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ACETOXYMERCURATION OF ACYLFERROCENES
A NOVEL SYNTHESIS OF 1,2-DISUBSTITUTED FERROCENES

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SUMMARY

Acetoxymercuration of a series of acylferrocenes has been found to produce appreciable amounts of 1,2- as well as 1,1'-mercurated products. The mercurated derivatives were readily converted into a variety of other unsymmetrical 1,2- and 1,1'-disubstituted ferrocenes. The 1,2-orientation of substituents was inferred by spectra data, and was confirmed by a comparison of products from the mercuration reactions with analogous products obtained from the 2-lithiation of [(dimethylamino)methyl]ferrocene. Both 2-(methoxycarbonyl)biferrocene and 2-acetylbiferrocene have been obtained from mixed Ullmann reactions of iodoferrocene with 2-iodo-1-(methoxycarbonyl)ferrocene and 2-iodo-1-acetylferrocene, respectively.

INTRODUCTION

Previous synthetic routes to 1,2-disubstituted ferrocenes have included the acid-catalyzed cyclization of (2-ferrocenylethyl)amine with formaldehyde, followed by Hoffman degradation to 2-substituted vinylferrocenes[1,2], and the 2-lithiation of diphenylferrocenylmethanol with n-butyllithium[3]. Other procedures involving electrophilic substitution lead to mixtures from which the 1,2-isomers are isolated in only very low yields[4-8].

The most convenient route presently available for 1,2-disubstituted ferrocenes involves the 2-metalation of [(dimethylamino)methyl]ferrocene with n-butyllithium[9]. Condensation of the 2-lithiated intermediate with appropriate electrophiles offers a route to a variety of 1,2-derivatives of ferrocene, since the methiodide derivatives of these compounds can be further converted to additional 1,2-disubstitution products[10-24]. The preparation of 1,2-disubstituted ferrocenes by this method, however, often involves a large number of successive reactions.

During an attempted synthesis of 1'-(chloromercuri)-1-(methoxycarbonyl)ferrocene (IIIa) via the acetoxymercuration of (methoxycarbonyl)ferrocene (Ia), we observed the formation of two isomeric monochloromercuri derivatives, one of which exhibited a *higher* R_f value than starting material (Ia). The isomer possessing an R_f value *lower* than (methoxycarbonyl)ferrocene was found to be the expected product, (IIIa) (24% yield), while the higher R_f material (20% yield) was subsequently identified as 2-(chloromercuri)-1-(methoxycarbonyl)ferrocene (IIa). These unexpected results

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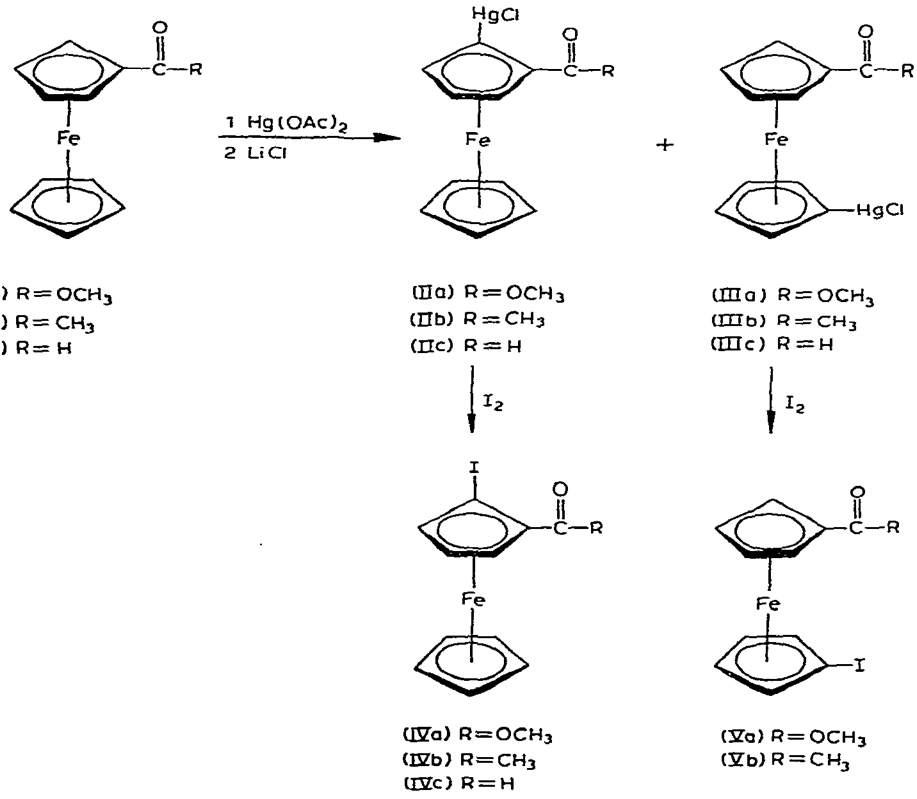
prompted us to study an extension of this mercuration reaction to a number of other acylferrocenes. The study has provided a novel route to 2-substituted acylferrocenes, as well as a convenient method for preparing other unsymmetrical 1,2-disubstituted ferrocenes and certain substituted biferrocenes. Most of the compounds available by this route are new, and would require many steps to be prepared by presently available methods. For this reason, we believe that the mercuration procedure supplements existing methods as a general route to compounds of this type.

RESULTS AND DISCUSSION

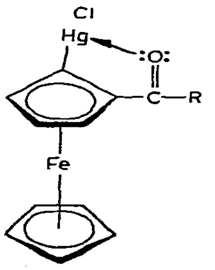
Acetoxymercuration of a variety of substituted ferrocenes (methoxycarbonyl-, acetyl- and formylferrocene) and subsequent treatment of the resulting products with lithium chloride produced appreciable amounts of 2- as well as 1-'chloromercurated acylferrocenes. The addition of small amounts of perchloric acid[25] to the reaction mixtures was found to improve the yields of mercurated products with the exception of formylferrocene (Ic), in which case it caused decomposition of the starting material. Reactions also occurred in the absence of perchloric acid, affording higher conversion to the 2-isomers, but the overall yields of products in these cases were substantially lower.



The crude reaction products were extracted with hexane to remove most of the starting material. Preparative thin layer chromatography was then utilized to resolve the mixture of mercurated products. In each separation, the band possessing the highest R_f contained the 2-(chloromercuri)-1-acylferrocenes (II). The chloromercuri derivatives did not possess sufficient solubility for the determination of NMR spectra. However, the corresponding iodinated derivatives were readily prepared, and exhibited NMR spectra which were completely consistent with a 1,2-structure. The IR spectra of the 2-substituted acylferrocenes showed absorptions at 1000 and 1110 cm^{-1}, which are indicative of an unsubstituted cyclopentadienyl ring[4,5,26]. A second band contained small amounts of unreacted starting material (I), while a third band possessing the lowest R_f value afforded the 1′-(chloromercuri)-1-acylferrocenes (III). The IR spectra of these products showed the absence of absorptions at 1000 and 1110 cm^{-1}, indicative of 1,1′-disubstitution.

An alternate workup procedure was subsequently devised which involves dry chromatography of the crude acetoxymercuri derivatives on a short column of silica gel (alumina causes decomposition). The highly polar mercurated compounds remain on the column while unreacted starting material is easily removed by elution with the appropriate solvent. The column is then stripped with a methanolic solution of lithium chloride, causing simultaneous conversion to the corresponding chloromercuri derivatives and elution of these from the column. The mixture of isomeric mono(chloromercuri)(acyl)ferrocenes is resolved by dry chromatography on a column of highly activated silica gel. This alternate procedure has proved to be more convenient than the preparative TLC method, and offers slightly higher yields of mercurated products.

The "anomalous" sequence of elution observed for the isomeric (chloromercuri)(acyl)ferrocenes can be explained by the postulation that coordination occurs between the carbonyl and the 2-chloromercuri groups, thereby decreasing electron density in the C=O bond. This result could cause a decrease in the affinity of the 2-chloromercuri isomers for the chromatographic substrate. Such a concept also explains the formation of sizable amounts of 2-mercurated derivatives, since the inductive effect of the carbonyl group would be expected to deactivate the ring toward further electrophilic substitution, and since the steric effect of this group might also be expected to inhibit attack at the 2-position. Since mercuration is generally assumed to occur by an electrophilic process, coordination of the carbonyl group with the incoming electrophile would thus direct substitution into the 2-position. In this regard, IR spectral evidence in two of the systems studied shows the



(II)

TABLE 1

IR CARBONYL STRETCHING FREQUENCIES (cm^{-1}) FOR VARIOUS ACYLFERROCENES[a]

R	$\text{Fc}{-}\overset{\text{O}}{\overset{\Vert}{\text{C}}}{-}\text{R}$	$\text{2-HgCl-Fcl}{-}\overset{\text{O}}{\overset{\Vert}{\text{C}}}{-}\text{R}$	$\text{1'-HgCl-Fcl}{-}\overset{\text{O}}{\overset{\Vert}{\text{C}}}{-}\text{R}$	$\text{2-I-Fcl}{-}\overset{\text{O}}{\overset{\Vert}{\text{C}}}{-}\text{R}$	$\text{1'-I-Fcl}{-}\overset{\text{O}}{\overset{\Vert}{\text{C}}}{-}\text{R}$
OCH_3	1720	1690	1715	1725	1715
CH_3	1670	1660	1670	1675	1670
H	1650	1650	1650	1670	

[a] Fc = ferrocenyl, $FeC_{10}H_9$; Fcl = ferrocenylene, $FeC_{10}H_8$.

carbonyl absorptions of both (IIa) and (IIb) are shifted to *lower* energy by 30 and 10 cm^{-1}, respectively, when compared with the unmercurated parent compounds (Table 1). The 1'-(chloromercuri)-1-acylferrocenes (IIIa) and (IIIb), on the other hand, exhibit carbonyl stretching frequencies very close to those of the parent compounds.

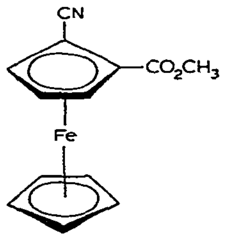
All the (chloromercuri)(acyl)ferrocenes studied underwent facile reaction with iodine in methylene chloride solution to form dark, soluble complexes. When these reaction mixtures were treated with aqueous sodium thiosulfate, the corresponding (iodo)(acyl)ferrocenes were obtained in yields ranging from 76–88%. The iodinated derivatives were unstable at room temperature, and were therefore prepared immediately before further use.

Table 1 illustrates the shifts which occur in the IR carbonyl stretching frequencies upon iodination of the (chloromercuri)(acyl)ferrocenes. Conversion of the 2-chloromercuri isomers to the corresponding 2-iodo derivatives shifts the carbonyl absorption peak to higher energy. This result is attributed primarily to a loss of coordination between the carbonyl and the 2-chloromercuri groups.

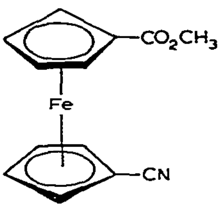
The NMR spectrum of 2-iodo-1-(methoxycarbonyl)ferrocene (IVa) exhibited the expected ABC system of multiplets for the three different protons on the substituted ring, a singlet integrating for five protons for the unsubstituted ring, and a singlet integrating for three protons for the methyl protons of the ester group. The spectrum of 2-iodo-1-acetylferrocene (IVb) was anomalous, exhibiting an A_2B pattern for the protons of the substituted ring (a downfield two-proton doublet and an upfield one-proton singlet). Conceivably, steric effects distort the carbonyl group from planarity and cause a merging of the individual proton chemical shifts, giving rise to the observed spectrum. The relative positions of the doublet and triplet are significant, since they indicate a 1,2-orientation of these two deshielding substituents. The NMR spectra of 1'-iodo-1-(methoxycarbonyl)ferrocene (Va) and 1'-iodo-1-acetylferrocene (Vb) were completely consistent with the proposed structures.

Reactions of 2- or 1'-iodo-1-(methoxycarbonyl)ferrocene with cuprous cyanide in *N*-methylpyrrolidone solution[27] afforded the corresponding cyano derivatives (VI) and (VII) in approximately 40% yield. Chromatography of the crude products on alumina yielded the isomeric (cyano)(methoxycarbonyl)ferrocenes as dark unstable oils, which slowly decomposed on standing. The IR spectra of each of the cyano derivatives exhibited both nitrile and ester absorption. Attempts to hydrolyze (VI) to 1,2-ferrocenedicarboxylic acid were unsuccessful.

In order to prove unequivocally the 1,2-orientation of substituents obtained by our mercuration procedure, we decided to compare several of the products with



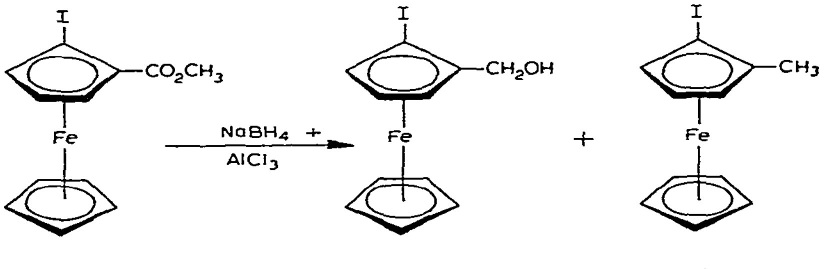
(VI)



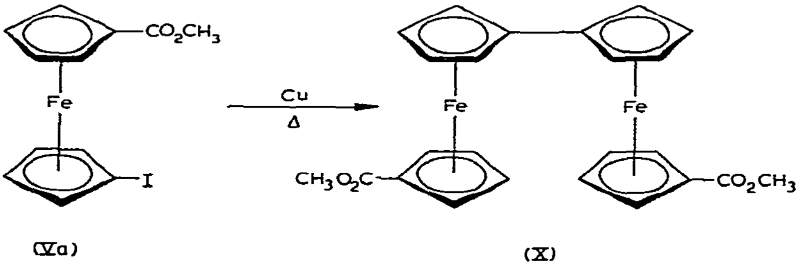
(VII)

similar compounds of known[9] 1,2-orientation. 2-Iodo-1-(hydroxymethyl)ferrocene (VIII) was chosen for comparison since it had recently been reported by Rockett and coworkers[10] and since it was readily available via the reduction of 2-iodo-1-(methoxycarbonyl)ferrocene (IVa).

Reduction of (IVa) with lithium aluminum hydride unfortunately caused carbon–iodine bond cleavage to occur, and yielded (hydroxymethyl)ferrocene as the only product. However, treatment of (IVa) with sodium borohydride in the presence of aluminum chloride yielded the desired product (VIII) in addition to significant amounts of 2-iodo-1-methylferrocene (IX). The two products could be separated on an alumina chromatographic column, and IR and NMR spectra of both were completely consistent with the proposed structures. A mixture melting point of (VIII) obtained in our studies with an authentic sample of (VIII) generously supplied by Dr. Rockett was undepressed, and the IR spectra and thin layer chromatograms of both compounds were identical. Sodium borohydride reduction of (IVc) also produced (VIII), which was likewise shown to be identical to the sample of (VIII) supplied by



(IVa) (VIII) (IX)

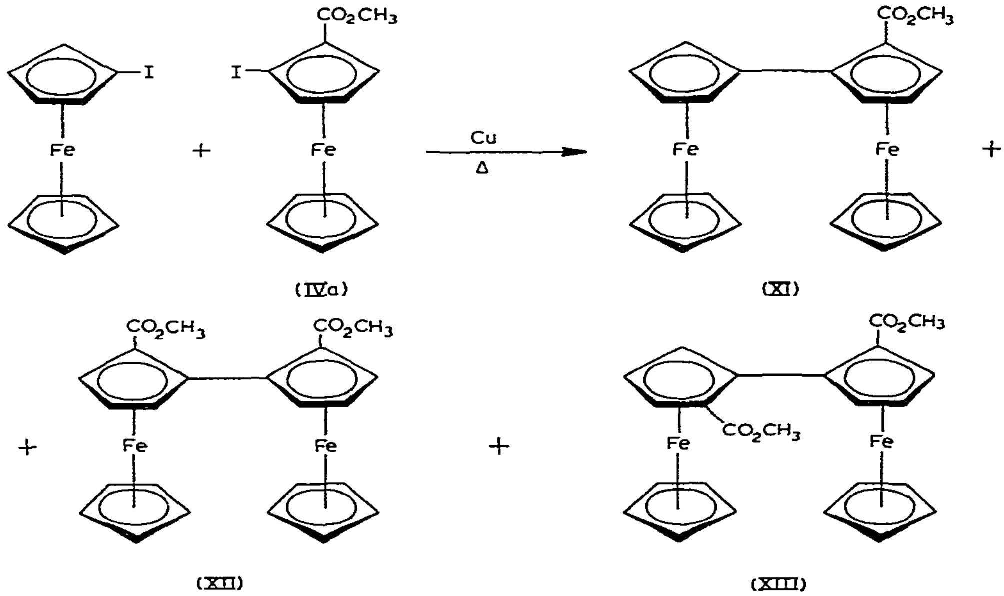


(Va) (X)

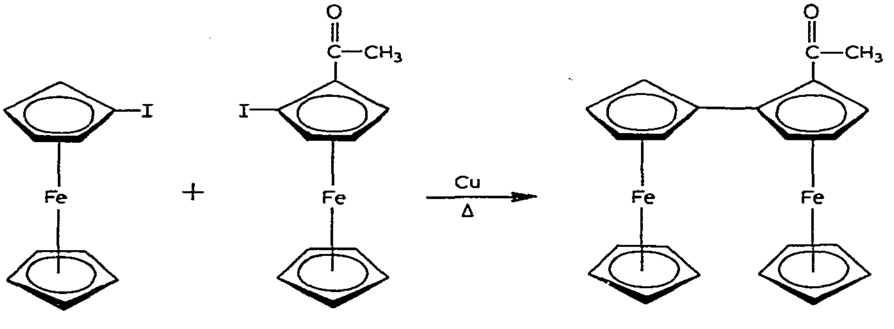
Dr. Rockett. The 1,2-orientation of substituents in our systems was therefore confirmed.

To further demonstrate the utility of 1'-iodo-1-acylferrocenes as precursors to 1',6'-disubstituted biferrocenes, 1'-iodo-1-(methoxycarbonyl)ferrocene (Va) was converted via Ullmann coupling into 1',6'-bis(methoxycarbonyl)biferrocene (X). Chromatography of the crude product and subsequent recrystallization afforded large red needles in 43% yield. The product was identical in properties to those previously reported for 1',6'-bis(methoxycarbonyl)biferrocene (X)^{28} and also with samples of (X) isolated from acylation and metalation reactions of biferrocene^{29,30}.

Two of the products isolated from recent acylation and metalation studies of biferrocene have been identified as 2- and 3-(methoxycarbonyl)biferrocene, respectively^{29,30}. A mixed Ullmann coupling reaction of iodoferrocene with 2-iodo-1-(methoxycarbonyl)ferrocene (IVa) was therefore carried out to provide an unequivocal synthesis of 2-(methoxycarbonyl)biferrocene (XI). An intimate mixture of iodoferrocene and (IVa) was heated in the presence of copper bronze at elevated temperatures. Chromatography of the crude product produced four well-resolved bands. The first band to be eluted yielded biferrocene, produced by the self-coupling of iodoferrocene. The second band afforded 2-(methoxycarbonyl)biferrocene (XI) in 55% yield. The IR and NMR spectra of (XI) were in agreement with the proposed structure. The product proved to be identical with a sample obtained from the methoxycarbonylation of biferrocene and previously assigned the structure (XI)^{29,30}. The third and fourth bands contained the diasteriomeric products 2,10-bis(methoxycarbonyl)biferrocene (XII) and 2,7-bis(methoxycarbonyl)biferrocene (XIII), respectively. The structures of these isomers have been assigned on the basis of their conversion to 2,10- and 2,7-dimethylbiferrocenes of known configuration$^{31-33}$, and will be the subject of a future publication.



The acetylation of biferrocene has been reported by several groups of investigators to produce isomeric monoacetylbiferrocenes; structural assignments have been made primarily on the basis of NMR data[34-37]. It was therefore of interest to undertake an unequivocal synthesis of 2-acetylbiferrocene (XIV) and to compare its properties with the products isolated from acetylation studies. The reaction between (IVb) and iodoferrocene in the presence of copper bronze, followed by column chromatography, produced three major bands. The first band contained biferrocene, identified by its IR spectrum. The second band to be eluted produced (XIV), m.p. 102–103°, in 37% yield. The product was found to be identical to the product of m.p. 102–103° assigned as 2-acetylbiferrocene from the biferrocene acetylation studies[36]. The monoacetylated product of m.p. 153–154°[36] (158–159°)[35] must therefore be 3-acetylbiferrocene, and the assignments of the three possible isomeric monoacetylbiferrocenes can thus be considered as firmly established. A third band was thought to contain a mixture of 2,7- and 2,10-diacetylbiferrocenes, however, the mixture of products in this band appeared to be very complex, and the investigation was not continued further. Ullmann coupling of 2-iodo-1-acetylferrocene (IVb) in a separate reaction yielded the same complex mixture.



(IVb) (XIV)

EXPERIMENTAL

IR spectra were recorded on a Beckman IR-10 spectrophotometer, and were calibrated using polystyrene. NMR spectra were recorded on a Varian A-60 spectrometer, using $CDCl_3$ as the solvent and TMS as an internal standard. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. Column chromatography was carried out using Matheson, Coleman and Bell or CAMAG activity grade I alumina. Preparative TLC was conducted on CAMAG silica gel, while Florisil was purchased from Fisher Scientific Co.

Mercuration of (methoxycarbonyl)ferrocene (Ia)

Into a 250 ml one-necked flask equipped with a magnetic stirrer and an equilibrated addition funnel was added 7.1 g (0.029 mole) of (methoxycarbonyl)ferrocene[38,39] and 50 ml of methylene chloride. Meanwhile, 7.0 g (0.022 mole) of mercuric acetate was suspended in 50 ml of methanol, and perchloric acid was added dropwise to the stirred suspension until the mercuric acetate had dissolved. This solution was then added dropwise to the reaction flask over a period of 1 h. Subsequently, 1.0 g (0.024 mole) of lithium chloride dissolved in 25 ml of methanol was added, and the mixture stirred for 15 min. An additional 100 ml of methylene chloride was added, and the contents of the flask transferred to a separatory funnel. The solution was washed with two 100 ml portions of water (to eliminate any perchlorate salts) and then filtered through a 1″ by 6″ column of Florisil. Evaporation of the solvent *in vacuo* resulted in the formation of a dark red oil. The latter was dissolved in a minimum amount of methylene chloride, 200 ml of heptane was added, and the solution heated on a steam bath until all the methylene chloride had boiled away. The resulting solution was cooled at 0° for 2 h and the extract decanted from the tarry residue which had precipitated. The residue was again dissolved in a minimum amount of methylene chloride, 200 ml of heptane added, and the procedure described above repeated, causing the residue to solidify. Virtually all the unreacted (methoxycarbonyl)ferrocene was removed by this method, leaving 4.70 g of solid containing a mixture of 2- and 1′-(chloromercuri)-1-(methoxycarbonyl)ferrocenes, together with small amounts of polymercurated products. The crude product was dissolved in a minimum amount of methylene chloride and subjected to preparative TLC (five silica gel plates of 1.5 mm thickness; eluted with methylene chloride). Development of the plates led to the formation of four distinct bands.

The first band (highest R_f) was extracted from the plate with methylene chloride, and the solvent evaporated *in vacuo* yielding 2.1 g (20%) of 2-(chloromercuri)-1-(methoxycarbonyl)ferrocene (IIa). Recrystallization of the product from heptane/methylene chloride afforded golden platelets, m.p. 203–204°. (Found: C, 29.88; H, 2.54; Fe, 11.82. $C_{12}H_{11}FeHgClO_2$ calcd.: C, 30.08; H, 2.32; Fe, 11.66%.) An IR spectrum (KBr) exhibited absorptions at 1690 (s), 1450 (s), 1335 (m), 1270 (s), 1205 (m), 1160 (s), 1110 (w), and 1000 (w) cm^{-1}. The second band produced 72 mg of (methoxycarbonyl)ferrocene (Ia), identified by its IR spectrum.

The third band afforded 2.57 g (24%) of 1′-(chloromercuri)-(1-methoxycarbonyl)ferrocene (IIIa). Recrystallization of the product from heptane/methylene chloride produced an orange powder, m.p. 174–175°. (Found: C, 29.80; H, 2.31. $C_{12}H_{11}FeHgClO_2$ calcd.: C, 30.08; H, 2.32%.) An IR spectrum (KBr) exhibited absorptions at 1715 (m), 1465 (m), 1275 (s), and 1135 (m) cm^{-1}; there were no absorptions at 1110 and 1000 cm^{-1}. Band four contained small amounts of polymercurated (methoxycarbonyl)ferrocene, but was not investigated further.

In other runs involving the mercuration reaction, an alternate work-up procedure was utilized which involved isolation and chromatography of the isomeric (acetoxymercuri)(methoxycarbonyl)ferrocenes on silica gel. For example, 2.0 g (8.2 mmoles) of (methoxycarbonyl)ferrocene was treated with mercuric acetate (8.2 mmoles) in the presence of perchloric acid according to the previously described method. The methylene chloride solution of acetoxymercurated ferrocenes was washed with water to remove perchlorate salts, filtered, and then evaporated to dryness. The residue which remained was subjected to dry-column chromatography on a 1″ by 12″ column of silica gel. Elution with methylene chloride removed virtually all the unreacted (methoxycarbonyl)ferrocene (0.8 g), leaving a residue of mercurated products on the column. The column was then treated with a methanolic solution of lithium chloride, which caused conversion to (chloromercuri)(methoxycarbonyl)ferrocenes and simultaneous elution of these products. The eluent was evaporated to dryness *in vacuo*, and the solid residue which remained was washed with water and then subjected to dry-column chromatography on a 2″ by 12″ column of highly activated silica gel (heated at 150° for 24 h). Elution with methylene chloride resolved the mixture into several distinct bands.

The first band yielded upon evaporation of the solvent 0.91 g (23%) of 2-(chloromercuri)-1-(methoxycarbonyl)ferrocene (IIa). Recrystallization of the product from hexane/methylene chloride afforded golden platelets, m.p. 203–204°. An IR spectrum (KBr) was identical to a spectrum of the product obtained previously. The second band contained 1.0 g (25%) of 1′-(chloromercuri)-1-(methoxycarbonyl)ferrocene (IIIa). Recrystallization of the product from hexane/methylene chloride produced an orange powder, m.p. 174–175°. An IR spectrum (KBr) of the product was identical to the spectrum obtained for 1′-(chloromercuri)-1-(methoxycarbonyl)ferrocene (IIIa) prepared previously. A third band contained polymercurated (methoxycarbonyl)ferrocene, and was not investigated further.

Iodination of 2-chloromercuri)-1-(methoxycarbonyl)ferrocene (IIa)

Into a 125 ml erlenmeyer flask equipped with magnetic stirrer was added 2.0 g (4.2 mmoles) of 2-(chloromercuri)-1-(methoxycarbonyl)ferrocene (IIa) and sufficient methylene chloride to dissolve the compound. A saturated solution of iodine in methylene chloride was added subsequently until the initially fading purple color persisted. The mixture was stirred for an additional 15 min, after which time the contents of the flask were transferred to a separatory funnel and shaken with two 100 ml portions of saturated sodium thiosulfate solution, followed by two 100 ml portions of water. The organic layer was then filtered through a 1″ by 6″ column of Florisil, and the eluent evaporated to dryness. The residual dark red oil was dissolved in a minimum amount of methylene chloride and subjected to preparative TLC (one plate; eluted with methylene chloride). The major band which developed was extracted from the plate with methylene chloride, and the extracts were evaporated *in vacuo*, producing 1.34 g (86%) of 2-iodo-1-(methoxycarbonyl)ferrocene (IVa) as a dark red oil which solidified below 0°. (Found: C, 39.08; H, 3.30. $C_{12}H_{11}FeIO_2$ calcd.: C, 38.96; H, 3.00%.) An IR spectrum of the product (film between salt plates) exhibited absorptions at 2915 (m), 1725 (s), 1450 (s), 1260 (s), 1275 (s), 1190 (m), 1150 (s), 1110 (w) and 1000 (w) cm^{-1}. An NMR spectrum ($CDCl_3$) exhibited a multiplet at τ 5.12 (one proton α to ester group), a multiplet at τ 5.26 (one proton α to iodine), a multiplet at τ 5.53 (one proton β to ester group and β to iodine), a singlet at τ 5.74 (five protons on unsubstituted ring), and a singlet at τ 6.13 (three protons on ester group).

Iodination of 1′-(chloromercuri)-1-(methoxycarbonyl)ferrocene (IIIa)

1′-(Chloromercuri)-1-(methoxycarbonyl)ferrocene (IIIa) (2.0 g, 4.2 mmoles) was iodinated in the manner described above, to produce after chromatography 1.4 g (90%) of 1′-iodo-1-(methoxycarbonyl)ferrocene (Va). Recrystallization of the product from methanol/water afforded orange needles, m.p. 71–72°. (Found: C, 39.03; H, 3.30. $C_{12}H_{11}FeIO_2$ calcd.: C, 38.96; H, 3.00%.) An IR spectrum (KBr) exhibited absorptions at 1715 (vs), 1460 (s), 1380 (m), 1275 (s), 1190 (m), 1140 (s), and 1025 (w) cm^{-1}. An NMR spectrum ($CDCl_3$) exhibited a triplet at τ 5.17 (two protons α to ester group), a multiplet at τ 5.58 (two protons β to ester group plus two protons α to iodine), a triplet at τ 5.80 (two protons β to iodine), and a singlet at τ 6.14 (three ester protons).

Reaction of 2-iodo-1-(methoxycarbonyl)ferrocene (IVa) with cuprous cyanide

A solution containing 0.30 g (0.81 mmole) of 2-iodo-1-(methoxycarbonyl)-ferrocene (IVa) dissolved in 2.0 ml of *N*-methylpyrrolidone was added to a test tube equipped with inlet and outlet tubes. Cuprous cyanide (0.25 g, 0.003 mole) was added, and the system flushed with nitrogen. The tube was immersed in an oil bath maintained at 110° for 3 h. The contents were then transferred to an erlenmeyer flask by rinsing with water, and 100 ml of a saturated ferric chloride solution in 1/1 hydrochloric acid/water was added. The mixture was extracted with three successive 50 ml portions of ethyl ether, and the combined extracts were filtered from the residue and washed with four 100 ml portions of water. The ether layer was separated, dried over sodium sulfate, and evaporated to dryness. The residue remaining was chromatographed on a 1" by 6" column of alumina. Elution of the column with benzene produced two bands. The first band contained 30 mg of (methoxycarbonyl)ferrocene, identified by its IR spectrum. The second band produced 90 mg (41%) of 2-cyano-1-(methoxycarbonyl)ferrocene (VI) as a dark brown oil, which was unstable in air. An IR spectrum (film between salt plates) exhibited absorptions at 2210 (s) (nitrile), 1725 (vs) (ester), 1460 (s), 1410 (m), 1270 (s), 1218 (s), 1105 (w), 1085 (w), 1020 (m), and 1000 (w) cm^{-1}).

Reaction of 1'-iodo-1-(methoxycarbonyl)ferrocene (Va) with cuprous cyanide

A reaction between 1'-iodo-1-(methoxycarbonyl)ferrocene (Va) (0.40 g, 1.1 mmoles) and cuprous cyanide (0.25 g, 3.0 mmoles) in 3.0 ml of *N*-methylpyrrolidone as described above produced 0.12 g (40%) of 1'-cyano-1-(methoxycarbonyl)ferrocene (VII) as an air-sensitive dark brown oil. An IR spectrum (film between salt plates) exhibited absorptions at 2215 (nitrile) and 1720 cm^{-1} (ester); there were no absorptions at 1105 and 1000 cm^{-1}.

Reduction of 2-iodo-1-(methoxycarbonyl)ferrocene (IVa) to (hydroxymethyl)ferrocene

A solution containing 0.10 g (0.27 mmole) of 2-iodo-1-(methoxycarbonyl)-ferrocene (IVa) dissolved in 1 ml of anhydrous ethyl ether was added under nitrogen to a suspension of 0.25 g (6.6 mmoles) of lithium aluminum hydride in ethyl ether. The solution immediately turned from dark orange to yellow. After 1 h, methanol was carefully added, followed by water. The resulting mixture was extracted with 10 ml of ether, and the extracts dried over sodium sulfate. Evaporation of the solution to dryness yielded 0.057 g of (hydroxymethyl)ferrocene, m.p. 79–81° (lit.[40] 81–82°). An IR spectrum (KBr) of the product was identical with that obtained for an authentic sample of (hydroxymethyl)ferrocene.

Reduction of 2-iodo-1-(methoxycarbonyl)ferrocene (IVa) to 2-iodo-1-(hydroxymethyl)-ferrocene (VIII) and 2-iodo-1-methylferrocene (IX)

Into a 25 ml erlenmeyer flask equipped with magnetic stirrer was added 25 ml of 1,2-dimethoxyethane, 1.5 g (0.04 mole) of sodium borohydride, and 1.8 g (0.01 mole) of aluminum chloride. The resulting slurry was stirred for 5 min, and then was added 2.0 g (5.4 mmoles) of 2-iodo-1-(methoxycarbonyl)ferrocene (IVa) dissolved in 10 ml of 1,2-dimethoxyethane. The reaction was stirred for 3 h after which time 100 ml of water was added, and the solution was extracted with three 10 ml portions of ether. The combined extracts were filtered, dried over sodium sulfate, and evaporated to dryness. The residue which remained was chromatographed on a 1" by 6" column of alumina.

Elution of the column with benzene produced an initial band which yielded 1.1 g (62%) of 2-iodo-1-methylferrocene (IX) as a dark red oil. (Found: C, 40.71; H, 3.54. $C_{12}H_{11}FeI$ calcd.: C, 40.53; H, 3.41%.) An IR spectrum of the product (film between salt plates) exhibited absorptions at 3110 (w), 2920 (w), 1460 (m), 1240 (w), 1110 (s), 1065 (m), 1040 (m), 1000 (m), 990 (m), 820 (s), and 800 (s) cm^{-1}. An NMR spectrum ($CDCl_3$) exhibited a triplet at τ 5.62 (one proton α to iodine), a singlet at τ 5.89 (five protons on unsubstituted ring plus one proton β to iodine plus one proton α to methyl group), and a singlet at τ 7.98 (three methyl protons).

Further elution of the column with methylene chloride produced a second band which contained 0.66 g (36%) of 2-iodo-1-(hydroxymethyl)ferrocene (VIII). Sublimation of the product at 100°/0.01 mm afforded yellow needles, m.p. 87–88° (lit.[10] 90–92°). A mixture melting point with authentic 2-iodo-1-(hydroxymethyl)-ferrocene was undepressed, and the IR spectra of both compounds were identical. An IR spectrum of the product (KBr) exhibited absorptions at 3360 (m), 3110 (w), 1110 (m), 1065 (m), 1000 (s), and 820 (m) cm^{-1}. The NMR spectrum ($CDCl_3$) exhibited multiplet absorption between τ 5.45–5.75 (three protons on disubstituted cyclopentadienyl ring plus two methylene protons), a singlet at τ 5.81 (five protons on unsubstituted ring), and a broad singlet at τ 8.05 (one hydroxyl proton).

Ullmann coupling of 1'-*iodo*-1-(*methoxycarbonyl*)*ferrocene* (*Va*)

A test tube with a side arm and equipped with an outlet tube was purged with nitrogen. An intimate mixture of 0.25 g (0.67 mmole) of 1'-iodo-1-(methoxycarbonyl)-ferrocene (Va) and 2.0 g (0.03 g atom) of activated copper bronze[41] was added, and the system was again flushed with nitrogen. The tube was then immersed in an oil bath maintained at 130° for 24 h. The contents of the tube were extracted repeatedly with methylene chloride until the extracts were colorless, and the combined extracts evaporated to dryness *in vacuo*. The dark residue which remained was subjected to preparative TLC using methylene chloride as the eluent. Extraction of the major band which developed with methylene chloride and subsequent evaporation of solvent produced 0.13 g (41%) of 1',6'-bis(methoxycarbonyl)biferrocene (X). Recrystallization of the product from heptane/mathylene chloride afforded large red needles, m.p. 193–194° (lit.[28] 184–184.5°). An IR spectrum of the product exhibited absorptions at 1712 (s) (ester), 1416 (m), 1280 (vs), 1138 (s), and 1030 (m) cm^{-1}; no absorptions occurred at 1110 and 1000 cm^{-1}. The NMR spectrum exhibited a triplet at τ 5.35 (four protons α to ester group), a triplet at τ 5.62 (four protons α to bridging carbons), a triplet at τ 5.78 (four protons β to ester groups plus four protons β to bridging carbons), and a singlet at τ 6.37 (six ester protons). (Found: C, 58.99; H, 4.81; mol. wt. (osmometric in benzene), 484. $C_{24}H_{22}Fe_2O_4$ calcd.: C, 59.29; H, 4.56%; mol. wt., 486.)

Ullmann coupling of 2-iodo-1-(methoxycarbonyl)ferrocene (IVa) with iodoferrocene; formation of 2-(methoxycarbonyl)biferrocene (XI)

As described above, an intimate mixture of 0.5 g (1.35 mmoles) of 2-iodo-1-(methoxycarbonyl)ferrocene (IVa), 1.0 g (3.2 mmoles) of iodoferrocene, and 4.0 g (0.064 g atom) of activated copper bronze[41] were heated under nitrogen in an oil bath maintained at 130° for 24 h. The contents of the tube were subsequently extracted repeatedly with 25 ml portions of methylene chloride until the extracts were colorless. The combined extracts were evaporated to dryness and the residue which remained was subjected to preparative TLC. Elution of the plates with methylene chloride produced four major bands.

The first band contained 0.40 g of biferrocene, m.p. 239–240°. The second band was extracted from the plates with methylene chloride and the solvent evaporated *in vacuo*, giving 0.31 g (55%) of 2-(methoxycarbonyl)biferrocene (XI) as a dark red oil. Prolonged trituration of the product with hexane afforded orange crystals, m.p. 78–79°. (Found: C, 61.48; H, 4.77. $C_{22}H_{20}Fe_2O_2$ calcd.: C, 61.72; H, 4.71%.) An NMR spectrum of the product ($CDCl_3$) exhibited a series of multiplets between τ 5.00 and τ 5.80, two singlets at τ 5.86 and τ 5.89 (ten protons on non-equivalent unsubstituted rings), and a singlet at τ 6.19 (three ester protons). The IR spectrum (film between salt plates) exhibited absorptions at 1730 (vs), 1450 (s), 1350 (w), 1275 (sh), 1250 (vs), 1130 (s), 1110 (m), 1030 (m), 1000 (m), and 815 (s) cm^{-1}.

The third band was extracted from the plates and the solvent evaporated, affording 0.34 g of 2,10-bis(methoxycarbonyl)biferrocene (XII). Recrystallization of the product from heptane/methylene chloride afforded orange needles, m.p. 174–175°. (Found: C, 59.22; H, 4.61; mol. wt. (osmometric in benzene), 490. $C_{24}H_{22}Fe_2O_4$: C, 59.29; H, 4.56%; mol. wt., 486.) An NMR spectrum of the product exhibited a multiplet at τ 4.96 (two protons α to ester groups), a multiplet at τ 5.13 (two protons β to ester groups and β to bridging carbons), a triplet at τ 5.52 (two protons α to bridging carbons), a singlet at τ 5.90 (ten protons on unsubstituted rings), and a singlet at τ 6.16 (six ester protons). The IR spectrum (KBr) exhibited absorptions at 1720 (s), 1445 (m), 1325 (m), 1240 (s), 1105 (w) and 1000 (w) cm^{-1}.

The fourth band contained 0.29 g of the isomer, 2,7-bis(methoxycarbonyl)-biferrocene (XIII). Recrystallization of the product from heptane/methylene chloride afforded orange needles, m.p. 191–192°. (Found: C, 59.40; H, 4.64; mol. wt. (osmometric in benzene), 486. $C_{24}H_{22}Fe_2O_4$ calcd.: C, 59.29; H, 4.56%; mol. wt. 486.) An NMR spectrum of the material exhibited a doublet at τ 5.12 (two protons α to ester group plus two protons α to bridging carbon), a triplet at τ 5.50 (two protons β to ester group, and β to bridging carbon), a singlet at τ 5.76 (ten protons on unsubstituted rings), and a singlet at τ 6.35 (six protons on ester groups). The IR spectrum (KBr) exhibited absorptions at 1710 (s), 1455 (m), 1440 (m), 1280 (m), 1150 (m), 1120 (m), 1110 (w), and 1000 (w) cm^{-1}.

Mercuration of acetylferrocene (Ib)

The procedure was analogous to that described above for the mercuration of (methoxycarbonyl)ferrocene (Ia), employing 10.1 g (0.044 mole) of acetylferrocene (Ib), 12.8 g (0.04 mole) of mercuric acetate, and 2.1 g (0.05 mole) of lithium chloride. The crude product was dissolved in a minimum amount of methylene chloride and subjected to preparative TLC (five plates; eluted twice with methylene chloride).

Development of the plates produced four distinct bands. The first band was extracted from the plates with methylene chloride, and the extracts evaporated *in vacuo* yielding 4.5 g (24%) of 2-(chloromercuri)-1-acetylferrocene (IVb). Recrystallization of the product from heptane/methylene chloride afforded golden platelets, m.p. 137–139°. (Found: C, 31.28; H, 2.55; Fe, 12.18; mol. wt. (osmometric in benzene), 490. $C_{12}H_{11}ClFeHgO$ calcd.: C, 31.12; H, 2.40; Fe, 12.06%; mol. wt., 463.) An IR spectrum (KBr) of the product exhibited absorptions at 1660 (s), 1435 (s), 1360 (m), 1335 (m), 1265 (s), 1140 (m), 1110 (w), and 1000 (w) cm^{-1}. The second band contained 0.20 g of acetylferrocene (Ib), identified by its IR spectrum.

The third band was extracted from the plate and the solvent evaporated *in vacuo* yielding 2.5 g (14%) of 1'-(chloromercuri)-1-acetylferrocene (IIIb). Recrystallization of the product from heptane/methylene chloride produced an orange powder, m.p. 178–179°. (Found: C, 30.85; H, 2.36. $C_{12}H_{11}ClFeHgO$ calcd.: C, 31.12; H, 2.40%.) An IR spectrum of the product exhibited absorptions at 1670 (s), 1460 (s), 1380 (m), 1365 (w) and 1280 (s) cm^{-1}; no absorptions were present at 1110 and 1000 cm^{-1}. The fourth band contained small amounts of polymercurated acetylferrocene, and was not investigated further.

Iodination of 2-(chloromercuri)-1-acetylferrocene (IIb)

2-(Chloromercuri)-1-acetylferrocene (IVb) (1.0 g, 2.1 mmoles) was iodinated in a manner described for the iodination of 2-(chloromercuri)-1-(methoxycarbonyl)-ferrocene (IIa). Preparative TLC (elution with methylene chloride) produced 0.63 g (82%) of 2-iodo-1-acetylferrocene (IVb) as a dark oil. Recrystallization of the product from methanol/water afforded orange crystals, m.p. 75–76° (Found: C, 40.96; H, 3.23. $C_{12}H_{11}FeIO$ calcd.: C, 40.72; H, 3.13%.) An IR spectrum (KBr) exhibited absorptions at 1675 (vs), 1430 (s), 1375 (m), 1355 (m), 1320 (m), 1265 (m), 1250 (s), 1110 (m), 1000 (m), and 825 (m) cm^{-1}. The NMR spectrum ($CDCl_3$) exhibited a doublet at τ 5.18 (one proton α to iodine plus one proton α to acetyl group), a triplet at τ 5.46 (one proton β to iodine and β to ester group), a singlet at τ 5.74 (five protons on unsubstituted ring), and a singlet at τ 7.50 (three protons on acetyl group).

Iodination of 1'-(chloromercuri)-1-acetylferrocene (IIIb)

1'-(Chloromercuri)-1-acetylferrocene (IIIb) (1.0 g, 2.1 mmoles) was iodinated in the manner described above to produce, after chromatography, 0.64 g (83%) of 1'-iodo-1-acetylferrocene (Vb) as a dark red oil. Recrystallization of the product from methanol/water afforded orange crystals, m.p. 51–52°. (Found: C, 40.48; H, 3.23. $C_{12}H_{11}FeIO$ calcd.: C, 40.72; H, 3.13%.) An IR spectrum (KBr) exhibited absorptions at 1670 (vs), 1455 (s), 1375 (m), 1350 (m), 1275 (vs), 1115 (m), and 1020 (m) cm^{-1}; no absorptions were noted at 1110 and 1000 cm^{-1}. The NMR spectrum ($CDCl_3$) exhibited a triplet at τ 5.24 (two protons α to acetyl group), a triplet at τ 5.49 (two protons α to iodine), a triplet at τ 5.56 (two protons β to acetyl group), a triplet at τ 5.79 (two protons β to iodine), and a singlet at τ 7.59 (three protons on acetyl group).

Ullmann coupling of 2-iodo-1-acetylferrocene (IVb) and iodoferrocene; formation of 2-acetylbiferrocene (XV)

As described above for 2-iodo-1-(methoxycarbonyl)ferrocene (IVa), an intimate mixture of 0.5 g (1.4 mmoles) of 2-iodo-1-acetylferrocene (IVb), 1.0 g (3.2 mmoles) of iodoferrocene, and 2.0 g (0.03 g. atom) of activated copper bronze[41] was heated under nitrogen in an oil bath maintained at 130° for 24 h. The contents of the tube were extracted repeatedly with 25 ml portions of methylene chloride until the extracts were colorless. The combined extracts were evaporated to dryness, and the residue which remained subjected to preparative TLC (elution with methylene chloride). Development of the plates produced three major bands. The first band contained 0.52 g of biferrocene, identified by its IR spectrum. The second band was extracted from the plate and the solvent evaporated to give 0.22 g (37%) of 2-acetylbiferrocene (XIV) as a dark red oil. Prolonged trituration of the product with hexane produced orange crystals, m.p. 102–103° (lit.[36] 102–103°). (Found: C, 64.10; H, 5.04. $C_{22}H_{20}Fe_2O$ calcd.: C, 64.12; H, 4.89%.) The produced appeared identical by TLC to a sample of 2-acetylbiferrocene (XIV) prepared by the acetylation of biferrocene[36]. An NMR spectrum of the product ($CDCl_3$) exhibited a multiplet centered at τ 5.20 (three protons α, β, and γ to acetyl group and bridging carbon), a multiplet at τ 5.51 (two protons α to bridging carbon), an apparent triplet at τ 5.79 (two protons β to bridging carbon), two singlets at τ 5.85 and τ 5.88 (ten protons of non-equivalent unsubstituted rings), and a singlet at τ 7.64 (three protons on acetyl group). The IR spectrum (KBr) exhibited absorptions at 1678 (vs), 1440 (m), 1360 (m), 1270 (sh), 1250 (m), 1110 (m), 1000 (m), and 815 (m) cm^{-1}.

Extraction of the third band from the plate with methylene chloride followed by subsequent evaporation of the solvent yielded 60 mg of a red powder, m.p. 148–149°. The NMR spectrum of this material was very complicated and characterization attempts were not continued.

Mercuration of formylferrocene (Ic)

Into a 125 ml erlenmeyer flask equipped with a magnetic stirrer wad added 1.5 g (0.007 mole) of formylferrocene, 1.91 g (0.006 mole) of mercuric acetate, 25 ml of methylene chloride, and 10 ml of methanol. The mixture was stirred for one h after which time a solution containing 0.43 g (0.01 mole) of lithium chloride dissolved in 20 ml of methanol was added. An additional 50 ml of methylene chloride was introduced and the solution filtered to remove decomposition products which had separated. The filtrate was transferred to a separatory funnel, and washed with two portions of water. The organic layer was filtered through a 1" by 4" column of Florisil, and the eluent evaporated to dryness. The residual oil was dissolved in a minimum amount of methylene chloride, and 200 ml of hexane was added. The solution was heated on a steam bath until all the methylene chloride had boiled away. The solution was then cooled to 0° for one hour, at which time the extracts were decanted from the residue which had precipitated, and the process repeated. Two successive extractions removed virtually all the unreacted formylferrocene (Ic), leaving a solid residue containing a mixture of isomeric (chloromercuri)(formyl)-ferrocenes together with small amounts of polymercurated products. The crude product was then subjected to preparative TLC (elution with methylene chloride); development of the plates produced four distinct bands.

The first band was extracted from the plate and the solvent evaporated to produce 0.39 g (13%) of 2-(chloromercuri)-1-formylferrocene (IIc). (Found: C, 29.16; H, 1.99. $C_{11}H_9ClFeHgO$ calcd.: C, 29.42; H, 2.02%.) An IR spectrum (KBr) of the product exhibited absorptions at 1650 (s), 1330 (w), 1100 (w), and 1000 (w) cm^{-1}. The second band contained 40 mg of formylferrocene (Ic), identified by its IR spectrum. The third band was extracted from the plate and solvent evaporated to produce 0.10 g (3.2%) of 1'-(chloromercuri)-1-formylferrocene (IIIc). (Found: C, 29.18; H, 1.77; Cl, 7.70; Hg, 44.59. $C_{11}H_9ClFeHgO$ calcd.: C, 29.42; H, 2.02; Cl, 7.89; Hg, 44.67%.) The product was recrystallized from heptane/methylene chloride as a red solid, m.p. 114–116°. An IR spectrum (KBr) exhibited absorptions at 1650 (s), 1440 (w), and 1235 cm^{-1} (w); no absorptions were present at 1110 and 1000 cm^{-1}.

Iodination of 2-(chloromercuri)-1-formylferrocene (IIc)

2-(Chloromercuri)-1-formylferrocene (IIc) (0.39 g, 0.86 mmole) was iodinated in the manner described above. Preparative TLC (elution with methylene chloride) gave 0.23 g (79%) of 2-iodo-1-formylferrocene (IVc) as a very unstable dark red oil which decomposed rapidly in air. An IR spectrum of the material exhibited absorptions at 1670 (vs), 1430 (m), 1245 (m), 1105 (w), 1000 (w), 820 (m), and 740 (m) cm^{-1}.

Reduction of 2-iodo-1-formylferrocene (IVc) to 2-iodo-1-(hydroxymethyl)ferrocene (VIII) using sodium borohydride

To a suspension of 0.25 g (6.6 mmoles) of sodium borohydride in 5 ml of methanol was added a solution containing 50 mg (0.15 mmole) of freshly prepared 2-iodo-1-formylferrocene (IVc) dissolved in 5 ml of methanol. After 30 min, 50 ml of water was added, and the mixture extracted with two 25 ml portions of ethyl ether. The combined extracts were dried over sodium sulfate and evaporated to dryness. The residue which remained was shown by TLC to be identical to authentic 2-iodo-1-(hydroxymethyl)ferrocene (VIII)[10] and to (VIII) prepared above. No starting material was detected.

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