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.

WRIGHT-PATTERSON AIR FORCE BASE, OHIO

[CONTRIBUTION FROM MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER]

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

MARVIN RAUSCH, MARTIN VOGEL, AND HAROLD ROSENBERG

Received January 15, 1957

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

---

[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.

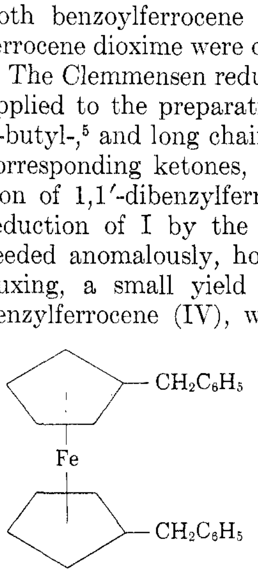
[4] R. Riemschneider and D. Helm, *Ber.*, **89**, 155 (1956).

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

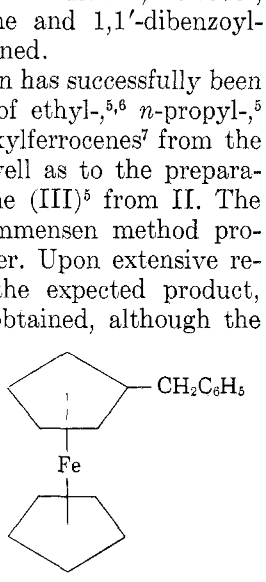
yields more satisfactory than any thus far reported.

Although Csendes[2] has reported the preparation of benzoylferrocene oxime, our attempts to prepare oximes, phenylhydrazones, and *p*-nitrophenylhydrazones by the usual methods were not successful. By resorting to more drastic conditions, however, both benzoylferrocene oxime and 1,1′-dibenzoylferrocene dioxime were obtained.

The Clemmensen reduction has successfully been applied to the preparation of ethyl-,[5,6] *n*-propyl-,[5] *n*-butyl-,[5] and long chain alkylferrocenes[7] from the corresponding ketones, as well as to the preparation of 1,1′-dibenzylferrocene (III)[5] from II. The reduction of I by the Clemmensen method proceeded anomalously, however. Upon extensive refluxing, a small yield of the expected product, benzylferrocene (IV), was obtained, although the primary reduction product was an as yet unidentified high melting orange-red solid (V). In several experiments V was the only product isolated from the reaction.



III



IV

The reaction of I with the binary mixture, magnesium–magnesium iodide, has been carried out in this laboratory and elsewhere[3] to produce small yields of a reduction product (VI) similar in appearance and properties to V. The ultraviolet and visible spectra of V and VI are completely identical, while the infrared spectra are very nearly identical.

It was initially suspected that the reduction products V and VI were the *sym*-pinacol, since the magnesium–magnesium iodide mixture is commonly used for the preparation of pinacols from aromatic ketones[8,9] and the Clemmensen reduction of aromatic ketones occasionally produces pinacols rather than hydrocarbons.[10] Numerous elemental analyses of both V and VI have indicated, however, that only carbon, hydrogen, and iron are present, eliminating the possibility of a pinacol or other oxygen-containing compound. The structures of V and VI are currently being investigated and detailed information will be published later.

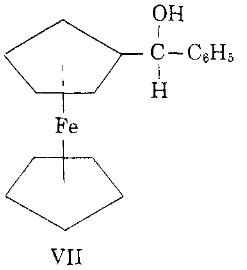
Attempts to reduce II using magnesium–magnesium iodide in ethyl ether–benzene solution either at room temperature or at reflux resulted in the formation of an insoluble complex, and after hydrolysis only starting ketone could be recovered. Preliminary experiments indicate that reduction of II does occur when solvents capable of producing higher temperatures are used.

While I did react with magnesium–magnesium iodide, it failed to undergo two other reactions which are commonly used to reduce aromatic ketones to bimolecular derivatives.[11–13] When I was stirred several days at 25° with powdered zinc and glacial acetic acid, only starting ketone was recovered. In an attempted photochemical reduction of I in 2-propanol, nearly all the ketone was recovered after 10 days exposure to sunlight, and only a very small amount of insoluble material resulted. This appeared to contain mostly iron oxide together with a trace of carbonaceous material. It has since been observed in this laboratory that certain derivatives of ferrocene in hydroxylic solvents are subject to photochemical decomposition. In a control photochemical experiment using benzophenone, a 97% yield of benzopinacol was obtained.

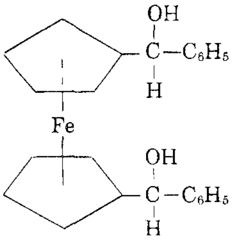
Both I and II could be reduced to the corresponding hydrocarbons IV and III by either catalytic hydrogenation or by "chemical" hydrogenation using sodium and ethanol. Although both reactions proceeded smoothly, the latter was more rapid and produced much better yields.

It has been reported[3] that the reaction of I with aluminum isopropoxide in isopropanol produced 1-propoxybenzylferrocene. In a similar experiment in which the reaction was carried out at higher temperatures using xylene as the solvent, we isolated a small yield of IV. In only one other case has the reduction of a ketone by aluminum isopropoxide been reported to yield a hydrocarbon, namely, the reduction of 9,9-dimethylanthrone-10 in xylene solution to 9,9-dimethyl-10,10-dihydroanthracene.[14]

The reduction of I with sodium borohydride in aqueous methanolic solution proceeded smoothly to produce the expected carbinol, 1-hydroxybenzylferrocene (VII). II was likewise reduced readily



VII



VIII

---

(6) F. S. Arimoto and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **77**, 6295 (1955).

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

(8) M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, **49**, 236 (1927).

(9) M. D. Rausch, W. E. McEwen, and J. Kleinberg, *Chem. Revs.*, in press.

(10) R. C. Fuson, *Advanced Organic Chemistry*, John Wiley and Sons, Inc., New York (1950), p. 361.

(11) W. E. Bachmann and F. H. Moser, *J. Am. Chem. Soc.*, **54**, 1124 (1932).

(12) R. P. Zelinski and M. Jurisch, *J. Am. Chem. Soc.*, **78**, 1015 (1956).

(13) W. E. Bachmann, *Org. Syntheses*, **Coll. Vol. II,** 71 (1943).

(14) A. L. Wilds, *Org. Reactions* **II,** 178 (1944).

with lithium aluminum hydride in ether-benzene solution, and the tarry residue which resulted was purified to yield 1,1′-di(1-hydroxybenzyl)ferrocene (VIII).

EXPERIMENTAL[15]

Benzoylferrocene (I). I was best prepared by the dropwise addition of a solution of equimolar quantities of benzoyl chloride and aluminum chloride to an equimolar quantity of ferrocene, using methylene chloride as the solvent. After hydrolysis and product workup, 70–75% yields of dark red needles of I were obtained by recrystallization from methanol, m.p. 108.1–108.3° (lit.[2] 111.5–112.0°). Extensive refluxing following the addition usually resulted in lower yields of I accompanied by increased amounts of tars.

1,1′-Dibenzoylferrocene (II). A modification of the procedure already reported[4] was adopted by adding the ferrocene in methylene chloride solution to slightly greater than two equivalents each of benzoyl chloride and aluminum chloride in the same solvent. In this manner, 81–91% yields of II were obtained in the form of purple needles, m.p. 106.5–106.7° (lit.[4] 105–106°).

1,1′-Dibenzoylferrocene dioxime. A solution of 2.0 g. of II, 4.0 g. of hydroxylamine hydrochloride, and 16.0 g. of potassium hydroxide in 100 ml. of 95% ethanol was refluxed for 4 hr. The reaction mixture was poured into 400 ml. of water and acidified with dilute hydrochloric acid. A yellow solid weighing 1.8 g. separated, m.p. 164–165° (uncorr.), with decomp. After several recrystallizations from methanol and water, the dioxime was collected in the form of golden-yellow crystals, m.p. 172–173°, with dec.

Anal. Calcd. for $C_{24}H_{20}FeN_2O_2$: C, 67.94; H, 4.75; Fe, 13.16; N, 6.60. Found: C, 68.12, 68.07; H, 4.65, 4.75; Fe, 12.86, 12.90; N, 6.36, 6.48.

Benzoylferrocene oxime. In a manner similar to the preparation of the dioxime, benzoylferrocene oxime was obtained as golden-yellow crystals, m.p. 159.6–160.0° (lit.[2] 160°).

Reduction of I by the Clemmensen method. A mixture of 60 g. of zinc dust, 4.5 g. of mercuric chloride, 3 ml. of concentrated hydrochloric acid and 75 ml. of water were stirred for 10 min. in a 1000-ml., 3-necked flask fitted with stirrer and reflux condenser. The aqueous phase was removed by a pipet and the amalgamated zinc was covered with 30 ml. of water, 60 ml. of concentrated hydrochloric acid and 100 ml. of toluene. There was then added 17.4 g. (0.06 mole) of I and the mixture was stirred under reflux for 72 hr. During this period, five 25-ml. portions of concentrated hydrochloric acid were added occasionally in order to replenish the concentration of acid. Upon cooling to room temperature an appreciable amount of yellow solid had separated, and the reaction mixture was filtered and extracted with hot toluene. The combined toluene portion was washed to neutrality with water and dried over anhydrous magnesium sulfate. The solid which remained after evaporation of the solvent was extracted with 200 ml. of hot methanol, the methanol solution was concentrated, and water was added to the cloud point. Upon cooling, 3.7 g. of benzylferrocene (IV) separated. IV was recrystallized from ethanol and water and was isolated as yellow crystals, m.p. 73–74° (lit.[16] 76°).

The methanol insoluble portion was recrystallized several times from either xylene and heptane, cyclohexane, or *n*-heptane to produce 5.0 g. of an orange-red solid (V). V did not melt when a melting point determination was made in the usual manner, but did slowly decompose when heated above 250°.

Anal. Found: C, 74.26, 74.38; H, 5.35, 5.13; Fe, 19.88, 19.92.

When the above reaction was carried out using less ketone and a shorter time of reaction, V was the only reduction product isolated.

Reduction of I by the binary mixture, magnesium–magnesium iodide. To a mixture of 1.7 g. (0.070 g. atom) of powdered magnesium in 50 ml. of ethyl ether and 50 ml. of dried benzene was added 5.6 g. (0.022 mole) of iodine with stirring. After the first few iodine crystals had been added the reaction mixture was warmed to initiate the reaction, which proceeded exothermically thereafter. After about 30 min. the reaction was complete and the mixture was nearly colorless. To this mixture was added 9.3 g. (0.032 mole) of I in 50 ml. of benzene. A deep violet color formed immediately upon contact of the ketone with the mixture, reminiscent of the color of the metal ketyls reported by Gomberg and Bachmann[8] and later workers. After shaking on a mechanical shaker overnight, the reaction mixture was hydrolyzed with 300 g. of ice containing 25 ml. of concentrated hydrochloric acid. The ether-benzene layer was washed with dilute sodium bicarbonate solution, dilute sodium bisulfite solution, water, and dried overnight over Drierite. The solvent was evaporated and the solid residue was extracted with 150 ml. of hot methanol. From the methanol extracts, 7.3 g. of crude I was obtained, m.p. 102–108° (uncorr.).

The methanol insoluble material was recrystallized several times from hot *n*-heptane to produce 0.7 g. of VI. VI was obtained as fine orange-red crystals, which did not melt but slowly decomposed at elevated temperatures.

Anal. Found: C, 74.35, 74.28; H, 5.08, 5.25; Fe, 19.92, 20.06.

Catalytic hydrogenation of I. In a 500-ml. hydrogenation bottle were placed 8.70 g. (0.03 mole) of I, 1.0 g. of 5% platinum on charcoal, and 250 ml. of redistilled 1-butanol. The mixture was placed on a Parr hydrogenation apparatus under a pressure of 35 psi.; after about 30 hr. a theoretical uptake of hydrogen was noted. The catalyst was filtered and the butanol solution was concentrated almost to dryness. Several recrystallizations of the residue from ethanol and water produced 5.8 g. (70% yield) of IV in the form of yellow leaflets, m.p. 72–73°.

Catalytic hydrogenation of II. A mixture of 11.8 g. (0.03 mole) of II, 2.0 g. of 5% platinum on charcoal and 250 ml. of redistilled 1-butanol was hydrogenated as described above under a pressure of 65 psi. After 17 hr. a theoretical hydrogen uptake was noted and the catalyst was filtered. Removal of the solvent and several recrystallizations of the residue from hot methanol produced long yellow needles of III weighing 5.4 g. (68% yield), m.p. 97–98° (lit.[16] 102°).

Reduction of I by sodium and ethanol. A mixture of 1.50 g. (0.0052 mole) of I and 50 ml. of absolute ethanol was warmed to about 60° during which time all the ketone dissolved. With stirring, about 5 g. of small clean chunks of sodium metal was added at such a rate as to maintain the reaction temperature between 60° and 70°. During the addition the reaction mixture changed from a red color characteristic of the ketone to a thick yellow-orange solution. Following addition of all of the sodium, 25 ml. of additional ethanol was added and the solution was stirred at room temperature for an additional hour. Water was then added until the solution became cloudy, and the solution was cooled. After filtering and drying, 1.40 g. (98% yield) of yellow leaflets of IV was collected, m.p. 72–73°. One recrystallization from ethanol and water raised the melting point to 73.5–74.0°.

Anal. Calcd. for $C_{17}H_{16}Fe$: C, 73.93; H, 5.85; Fe, 20.22. Found: C, 74.07, 74.01; H, 6.06, 6.08; Fe, 20.11, 20.36.

In another experiment, a 95% yield of IV was obtained by this procedure.

Reduction of II by sodium and ethanol. In a manner similar

---

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

(16) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 3030 (1956).

to that described for the reduction of I, about 7.5 g. of sodium was added to a solution of 2.00 g. (0.0051 mole) of II in 75 ml. of absolute ethanol at 60–70°. Following addition of the sodium, 25 ml. of additional ethanol was added to the thick yellow solution and the mixture was stirred for 1 hr. at room temperature. Water was added and the yellow crystals which separated were dried and recrystallized from hot ethanol. Long yellow needles of III were obtained weighing 1.00 g., m.p. 105–106°. From the methanol mother liquor an additional 0.49 g. of III was recovered, for a total yield of 80%.

Anal. Calcd. for $C_{24}H_{22}Fe$: C, 78.70; H, 6.06; Fe, 15.24. Found: C, 78.40, 78.35; H, 6.16, 6.16; Fe, 15.05, 15.02.

A mixed melting point test of a sample of III prepared above and a sample obtained by means of catalytic hydrogenation melted intermediate between the two melting points. The infrared spectra of the two samples were identical.

In another experiment, a 72% yield of III was obtained by this procedure.

Reduction of II by lithium aluminum hydride. To a slurry of 1.52 g. (0.04 mole) of powdered lithium aluminum hydride in 250 ml. of ether was added 11.8 g. (0.030 mole) of II in 150 ml. of benzene and 50 ml. of ether over a 1 hr. period. The reaction mixture was refluxed with stirring for 16 hr., cooled, and moist ether followed by dilute ammonium chloride solution was added. After filtering, the ether phase was washed with water and dried over Drierite. The solvent was evaporated leaving a dark viscous oil which was induced to crystallize by dissolving it in hot methanol and rapidly cooling in a Dry Ice-acetone bath. Seven g. of a yellow solid was thus obtained, m.p. 115–125° (uncorr.). After repeated crystallization from either methanol or ethanol, 5.0 g. of VIII was obtained in the form of yellow leaflets, m.p. 136–137°.

Anal. Calcd. for $C_{24}H_{22}FeO_2$: C, 72.37; H, 5.57; Fe, 14.02. Found: C, 72.42, 72.62; H, 5.85, 5.86; Fe, 14.04, 14.04.

Reduction of I by sodium borohydride. To a solution of 2.90 g. (0.01 mole) of I in 80 ml. of methanol was added 3.8 g. (0.10 mole) of sodium borohydride in 20 ml. of water. The mixture was stirred for 2 hr. and then filtered. The filtrate was cooled in ice and the excess sodium borohydride was decomposed with acetone. Following the addition of 50 ml. of water and 100 ml. of ether, the ether portion was washed with water and dried over anhydrous sodium sulfate. Removal of the solvent and two recrystallizations from ether–petroleum ether produced 1.9 g. (66% yield) of yellow crystals of VII, m.p. 80.3–80.5°.

Anal. Calcd. for $C_{17}H_{16}FeO$: C, 69.88; H, 5.52; Fe, 19.12. Found: C, 70.10, 69.92; H, 5.57, 5.67; Fe, 19.18, 19.22.

Reduction of I by aluminum isopropoxide. A solution of 4.37 g. (0.015 mole) of I and 7.4 g. (0.036 mole) of aluminum isopropoxide in 150 ml. of redistilled isopropyl alcohol was slowly distilled for 1 hr.; however, the presence of acetone in the distillate could not be detected. In order to raise the reaction temperature, 300 ml. of xylene was added and the isopropyl alcohol was removed by distillation. Continued slow distillation at 134–135° produced a distillate containing acetone. After hydrolysis with 150 ml. of 10% hydrochloric acid, the organic phase was washed with water and the solvent evaporated. Recrystallization of the residue produced 0.6 g. of benzylferrocene (IV), m.p. 73–74°. A mixed melting point test with an authentic sample was not depressed.

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. Roy Pruett of the Linde Co., and to Dr. Eric Barthel of the E. I. du Pont de Nemours & Co., Inc., for generous samples of ferrocene used in our research program.

WRIGHT-PATTERSON AIR FORCE BASE, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Some Typical Aldehyde Addition and Condensation Reactions of Formylferrocene[1]

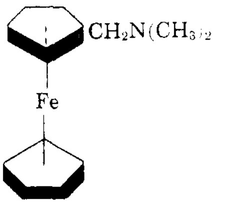
CHARLES R. HAUSER AND JACQUE K. LINDSAY

Received February 8, 1957

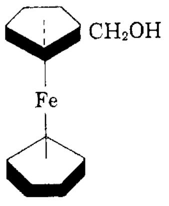
Formylferrocene was found to undergo typical addition and condensation reactions with methylmagnesium iodide, dimethylamine and sodium cyanide, lithio *t*-butyl acetate, and acetophenone and alkali. These processes together with further reactions of certain of the products illustrate useful methods for the synthesis of a number of ferrocene derivatives. Formylferrocene failed to condense with acetophenone in the presence of boron fluoride.

Recently[2] *N*,*N*-dimethylaminomethylferrocene (I) was prepared from ferrocene and the methiodide of this tertiary amine converted to the corresponding alcohol and aldehyde, II and III, respectively.

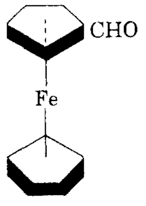
In the present investigation aldehyde III (formylferrocene) was shown to undergo the addition and condensation reactions represented in Chart I. The crude aldehyde, which was obtained by the oxidation of alcohol II with manganese dioxide, was employed in these reactions, the yields being based on the alcohol.



I



II



III

It can be seen from Chart I that the yields of the products (IV–VII) were good to excellent (63–

---

[1] Supported by the Office of Ordnance Research, U. S. Army.

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