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Alkoxylation of Ferrocene by Photolysis of Haloferrocenes in Aqueous Alcohols

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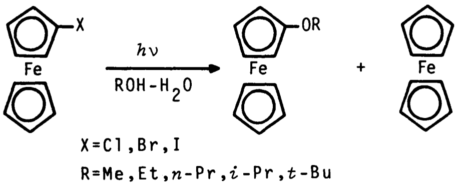
Synopsis. The UV irradiation of haloferrocenes in aqueous alcohols resulted in an alcoholysis with the formation of the corresponding alkoxyferrocenes accompanied by the formation of ferrocence. The order of the reactivities of haloferrocenes was I>Br>Cl.

Considerable attention has been directed to the realm of photosubstitution of aromatic compounds.1) However, photosubstitution of ferrocene derivatives has not been extensively studied.2) In this paper, we report the photolysis of haloferrocenes in aqueous alcohols. The photochemical substitution of halogens with alkoxyl groups occurred.

The irradiation of an aqueous methanol solution of bromoferrocene in the presence of sodium carbonate afforded methoxyferrocene(60%) and ferrocene(8%). Similarly, iodo- and chloroferrocenes produced methoxyferrocene. Photolysis of these haloferrocenes in other alcohols also gave mixtures of the corresponding alkoxyferrocenes and ferrocene.

The photoreactions are generalized in Scheme 1. The results are summarized in Table 1. The reactivities of halogens are I>Br>Cl for both photosubstitution and photoreduction.



Scheme 1.

Table 1. Photochemical reactions of haloferrocenes with alcohols

FcX a) X	ROH b) R	Time of irradn/h c)	Conversion/%	Yield/% d) FcOR	 FcH
Cl	Me	10	69	46	5
	i-Pr	10	40	20	8
Br	Me	1.5	87	60	8
	Et	1.5	75	37	10
	n-Pr	1.5	59	14	13
	i-Pr	1.5	64	21	15
	t-Bu	1.5	45	8	18
I	Me	1.0	93	47	25
	i-Pr	1.0	74	18	28

a) [FcX] = 1.8 mmol dm^{-3}. b) The solutions contained 10% of water and 10 mmol dm^{-3} of Na_2CO_3. c) High pressure Hg arc lamp with a Pyrex filter. d) Yields were determined by GLC and based on unrecovered haloferrocene.

The nucleophilic substitution of ferrocene derivatives takes place with difficulty, and few cases have been reported.3) The alkoxyferrocenes, other than methoxyferrocene, have not been synthesized. This type of reaction affords a new route for the introduction of alkoxyl groups into the ferrocene ring: The reactivity of chloroferrocene is too small. The reaction of iodoferrocene gave a considerable amount of ferrocene. Consequently, bromoferrocene is adequate for the synthesis of alkoxyferrocenes.

Experimental

The melting points were measured with a Mettler FR-2 melting point apparatus and are uncorrected. IR spectra were obtained with a JASCO A-302 spectrometer. ^{1}H NMR spectra were taken with a Hitachi R-22 apparatus an chemical shifts are given in ppm from TMS internal standard. GLC analysis were carried out by means of a Shimadzu 4C-PF apparatus. Mass spectra were obtained using a Hitachi M-52 mass spectrometer at 20 eV.

Materials. Bromo- and iodoferrocenes were synthesized by the reaction of *N*-halosuccinimides with ferrocenylmercury(II) chloride.4) Bromoferrocene; mp 31.5—32 °C (lit,4) 30—31 °C). Iodoferrocene; mp 46—47 °C (lit,4) 45.5—46 °C). Chloroferrocene was prepared by refluxing iodoferrocene with copper(I) chloride in pyridine.5) mp 57—57.5 °C (lit,5) 56—56.5 °C).

Irradiation of Haloferrocenes. A solution of haloferrocene(1.8 mmol dm^{-3}) in alcohol-water(9:1 v/v, 200 cm^3) in the presence of sodium carbonate(5 mmol dm^{-3}) was irradiated in a Pyrex vessel with a 300 W high pressure Hg arc lamp (Eikosha) externally at room temperature. The reaction mixture was extracted with benzene, and resultant benzene solution was washed with water and dried (Na_2SO_4). After removal of the solvent, products were isolated by means of preparative TLC (Merck Silica Gel 60 PF_{254}–hexane).

Methoxyferrocene: Mp 40—41 °C (lit,4) 39—40.5 °C). Found: M$^+$ 216.

Ethoxyferrocene: An orange oily substance. IR (neat) 3120, 2995, 1108, 1025, 1003, 816, 688 (Fc ring), 2950, 1476, 1382, 1251, and 1065 cm^{-1} (EtO); ^{1}H NMR ($CDCl_3$) δ=1.32 (t, 3H), 3.81 (q, 2H), 3.75—3.95 (m, 2H), 4.0—4.15 (m, 2H) and 4.16 (s, 5H); MS *m/z* (rel intensity) 230 (M$^+$, 100), 202 (76), 172 (33), and 121 (33). Found: C, 62.38; H, 6.01. Calcd for $C_{12}H_{14}OFe$: C, 62.64; H, 6.13.

Propoxyferrocene: An orange oily substance; IR (neat) 3105, 2970, 1104, 1000, 815, 682 (Fc ring), 2940, 2880, 1472, 1387, 1250, and 1060 cm^{-1} (*n*-PrO); ^{1}H NMR ($CDCl_3$) δ=1.00 (t, 3H), 1.73 (sex, 2H), 3.76 (t, 2H), 3.86 (s, 2H), 4.10 (s, 2H), and 4.20 (s, 5H); MS *m/z* (rel intensity) 244 (M$^+$, 59), 202 (75), 172 (18), and 121 (100). Found: C, 63.62; H, 6.45. Calcd for $C_{13}H_{16}OFe$: C, 63.96; H, 6.61.

Isopropoxyferrocene: An orange oily substance; IR (neat) 3120, 3000, 1003, 819, 629 (Fc ring), 2955, 2870, 1388, 1378, 1255, 1122, 1045, and 918 cm^{-1} (*i*-PrO); ^{1}H NMR ($CDCl_3$) δ=1.28 (d, 6H), 3.8—4.0 (m, 2H), 4.0—4.2 (m, 3H), and 4.19 (s, 5H); MS *m/z* (rel intensity) 244 (M$^+$, 100), 202 (76), 172 (33), and 121 (33). Found:

C, 63.57; H, 6.48. Calcd for $C_{13}H_{16}OFe$: C, 63.96; H, 6.61.

t-Butoxyferrocene: mp 68—68.5 °C; IR (KBr) 3110, 2995, 1110, 1012, 802 (Fc ring), 2950, 2880, 1460, 1373, 1365, 1246, and 1055 cm^{-1} (*t*-BuO); ^{1}H NMR ($CDCl_3$) δ=1.13 (s, 9H), 3.8—4.0 (m, 2H), and 4.05—4.3 (m, 7H), MS *m/z* (rel intensity) 258 (M^+, 100), 202 (98), 172 (50), and 121 (33). Found: C, 65.01; H, 7.07. Calcd for $C_{14}H_{18}OFe$: C, 65.14; H, 7.03.

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