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]

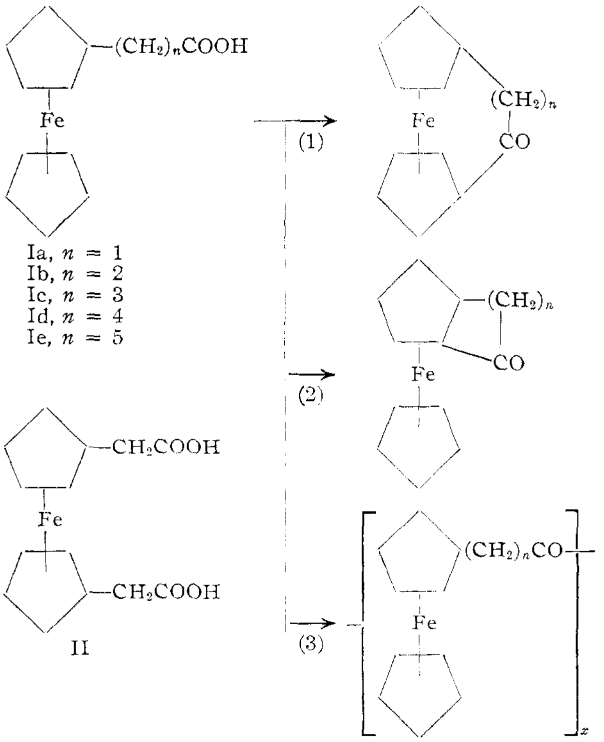
Organic Chemistry of Ferrocene. II. The Preparation of ω-Ferrocenyl Aliphatic Acids[1]

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

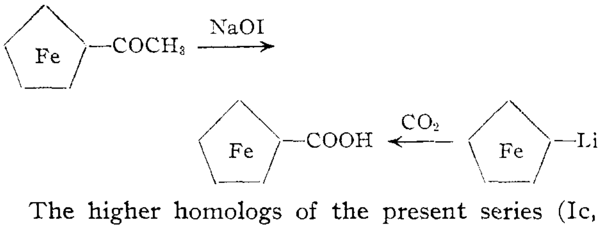
RECEIVED JANUARY 28, 1957

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).



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).

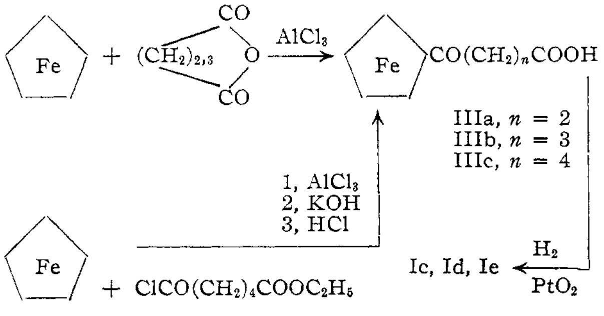
(5) M. Rosenblum, Ph.D. Thesis, Harvard University, August, 1953.

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

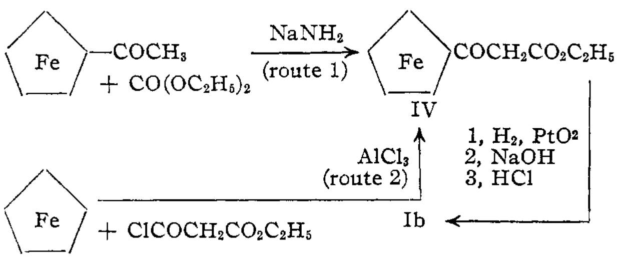
(7) R. A. Benkeser, D. Goggin and G. Schroll, *ibid.*, **76**, 4025 (1954).

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

rocene with a limited amount of appropriate acid derivatives under conditions designed to give principally monoacylation.[3] Thus, ferrocene and succinic anhydride gave β-ferrocenoylpropionic acid (IIIa), and ferrocene and glutaric anhydride gave γ-ferrocenoylbutyric acid (IIIb), while ferrocene and δ-carbethoxyvaleryl chloride gave δ-ferrocenoylvaleric acid (IIIc). Yields from the anhydrides approximated 90%, while that from the half-ester acid chloride was 70%. Hydrogenation of each keto acid was effected in good yield.

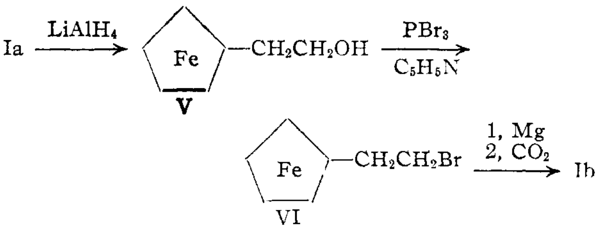


A similar procedure has been employed for the synthesis of β-ferrocenylpropionic acid by Woodward and Csendes,[9] who acylated ferrocene with carbethoxyacetyl chloride (route 2, below) to give the β-keto ester ethyl ferrocenoylacetate (IV) in good yield. Since carbethoxyacetyl chloride is inconvenient to prepare,[10] alternative routes have been investigated in the present study. The most convenient proved to be the carbethoxylation of acetylferrocene, employing diethyl carbonate and sodium amide catalyst[11] (route 1, below).

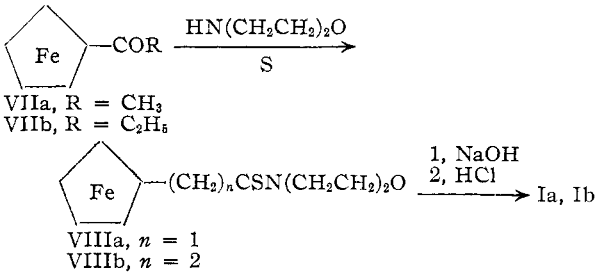


The β-keto ester IV was not isolated but was hydrogenated, then hydrolyzed directly to β-ferrocenylpropionic acid. No attempt was made to establish optimum conditions, but the ready availability of the starting materials render this approach particularly attractive.

Two alternative routes to β-ferrocenylpropionic acid were investigated but proved considerably less successful. One, the Willgerodt reaction of propionylferrocene, gave the acid, but in only very low yield, as described in the next paragraph. The second, below, was abandoned when the attempted conversion of β-ferrocenylethyl alcohol (V) to the corresponding bromide VI gave a complex mixture of products.



The Willgerodt reaction[12] was employed with success in the preparation of both ferrocenylacetic acid[13] and β-ferrocenylpropionic acid, from acetylferrocene (VIIa) and propionylferrocene (VIIb), respectively. The usual conditions[14] for the Kindler variation[15] of the Willgerodt reaction were modified slightly by the addition of dioxane to lower the reflux temperature, as the intermediate thiomorpholide was found to decompose at the normal reflux temperatures. Ferrocenylacetothiomorpholide (VIIIa) was obtained in 40% yield from one run and could be hydrolyzed in alkali to the corresponding acid. In other runs the thiomorpholide was not isolated, and the crude reaction mixture was hydrolyzed to give ferrocenylacetic acid in approximately 20% over-all yield.



No attempt was made to isolate β-ferrocenylpropionothiomorpholide (VIIIb), but the yield of β-ferrocenylpropionic acid from hydrolysis of the crude reaction mixture was only 4%, reflecting the usually lower yields of product obtained from higher alkyl aryl ketones compared to those from methyl aryl ketones.[12]

The dicarboxylic acid 1,1'-ferrocenediacetic acid was prepared by the same procedure in 13% over-all yield and was characterized as its dimethyl ester.

Infrared spectra are consistent with those anticipated for compounds of the structures given.[16] Thus, the spectra of the acids contain carboxyl carbonyl bands in the 1712–1705 cm.$^{-1}$ region, while those of the ketonic compounds, with carbonyl adjacent to the ferrocene nucleus, have bands between 1667–1663 cm.$^{-1}$.[17] The spectrum of

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[9] R. B. Woodward and E. Csendes, personal communication.

[10] H. Staudinger and H. Becker, *Ber.*, **50**, 1016 (1917).

[11] R. Levine and C. R. Hauser, THIS JOURNAL, **66**, 1768 (1944).

[12] M. Carmack and M. A. Spielman in "Organic Reactions," Vol. III, R. Adams, ed., John Wiley and Sons, New York, N. Y., 1946, p. 83.

[13] Nesmeyanov has reported the isolation of ferrocenylacetothiomorpholide from the Willgerodt reaction of acetylferrocene, but has given no experimental details or physical properties (A. N. Nesmeyanov, XIVth International Congress of Pure and Applied Chemistry, Zurich, July 21–27, 1955; *cf.* Abstracts of Papers, p. 193).

[14] Reference 12, p. 97.

[15] K. Kindler, *Ann.*, **431**, 187 (1923).

[16] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

[17] Exceptions to these values are found in the spectra of ferrocenylacetic acid and ε-ferrocenylcaproic acid, which show carboxyl carbonyl absorption at 1698 and 1694 cm.$^{-1}$, respectively, when determined in mulls. However, spectra of these compounds in chloroform solution have carboxyl bands at the normal positions. Also exceptional are the mull spectra of δ-ferrocenoylvaleric acid, which has two carboxyl bands, at 1723 and 1702 cm.$^{-1}$, and two ketone bands at 1658 and 1638 cm.$^{-1}$, and, to a lesser extent, the mull spectrum of β-ferrocenoylpropionic acid, with two ketone bands, at 1657 and 1640 cm.$^{-1}$. In these compounds, too, the abnormalities are absent from the spectra of chloroform solutions.

ferrocenylethyl alcohol shows hydroxyl absorption at 3220 cm.$^{-1}$ and that of dimethyl 1,1′-ferrocenediacetate displays ester carbonyl absorption at 1740 cm.$^{-1}$, while the thiomorpholide spectra contain bands near 1500 cm.$^{-1}$, attributed to the –CSN= group.[18]

Bands previously associated with substituted ferrocenes[3,19] are also found in the spectra of the compounds in the present series. The carbon–hydrogen stretching band[19] is found between 3090 and 3040 cm.$^{-1}$, usually near 3060 cm.$^{-1}$, for every compound and carbon–hydrogen bending bands[19] in the narrow region 828–820 cm.$^{-1}$. All of the compounds with one unsubstituted cyclopentadienyl ring have bands near 1110 and 1005 cm.$^{-1}$ (9–10 μ rule),[20] although in some cases the 10 μ band is very weak. Thus the *absence* of *both* bands would be strong indication of substitution on both rings. However, the *presence* of one or more bands in these positions cannot be taken conclusively as proof of an unsubstituted ring. For example, in the present series dimethyl 1,1′-ferrocenediacetate has a band at 1015 cm.$^{-1}$, while 1,1′-ferrocene-diacetodithiomorpholide has bands at both 1111 and 1006 cm.$^{-1}$.[21] Further bands are found in the 1000–900 cm.$^{-1}$ region previously found useful for characterizing alkyl- and acyl-substituted ferrocenes.[3] This region is of little value for the present compounds, however, since broad carboxyl bands[22] are also found between 1000–900 cm.$^{-1}$ in many of these compounds.

Experimental[23]

Preparation of Ferrocenylacetic Acid.—A mixture of 20 g. of acetylferrocene, 7 g. of sulfur, 50 ml. of dioxane and 150 ml. of morpholine was heated at reflux for 18 hr. under nitrogen. The reaction mixture was filtered and evaporated to small volume under reduced pressure, then transferred to an alumina column and eluted in two fractions with benzene. From the first fraction was obtained 10.2 g. (35%) of **ferrocenylacetothiomorpholide**, m.p. 126–128°, and from the second fraction 1.0 g. (5%) of recovered acetylferrocene. Ferrocenylacetothiomorpholide, recrystallized from ether, had m.p. 130–131°.

Anal. Calcd. for $C_{16}H_{19}FeNOS$: C, 58.29; H, 5.80; N, 4.25. Found: C, 58.71, 58.52; H, 5.86, 5.75; N, 4.55.

The crude thiomorpholide was heated under reflux for 4 hr. with 2 *N* aqueous sodium hydroxide, then filtered, washed with ether and acidified with hydrochloric acid. The precipitated acid was extracted into ether, and the ether extracts were washed with water, dried and evaporated to small volume. Addition of pentane gave 5.5 g. (73% from the thiomorpholide) of precipitated ferrocenylacetic acid. The yellow acid, recrystallized from ether–pentane, darkened 125–135° and sintered 135–140°.

Anal. Calcd. for $C_{12}H_{12}FeO_2$: C, 59.05; H, 4.96. Found: C, 59.40; H, 5.34.

In subsequent runs the thiomorpholide was not isolated, but the reaction mixture from the Willgerodt procedure was filtered, then hydrolyzed directly with refluxing 4 *N* aqueous sodium hydroxide. The basic mixture was acidified and extracted with ether. The organic acid was extracted from ether with sodium carbonate and reprecipitated upon acidification. The ether–carbonate extraction sequence was repeated to give the pure acid; yields from six runs employing this procedure varied from 14 to 26%.

β-Ferrocenylethyl alcohol was prepared in quantitative yield from ferrocenylacetic acid by reduction at room temperature with lithium aluminum hydride. The yellow alcohol was recrystallized from ether–pentane and had m.p. 49–50°.

Anal. Calcd. for $C_{12}H_{14}FeO$: C, 62.64; H, 6.13. Found: C, 62.87; H, 6.41.

An attempt was made to convert the alcohol to the corresponding bromide by reaction with phosphorus tribromide and pyridine at −5°. Chromatography of the product over alumina gave three distinct bands, which were eluted and concentrated to red oils, not further investigated.

Preparation of 1,1′-Ferrocenediacetic Acid.—A mixture of 10 g. of 1,1′-diacetylferrocene, 10 g. of sulfur, 18 ml. of dioxane and 83 ml. of morpholine was heated at reflux for 18 hr. under nitrogen. The reaction mixture was filtered and evaporated to dryness under reduced pressure. The residue was dissolved in chloroform and reprecipitated with pentane. This process was repeated to give an analytical sample (0.32 g., 2%) of 1,1′-ferrocenediacetodithiomorpholide, which darkened 175–190°, sintered 200°.

Anal. Calcd. for $C_{22}H_{28}FeN_2O_2S_2$: C, 55.93; H, 5.96; N, 5.93. Found: C, 56.12; H, 6.10; N, 6.04.

The purified material was combined with the residue from the evaporated chloroform–pentane filtrates and hydrolyzed with sodium hydroxide as described above for the preparation of ferrocenylacetic acid. The yield of 1,1′-ferrocenediacetic acid was 1.4 g. (13%). The yellow acid, recrystallized from ether–pentane, darkened below 137° and sintered 140–143° with decomposition.

Anal. Calcd. for $C_{14}H_{14}FeO_4$: C, 55.64; H, 4.67. Found: C, 55.53; H, 4.75.

In subsequent runs no attempt was made to isolate the dithiomorpholide, but the crude reaction mixture was filtered, hydrolyzed with 4 *N* sodium hydroxide and worked up as described above. From five runs, in which amounts varying from 3–30 g. of diacetylferrocene were employed, yields ranged from 10–14%.

One run was made employing the ammonia–pyridine procedure[24] for the Willgerodt reaction. When 3 g. of diacetylferrocene, 11 ml. of concentrated aqueous ammonia, 4 g. of sulfur and 32 ml. of pyridine were heated at 165° for 4 hr. in a sealed tube, only 20 mg. of poorly characterized product could be obtained and the procedure was not further explored.

Dimethyl 1,1′-ferrocenediacetate was prepared in 75% yield by the reaction of 1,1′-ferrocenediacetic acid with diazomethane. The product was eluted from a Celite column with benzene and concentrated to the brown liquid diester. The infrared spectrum shows strong ester carbonyl absorption at 1740 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{18}FeO_4$: C, 58.20; H, 5.49. Found: C, 58.43; H, 5.81.

Preparation of β-ferrocenylpropionic acid was effected *via* the β-keto ester obtained by carbethoxylation[11] of acetylferrocene. A solution of sodium amide[25] was prepared from 2.3 g. of sodium and 100 ml. of liquid ammonia. After the blue color had disappeared a solution of 10 g. of acetylferrocene in 100 ml. of absolute ether and 25 ml. of diethyl carbonate was added. The resulting mixture was stirred for 2 hr. under reflux, then poured over ice and acetic acid. The ether phase was washed with sodium carbonate, concentrated under reduced pressure and purified by elution with benzene from a Celite column. Benzene was removed in vacuum to give a red oil.

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(18) Reference 16, p. 294.

(19) E. R. Lippincott and R. D. Nelson, THIS JOURNAL, **77**, 4990 (1955).

(20) This rule was proposed by Rosenblum,[5] who attributed sharp infrared bands at 9 and 10 μ to the presence of one or more unsubstituted cyclopentadienyl rings in the ferrocene molecule. Lippincott and Nelson[19] assign bands near 9 μ to ring breathing and bands near 10 μ to C–H bending parallel to the plane of the ring.

(21) It may be noted that 1,1′-dimethyl-2-ferrocenecarboxylic acid and the corresponding 3-carboxylic acid,[3] in which both rings are substituted, also have bands at 1104 cm.$^{-1}$.

(22) Reference 16, p. 148.

(23) Melting points are uncorrected. We are indebted to Mr. Jozsef Nemeth, Mrs. Maria Benassi, Mrs. Ruby Ju and Miss Claire Higham for microanalyses, and to Mr. James Brader, Mrs. Louise Griffing and Mr. Sy Portnow for infrared spectra. The spectra, which are on file in the Infrared Laboratory, were obtained for solids in Nujol mulls, for liquids as smears, with a recording Perkin–Elmer infrared spectrophotometer, model 21.

(24) D. F. DeTar and M. Carmack, THIS JOURNAL, **68**, 2025, 2029 (1946).

(25) K. W. Greenlee and A. L. Henne, *Inorg. Syntheses*, **2**, 128 (1946).

A portion (4.0 g.) of the crude residue was dissolved in acetic acid and hydrogenated at four atmospheres pressure over 800 mg. of platinum oxide catalyst. After 48 hr. the mixture was filtered, diluted with water and extracted with ether. The ethereal solution was washed with sodium carbonate and concentrated. The residue was hydrolyzed with refluxing aqueous potassium hydroxide. The cooled basic solution was extracted with ether, then acidified to give crude β-ferrocenylpropionic acid, which was purified by passing the sodium salt through Celite, re-precipitation with acid and recrystallization from ether–pentane. A total of 1.73 g. was obtained of yellow-orange, crystalline β-ferrocenylpropionic acid, m.p. 115–116°,[26] together with an additional 340 mg. of less pure material.

Anal. Calcd. for $C_{13}H_{14}FeO_2$: C, 60.49; H, 5.47. Found: C, 60.44; H, 5.62.

The ether extract of the saponification mixture was concentrated and eluted from an alumina column with benzene. A small amount of ethylferrocene[27] was obtained, together with 580 mg. of recovered acetylferrocene.

A second portion of the crude β-keto ester was saponified with ethanolic potassium hydroxide at room temperature, then diluted with water. The orange aqueous layer was washed with ether, then acidified. The precipitated acid was extracted into ether, but apparently was decarboxylated readily as only acetylferrocene, m.p. 84–85°,[28] could be isolated from the ether solution.

A third portion of the crude β-keto ester was transferred to an alumina column. In addition to recovered acetylferrocene, a small amount of red oil[29] was obtained; the infrared spectrum of this material showed typical ferrocene bands at 3100 and 826 cm.$^{-1}$ [19] and carbonyl absorption, consistent with that of a β-keto ester, at 1739 and 1665 cm.$^{-1}$.[30,31]

Propionylferrocene was prepared by the Friedel–Crafts acylation of ferrocene with propionic anhydride. To a mixture of 34.5 g. of aluminum chloride and 300 ml. of methylene chloride was added a solution of 44.3 g. of ferrocene and 15.6 g. of propionic anhydride in 300 ml. of methylene chloride. The mixture was stirred for 2 hr. at room temperature, then decanted over ice and worked up in the usual manner. The methylene chloride solution was concentrated and the residue dissolved in benzene and transferred to an alumina column, which was eluted with benzene. The first of two bands gave 21.4 g. (48%) of recovered ferrocene, while the second band yielded 15.3 g. (53%) of propionylferrocene as a red oil, which crystallized from pentane at Dry Ice temperature, m.p. 38–39°.

Anal. Calcd. for $C_{13}H_{14}FeO$: C, 64.49; H, 5.83. Found: C, 64.66; H, 6.08.

Propionylferrocene was converted to β-ferrocenylpropionic acid by the Willgerodt procedure described above for the preparation of ferrocenylacetic acid, but the yield of the substituted propionic acid was small (*ca.* 4%), and the material was impure (m.p. 112–114°). The infrared spectrum was, however, nearly identical with that of β-ferrocenylpropionic acid, obtained from the carbethoxylation sequence above.

β-Ferrocenoylpropionic acid[32] was prepared, by the procedure described above for the synthesis of propionylferrocene, from 7.4 g. of ferrocene, 2.0 g. of succinic anhydride and 5.8 g. of aluminum chloride.[33] The crude acid was extracted from methylene chloride with sodium carbonate, filtered through Celite and re-precipitated with dilute hydrochloric acid; yield 5.0 g. (87%). A sample of orange β-ferrocenoylpropionic acid, recrystallized from methanol-benzene, had m.p. 166.5–167.5°.

Anal. Calcd. for $C_{14}H_{14}FeO_3$: C, 58.78; H, 4.93; Fe, 19.52. Found: C, 58.74; H, 5.20; Fe, 19.24.

In an alternative procedure the order of addition of reagents was ferrocene (74.7 g.), aluminum chloride (58.8 g.), succinic anhydride (20.0 g.). Reaction was allowed to proceed for 20 hr. at room temperature. The yield of pure keto acid from this procedure was 11.8 g. (21%).

γ-Ferrocenylbutyric acid was prepared by hydrogenation of β-ferrocenoylpropionic acid, as described above for the preparation of β-ferrocenylpropionic acid. The diluted reaction mixture was extracted with ether, and the ether phase was in turn extracted with sodium carbonate. γ-Ferrocenylbutyric acid precipitated in yellow crystals on acidification of the carbonate extracts and was purified by repeated ether–carbonate extractions; yield 0.88 g. (93%, from 1.0 g. of keto acid), m.p. 115–116°.

Anal. Calcd. for $C_{14}H_{16}FeO_2$: C, 61.79; H, 5.93. Found: C, 61.79; H, 5.73.

γ-Ferrocenoylbutyric acid was prepared by the procedure described above for the preparation of β-ferrocenoylpropionic acid. From 33 g. of ferrocene, 10 g. of glutaric anhydride[34] and 26 g. of aluminum chloride the yield of γ-ferrocenoylbutyric acid was 24.1 g. (92%), m.p. 136–137°.

Anal. Calcd. for $C_{15}H_{16}FeO_3$: C, 60.05; H, 5.36; Fe, 18.59. Found: C, 59.75; H, 5.35; Fe, 18.52.

δ-Ferrocenylvaleric acid was prepared from γ-ferrocenoylbutyric acid by the hydrogenation procedure employed above for the preparation of γ-ferrocenylbutyric acid. From 1.0 g. of the orange keto acid was obtained 0.80 g. (84%) of yellow δ-ferrocenylvaleric acid, m.p. 109–110°.

Anal. Calcd. for $C_{15}H_{18}FeO_2$: C, 62.95; H, 6.34. Found: C, 62.69; H, 6.54.

δ-Ferrocenoylvaleric acid[32] was prepared by the acylation of ferrocene with δ-carbethoxyvaleryl chloride. Ethyl hydrogen adipate (b.p. 130–131° (2 mm.), m.p. 28–29.5°; lit.[35] b.p. 140–145° (2 mm.), m.p. 28–29°) was prepared by the procedure of Brown, *et al.*,[35] from diethyl adipate, adipic acid and ethanol and converted to the acid chloride (b.p. 70–73° (0.7 mm.); lit.[35] b.p. 120° (15 mm.)) by thionyl chloride.

Acylation was effected by the procedure described for the synthesis of propionylferrocene and employed 34.7 g. of δ-carbethoxyvaleryl chloride, 67.5 g. of ferrocene and 52.0 g. of aluminum chloride. After the reaction mixture had been worked up, the methylene chloride solution, containing ferrocene and keto ester, was allowed to stand for 60 hr. with 1 *N* ethanolic potassium hydroxide. Addition of water gave the sodium salt of δ-ferrocenoylvaleric acid in the aqueous layer. The orange acid precipitated on addition of glacial acetic acid and was extracted into ether, and recovered upon concentration; yield 43.5 g. (71%). An analytical sample, recrystallized from ether–pentane, had m.p. 83.5–84.5°.

Anal. Calcd. for $C_{16}H_{18}FeO_3$: C, 61.17; H, 5.78. Found: C, 61.48; H, 5.33.

In a second run the yield of keto acid was 65%.

ε-Ferrocenylcaproic acid[32] was prepared from δ-ferrocenoylvaleric acid by the hydrogenation procedure employed above for the preparation of γ-ferrocenylbutyric acid. From 5.0 g. of keto acid the yield of ε-ferrocenylcaproic acid was only 3.3 g. (70%) due to mechanical loss on bumping. The melting point behavior of ε-ferrocenylcaproic acid indicates polymorphism. Sharp yellow crystals, obtained from ether–pentane, had m.p. 92–93°; after re-solidification this material melted 85–86°. Microcrystals, obtained after grinding and prolonged drying, had m.p. 83–84°; after re-solidification this material melted 91.5–92.5°.

Anal. Calcd. for $C_{16}H_{20}FeO_2$: C, 64.03; H, 6.72. Found: C, 64.07; H, 6.57.

Acknowledgments.—The authors wish to express

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[26] Woodward and Csendes[9] also have found m.p. 115–116° for this acid.

[27] K. L. Rinehart, Jr., Sung Moon and K. L. Motz, in preparation.

[28] The high degree of purity of this material [lit.[3] m.p. 86–87°] is in agreement with the formulation of the acidic product as ferrocenoylacetic acid.

[29] The oil did not yield readily to crystallization, presumably due to impurities. Woodward and Csendes[9] found ethyl ferrocenoylacetate to have m.p. 50–51°.

[30] R. S. Rasmussen and R. R. Brattain, THIS JOURNAL, **71**, 1073 (1949).

[31] N. J. Leonard, H. S. Gutowsky, W. J. Middleton and E. M. Peterson, *ibid.*, **74**, 4070 (1952).

[32] We thank Messrs. P. W. K. Woo and R. W. Bush for assistance with the preparation of these compounds.

[33] We are indebted to Dr. R. H. Mazur of G. D. Searle and Co. for helpful suggestions regarding certain details of the experimental conditions employed.

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[CONTRIBUTION FROM THE CHEMICAL CORPS, CHEMICAL RESEARCH DIVISION, CHEMICAL WARFARE LABORATORIES]

Fluorocarbon Derivatives. I. Derivatives of Sulfur Hexafluoride[1]

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The electrofluorination of dialkyl and cyclic sulfides and dialkyl disulfides in anhydrous hydrogen fluoride by the Simons process was investigated. Dialkyl sulfides were found to yield the corresponding di-perfluoroalkyl sulfur tetrafluorides, $(R_F)_2SF_4$ (I), together with degradation products. Dialkyl disulfides failed to give the corresponding di-(perfluoroalkyl) disulfur decafluorides, $(R_FSF_4)_2$, but yielded instead I and cleavage products.

Introduction

Direct as well as cobalt trifluoride fluorination of both methyl mercaptan and carbon disulfide result in the formation of trifluoromethyl sulfur pentafluoride, CF_3SF_5[3] (II). Clifford, El-Shemy, Emeleus and Haszeldine[4] obtained the same compound by electrochemical fluorination of dimethyl sulfide in anhydrous hydrogen fluoride (Simons process)[5] together with bis-(trifluoromethyl) sulfur tetrafluoride, $(CF_3)_2SF_4$ (III), the fully fluorinated analog of the starting material. II and III, which can be regarded as mono- and di-(perfluoroalkyl) derivatives of sulfur hexafluoride, respectively, seem to be the only representatives of these two classes of compounds reported in the literature.

The successful conversion of dimethyl sulfide to III and to the cleavage product II suggested that the relatively mild conditions prevailing in the Simons cell might permit the preparation of higher homologs of the two series of sulfur hexafluoride derivatives, $(R_F)SF_5$ (I) and $(R_F)_2SF_4$, (IV), respectively, from the corresponding dialkyl sulfides. Therefore, the behavior of several open-chain and cyclic sulfides and of three dialkyl disulfides during low-voltage electrolysis in anhydrous hydrogen fluoride was studied in the course of a program for the investigation of new sulfur- and nitrogen-containing fluorocarbon derivatives. This investigation resulted in the synthesis of several open-chain and one cyclic fluorocarbon derivatives of sulfur hexafluoride. The physical constants and analyses of these new compounds are listed in Table I.

After the Experimental part of our investigation had been completed, Severson, Brice and Coon[6] reported the preparation of $(C_4F_9)_2SF_4$ (X), $C_4F_9SF_5$ (IX) and $\overline{CF_2CF_2OCF_2CF_2SF_4}$ (XI) by the Simons process. These compounds also had been obtained in our study.

Experimental

Apparatus.—The large scale runs were performed in a cell of 3600-ml. capacity and a nominal rating of 50 amperes (cell A). The cell casing was constructed of nickel with an electrode pack of alternating anodes and cathodes (9 each, spaced $^1/_8$ inch apart) of 8.9 × 17.8 × 0.16 cm. nickel sheeting and was provided at the bottom with a valve for the removal of insoluble liquid fluorinated product. Any gaseous reaction product, or low boiling materials entrained in the effluent hydrogen, were condensed in attached traps cooled with Dry Ice–acetone and liquid nitrogen. The effluent from the cell was passed through a low temperature reflux condenser and subsequently through a bed of sodium fluoride pellets in order to remove hydrogen fluoride from the gas stream before condensation in the attached cold traps.

Small cell runs were carried out in either of two nickel cells provided with Kel-F windows for observation of the electrolyte during the reaction. One of the cells (cell B), of 900-ml. capacity, had a cathode area of 250 sq. cm., the cell body served as the anode and the cell was rated at 10 amperes. The other small cell (cell C), of 1000-ml. capacity, was equipped with four anodes and four cathodes (14.0 × 12.7 × 0.16 cm. each) arranged alternatingly and was rated at 25 amperes. Cells A and C were provided with a mantle through which a refrigerant could be circulated. The coolant for the cell condensers and jacket was obtained from a Mayer Junior Chil-er (Mayer Refrigerating Engineers) model J-4, using a brine of ethylene glycol and water.

The power for cell A was supplied by a Sorenson Nobatron model E-6-100a and for cells B and C by a Mallory Rectopower, model 6RS25-1.

Materials.—The organic starting materials used in the electrofluorination were commercial products or were synthesized by conventional methods.

The hydrogen fluoride employed was commercial grade anhydrous hydrogen fluoride (Mathieson Chemical Corp. and Pennsylvania Salt Manufacturing Co.) which was distilled before use through a 122-cm. Monel column of 12.7 cm. inside diameter and packed with nickel Heli-pak (Podbielniak, Inc.).

The sodium fluoride pellets used for the removal of entrained hydrogen fluoride from the effluent gas stream were obtained as NaF·HF pellets (Harshaw Chemical Co.) and converted to NaF by the passage of dry air or nitrogen over the pellets at 450° for 10 hr.

Operation of the Cells.—Drying of the distilled anhydrous hydrogen fluoride (which contained approximately 0.5% of water) was accomplished by electrolyzing the cell charge of hydrogen fluoride at 5.5 to 6.0 volts. During the drying of the hydrogen fluoride some care had to be exercised to avoid undesirable explosions due to the formation of oxygen difluoride. The tendency for explosions was greatest during low flow rates of the effluent gases and could be prevented by increasing the gas flow with dry nitrogen.

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