BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1976—1981 (1969)

The Reaction of Haloferrocenes with Copper(I) Salts in Pyridine

Masaru SATO, Takehiko ITO, Izumi MOTOYAMA, Ken-ichi WATANABE and Kazuo HATA

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya, Tokyo

(Received November 5, 1968)

The halogen exchange reaction of haloferrocene series with copper(I) salts (halide, cyanide) in an organic base was studied in comparison with that of the halobenzene series, which is regarded as a kind of nucleophilic substitution. Chloro-, bromo-, and cyanoferrocene were all obtained from iodoferrocene by this reaction in good yields. The reactivity of the ferrocene series was much higher than that of the benzene series. The order of the reactivity of halogen, I>Br>Cl, was similar to that of the benzene series. On the other hand, the substituent effects in the comparative reactivity of 1′-substituted-1-chloroferrocene with copper(I) cyanide was observed to be as follows: Et>H>Cl>Ac. This order in the ferrocene series was opposite to that in the *p*-substituted bromobenzene series: CN>Ac>Br>H>Me. In view of the electrophilic tendency in the ferrocene series and its high reactivity, the reaction mechanism is discussed.

Since the discovery of the aromaticity of ferrocene many interesting findings on the reactions of ferrocene derivatives have been reported. Ferrocene itself has a greater reactivity in the electrophilic substitution than does benzene. For example, it is acetylated with acetyl chloride and anhydrous aluminum chloride 10^6 times faster than benzene.[1] However, the nucleophilic substitution of ferrocene derivatives seems to take place with much difficulty, and few have been reported. Chloroferrocene, for example, reacts neither with potassium amide in liquid ammonia[2] nor with potassium hydroxide or potassium acetate.[3] It is interesting to note, however, that copper or copper salts have been found to participate in the reactions of haloferrocenes. The Ullmann aryl-coupling reaction of iodoferrocene took place at 60°C to afford biferrocenyl in a high yield,[4] but that of iodobenzene took place only at 200°C. The reaction of bromo- and chloroferrocene with copper(II) acetate gave ferrocenyl acetate with ease.[3] Nesmeyanov *et al.* have obtained cyanoferrocene in a good yield by the reaction of bromo- or chloroferrocene with copper(I) cyanide.[3] Thus, the substitution reactions of haloferrocenes including chloroferrocene with copper(I) salts seem to occur more easily than those of the benzene series, while the reaction of chlorobenzene with copper(I) cyanide hardly ever takes place under ordinary reaction conditions, such as with iodo- or bromobenzene.

In our previous reports,[5,6] some information on the Rosenmund-von Braun reaction of halobenzene with a complex of copper(I) cyanide and an organic base in nitrobenzene was presented, along with a discussion of the reaction mechanism. It has been reported that this reaction proceeds easily in dimethylformamide or *N*-methylpyrrolidone.[7] The reactions of halobenzene with copper(I) halides as well as with cyanide in an organic base have also been reported by Bacon and Hill.[8]

In this study, haloferrocenes were submitted to similar reactions, and the results were examined in comparison with those in the benzene series.

Syntheses of Haloferrocenes

Haloferrocenes can not be synthesized by the direct halogenation of ferrocene. Therefore, they have hitherto been obtained through the reaction of chloromercuriferrocene with halogen[9,10] or

---

[1] M. Rosenblum, J. O. Santer and W. G. Howells, *J. Am. Chem. Soc.*, **85**, 1450 (1963).

[2] J. W. Huffman, L. H. Keith and R. L. Asbury, *J. Org. Chem.*, **30**, 1600 (1965).

[3] A. N. Nesmeyanov, V. A. Sazonova and V. N. Drozd, *Chem. Ber.*, **93**, 2717 (1960).

[4] M. D. Rausch, *J. Org. Chem.*, **26**, 1802 (1961).

[5] T. Ito and K. Watanabe, This Bulletin, **41**, 419 (1968).

[6] N. Akanuma, H. Amemiya, T. Hayashi, K. Watanabe and K. Hata, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **81**, 333 (1960).

[7] L. Friedmann and H. Shechter, *J. Org. Chem.*, **26**, 2522 (1961); M. S. Newman and H. Boden, *ibid.*, **26**, 2525 (1961).

[8] R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, **1964**, 1097.

[9] A. N. Nesmeyanov, E. G. Perevalova and O. A. Nesmeyanova, *Dokl. Akad. Nauk S. S. S. R.*, **100**, 1099 (1955).

[10] H. Shechter and J. F. Helling, *J. Org. Chem.*, **26**, 1034 (1961).

TABLE 1. THE HALOGEN EXCHANGE REACTIONS OF HALOFERROCENES
Reaction temperature: 117°C

Exp. No.	Iodoferrocene	(g)	Copper(I) salt	(g)	Pyridine (m*l*)	Reaction time (hr)	Product	Yield (%)
1	Iodoferrocence	3.12	CuCl	1.98	30	3	Chloroferrocene	88.3
2	Iodoferrocence	3.12	CuBr	2.87	30	3	Bromoferrocene	94.2
3	Iodoferrocence	3.12	CuCN	3.6	20	3	Cyanoferrocene[a)]	83
4	1,1′-Diiodoferrocene	18.0	CuCl	30	200	3	1,1′-Dichloroferrocene	77.4
5	1,1′-Diiodoferrocene	2.19	CuCN	2.24	20	2	1-Iodo-1′-cyanoferrocene[b)]	40.2

a) Along with an unidentified product 0.15 g, mp 157—158°C.
b) Along with 37.5% recovery.

N-halosuccinimide,[11] or through the reaction of ferroceneboronic acid with copper(II) halide.[3,12] Among the haloferrocenes, however, iodoferrocene is easily obtained in a high yield by the treatment of chloromercuriferrocene with iodine.[10]

On the other hand, it is well known that iodobenzene easily undergoes a halogen exchange reaction with copper(I) halides to give bromo- or chlorobenzene in a good yield. Thus, chloro- and bromoferrocene may be expected to be successfully obtained by the reaction of iodoferrocene with copper(I) chloride and bromide respectively. The halogen exchange reactions were achieved only by refluxing the mixtures of iodoferrocene and copper(I) halides in pyridine for a few hours under an oxygen-free nitrogen atmosphere. Cyanoferrocene was also obtained using copper(I) cyanide instead of copper(I) halides.[*1] The experimental results are summarized in Table 1.

Thus, these reactions are sufficiently useful as a method of synthesizing bromo-, chloro- or cyanoferrocene, since iodoferrocene is obtainable with considerable ease. On the other hand, the fact that the reaction of 1,1′-diiodoferrocene with copper(I) cyanide afforded 1′-cyano-1-iodoferrocene as the sole isolable product suggests a new method to synthesizing various 1′-substituted haloferrocenes.

TABLE 2. THE REACTION OF HALOFERROCENES WITH COPPER(I) CYANIDE
Haloferrocenes: 0.4 g in each run, Reaction time: 2 hr

Exp. No.	Haloferrocene	CuCN (g)	Pyridine (m*l*)	Reaction temp. (°C)	Yield of cyanoferrocene	Recovered (%)
1	FcI	2	10	118	63	+
2	FcBr	2	10	118	32	35
3	FcBr	3	3	140	64	+
4	FcCl	2	10	118	Trace	*ca.* 100
5	FcCl	3	3	140	34	66

A small amount of unidentified product (mp 157°C) was obtained in every case.
The formation of ferrocene by the decomposition of haloferrocenes was observed in Exps. 1, 2 and 3.

TABLE 3. THE REACTION OF HALOBENZENES WITH COPPER(I) CYANIDE
Halobenzenes: 0.5 m*l* in each run, Reaction time: 2 hr

Exp. No.	Halobenzene	CuCN (g)	Pyridine (m*l*)	Reaction temp. (°C)	Yield of benzonitrile[a)] (%)
1	PhI	2	10	118	98
2	PhBr	2	10	118	Trace
3	PhBr	2	10	118	2.5[b)]
4	PhCl	2	10	118	—
5	PhI	3	3	140	*ca.* 100
6	PhBr	3	3	140	43[c)]
7	PhCl	3	3	140	—

a) Calculated by the gas chromatographic analysis.
b) The reaction time, 10 hr.
c) When heated for 9 hr at 140—150°C, the yield was 85%.

The Rosenmund-von Braun Reaction of Haloferrocenes in Comparison with the Benzene Series. With a view to elucidating the character of the substitution reaction of haloferrocenes with copper(I) salts, the results of the reaction of haloferrocenes with copper(I) cyanide in pyridine under somewhat different conditions were compared with those of the same reaction with halobenzenes. The results of the experiments are shown in Tables 2 and 3. The relatively fast decomposition of iodoferrocene at 118°C may reduce the yield of cyanoferrocene to below that of benzonitrile from iodobenzene. Chloroferrocene gave a 34% yield of cyanoferrocene at 140°C (Exp. 5 in Table 2), while chlorobenzene did not react at all (Exp. 7 in Table 3).[*2] A similar contrast was also evident in the reactions of bromo-compounds. In general, the higher the reaction temper-

---

11) R. W. Fish and M. Rosenblum, *J. Org. Chem.*, **30**, 1253 (1965).

12) A. N. Nesmeyanov, V. A. Sazonova and V. N. Drozd, *Dokl. Akad. Nauk S. S. S. R.*, **126**, 1004 (1959).

[*1] Nesmeyanov *et al.*[3] performed this reaction at 135—140°C without any solvent.

[*2] Chlorobenzene was hardly ever changed by heating at 140—150°C for 14 hr. Upon reaction in an autoclave at 250°C for 9 hr, the yield of the nitrile was 34%.[5]

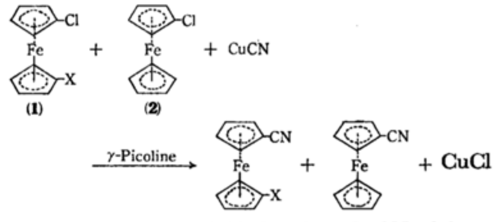
ature, the greater the increase in the yield of nitriles, and the reactivity of the halogens in both the ferrocene and the benzene series was in the same order: I>Br>Cl.*3

The ease of the displacement of halogens from the benzene nucleus was also shown to be the same order by Bacon and Hill.[8] This order is the inverse of that of the reactivities of activated aryl halides in the nucleophilic substitution. This implies that the reactions of haloferrocenes with copper(I) salts proceed in a manner similar to those of halobenzenes, at least at certain steps. On the other hand, the higher reactivity of the ferrocene series, together with that of the Ullmann coupling and Ullmann condensation of haloferrocenes,[4] suggests the contribution of a characteristic factor of ferrocene molecules to this reaction.

Effects of Substituents. In order to examine the electronic factor in this reaction, the reactions of *p*-substituted halobenzenes and of 1′-substituted haloferrocenes with copper(I) cyanide were carried out, and the effect of the substituents was discussed.

1′-Ethyl-, 1′-chloro-, and 1′-acetyl-1-chloroferrocene were synthesized, and competitive reactions of each of them with chloroferrocene were carried out in γ-picoline.*4 Similarly, the competitive reactions of *p*-methyl-, *p*-bromo-, and *p*-acetylbromobenzene with bromobenzene were all examined in the same solvent. The nitriles produced were analyzed by gas chromatography; the results are shown in Tables 4 and 5 in terms of the relative reactivity.

TABLE 4. THE RELATIVE REACTIVITY OF 1′-SUBSTITUTED CHLOROFERROCENE

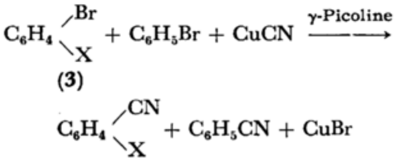


1: 0.0015 mol, **2**: 0.0015 mol, CuCN: 3.0 g, γ-Picoline: 3.0 m*l*, Biphenyl[a]: 0.0015 mol, Reaction temp.: 145°C, Reaction time: 2 hr, in N_2 atmosphere.

Exp. No.	Substituent X	Relative reactivity
1	C_2H_5	1.65
2	H	1.00
3	Cl	0.04[b]
4	$COCH_3$	—

a) Added as an internal standard in the gas chromatographic analysis.
b) Only 1′-chloro-1-cyanoferrocene was obtained.

TABLE 5. THE RELATIVE REACTIVITY OF *p*-SUBSTITUTED BROMOBENZENE



$$C_6H_4\genfrac{}{}{0pt}{}{\diagup Br}{\diagdown X} + C_6H_5Br + CuCN \xrightarrow{\gamma\text{-Picoline}}$$
$$(\mathbf{3})$$
$$C_6H_4\genfrac{}{}{0pt}{}{\diagup CN}{\diagdown X} + C_6H_5CN + CuBr$$

3: 0.02 mol, C_6H_5Br: 0.02 mol, CuCN: 3.0 g, γ-Picoline: 4.0 m*l*, Reaction temp.: 147°C, Reaction time: 3 hr

Exp. No.	Substituent X	Relative reactivity
1	CH_3	0.92
2	H	1.00
3	Br	1.21[a]
4	$COCH_3$	1.90
5	CN	2.03[b]

a) *p*-Bromobenzonitrile and terephthalonitrile were obtained.
b) The relative rate of *p*-bromobenzonitrile was calculated not from the direct competitive reaction, but from the result of No. 3 in this table, on the assumption that *p*-bromobenzonitrile is initially formed from *p*-dibromobenzene, followed by further substitution to terephthalonitrile.

It is very interesting that a remarkable electrophilic character was observed in the reaction of the ferrocene series, while the nucleophilic character was observed in that of the benzene series. Bacon and Hill also reported that the effect of substituents in the latter was slightly nucleophilic.[8] In view of the model proposed in our earlier paper,[5] the interaction of the cyano group with the carbon atom in benzene nuclei may be nucleophilic. Therefore, the trend and the order of substituent effcet shown in Table 5 seems reasonable. However, the nucleophilic character of this reaction, caused by the activation by the base-CuCN complex, is not as conspicuous as in an ordinary nucleophilic substitution of activated halobenzenes.

In the reactions of the ferrocene series (Table 4), the electron-withdrawing acetyl and also chloro groups exert a strong suppressive effect. The fact that dichloroferrocene only afforded a monocyano compound can be interpreted in terms of the interfering effect of a strong electron-withdrawing cyano group which has previously been substituted in another cyclopentadienyl ring. A similar result is found in the case of diiodo derivatives (Exp. 5 in Table 1). Thus, the fact that the electron-withdrawing group displays a suppressive effect on the substitution reaction of the ferrocene series, contrary to that of the benzene series,

---

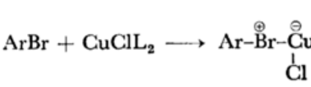
*3 I>Br>Cl>F: Fluorobenzene is never replaced by this reaction.[5] The reactivity order was estimated on the basis of the yields of nitriles from the corresponding halides.

*4 It was used because its boiling point is higher than that of pyridine (bp 145°C).

offers an important suggestion for discussing the mechanism of this reaction in close relationship with the superior reactivity of the ferrocene series.

Discussion

The halogen exchange reaction of haloferrocene participated with copper(I) salt is considered to be a kind of nucleophilic substitution, analogous to that of halobenzene under the same conditions. Nevertheless, the displacement of halogen from the ferrocene nucleus was found to be facile in the order: I>Br>Cl, an order similar to that observed in halobenzenes. This kind of metal-assisted aromatic replacement reaction has been extensively studied by Bacon and Hill,[8] who established that the reaction was initiated by bonding between the halogen in aryl halide and copper, thus giving an "onium" structure (**4**), followed by the formation of a four-centered cyclic intermediate or an ion pair, or by a homolytic fission, and that an electron-withdrawing group on the aryl halide had only a small accelerating effect on the reaction rate.



$$\mathrm{ArBr} + \mathrm{CuClL_2} \longrightarrow \mathrm{Ar{-}\overset{\oplus}{Br}{-}\underset{\displaystyle\mathrm{Cl}}{\overset{\ominus}{Cu}}L_2}$$

L: Ligand (**4**)

It may be concluded that, within the range of conditions employed in this investigation, copper(I) salt is present in the reaction mixture in the form of a complex with a pyridine base.[5] It has also been shown that the nature of the pyridine base in the copper complex affects the rate of the substitution reaction remarkably. Under the circumstances, an electronic state of the halogen atom in aryl halide, like one of the copper atom in the complex, will seriously affect the first stage of the reaction. The cyclopentadienyl ring in ferrocene has a higher electron density than the benzene ring, so the halogen in haloferrocene may be expected to be more strongly coordinated to the copper atom than that in the corresponding halobenzene under the same conditions. The expected higher reactivities of haloferrocenes were actually observed in this investigation.

As is shown in Table 4, the effect of 1′-substituents observed in haloferrocenes was contrary to what was expected from the nucleophilic feature of this reaction. That is, the reaction was accelerated with an electron-releasing group, while it was retarded with an electron-withdrawing one.

In view of these results, the halogen exchange reaction in the ferrocene series seems to be more complicated than that in the benzene series. However, on the assumption that the principal mechanism of this reaction is not different between the two series, the anomalism observed in the substituent effect of haloferrocenes can reasonably be explained as follows: In haloferrocenes, a particular interaction between the copper(I) salt-base complex and haloferrocene precedes the formation of an "onium"-type intermediate (**4**) by an attack of the halogen in the haloferrocene on the copper atom in the complex, and exerts a controlling effect on the rate of the reaction. Since haloferrocene acts as an electron donor in this reaction, an electron-withdrawing substituent on haloferrocene retards the above-mentioned interaction, thus reducing the rate of the reaction. This explanation is consistent with the experimental results obtained in this study, and similar interaction has been observed in several members of the ferrocene series.[13] Therefore, it seems reasonable to assume a precedence of such an interaction in the halogen exchange reactions, although there is no direct evidence to support this assumption.

Further work on this subject is in progress and a more detailed discussion will be reported later.

Experimental

Materials. Commercial copper(I) chloride and bromide were used without any further purification. The copper(I) cyanide was prepared from copper(II) sulfate and potassium cyanide. Commercial pyridine, γ-picoline, and halobenzenes were purified by distillation under reduced pressure. The purity of all the organic reagents was checked by gas chromatography.

Iodoferrocene. Iodoferrocene was prepared, by a modification of the procedure reported by Shechter and Helling,[10] in a much improved yield, 71—91%; mp 48—49°C (lit. 44—45°C,[9] 49—49.5°C[4]).

Chloroferrocene. To a solution of 3.12 g (0.01 mol) of iodoferrocene in 30 m*l* of pyridine, 1.98 g (0.02 mol) of copper(I) chloride were added and then the mixture was refluxed with stirring for 3 hr under a nitrogen atmosphere. At the end of the reaction, 100 m*l* of *n*-hexane were added. Then, the reaction mixture was filtered, and the precipitate collected on a filter was washed several times with *n*-hexane. The filtrate and the washings were combined and washed with dilute hydrochloric acid and water successively. The organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent, the residual crude product was chromatographed on alumina to afford 1.95 g chloroferrocene. Yield, 88.3%; mp 56—56.5°C (lit. 58—59°C[3]).

Bromoferrocene. Following the procedure described above, bromoferrocene was prepared from iodoferrocene and copper(I) bromide in pyridine. Yield, 94%; mp 29—30°C (lit. 32—33°C[3]).

Cyanoferrocene. Iodoferrocene (3.1 g, 0.01 mol) and copper(I) cyanide (3.6 g, 0.04 mol) were treated in 20 m*l* of pyridine by the procedure used for the preparation of chloroferrocene. The crude product thus obtained was chromatographed on Florisil to give 1.75 g of cyanoferrocene. Yield, 83%; mp 106—107°C (lit.

---

13) V. L. Wolf and H. Hennig, *Z. Anorg. Allgem. Chem.*, **341**, 1 (1965).

107—108°C[3]). Unidentified yellow crystals were obtained as a by-product (0.15 g), mp 157—158°C.

1,1′-Diiodoferrocene. Following the procedure reported by Nesmeyanov *et al.*,[9] 1,1′-diiodoferrocene was prepared in a much improved yield. Purification by means of chromatography gave 5.77 g of 1,1′-diiodoferrocene as an orange liquid. Yield, 65.5%; bp 85°C/0.003 mmHg, n^{23} 1.6850.

1,1′-Dichloroferrocene. 1,1′-Dichloroferrocene was prepared by the reaction of 1,1′-diiodoferrocene with copper(I) chloride in pyridine following the procedure previously described for the preparation of chloroferrocene. Yield, 77.4%; mp 76—77°C (lit. 75—77°C[3]).

1′-Cyano-1-iodoferrocene. To a solution of 2.19 g (0.005 mol) of 1,1′-diiodoferrocene in 20 m*l* of pyridine, there were added 2.24 g (0.0025 mol) of copper(I) cyanide, and then the mixture was refluxed for 2 hr under a nitrogen atmosphere. After a treatment similar to that for chloroferrocene, the crude product was chromatographed on Florisil to give 0.8 g of the starting material and 0.68 g of 1′-cyano-1-iodoferrocene. The yield of the latter, 40.2%; mp 43.5—45°C.

Found: C, 39.72; H, 2.56; N, 4.25%. Calcd for $C_{11}H_8NIFe$: C, 39.20; H, 2.39; N, 4.16%.

1′-Acetyl-1-chloroferrocene. A solution of 7.6 m*l* (0.06 mol) of boron trifluoride etherate in 10 m*l* of dry dichloromethane was added to a solution of 5.5 g (0.025 mol) of chloroferrocene and 5.65 m*l* (0.06 mol) of acetic anhydride in 100 m*l* of dry dichloromethane over a 7-min period under a nitrogen atmosphere and in an ice bath. After the reaction mixture had been stirred for 30 min in the ice bath and then for 5.5 hr at room temperature, it was poured into ice water. The dichloromethane layer was washed repeatedly with water and dried over anhydrous magnesium sulfate. After the solvent had been removed, the residue was chromatographed on alumina to give 2.80 g of cholroferrocene and 3.20 g of 1′-acetyl-1-chloroferrocene. The yield of the acetyl compound, 48.6%; mp 55.5°—56.7°C (lit. 53—55°C[14]).

1′-Ethyl-1-chloroferrocene. Zinc (1.0 g) was amalgamated by stirring it with 0.1 g of mercury(II) chloride in 4 m*l* of dilute hydrochloric acid (1:20) for 10 min. After the aqueous phase had then been decanted off, a solution of 0.25 g of 1′-acetyl-1-chloroferrocene in 2.5 m*l* of conc. hydrochloric acid and 2.5 m*l* of acetic acid was added to the amalgamated zinc. The mixture was refluxed for 5 min and then cooled to room temperature. Then the zinc was filtered off and washed with ether. The filtrate was extracted with ether. The combined ethereal solution was washed with water, dilute aqueous potassium hydroxide, and water successively, and dried over anhydrous magnesium sulfate. After the ether had then been evaporated away, the residue was chromatographed on alumina with *n*-hexane, there was thus obtained 0.19 g of 1′-ethyl-1-chloroferrocene. Yield, 81.0%; bp 65—66°C/0.006 mmHg, n^{23} 1.6048.

Found: C, 58.10; H, 5.23%. Calcd for $C_{12}H_{13}ClFe$: C, 57.95; H, 5.23%.

1′-Ethyl-1-cyanoferrocene. To a solution of 0.67 g (0.0027 mol) of 1′-ethyl-1-chloroferrocene in 1.5 m*l* of γ-picoline, 1.21 g (0.0135 mol) of copper(I) cyanide were added. The reaction mixture was heated for 3 hr at 140—145°C under a nitrogen atmosphere, and cooled after the addition of 10 m*l* of pyridine at the end of the reaction. After a treatment similar to that described for the preparation of chloroferrocene, the crude product was chromatographed on silica gel to give 0.375 g of the starting material and 0.159 g of 1′-ethyl-1-cyanoferrocene. The yield of the cyano compound, 24.8%; 99—100°C/0.045 mmHg (lit. 152—156°C/5 mmHg[3]).

The Reaction of Haloferrocene with Copper(I) Cyanide (Table 2, Exp. 2). A mixture of 0.40 g of bromoferrocene, 2.0 g of copper(I) cyanide, and 10 m*l* of pyridine was stirred for 2 hr at 118°C. After the reaction was over, 30 m*l* of ether was added to the hot reaction mixture and the whole was refluxed for 10 min while being stirred well. The copper(I) salt-pyridine complex thus precipitated was filtered off and washed well with ether. The extraction with fresh ether was repeated three times in order to ensure the extraction of the product from the reaction mixture. All the ethereal solutions were then combined, washed three times with dilute hydrochloric acid and then with water, and dried over anhydrous magnesium sulfate. After the ether had been distilled off, the residue was chromatographed on silica gel with a mixture of *n*-hexane and benzene (1:1) to give 0.10 g (32%) of cyanoferrocene, mp 106—107°C, and 0.14 g (35%) of the recovered bromoferrocene.

In the case of the reaction of chloroferrocene, the products were analyzed by gas chromatography; by this means the quantities of cyanoferrocene and the recovered chloroferrocene were determined precisely.

The Reaction of Halobenzene with Copper(I) Cyanide (Table 3, Exp. 6). A mixture of 0.5 m*l* of bromobenzene, 3.0 g of copper(I) cyanide and 3.0 m*l* of pyridine was stirred at 140°C for 2 hr. Then the reaction mixture was treated similarly as in the case of haloferrocenes. The ethereal solution thus obtained was analyzed by gas chromatography. The yield of benzonitrile was 43%.

The Competitive Reaction of Haloferrocenes (Table 4, No. 1). A mixture of 3.0 g of copper(I) cyanide, 3.0 m*l* of γ-picoline, 0.377 g (0.0015 mol) of 1′-ethyl-1-chloroferrocene, 0.336 g of chloroferrocene, and 0.203 g of biphenyl (internal standard for gas chromatography) was stirred for 2 hr at 145°C. After the reaction was over, 6 m*l* of pyridine and 20 m*l* of ether were added to the hot reaction mixture, and the whole was refluxed for 10 min while being stirred well. A copper(I) salt-pyridine complex precipitated from the reaction mixture. The precipitate was filtered off and washed with ether. To complete the collection of the product, the precipitate was extracted twice more. The ethereal solutions thus obtained were combined, washed with dilute hydrochloric acid, and then with water, and dried over anhydrous magnesium sulfate. The solution was concentrated and analyzed by gas chromatography.

The Relative Reactivities of Haloferrocenes. After the competitive reaction between chloroferrocene and 1′-substituted chloroferrocene, the yields of both nitriles were calculated from the ratio of each peak area of the nitriles to the internal standard (biphenyl). When a large excess of copper(I) cyanide over haloferrocene was used, the reaction was apparently first-order in haloferrocenes. Therefore, on the assumption

---

14) D. W. Hall and J. H. Richards, *J. Org. Chem.*, **28**, 1549 (1963).

that the reaction would be approximately first-order in haloferrocenes under the conditions employed in the present experiments, the rate constants were calculated from the yields of the nitriles. The relative reactivities of 1′-substituted chloroferrocene and chloroferrocene are shown in Table 4. Similarly, the relative reactivities of *p*-substituted bromobenzene and bromobenzene were found to be as shown in Table 5.

Analytical Conditions for Gas Chromatography. Apparatus: Ohkura Model 1100. Column: 2 m × 6 mm stainless-steel column packed with 10% Silicon Grease on Daichrom W with 60—80 meshes. Temperature: 180—200°C (130°C for halobenzene). Carrier gas: H_2. Flow rate: 40—60 m*l*/min. Relative retention time: FcH (1); Biphenyl (1.16); FcCl (1.57); 1′-Et-1-Cl-ferrocene (2.43); 1,1′-Cl_2-ferrocene (2.48); FcCN (2.77); $FcCOCH_3$ (3.45); 1′-Et-1-CN-ferrocene (4.32); 1′-Cl-1-CN-ferrocene (4.43); 1′-Ac-1-CN-ferrocene (5.23).

For the substituted halobenzenes, the following conditions were employed. Column: 2 m × 6 mm stainless-steel column packed with 10% Carbowax 1500 on Chromosorb W with 60—80 meshes. Temperature: 180—190°C. Carrier gas: H_2. Flow rate: 40 m*l*/min.