting point was unchanged upon two recrystallizations from toluene.

Anal. Calcd. for $C_{14}H_{14}FeO_4$: C, 55.65; H, 4.67; Fe, 18.49. Found: C, 55.56; H, 4.67; Fe, 18.62.

Ethyl ferrocenoate (VI). A mixture of 37.2 g. (0.17 mole) of crude ferrocenoic acid[7] (X), 580 ml. of ethanol, and 8.5 ml. of concentrated sulfuric acid was refluxed for 4 hrs., the ethanol removed *in vacuo*, and the residue dissolved in ether. After extraction with 5% sodium bicarbonate solution and washing with water, the solution was dried with magnesium sulfate and solvent was removed under vacuum. Distillation of the solid residue and recrystallization of the fraction boiling at 110–117°/0.15 mm. from ethanol-water (2:1) gave 23.6 g. (56%) of VI, m.p. 62.5–64°. After recrystallization, the ester melted at 63–64° (lit., m.p. 61–62° [8]).

Anal. Calcd. for $C_{13}H_{14}FeO_2$: C, 60.49; H, 5.47; Fe, 21.64. Found: C, 60.09; H, 5.37; Fe, 21.76.

Ferrocenoic acid (X). Ethyl ferrocenoate (VI) (45.3 g.; 0.197 mole) in a solution of 35 g. (0.88 mole) of sodium hydroxide in 350 ml. of water and 350 ml. of ethanol was refluxed for 2.5 hr., cooled, and diluted with 2000 ml. of water. The solution was extracted with ether, filtered, and the filtrate acidified. Filtration, washing the solid with water, and recrystallization of the dried solid from toluene yielded 36.1 g. (80%) of X, m.p. 224–225° (slow dec.)[21] (lit., m.p. 225–230°[8]; 210°, dec.[10]; and 208.5°, dec.[11]).

Anal. Calcd. for $C_{11}H_{10}FeO_2$: C, 57.43; H, 4.38; Fe, 24.28; neut. equiv. 230. Found: C, 57.54; H, 4.50; Fe, 24.27; neut. equiv. 240.

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(19) R. G. Jones and H. Gilman, *Organic Reactions*, 6, 339 (1951).

(20) Evolution of gas was apparently a result of decomposition of ethyl chloroformate by aluminum chloride; cf. C. A. Thomas, *Anhydrous Aluminum Chloride in Organic Chemistry*, Reinhold, New York, 1941, p. 136.

(21) Taken at 1°/min. from 214°. When taken in air or nitrogen very slowly from 220°, the m.p. was 222–222.5°.

Determination of micro boiling points. For determination of micro boiling points a common method[22] was used, with an atmosphere of nitrogen above the sample. The method involved placing the sample in a glass tube 20-cm. long, degassing the tube and an inserted capillary, and introducing nitrogen, prior to heating the tube (now open to the air) in a hot air bath. In instances in which ferrocene sublimed from the sample area, identification was made by infrared comparison.

Thermal decomposition of ferrocenoic acid (X). *Ferrous ferrocenoate* (XI). A bulb was blown in the end of a 20-cm. length of 7 mm. tubing and 0.50 g. of analytically pure X was introduced. The tubing was evacuated, nitrogen introduced, and this process repeated twice. With the end open to the air, the bulb was quickly placed in a Wood's-metal bath at 360°. After the sample melted, there was vigorous evolution of gas, yellow solid sublimed from the bulb, and a tan powder remained. After two min. near 340°, the bulb was cooled, separated from the tubing, and the residue placed under vacuum to remove any condensed cyclopentadiene. The residue, ferrous ferrocenoate (XI), was insoluble in common solvents and did not melt below 300°.

Anal. Calcd. for $C_{22}H_{18}Fe_3O_4$: C, 51.41; H, 3.53; Fe, 32.60. Found: C, 51.42, 51.34; H, 3.56, 3.44; Fe, 32.1, 32.3.

In an initial experiment the yield of XI was 0.28 g. (75%). The infrared spectrum showed a strong band at 1550 cm.$^{-1}$ (carboxylate) and a weak band at 1650 cm.$^{-1}$ (trace of carboxyl). The intensity of the weak band was only slightly reduced by extraction of the sample with boiling toluene to remove X.

When 0.10 g. of XI was shaken for 30 min. with 4 ml. of 5% sodium hydroxide solution, filtered, and the filtrated acidified, 0.08 g. (90%) of X was obtained and identified by infrared comparison.

Decomposition of X also occurred to some degree at 250°, inasmuch as the infrared spectrum of the residue from a sample which had boiled near 250° showed a new medium band at 1550 cm.$^{-1}$ in addition to the expected strong band at 1650 cm.$^{-1}$

Thermal decomposition of 2-hydroxybenzoylferrocene (III). Treatment of 0.50 g. of III as described above for X yielded 0.41 g. of residue. Extraction with benzene left 0.36 g. of brittle glass, the infrared spectrum of which was complex; a strong new band was present at 1500 cm.$^{-1}$ A small amount of ferrocene and III distilled from the sample area during the test and were identified by infrared comparison.

Diferrocenylmethanol (XIII). A mixture of 9.3 g. (0.05 mole) of ferrocene and 29.6 g. (0.2 mole) of ethyl orthoformate in 65 ml. of ethylene chloride at 50° under nitrogen was treated with 13.3 g. (0.10 mole) of aluminum chloride in one portion and a cold bath was applied to control the immediate exothermic reaction. The mixture was refluxed 1 hr., cooled, and added to a cold solution of 37.5 g. of sodium hydroxide in 750 ml. of water in an ice bath; the temperature rose to 15°. After the mixture was stirred 10 min., the aqueous layer was extracted with chloroform, and the organic solutions were combined, dried, and evaporated *in vacuo*. Chromatography of the residue on alumina by elution with petroleum ether–benzene (1:1) yielded 5.43 g. (58%) of recovered ferrocene (infrared comparison). Subsequent elution with chloroform and recrystallization of the eluted solid from toluene furnished 2.02 g. (10%) of diferrocenylmethanol (XIII), m.p. 170–175° (dec.); after two recrystallizations, it melted at 175–180° (dec.) (lit., m.p. 166–167°[14]). The infrared spectrum showed a medium band at 3500 cm.$^{-1}$ (hydroxyl) and strong bands at 1100 and 1000 cm.$^{-1}$ (monosubstituted ferrocene).

Anal. Calcd. for $C_{21}H_{20}Fe_2O$: C, 63.04; H, 5.04; Fe, 27.92. Found: C, 63.11; H, 5.01; Fe, 27.3.

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WYANDOTTE, MICH.

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[22] R. L. Shriner and R. C. Fuson, *Systematic Identification of Organic Compounds*, 3rd ed., Wiley, New York, 1948, p. 27.

[CONTRIBUTION NO. 1089 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Quantitative Estimates of the Strong Electron Donor Properties of Metallocenyl Nuclei[1,2]

EDWARD McCOLLIN ARNETT AND RONALD D. BUSHICK

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The pK_a's of the conjugate acids of acetylferrocene (−2.80) and diferrocenyl ketone (−2.55) have been determined in aqueous sulfuric acid solutions. These two results demonstrate the extraordinary ability of the ferrocenyl nucleus to stabilize carbonium ions and indicate that the σ^+ substituent parameter for the ferrocenyl group in this reaction is about −1.3 (relative to phenyl as 0.00). Estimates for the σ parameter of −0.20 and −0.42 for the ferrocenyl nucleus are also made from dissociation constants of ferrocene carboxylic acid in the literature. It is concluded that the ferrocenyl nucleus is one of the most powerful electron donating aromatic nuclei known. Data in the literature also suggest that there may be two classes of electrophilic substituent constants for metallocene compounds, one of which is even larger than we report and which is associated with direct participation by the metal in carbonium ion stabilization in the order Os > Ru > Fe. The value of σ^+ we report may be associated with indirect metal stabilization through the rings and is expected to follow the order Fe > Ru > Os. Unsuccessful attempts were made to measure the basicities of ferrocenyl ruthenocenyl ketone and ferrocene itself.

The explosive growth of research and interest in the properties of metallocene systems has been recorded in a plethora of reviews.[3–10]

It is by now clear that as an aromatic system the ferrocenyl nucleus is an unusually powerful electron donor, and that it far outstrips the *p*-methoxyphenyl group in this capacity. Probably the most persuasive quantitative evidence of this fact has

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[1] Stereoelectronic Effects in Organic Bases V. Previous paper in this series, E. M. Arnett, T. Cohen, A. A. Bothner-By, R. D. Bushick, and G. Sowinski, *Chem. & Ind.* (*London*), 1961, 473.