Some Oxygen-Containing Ferrocenes

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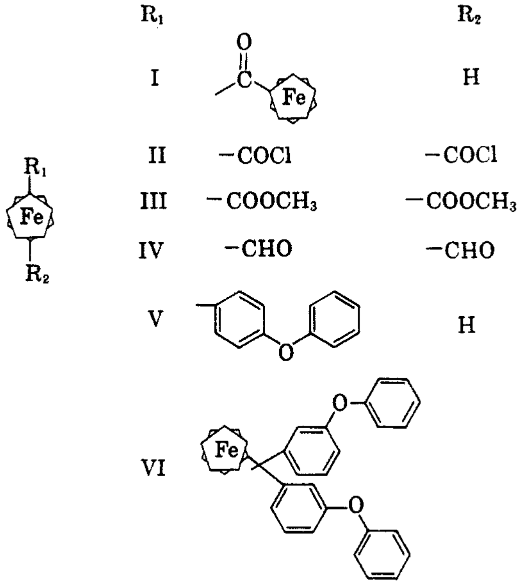
In connection with this Laboratory's research program, the oxygen-containing ferrocene derivatives, I–VI, were prepared. Of these only IV, V and VI have not been previously described.

Present interest in the known compounds, I, II and III, lies in the methods used to prepare them. Thus, I[2] was obtained from treatment of ferrocene with oxalyl chloride in the presence of aluminum chloride. Preparation of I by this reaction[3] is analogous to the similar reaction of benzene which yielded diphenylketone.[4]



The diacid chloride, II, was obtained from treatment of ferrocenedicarboxylic acid with PCl_3. Use of this reagent instead of the more conventional reagents, PCl_5 or $SOCl_2$, gave II in almost quantitative yield with no sign of decomposition.[5] Successful preparation of II was shown by treatment of the crude product with methanol followed by isolation and characterization of the known diester, III. The yield, therefore, is reported for the pure diester derivative.

While several accounts of the preparation of formylferrocene have appeared in the literature[6,7,8,9], preparation of 1,1′-diformylferrocene (IV) has not been reported. In the present work, II was treated with lithium tri-*tert*-butoxyaluminohydride, a reagent known to effect conversion of acid chlorides to the corresponding aldehydes.[10] Although it was not possible to obtain a pure sample of IV, its existence was strongly indicated by the infrared spectrum prepared from the crude material. No absorption was present in the O—H stretching region, while a strong band at 6.00 μ was observed. Infrared absorption of the carboxyl-carbonyl in 1,1′-ferrocenedicarboxylic acid, the starting material, occurs at 6.12 μ,[11] while that of the aldehyde-carbonyl in formylferrocene is reported as occurring at 5.91 μ,[6] 5.95 μ,[7] 5.9–6.0 μ[8] and 6.02 μ.[9] Additional evidence which showed the product not to be the starting diacid was its total insolubility in aqueous base.

Compound V, obtained *via* treatment of ferrocene with diphenyl ether-4-diazonium chloride, was of interest because it gave rise to an infrared spectrum (KBr disc) which possessed a band near 9 μ but not near 10 μ (9–10 Rule[12]). When the spectrum was obtained from a carbon disulfide solution of V, however, both the 9-band and the 10-band were present; so that the absence of the 10-band in the former case was attributed to a solid state effect, and not to an inconsistency with the 9–10 Rule.

Compound VI was prepared by the same technique as was V. In this case the diazonium salt of 3-phenoxyaniline was used, and the product obtained, VI, contained two phenoxyphenyl substituents. Presence of absorption at 9 and 10 microns in the infrared spectrum of the liquid compound showed it to possess an unsubstituted cyclopentadienyl ring.[12]

EXPERIMENTAL[13]

Reaction of Oxalyl Chloride and Ferrocene. Diferrocenylketone (I). To a vigorously stirred solution of ferrocene (5.58 g.; 30 m.moles) and 50 ml. of pure dry methylene dichloride, cooled to 0°, was added anhydrous aluminum chloride (2.67 g.; 20 m.moles) in small portions over a 1 hr. period. A cold (0°) solution of oxalyl chloride (1.27 g.; 10 m.moles) and 50 ml. of methylene chloride was slowly added (1 hr.) to the above described suspension. The dark violet colored reaction mixture was stirred while it gradually reached room temperature (approx. 2 hr.). After the mixture was rapidly poured onto 100 ml. of crushed ice and water, it was phase

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(2) E. Csendes in M. Rosenblum's Doctoral Dissertation, Harvard University, 1953.

(3) R. Riemschneider and D. Helm, *Chem. Ber.*, **89**, 155 (1956), reported that no reaction occurred between ferrocene and oxalyl chloride in the presence of aluminum chloride.

(4) H. Staudinger, *Chem. Ber.*, **41**, 3558 (1908).

(5) After the completion of this work, A. N. Nesmeyanov and O. A. Reuton, *Doklady Akad. Nauk S. S. S. R.*, **120**, 1267 (1958), described a very similar procedure for the preparation of II.

(6) J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **22**, 355 (1957).

(7) M. Rosenblum, *Chem. and Ind.* (*London*), 72 (1957).

(8) P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson, and G. M. Whitman, *J. Amer. Chem. Soc.*, **79**, 3416 (1957).

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(10) H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, **80**, 5377 (1958).

(11) E. F. Wolfarth, *Anal. Chem.*, **30**, 185 (1958).

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(13) All melting points are uncorrected. Analyses by Hufman Microanalytical Laboratories, Wheatridge, Colo.

separated. The organic phase (deep red) was dried and evaporated to a mass of orange-red colored crystalline material from which unchanged ferrocene was separated by means of vacuum sublimation. The red-colored residue, after chromatography on alumina followed by several recrystallizations from benzene, gave rise to pure I (200 mg., 0.5%), m.p. 206.5–207.0° (liter, 206–208°[2]). This product, when melted in admixture with a sample of I, prepared *via* the Friedel-Crafts Reaction of ferrocene and ferrocenoyl chloride,[14] exhibited no melting point depression; and, both materials gave rise to identical infrared spectra.

Anal. Calcd. for $C_{21}H_{18}Fe_2O$: C, 63.39; H, 4.56; Fe, 28.1. Found: C, 63.34; H, 4.47; Fe, 28.9.

1,1′-Bis(chlorocarbonyl)-ferrocene (*II*). 1,1′-Ferrocenedicarboxylic acid (276 mg.; 1.0 m.moles) was added to an excess of PCl_3 (approx. 10 ml.), and heated in an atmosphere of dry nitrogen under reflux during 24 hr. At the end of that time—the diacid was dissolved and the reaction mixture assumed a deep red-coloration—the excess PCl_3 was evaporated *in vacuo*, and the red solid residue obtained was cooled to 0°. The crude II was carefully treated with methanol—a procedure which gave rise to a vigorous reaction, including evolvement of HCl gas. The reaction mixture was evaporated to dryness *in vacuo*, and the solid residue obtained was found to be completely insoluble in aqueous base. It did, however, dissolve in ether, and no trace of the ether-insoluble ferrocene diacid was observed. The ethereal solution was evaporated to a red-colored residue which, when chromatographed on alumina, yielded, from the benzene-methanol (50:1) eluant, II (265 mg.; 88%). The product was recrystallized from cyclohexane and gave orange-red colored needles, m.p. 114.0–114.6° (lit., 116.5–117.5°,[15] 114–115°[16,17,18]).

Anal. Calcd. for $C_{14}H_{14}FeO_4$: C, 55.66; H, 4.67. Found: C, 55.67, 55.56; H, 4.81, 4.69.

1,1′-Diformylferrocene (*IV*). 1,1′-Ferrocenedicarboxylic acid (2.76 g.; 10.0 m.moles) was converted to II as described above. The crude product, free of PCl_3 and dissolved in 50 ml. of pure dry diglyme,[19] was cooled to −78° by means of a Dry Ice-acetone bath, and slowly treated with a cold (−78°) solution of lithium tri-*tert*-butoxyaluminohydride[10] (30 m.moles) and 15 ml. of diglyme during 1 hr. The mixture, vigorously agitated by means of a magnetically operated stirrer, was allowed to warm to room temperature and remain overnight. Addition of 200 ml. of a mixture of crushed ice and water produced a mass of red crystalline precipitate which was collected and triturated with several portions of dilute sodium hydroxide solution to remove any unreacted ferrocene diacid. After the residue was washed with water to free it of residual base, it was treated with portions of hot ethanol (total volume, approx. 300 ml.) which eventually dissolved all but a trace of the material. The ethanolic solution was evaporated to a red crystalline residue, presumed to be crude IV (1.75 g., 73%). This product decomposed when heated above 200°. Its infrared spectrum (KBr disc) was found to be different from that of the starting diacid. The material was so difficultly soluble in the variety of solvents tried, that a large volume of solvent (methanol or ethanol were best) was necessary to dissolve a small sample. Crystallization under these conditions could not be induced. Attempts to purify the product by means of vacuum sublimation only resulted in its decomposition. Preparation of a pure sample for combustion analysis was not possible, and analysis of the crude material gave equivocal results.

4-Ferrocenyldiphenyl Ether (*V*). A solution of 4-aminodiphenyl ether[20] (2.97 g.; 16 m.moles) and 175 ml. of water containing 10 ml. of conc. HCl, cooled to −5°, was treated with sodium nitrite (1.28 g.; 17.5 m.moles) to form the diazonium salt from the amine. The temperature of the reaction mixture was not allowed to rise above 0°, excess nitrous acid was destroyed by addition of urea and the mixture finally neutralized with sodium acetate solution. This solution of diazonium salt was then rapidly added to a cold (0°) ethereal solution of ferrocene (3.36 g.; 16 m.moles) and vigorously stirred during 30 min. After the blue-black colored reaction mixture was allowed to warm to room temperature (40 min.), it was phase-separated. The deep blue colored aqueous phase was treated with zinc and conc. HCl until the blue coloration, characteristic of the presence of ferricium ion,[21] was discharged. Ether extraction of the *leuco*-aqueous mixture yielded 1.89 g. of a soft dark-colored substance which was combined with similar material (2.32 g.) obtained by evaporation of the original ether phase. This crude product was then submitted to continuous extraction by petroleum ether (40–50°) in a Soxhlet Apparatus during 5 days.

Evaporation of the petroleum ether extract yielded a residue of orange-colored crystalline material (3.19 g.) from which unchanged ferrocene (1.39 g.) was sublimed. Several recrystallizations of the sublimation-residue from *n*-propanol raised its melting point from 125–127° to 129.5–130.5°, and afforded pure V (1.74 g.; 31%).

Anal. Calcd. for $C_{22}H_{18}FeO$: C, 74.60; H, 5.12. Found: C, 74.68, 74.61; H, 5.08, 5.00.

Bis(3-phenoxyphenyl)-ferrocene (*VI*). A solution of 3-phenoxyaniline[22] (3.70 g.; 20 m.moles) in 15 ml. of water containing 50 m.moles of conc. HCl was diazotized as described above. The solution of diazonium salt was rapidly added to a cold (0°) solution of ferrocene (3.72 g.; 20 m. moles) in 70 ml. of ether. The reaction mixture was worked up as in the previous case, and the partially purified product, VI, was obtained from a column-chromatogram of the crude reaction product. Pure VI (883 mg.; 8.5%) was collected after two molecular distillations in a Späth Bulb. The red-colored fluid slowly vaporized at 150° under a pressure of 0.05 mm.

Anal. Calcd. for $C_{34}H_{26}FeO_2$: C, 78.17; H, 5.02; Fe, 10.7. Found: C, 77.82; H, 5.21; Fe, 11.0.

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(19) 2,5,8-Trioxanonane, also known as the dimethyl ether of diethylene glycol.

(20) Prepared by means of the reduction of 4-nitrodiphenyl ether according to the procedure reported by Hazlet and Dornfeld, *J. Chem. Soc.*, 1781 (1944).

(21) The oxidized form of ferrocene, or the dicyclopentadienyl iron (III) cation.

(22) Obtained from The Merck Chemical Co., Rahway, N. J.; m.p. 37.8–38.2°.