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Reactions of Haloferrocenes. III. The Reaction of Haloferrocenes with Copper(I) Benzenethiolate, Thiocyanate, Acetate, and Benzoate

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Iodoferrocene reacted with copper(I) benzenethiolate in boiling pyridine to give ferrocenyl phenyl sulfide in a quantitative yield. The reaction of iodoferrocene with copper(I) thiocyanate gave diferrocenyl disulfide. The behavior of copper(I) acetate and benzoate toward haloferrocene was found to be different from those of the other copper(I) salts: the reactions in boiling pyridine gave the corresponding ferrocenyl ester, together with a small quantity of ferrocene, while the reaction in boiling toluene produced biferrocenyl as the main product. The reaction mechanism of the ferrocenyl ester and biferrocenyl formations was discussed.

It has been shown that haloferrocene has a high reactivity in the reaction with copper(I) salts in pyridine, and that chloro-, bromo-, and cyanoferrocene were obtained in good yields from the reaction of iodoferrocene with, respectively, copper(I) chloride, bromide, and cyanide in boiling pyridine.$^{1)}$ Bromoferrocene was 10^3 times more reactive than bromobenzene in the reaction with copper-

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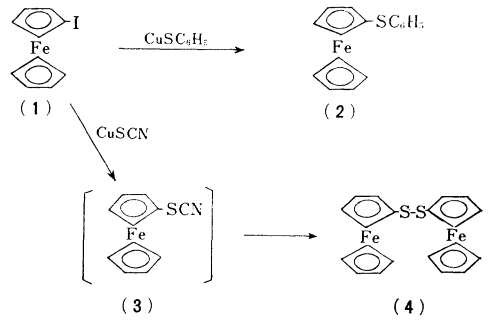
1) M. Sato, T. Ito, I. Motoyama, K. Watanabe and K. Hata, This Bulletin, **42**, 1976 (1969). Part I in this series.

(I) chloride - pyridine complex in bromobenzene.[2] According to Bunnett and Zahler,[3] the reaction of this kind is classified as a nucleophilic substitution reaction participated by transition metal through an uncertain mechanism. It is surprising that haloferrocene has a high reactivity even in the nucleophilic reaction, whereas ferrocene itself shows a much higher reactivity than benzene in an electrophilic reaction such as the Friedel-Crafts acylation. In order to elucidate the nature of this reaction, the reactions of haloferrocene with copper(I) benzenethiolate, thiocyanate, acetate, and benzoate were investigated.

Results and Discussion

The treatment of iodoferrocene (**1**) with copper(I) benzenethiolate in boiling pyridine for two hours gave ferrocenyl phenyl sulfide (**2**) in a quantitative yield. Similar results have been observed in the reaction of aryl halide with copper(I) benzenethiolate.[4] No particular high reactivity of iodoferrocene over other aryl halides was observed in this reaction, although it has been found[1] that haloferrocenes generally have a higher reactivity toward copper(I) salts than do the corresponding halobenzenes. This has been supposed to be due to the special high reactivity of benzenethiolate toward both halides. Thus, this reaction is considered to be as useful as the copper-catalyzed reaction between iodoferrocene and sodium benzenethiolate[5] for the preparation of ferrocenyl phenyl sulfide.

The reaction of iodoferrocene (**1**) with copper(I) thiocyanate in boiling pyridine for two hours gave diferrocenyl disulfide (**4**) in a 48% yield instead of the expected product, ferrocenyl thiocyanate (**3**), with a 42% recovery of iodoferrocene.



It is known that aryl halides are converted to the diaryl disulfides by the action of copper(I) thiocyanate under severe conditions[6] and that aryl thiocyanates are reduced to the corresponding disulfides with copper(I) salt.[7] The formation of diferrocenyl disulfide (**4**) is probably due to the rapid reduction of the intermediary ferrocenyl thiocyanate (**3**) to the disulfide (**4**) by an excess of copper(I) salt. The reactivity of iodoferrocene toward thiocyanate seems to be usually high, since 1-bromonaphthalene hardly reacts with copper(I) thiocyanate under similar conditions.[8] This process can be used for the preparation of diferrocenyl disulfide which was previously prepared by the oxidation of ferrocenethiol.[9]

Table 1. The reaction of haloferrocene with copper(I) acetate and benzoate
Haloferrocene: 0.005 mol; copper(I) salts: 0.01 mol; solvent: 15 m*l*;
reaction temp.: 120°C±5°C; reaction time: 0.5 hr

Exp. No.	Haloferrocene	Copper(I) salt	Solvent	Starting material recovered (%)	Product (%)		
					Ester	Biferrocenyl	Ferrocene
1[a]	FcI	CuOAc	Pyridine	None	62.3	4.3	20.0
2[b]	FcI	CuOBz	Pyridine	35.5	54.9	Trace	1.8
3[a]	FcBr	CuOAc	Pyridine	None	62.3	None	20.7
4	FcCl	CuOAc	Pyridine	76.8	9.6	None	11.7
5	FcI	CuOAc	Toluene	None	7.4	74.4	12.8
6[b]	FcI	CuOBz	Toluene	None	24.2	67.0	Trace
7	FcBr	CuOAc	Toluene	15.2	15.6	68.0	2.1

a) 20 m*l* of solvent was used.

b) A minor quantity of chloroferrocene was found in the reaction product. This halogen-exchange must be caused by hydrochloric acid during the treatment, but the reason of the exchange is not clear.

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2) M. Sato, I. Motoyama and K. Hata, This Bulletin, **43**, 1860 (1970).

3) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951).

4) R. Adams, W. Reifschneider and M. D. Nair, *Coastica Chem. Acta*, **1957**, 29.

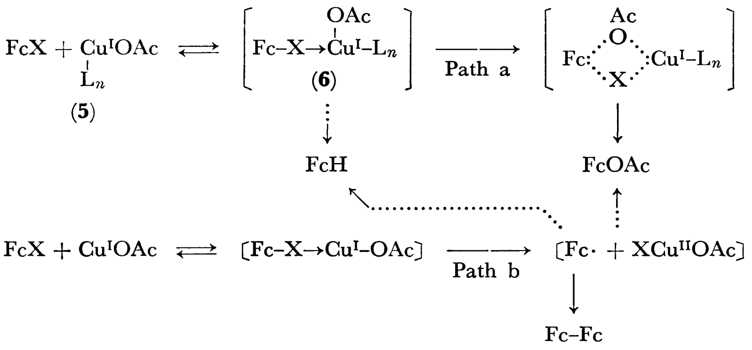
5) M. D. Rausch, *J. Org. Chem.*, **26**, 3579 (1961).

6) K. W. Rosenmund and H. Harms, *Ber.*, **53**, 2226 (1920).

7) R. G. R. Bacon, S. C. Rennison and O. J. Stewart, *Proc. Chem. Soc.*, **1964**, 409.

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

9) G. R. Knox and P. L. Pauson, *ibid.*, **1958**, 692.



(Fc=ferrocenyl, L=ligand)
⟶ major process ⋯⋯→ minor process

Scheme 1

The behavior of copper(I) acetate and benzoate toward haloferrocene was found to be different from that of the other salts, as is summarized in Table 1. When iodoferrocene was treated with copper(I) acetate in boiling pyridine for 0.5 hr, ferrocenyl acetate was obtained in a moderate yield, together with a small quantity of ferrocene and biferrocenyl. The formation of these by-products was not observed in the reaction described above or in the previous paper.1) The reaction of bromo- or chloroferrocene with copper(I) acetate did not afford biferrocenyl, but it did give ferrocene in addition to ferrocenyl acetate. The reactivities of haloferrocenes toward the copper(I) acetate were in the order: FcI> FcBr>FcCl. When copper(I) benzoate, instead of copper(I) acetate, was refluxed for 0.5 hr with iodoferrocene in pyridine, ferrocenyl benzoate was similarly obtained in a moderate yield, along with traces of ferrocene and biferrocenyl. Since a considerable amount of iodoferrocene was recovered in this reaction, the reactivity of copper(I) benzoate toward iodoferrocene seems to be considerably smaller than that of copper(I) acetate.

As has been mentioned above, the reaction of haloferrocene with copper(I) acetate and benzoate in pyridine gave ferrocenyl acetate and benzoate respectively. Those results are very different from those of the halobenzene series. It has been reported that reactions of aryl halides with copper(I) acetate in pyridine generally give dehalogenation products as a sole product.10,11) For example, naphthalene was obtained in a 60% yield by the treatment of 1-bromonaphthalene with copper(I) acetate in boiling pyridine.10) When *o*-iodonitrobenzene, which is as reactive as iodoferrocene in the Ullmann coupling reaction,12) was treated with copper(I) acetate in boiling pyridine, 2,2′-dinitrobiphenyl was obtained in an 84% yield, but no detectable amount of *o*-nitrophenyl acetate was produced.

The reaction of haloferrocenes with copper(I) acetate and benzoate also gave rise to the formation of ferrocene and biferrocenyl, but the formation of the latter was only observed in the reaction of iodoferrocene. The fact may be explained as follows: active copper, which was produced by the decomposition or disproportionation of copper(I) acetate, causes the coupling of iodoferrocene, just as in the reaction of iodoferrocene with active copper powder13) prepared from copper(II) sulfate and zinc dust to give biferrocenyl. However, we cannot exclude the possibility of the process involving the reduction of iodoferrocene with copper(I) salts, followed by the coupling reaction to be described below.

The route of the reaction of haloferrocene with copper(I) acetate or benzoate in pyridine may be similar to that with the other copper(I) salts.2) The coordination of the halogen atom of haloferrocene to the copper(I) salt-pyridine complex (**5**) may give a metastable intermediate (**6**), through which a ligand-exchange reaction leads to ferrocenyl acetate or benzoate as is shown in Path a of Scheme 1.

The fact that the dehalogenation product, *i.e.*, ferrocene, was not detected in the reaction of haloferrocene with copper(I) salts other than acetate or benzoate indicates that the existence of an acetate or benzoate ligand on the copper(I) complex (**5**) is essential for the formation of the dehalogenation product. It is considered that the dehalogenation may proceed through an intramolecular hydride shift within the intermediate complex (**6**) similar to that which was proposed by Bacon and Hill11) in the benzene series. This consideration is supported by the fact that a larger amount of ferrocene is formed in the reaction with copper(I) acetate than with benzoate; it is possible that the hydride shift takes place more easily in the former than in the latter.

In order to examine the function of pyridine in

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10) W. G. H. Edwards and R. G. Stewart, *Chem. Ind.* (London), **1952**, 472.

11) R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, **1964**, 1112.

12) M. D. Rausch, *J. Org. Chem.*, **26**, 1802 (1961).

13) R. Q. Brewster and R. Groening, "Organic Syntheses," Coll. Vol. 2, p. 445 (1943).

these reactions, haloferrocenes were treated with copper(I) acetate or benzoate in boiling toluene (Table 1, Nos. 5, 6, and 7). In every case, the main product was biferrocenyl, while ferrocene and ferrocenyl ester were produced as minor by-products. The remarkable difference in the product ratio observed between the reactions in pyridine and those in toluene suggests that the coordinating ability of the solvent may be significant in these reactions. It has been established that the coordination of pyridine to copper(I) salt affords a copper(I) salt-pyridine complex (**5**). The reaction of haloferrocene with copper(I) acetate or benzoate was considered to proceed through this complex to afford the ferrocenyl ester as a main product. On the other hand, as the coordination of toluene must proceed through another process. During the reaction in toluene, a color change in the reaction mixture from orange to green was observed as the reaction proceeded. This is probably due to the formation of some copper(II) species. As no such color change was observed by refluxing copper(I) benzoate alone in toluene, the coexistence of haloferrocene seems to be necessary for the formation of the copper(II) species. On the basis of the results presented above, Path b in Scheme 1 was assumed to be a possible process: haloferrocene is reduced by some participation of copper(I) acetate or benzoate (for instance, the unstable complex-formation shown in Scheme 1) to give a ferrocenyl radical, which may interact with the excess of the salt to form ferrocenylcopper species. The ferrocenyl radicals thus formed couple with each other to give biferrocenyl, on the one hand, and abstract an acetoxy group from copper(II) acetate to give ferrocenyl acetate, on the other hand.

A similar process has been proposed for the reduction of benzyl chloride with copper(I) ion[14] or chrom(II) ion.[15] It is not apparent, however, whether or not the formation of the ferrocenyl ester is exclusively due to the process involving the ferrocenyl radical. Perhaps the ligand-exchange process through complex-formation discussed above will simultaneously contribute to the formation of the ester.[16]

Considering the results of the reactions of haloferrocenes with various copper(I) salt-pyridine complexes described in the present paper, together with those described in the previous paper,[1] it was found that the affinity of various ligands to ferrocene nucleus was in the following order: $SC_6H_5 > Cl > Br > CN > OAc > OBz > SCN$. It was also reconfirmed that haloferrocenes have a higher reactivity toward various copper(I) salt-pyridine complexes than do halobenzenes.

Experimental

Materials. Iodoferrocene was prepared from chloromercuriferrocene by a modification of a previously-reported procedure.[1] Bromoferrocene and chloroferrocene were prepared by the procedure described in a previous paper.[1] Copper(I) benzenethiolate,[4] thiocyanate,[17] acetate,[18] and benzoate[16] were prepared according to the literatures. Pyridine was distilled just before use after desiccation over potassium hydroxide.

Ferrocenyl Phenyl Sulfide. Iodoferrocene (1.56 g, 0.005 mol) and copper(I) benzenethiolate (1.73 g, 0.01 mol) were refluxed for 2 hr in 15 m*l* of pyridine. After the reaction had been completed, 80 m*l* of benzene was poured into the hot reaction mixture. The precipitate thus formed was filtered and washed with benzene. The combined benzene solution was repeatedly washed with water until the aqueous layer became neutral; then the solution was dried over anhydrous magnesium sulfate. After benzene had been evaporated off, the residue was chromatographed on alumina with hexane - benzene (1 : 1) to give 1.6 g of yellow crystals, which were then recrystallized from hexane - benzene, mp 110.0—110.5°C (lit, 111.5—112°C). Finally, 1.38 g (93.9% yield) of ferrocenyl phenyl sulfide were obtained.

The Reaction of Iodoferrocene with Copper(I) Thiocyanate in Pyridine. A mixture of 1.56 g (0.005 mol) of iodoferrocene, 1.22 g (0.01 mol) of copper(I) thiocyanate, and 15 m*l* of pyridine was refluxed for 2 hr under an atmosphere of nitrogen. Then, 80 m*l* of ether was added and the reaction mixture was filtered. The filtrate was washed with water, then with 2N hydrochloric acid to remove pyridine, and again with water. After the removal of the solvent, the residue was chromatographed on alumina. Iodoferrocene (0.65 g, 41.7%) was recovered, and diferrocenyl disulfide (0.52 g, 47.9%) was obtained as yellow crystals, which were subsequently recrystallized from hexane - benzene, mp 190—191°C (lit, 192°C,[9] 192—193°C[5]).

A General Procedure for the Reactions of Haloferrocenes with Copper(I) Acetate or Benzoate in Pyridine. Haloferrocene (0.005 mol) was refluxed, together with copper(I) acetate or benzoate (0.01 mol), in 15 m*l* of pyridine under an atmosphere of nitrogen. After 30 min, 80 m*l* of ether was added to the cooled reaction mixture, and then the mixture was filtered. The filtrate thus obtained was washed successively with water, 2N hydrochloric acid, and again with water, and then dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was separated into individual compounds by chromatography.

Procedure for Exp. 1 in Table 1. The reaction product was chromatographed on silica gel with hexane - benzene (2 : 1). The product obtained from the first fraction was again chromatographed on alumina with the same solvent to give 0.24 g of yellow crystals and 0.04 g (4.3% yield) of biferrocenyl. The gas-chromatographic analysis of the former was carried out under the conditions described in a previous paper,[2] and the yellow crystalline substance was found to be a mixture

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[14] K. Wada and S. Hashimoto, This Bulletin, **41**, 3001 (1968).

[15] J. K. Kochi and D. D. Davis, *J. Amer. Chem. Soc.*, **86**, 5264 (1964).

[16] T. Cohen and A. H. Lewin, *ibid.*, **88**, 4521 (1966).

[17] R. L. Demmerle, W. A. Taebel and W. F. Anderson, *Ind. Eng. Chem.*, **42**, 2 (1950).

[18] M. Calvin and W. K. Wilmarth, *J. Amer. Chem. Soc.*, **78**, 1301 (1956).

of ferrocene (0.19 g, 20.0% yield) and chloroferrocene (0.05 g, 4.5% yield). The second fraction of chromatography gave ferrocenyl acetate (0.76 g, 62.3% yield), which was subsequently recrystallized from hexane, mp 66—67.5°C (lit,[19] 64.5—66.5°C).

The Reaction of Iodoferrocene with Copper(I) Benzoate in Toluene. (Table 1, Exp. 6). Iodoferrocene (1.56 g, 0.005 mol) was refluxed with copper(I) benzoate (1.85 g, 0.01 mol) in 20 m*l* of toluene under an atmosphere of nitrogen. After 30 min, the cooled reaction mixture was extracted with benzene by using a Soxhlet extractor. The concentration of the extract under reduced pressure, followed by filtration, gave orange crystals (0.56 g), which were identified as biferrocenyl on the basis of their melting point (238—240°C, lit,[12] 240—241°C) and their IR spectrum. The residue obtained from the filtrate on evaporation was chromatographed on silica gel with hexane-benzene (2:1). The first fraction was again chromatographed on alumina with the same solvent to give a trace of ferrocene and 0.06 g of biferrocenyl. The second fraction afforded 0.37 g (24.2% yield) of ferrocenyl benzoate. The total yield of biferrocenyl amounted to 0.62 g (67.0%).

The Reaction of *o*-Iodonitrobenzene with Copper(I) Acetate in Pyridine. The residue obtained from the reaction of *o*-iodonitrobenzene with copper(I) acetate under the conditions described above in the general procedure was chromatographed on silica gel with hexane-benzene (2:1) to give 0.12 g of a yellow liquid as a first fraction and 0.51 g (83.6%) of 2,2′-dinitrobiphenyl as a second fraction. The yellow liquid obtained from the first fraction was supposed to be a mixture of nitrobenzene and *o*-iodonitrobenzene, though attempts at identification failed because of the difficulty of separation.

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