[CONTRIBUTION FROM MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER]

Derivatives of Ferrocene. I. The Metalation of Ferrocene

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The metalation of ferrocene by means of *n*-butyllithium and mercuric acetate has been further investigated. The lithiation reaction has been extended for the preparation of trimethylsilylferrocene and 1,1′-di(trimethylsilyl)ferrocene. In the mercuration reaction, the ratio of starting materials has been varied in order to obtain optimum yields of either chloromercuriferrocene or 1,1′-dichloromercuriferrocene. Chloromercuriferrocene has been converted to diferrocenylmercury by means of dispersed sodium, sodium stannite, and sodium iodide in ethanol.

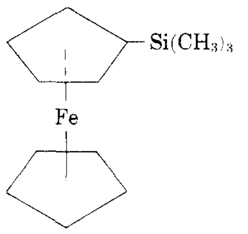
Since the discovery of ferrocene[1-3] in 1951, over one hundred technical publications have appeared in the literature concerning cyclopentadienylmetal compounds.[4] In this and subsequent papers we wish to report some new derivatives of ferrocene, as well as discuss the various synthetic methods by which substituted ferrocenes can be made.

One method for the preparation of ferrocene derivatives is by metalated intermediates. Benkeser, Goggin, and Schroll,[5] and Nesmeyanov *et al.*[6] have lithiated ferrocene using *n*-butyllithium to produce a mixture of mono- and dilithioferrocene. These metalated intermediates have been converted to carboxy,[5,6] triphenylsilyl,[5] and amino[7] derivatives. Nesmeyanov *et al.* have also mercurated ferrocene[6] and have converted the mercurated intermediates to bromo and iodo derivatives.[8]

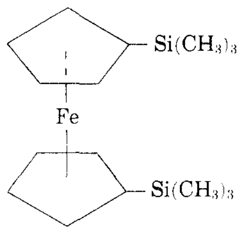
The present investigation was undertaken to determine the usefulness of these two reactions as practical methods for the preparation of mono- and disubstituted derivatives of ferrocene; part of our results are discussed herein. Initial experiments were directed toward improving the yields of mono- and dilithioferrocene, these metalated derivatives being characterized by carbonation to the mixed mono- and dicarboxyferrocenes. In numerous experiments in which experimental conditions were varied, however, the total yield of mixed acids could not be increased to more than about 30%. These yields are consistent with the yields of ferrocene acids reported by the other investigators.[5,6]

Benkeser *et al.*[5] have also reported that the mixture of mono- and dilithioferrocene obtained from the reaction of ferrocene and *n*-butyllithium in ether reacts with triphenylchlorosilane to produce triphenylsilylferrocene and 1,1′-di(triphenylsilyl)ferrocene. These two compounds were obtained in yields of 27% and 7%, respectively, or a total yield of 34%.

We have found that this reaction can also be applied to the synthesis of trialkylsilylferrocenes, and wish to report here the synthesis of trimethylsilylferrocene (I)[9] and 1,1′-di(trimethylsilyl)ferrocene (II). Both I and II were isolated as mobile, distillable, orange-red liquids, possessing mild odors. Both appeared to be completely stable in light and in air, in contrast to several low molecular weight alkyl derivatives of ferrocene.[10-12] The yields of I and II obtained were somewhat higher than the yields of carboxy- and triphenylsilylferrocenes obtained by this method. It is also interesting to note that more disubstituted product was obtained than monosubstituted product, in contrast to the above results.



I



II

The infrared spectra of I and II were very

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(1) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

(2) S. A. Miller, J. A. Tebboth, and J. F. Tremaine, *J. Chem. Soc.*, 632 (1952).

(3) In this and subsequent papers from this laboratory, the generic name ferrocene will be used instead of the more formal dicyclopentadienyliron (II). Furthermore, the system of nomenclature as outlined by Rosenblum[10] has been adopted.

(4) For excellent reviews on the subject, see: E. O. Fischer, *Angew. Chem.*, **67**, 475 (1955); P. L. Pauson, *Quart. Revs.* (*London*), **9**, 391 (1955).

(5) R. A. Benkeser, D. Goggin, and G. Schroll, *J. Am. Chem. Soc.*, **76**, 4025 (1954).

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

(7) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and L. S. Shilovtseva, *Doklady Akad. Nauk SSSR*, **102**, 535 (1955).

(8) A. N. Nesmeyanov, E. G. Perevalova, and O. A. Nesmeyanova, *Doklady Akad. Nauk SSSR*, **100**, 1099 (1955).

(9) The structural configuration which is shown for ferrocene is used for convenience only; the exact nature of the bonding is still in dispute.[4]

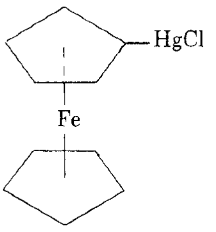
(10) M. Rosenblum, Ph.D. Thesis, Harvard University, 1953.

(11) A. N. Nesmeyanov and N. A. Vol'kenau, *Doklady Akad. Nauk SSSR*, **107**, 262 (1956).

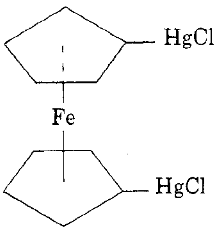
(12) M. Vogel, M. D. Rausch, and H. Rosenberg, unpublished results.

similar, the only notable difference being strong absorption bands at 9.00 and 9.95 μ in the spectrum of I. Both bands were totally absent in the spectrum of II. These results are in good accord with the data of Rosenblum[10] and of Pauson[13] who have found that the bands at 9.00 and 9.95 μ are present in both ferrocene itself and in derivatives in which only one cyclopentadienyl ring is substituted, but are absent in derivatives in which both rings are substituted. Among the absorption bands in both spectra were strong bands at 8.0 μ, 13.2 μ, and strong absorption from 11.6 to 12.4 μ. These three regions of absorption may be assigned to CH_3—Si stretching and rocking vibrations.[14]

The mercuration of ferrocene in either ether-alcohol or benzene-alcohol has been reported by Nesmeyanov *et al.* to produce a mixture of both chloromercuriferrocene (III) and 1,1′-dichloromercuriferrocene (IV).[6] A study of this reaction indicates that the relative proportions of III and IV produced can be conveniently controlled by varying the ratio of the starting materials. Table I summarizes these results.



III



IV

TABLE I

MERCURATION OF FERROCENE

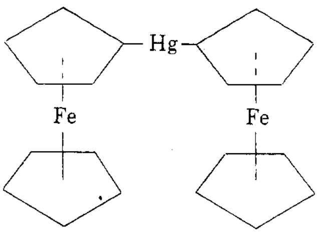
$FeC_{10}H_{10}$, Moles	$Hg(OAc)_2$, Moles	MCl,[a,b] Moles	Yield of III, %	Yield of IV, %
0.100[a]	0.050	0.055	14	14
0.500[b]	0.500	0.520	19	64
0.200[b]	0.100	0.105	32	39
0.500[b,c]	0.100	0.105	50	11

[a] Glacial acetic acid used as the solvent, M = K. [b] Ethyl ether-methanol used as the solvent, M = Li. [c] Extensive extraction with hot methanol was required to completely remove the unreacted ferrocene.

The mercuration of ferrocene to form III and IV can likewise be carried out in glacial acetic acid. This reaction requires no pressure vessel or additional high boiling solvent as does the well-known mercuration of benzene.[15,16] Under these conditions, however, some oxidation of ferrocene to the ferricinium ion, $(FeC_{10}H_{10})^+$, occurred, and the combined yield of III and IV was low. The use of ether-methanol as the solvent offers many advantages, avoiding oxidation of ferrocene and producing an excellent combined yield of III and IV. The facile formation and separation of these mercurated derivatives suggest them as useful intermediates in the preparation of additional ferrocene compounds in which either one or both cyclopentadienyl rings are substituted. Further studies along these lines are currently in progress in this laboratory.

The direct reaction of organomercury compounds with active halogen compounds such as alkyl halides, acid halides, *etc.*, has been reported in only a few instances to yield the desired derivatives,[17] these compounds being among the least reactive organometallics known.[18,19] Attempts to react III with acetyl chloride and trimethylchlorosilane in toluene solution were likewise not successful and considerable oxidation occurred. In both instances, insoluble blue solids separated which were identified as ferricinium salts by means of their solubility characteristics, reactions, and ultraviolet spectra.

In an attempt to *trans*-metalate III using dispersed sodium, several unexpected results were obtained. When III was reacted with a 10-molar excess of dispersed sodium (40% in *n*-nonane) diluted with benzene and the reaction mixture hydrolyzed at room temperature, quantitative yields of ferrocene were obtained. In a similar experiment in which the reaction mixture was first carbonated with a Dry Ice-ether mixture and then hydrolyzed, a 70% yield of diferrocenylmercury (V) was isolated. This result is not entirely anomalous, since both sodium and sodium amalgam have been reported to convert compounds of the type RHgX to the symmetrical R_2Hg derivatives.[18] It was subsequently found that contact of the reaction mixture with Dry Ice ether was not necessary to obtain V; direct hydrolysis at the low temperatures afforded by this refrigerant produced comparable results. No carboxyferrocene was isolated from



V

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(13) P. L. Pauson, *J. Am. Chem. Soc.*, **76**, 2187 (1954).

(14) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, pp. 274–277, John Wiley and Sons, Inc., New York (1954).

(15) F. C. Whitmore, *Organic Compounds of Mercury*, pp. 35, 171, Chemical Catalog Co., New York (1921).

(16) K. A. Kobe and P. F. Lueth, *Ind. Eng. Chem.*, **34**, 309 (1942).

(17) For example, see W. D. Schroeder and R. Q. Brewster, *J. Am. Chem. Soc.*, **60**, 751 (1938).

(18) F. C. Whitmore, *Organic Compounds of Mercury*, pp. 38–84, Chemical Catalog Co., New York (1921).

(19) H. Gilman, *Organic Chemistry*, Vol. I, p. 550, John Wiley and Sons, Inc., New York (1943).

these reactions, indicating that probably *trans*-metalation did not occur.

In a manner analogous to other compounds of the type RHgX,[18,20] III reacted readily with a solution of sodium stannite to produce V in good yield. III also reacted rapidly with sodium iodide in ethanol, another reagent which is frequently used to convert RHgX compounds to R_2Hg compounds.[18] In this reaction, two stable forms of V with different melting points were isolated.

Attempts to metalate ferrocene directly using either lithium metal in *n*-butyl ether or dispersed sodium in tetrahydrofuran were unsuccessful. In the latter reaction considerable destruction of ferrocene occurred, and small amounts of ferric oxide were isolated.

EXPERIMENTAL[21]

Lithiation of ferrocene and subsequent carbonation. In general, the procedure followed was similar to that described by Benkeser, Goggin, and Schroll.[5] For example, in a typical experiment in which 0.123 mole of *n*-butyllithium in 175 ml. of anhydrous ethyl ether was reacted with 17.7 g. (0.095 mole) of ferrocene in 200 ml. of ether, 11.0 g. of ferrocene and 5.0 g. of the crude acid were obtained. The neutralization equivalent of the crude acid, determined potentiometrically in aqueous ethanol solution, was 196, indicating a mixture of about 3 parts carboxyferrocene to 1 part dicarboxyferrocene, assuming these are the only two acids present.

Trimethylsilylferrocene (I) *and 1,1'-di(trimethylsilyl)ferrocene* (II). A suspension of 139.5 g. (0.75 mole) of ferrocene in 1200 ml. of anhydrous ethyl ether (dried and distilled over sodium) was placed in a 3-liter, 3-necked flask, fitted with a stirrer, reflux condenser, addition funnel, and nitrogen inlet. Over a 1-hr. period was added 1000 ml. of a 1.55-molar solution of *n*-butyllithium in anhydrous ether. Following the addition, all the ferrocene appeared to be dissolved. The reaction mixture was then stirred under a nitrogen atmosphere for 44 hr. at room temperature, during which time an orange precipitate separated from the ether solution. With stirring, 163.0 g. (1.50 moles) of trimethylchlorosilane was added over a period of about 5 hr., in order to maintain gentle reflux. The reaction mixture was then refluxed for 15 hr., hydrolyzed with ice, and the aqueous and ether phases separated. The aqueous layer was extracted once with ether and the combined ether phase washed repeatedly with water to neutrality and dried over Drierite.

The ether was evaporated leaving a dark orange-red liquid and precipitated ferrocene. This mixture was chilled in a Dry Ice-acetone bath in order to freeze out as much ferrocene as possible, filtered, and the ferrocene washed with a little ether. After drying the ferrocene weighed 35.1 g., m.p. 173–174°. The filtrate was placed in a 500-ml. flask fitted with a 12-inch Vigreux column and warmed under a pressure of 0.1 to 0.2 mm. of mercury. After about 1 hr. additional unreacted ferrocene had sublimed onto the column. Atmospheric pressure was then restored and the column was removed, rinsed with acetone, dried, and replaced. This procedure was repeated several times until all the ferrocene appeared to have sublimed, and only refluxing liquid was observed. From the acetone washings an additional 6.5 g. of ferrocene was isolated, for a total recovery of 41.6 g.

The remaining liquid was fractionally distilled using a packed column and a distillation head equipped for total reflux. After initial separation into low and high boiling fractions, both fractions were redistilled through a 12-inch Vigreux column equipped with a straight take-off head.

Following redistillation, 36.9 g. (19% yield) of I was obtained as a dark orange-red mobile liquid possessing a mild cedar-like odor, b.p. 64–65° (uncorr.) at 0.045 mm. of mercury, m.p. 23°, n_D^{25} 1.5696.

Anal. Calcd. for $C_{13}H_{18}SiFe$: C, 60.47; H, 7.03; Fe, 21.63; Si, 10.88. *Found:* C, 60.58, 60.69; H, 7.17, 7.17; Fe, 21.95, 21.69; Si, 10.64, 10.89.

The higher boiling fraction produced 66.5 g. (27% yield) of II, b.p. 87–88° (uncorr.) at 0.060 to 0.070 mm. of mercury, m.p. 16°, n_D^{25} 1.5454. II was similar in appearance to I, although its odor was very faint.

Anal. Calcd. for $C_{16}H_{26}Si_2Fe$: C, 58.16; H, 7.93; Fe, 16.90; Si, 17.00. Found: C, 58.50, 58.13; H, 7.97, 7.98; Fe, 16.63, 16.60; Si, 16.80, 16.82.

Chloromercuriferrocene (III) *and 1,1'-di(chloromercuri)-ferrocene* (IV). (*A*) *Methanol-ethyl ether as the solvent.* In general, modifications of the procedure described by Nesmeyanov *et al.*[6] were used, by varying the ratio of the reactants as illustrated in Table I. III was obtained in the form of golden-yellow leaflets, m.p. 193–194°, with decomp. (lit.[6] m.p. 194–196°). IV was isolated as a yellow powdery solid which did not melt at temperatures up to 300°. When heated at elevated temperatures over a period of time, however, slow decomposition was observed with ferrocene subliming on the tube.

(*B*) *Glacial acetic acid as the solvent.* A solution of 18.6 g. (0.10 mole) of ferrocene in 400 ml. of glacial acetic acid was heated to reflux, and a solution of 15.9 g. (0.05 mole) of mercuric acetate in 100 ml. of hot glacial acetic acid was added with stirring over a period of 1.25 hr. Following the addition the reaction mixture was refluxed for 0.5 hr. and then stirred for 16 hr. at room temperature. After filtering from a small amount of metallic mercury which had separated (0.4 g.), the filtrate was mixed with a solution of 4.1 g. (0.055 mole) of potassium chloride in 100 ml. of a 1:1 mixture of ethanol and water. A brown solid separated (A), which was washed with benzene to remove ferrocene; after drying the solid weighed 9.5 g.

The blue acidic filtrate was diluted with 500 ml. of water and a yellow solid separated, which after filtering, washing with water, and recrystallizing from cyclohexane produced a small amount of ferrocene. The filtrate was stirred with 50 g. of powdered zinc for about 2 hr. during which time the blue color was discharged. Extraction with benzene and removal of the solvent produced an additional 1.4 g. of ferrocene. From A, both III and IV were obtained by recrystallization from hot 1-butanol. The total amount of III isolated was 3.0 g., m.p. 192–193°, with decomp., or a yield of 14%. The total amount of IV isolated was 2.2 g., or a total yield of 14%.

Attempted reaction of III with trimethylchlorosilane. To a warm solution of 2.1 g. (0.005 mole) of III in 100 ml. of toluene (dried over sodium) was added 5.4 g. (0.05 mole) of trimethylchlorosilane. The reaction mixture was stirred under a nitrogen atmosphere for 3 hr. at 70°. During this period the solution darkened and a blue solid separated. The reaction mixture was diluted with 100 ml. of cold water and filtered. The light blue solid which was collected was washed with water and with toluene and dried, weighing 1.2 g. This solid was insoluble in common organic solvents, only slightly soluble in water, and was moderately soluble in dilute hydrochloric acid, forming a blue solution. The blue color was readily discharged upon addition of an excess of sodium hydroxide solution. The ultraviolet spectrum of a small sample in dilute hydrochloric acid was similar to that reported for the ferricinium ion.[10] From the toluene layer 0.7 g. of ferrocene was recovered.

A similar experiment was carried out using acetyl chloride in place of trimethylchlorosilane. In this reaction also,

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(20) J. L. Maynard, *J. Am. Chem. Soc.*, **46**, 1510 (1924).

(21) All melting points and boiling points are corrected unless otherwise noted. Analyses were made by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

a similar blue solid was isolated and ferrocene was recovered.

Reaction of III with dispersed sodium. (*A*). *Isolation of ferrocene.* In a 3-necked 250-ml. flask was placed 2.9 g. (0.05 mole) of sodium dispersion (40% in *n*-nonane), and the dispersion diluted with 50 ml. of benzene (dried over sodium). With stirring and under a nitrogen atmosphere, 2.1 g. (0.005 mole) of III in 100 ml. of warm dried benzene was added over a period of 15 min., and the reaction mixture stirred at 25° for 3.5 hr At the end of this period 35 ml. of 95% ethanol was cautiously added, followed by 50 ml. of water. The hydrolyzed mixture was filtered with suction and washed thoroughly with hot water and with benzene. The residue which remained (0.82 g.) appeared to be a gray powder containing small globules of mercury. The filtrate was separated into layers, the aqueous phase extracted with benzene, the combined benzene portion washed with water, and then the benzene solution dried over anhydrous magnesium sulfate. Filtration of the drying agent and evaporation of the solvent left 0.92 g. (99% yield) of ferrocene, m.p. 171–174° (uncorr.).

(*B*). *Isolation of diferrocenylmercury* (V). The apparatus and quantities of reactants were the same as outlined in (A). After stirring at 25° for 3.5 hr., the reaction mixture was poured onto a mixture of Dry Ice and ether. After cautious hydrolysis with 95% ethanol and with water, the mixture was vacuum-filtered. The aqueous and benzene phases were separated, and the benzene phase washed and dried over anhydrous magnesium sulfate. Removal of the solvent by evaporation left a yellow-orange solid. This solid and the initially insoluble material were extracted with a small quantity of boiling xylene, filtered, and the filtrate cooled to produce 1.0 g. (70% yield) of orange crystals of V, m.p. 235–236°, with decomp. (lit.[6] m.p. 233–234°). Acidification of the basic aqueous phase produced no trace of solid acidic material.

When the above reaction was carried out at 50° instead of 25°, carbonation and hydrolysis produced some V and some light yellow powdery solid which was insoluble in hot xylene and in dilute potassium hydroxide solution, but which did react with hydrochloric acid to give a blue solution. Acidification of the aqueous layer produced a trace of insoluble yellow material.

Reaction of III with sodium stannite. To a suspension of 2.1 g. (0.005 mole) of III in 20 ml. of 95% ethanol and 50 ml. of water was added a solution of sodium stannite, previously prepared by mixing 5.0 g. of sodium hydroxide in 25 ml. of water with 1.8 g. of stannous chloride dihydrate in 25 ml. of water. The yellow-orange color was immediately discharged and a gray-black solid separated. After stirring for 3 hr., the mixture was vacuum filtered, the solid washed well with water, dried, and digested with a little boiling xylene. The residue consisted of a dark gray solid containing globules of mercury. Upon cooling the xylene solution, 1.0 g. (70% yield) of V separated as yellow-orange crystals, m.p. 230–233° (uncorr.). Recrystallization from xylene raised the melting point to 234–235°, with decomp.

Reaction of III with sodium iodide in ethanol. A mixture of 600 ml. of 95% ethanol, 10.5 g. of sodium iodide, and 2.1 g. (0.005 mole) of III was refluxed for 2 hr. After filtering the hot mixture a yellow-orange solid separated, m.p. 215–225° (uncorr.). Two recrystallizations from xylene produced 0.9 g. (64% yield) of V, m.p. 235–236°, with decomp. Upon cooling and concentrating the ethanolic filtrate there was obtained 0.5 g. (35% yield) of an orange crystalline solid, m.p. 245–248°. Recrystallization from xylene produced a second form of V, m.p. 248–249°, with decomp.

Anal. Calcd. for $C_{20}H_{18}Fe_2Hg$: C, 42.09; H, 3.18; Fe, 19.57; Hg, 35.16. Found: C, 42.01, 41.99; H, 3.28, 3.15; Fe, 19.46, 19.41; Hg, 35.10, 35.24.

In two additional experiments both forms of V were obtained in each case. The infrared spectra of both forms of V (mulls in Nujol) were completely identical.

Acknowledgment. The authors wish to express their appreciation to Mr. F. F. Bentley and Mrs. N. E. Srp for the infrared spectra. We are also very grateful to Dr. Eric Barthel of the E. I. du Pont de Nemours and Co., Inc., and to Dr. Roy Pruett of the Linde Co., for generous samples of ferrocene which have been used in our research program.

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[CONTRIBUTION FROM MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER]

Derivatives of Ferrocene. II. Some Reduction Products of Benzoylferrocene and 1,1'-Dibenzoylferrocene[1]

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The reduction of benzoyl- and 1,1'-dibenzoylferrocene to benzyl- and 1,1'-dibenzylferrocene has been accomplished by either catalytic hydrogenation or by reduction with sodium and ethanol. 1-Hydroxybenzylferrocene has been prepared by the sodium borohydride reduction of benzoylferrocene, while the reduction of 1,1'-dibenzoylferrocene with lithium aluminum hydride has produced 1,1'-di(1-hydroxybenzyl)ferrocene. The action of a number of other reducing agents on these aryl ferrocenyl ketones is discussed.

In the Friedel-Crafts reaction of ferrocene, benzoyl chloride, and aluminum chloride, both benzoylferrocene (I)[2,3] and 1,1'-dibenzoylferrocene (II)[2,4,5] have been reported to be formed. We have further investigated this reaction and have found that by varying the method of addition and the molar ratio of the reactants, both I and II can be prepared in

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[1] Presented in part at the 131st Meeting of the AMERICAN CHEMICAL SOCIETY, Miami, Fla., April 7 to 12, 1957; see Abstracts of Papers, p. 47–O.

[2] M. Rosenblum, Ph.D. Thesis, Harvard University, 1953 (see Appendix).

[3] N. Weliky and E. S. Gould, New York Section, AMERICAN CHEMICAL SOCIETY, Meeting in Miniature, March 16, 1956.

[4] R. Riemschneider and D. Helm, *Ber.*, **89**, 155 (1956).

[5] A. N. Nesmeyanov and N. A. Vol'kenau, *Doklady Akad. Nauk SSSR*, **107**, 262 (1956).