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Photochemical Substitution of Ferrocene in Halogenated Hydrocarbon-Ethanol Solutions

Takeo AKIYAMA, Yoshiyuki HOSHI,* Satoshi GOTŌ,** and Akira SUGIMORI

Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioi-cho 7, Chiyoda-ku, Tokyo 102

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The photochemical substitution of ferrocene in several halogenated hydrocarbon–ethanol solutions was investigated. Ethoxycarbonyl, formyl, ethoxymethyl, benzyl and allyl groups were photochemically introduced into ferrocene in 25—53% yields by the UV-irradiation of ferrocene in carbon tetrachloride–, chloroform–, dichloromethane–, benzyl chloride–, and allyl bromide–ethanol solutions, respectively. The reactions proceeded effectively by the excitation of the charge transfer complexes formed between ferrocene and halogenated hydrocarbons.

Investigations have been made on the chemistry of ferrocene but only a few reports have appeared on the photochemical reactions of ferrocene. Nesmeyanov and his co-workers reported on the photochemical decomposition of several ferrocene derivatives.[1a–c]

van Riel *et al.* reported on the elimination of boric acid in the photolysis of ferroceneboronic acid in an aqueous alkaline solution.[2] Brand and Snedden observed a dissociative charge transfer absorption of ferrocene in a carbon tetrachloride solution.[3] Körner von Gustorf and his co-workers found that UV-irradiation of ferrocene in carbon tetrachloride gave ferrocenium tetrachloroferrate (III) almost quantitatively and they discussed the mechanism of its formation.[4] Spilners also reported the formation of ferrocenium tetrachloroferrate (III) in the photolysis of ferrocene in hexachlorocyclopentadiene.[5] Traverso and Scandola reported on the photochemical oxidation of ferrocene to ferrocenium ion in a carbon tetrachloride–ethanol solution, but they did not refer to the reaction product.[6] We reported the photochemical substitution of ferrocene in several organic halide–ethanol solutions.[7] The present paper deals with the photochemical introduction of ethoxycarbonyl, formyl, ethoxymethyl, benzyl, and allyl groups into ferrocene nucleus by UV-irradiation.

Experimental

Materials. Ferrocene was prepared from cyclopentadiene and iron(III) chloride by the method of Wilkinson *et al.*,[8] and was purified by column chromatography on silica gel. Mp 172—173 °C (lit,[9] 174 °C).

Carbon tetrachloride, chloroform and dichloromethane were purified by the method given in literature.[10] Benzyl chloride, benzal chloride, benzotrichloride, chlorobenzene, *n*-butyl chloride, *t*-butyl chloride, allyl chloride and allyl bromide were washed with aqueous alkaline solution and water, dried over calcium chloride and then distilled under reduced pressure just before use. Commercial *p*-nitrobenzyl chloride (Tokyo Kasei, Reagent Grade) was used without further purification.

Irradiation (General Procedure). A sample solution in a vessel equipped with gas inlet tube was irradiated internally with a high pressure mercury lamp (100 W high pressure mercury lamp, Ushio Denki, or 150 W high pressure mercury lamp, Taika Kogyo) with a quartz or a Pyrex jacket for cooling water, or a low pressure mercury lamp (120 W low pressure mercury lamp, Taika Kogyo) immersed in a sample solution. The reaction vessel was cooled externally by current water. During the course of irradiation nitrogen was bubbled through the solution. For irradiation of a comparatively small amount of solution, the sample solution in a quartz vessel was irradiated externally at the center of the spiral light source (16 W low pressure mercury lamp, Taika Kogyo) which was placed in a water bucket for cooling.

Separation of the Photoproducts (General Procedure). The irradiated solution was immediately washed with 0.1 M aqueous hydrochloric acid solution and extracted with *n*-hexane. The *n*-hexane solution was concentrated under reduced pressure below 45 °C and the residue was subjected to column chromatography on silica gel.

In the treatment of the reaction mixture from the photoreaction with less volatile chlorides such as benzyl, benzal and benzotrichloride, ether solution of anhydrous iron(III) chloride was added to the *n*-hexane solution to convert all the ferrocene and its derivatives into the corresponding ferrocenium salts. Ferrocenium salts and excess iron(III) chloride were extracted with water and then the ferrocenium salts were reconverted into ferrocene derivatives with sodium bisulfite. The reduced compounds were again extracted with *n*-hexane and dried over anhydrous sodium sulfate. After the solvent was removed, the residue was subjected to column chromatography on silica gel.

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* Present Address: Fuji Photo Film Co., Ltd., Nakanuma 210, Minami-ashigara-cho, Ashigara-shi, Kanagawa.

** Present Address: Konishiroku Photo Industry Co., Ltd., Hino-shi, Sakura-cho 1, Tokyo.

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Identification of the Photoproducts. *Ethyl Ferrocenecarboxylate*: The compound was obtained in the photoreaction of ferrocene in carbon tetrachloride–ethanol solution. It was obtained as a yellow crystalline solid from the benzene fraction of column chromatography. Mp 58—61 °C. IR (KBr), 1690 cm^{-1} ($\nu_{C=O}$), 1100, 1040, 1000 cm^{-1} (mono substituted ferrocene). NMR (CCl_4), δ 4.70 (t), 2H (2,5H of the cyclopentadienyl ring of ferrocene); 4.22 (q), 2H (3,4H of the cyclopentadienyl ring of ferrocene); 4.10 (s), 5H (C_5H_5); 4.1 (q), 2H ($-CH_2-$); 1.32 (t), 3H ($-CH_3$).

Found: C, 58.0; H, 5.51%.

Formylferrocene: The compound was obtained in the photoreaction of ferrocene in chloroform–ethanol solution. Yellow orange substance was eluted with benzene on column chromatography. Mp 124—125 °C (lit,[11] 124.5 °C). IR spectrum was identical with that of the sample prepared by the method given in literature.[11]

Ethoxymethylferrocene: The compound was obtained in the photoreaction of ferrocene in dichloromethane–ethanol solution. It was eluted with *n*-hexane–benzene (9: 1) on column chromatography. Deep orange oil. Bp 112—113 °C/2 mmHg (lit,[12] 112—113.5 °C/2 mmHg). IR (direct), 2850, 1090, 920 cm^{-1} (ether), 1480, 1380 cm^{-1} ($-CH_2-$), 1100, 1020, 1000 cm^{-1} (mono substituted ferrocene). NMR (CCl_4), δ 4.11 (m), 6H ($C_5H_4-CH_2-$); 4.00 (s), 5H (C_5H_5); 3.39 (q), 2H ($-CH_2-$); 1.13 (t), 3H ($-CH_3$).

Found: C, 61.35; H, 6.39%.

1,1′-Diethoxymethylferrocene: The compound was obtained in the photoreaction of ferrocene in dichloromethane–ethanol solution. It was eluted with *n*-hexane–benzene (1: 1) after monoether had been eluted. Yellow oily substance. IR (direct), 2840, 1090, 930 cm^{-1} (ether), 1450, 1380 cm^{-1} ($-CH_2-$). The IR spectrum of this compound was nearly the same as that of monoether except for the peak at 1000 cm^{-1} which is characteristic of mono substituted ferrocene and ferrocene. NMR (CCl_4), δ 4.10 (m), 12H ($C_5H_4-CH_2-$); 3.96 (q), 4H ($-CH_2-$); 1.12 (t), 6H ($-CH_3$).

Found: C, 63.36; H, 7.14%. Calcd for $C_{16}H_{22}O_2Fe$: C, 63.59; H, 7.14%.

Benzylferrocene: The compound was obtained in the photoreaction of ferrocene in benzyl chloride–ethanol (20: 140 v/v) solution. It was obtained as a yellow orange crystalline solid (160 mg) from *n*-hexane–benzene (1: 1) fraction of column chromatography. Mp 75—76 °C (lit,[13] 74.5—76 °C). IR (KBr), 3020, 2920, 1603, 1495, 720, 699 cm^{-1} ($-CH_2-C_6H_5$), 1100, 1020, 1000 cm^{-1} (mono substituted ferrocene). NMR (CCl_4), δ 7.12 (s), 5H (C_6H_5-); 4.00 (s), 9H (C_5H_4-, C_5H_5); 3.64 (s), 2H ($-CH_2-$).

Found: C, 74.31; H, 6.39%.

Dibenzylferrocene: The compound was obtained as in the reaction described above. It was obtained as a yellow crystalline solid (50 mg) from benzene fraction of column chromatography, and was found to be a mixture of 1,2- and 1,3-dibenzylferrocene. IR (KBr), 3027, 2920, 1603, 1495, 700 cm^{-1} ($C_6H_5-CH_2-$), 1100, 1035, 1020, 1000, 940, 925, 920 cm^{-1} (homo annularly substituted ferrocene.[14]) NMR (CCl_4), δ 7.13 ($C_6H_5-CH_2-$); 7.05 ($C_6H_5-CH_2-$); 3.93 (s), (C_5H_5, C_5H_3-); 3.69 ($-CH_2-$); 3.60 ($-CH_2-$).

p-*Nitrobenzylferrocene*: The compound was obtained in the photoreaction of ferrocene with *p*-nitrobenzyl chloride in ethanol. It was obtained as a brown red substance (3.0 mg) from benzene fraction. IR (KBr), 2900, 1603, 1590, 1510, 1340, 710 cm^{-1} (p-$NO_2C_6H_4-CH_2-$), 1100, 1020, 1000 cm^{-1} (mono substituted ferrocene).

Phenylferrocene: The compound was obtained in the photoreaction of ferrocene in chlorobenzene–ethanol (10:110 v/v) solution. It was obtained as an orange crystalline solid (15 mg) from *n*-hexane–benzene (1: 1) fraction of column chromatography. IR (KBr), 3027, 1603, 1510, 690 cm^{-1} (C_6H_5-), 3080, 1100, 1020, 1000 cm^{-1} (mono substituted ferrocene). NMR (CCl_4), δ 7.20 (m), 5H (C_6H_5-); 4.50 (t), 2H (2,5H of the cyclopentadienyl ring of ferrocene); 4.16 (t), 2H (3,4H of the cyclopentadienyl ring of ferrocene); 3.90 (s), 5H (C_5H_5).

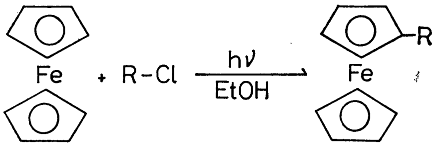
Found: C, 73.72; H, 5.20%.

Allylferrocene: The compound was obtained in the photoreaction of ferrocene in allyl bromide–ethanol (30: 250 v/v) solution. It was obtained as a dark orange liquid substance (900 mg) from *n*-hexane–benzene (2: 1) fraction of column chromatography. IR (direct), 3080, 3010, 2910, 1640, 1430, 1410 cm^{-1} (allyl group), 1100, 1020, 1000 cm^{-1} (mono substituted ferrocene). NMR (CCl_4), δ 5.70 (m), 1H ($-\underline{CH}=CH_2$); 4.90 (m), 2H ($-CH=\underline{CH_2}$); 3.96, 9H (C_5H_4-, C_5H_5); 2.98 (d), ($-CH_2-$).

Measurement. The electronic absorption spectra were measured with a Hitachi Model 124 UV–VS spectrophotometer. The NMR and IR spectra were obtained on a JEOL H-60 NMR spectrometer and a Hitachi Model 215 grating infrared spectrophotometer, respectively.

Results and Discussion

Although the UV-irradiation of ferrocene in carbon tetrachloride gave blue-gray precipitate of ferrocenium tetrachloroferrate (III) as was reported by Körner von Gustorf and his co-workers,[4] the UV-irradiation of ferrocene in a carbon tetrachloride–ethanol solution in the atmosphere of nitrogen gave ethyl ferrocenecarboxylate, a substitution product. Similar reactions were observed in the UV-irradiation of ferrocene in chloroform- and dichloromethane–ethanol solutions. Results of the reactions in these solvents are summarized in Table 1. The photoreactions can be generalized as follows.



$R = -CCl_3$ $R' = -CO_2Et$
$R = -CHCl_2$ $R' = -CHO$
$R = -CH_2Cl$ $R' = -CH_2OEt$

These reactions are formally the substitution at the cyclopentadienyl ring of ferrocene by halomethyl radicals formed by the fission of R–Cl bond of halomethanes, followed by the ethanolysis of halomethyl groups. This type of reaction affords a new route for the introduction of ethoxycarbonyl, formyl and ethoxymethyl groups into ferrocene ring.

However, it was not effective for alkyl and aryl monochlorides such as *t*-butyl chloride and chlorobenzene. Of phenyl substituted chloromethanes,

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TABLE 1. PHOTOCHEMICAL REACTIONS OF FERROCENE IN HALOGENATED HYDROCARBON–ETHANOL 1:1 SOLUTIONS

Run	FcH[a)] (g)	Solvent (ml)	Light (W)	FcH reacted (%)	Product	Yield[b)] (%)
1	3.7	CCl_4–EtOH (280)	LP(16)[c)] 48 hr	57	FcCOOEt	20
2	3.0	CCl_4–EtOH (140)	HP(150)[d)] 8 hr	35	FcCOOEt	38
3	1.9	CCl_4–EtOH (400)	HPpy(100)[e)] 7 hr	34	FcCOOEt	32
4	3.0	$CHCl_3$–EtOH (220)	LP(120) 7 hr	84	FcCHO	42
5	2.0	$CHCl_3$–EtOH (140)	HP(150) 5 hr	35	FcCHO	trace[f)]
6	4.0	CH_2Cl_2–EtOH (220)	LP(120) 7 hr	72	$FcCH_2OEt$ $(C_5H_4CH_2OEt)_2Fe$[g)]	43 36
7	1.0	CH_2Cl_2–EtOH (140)	HP(150) 3 hr	9	$FcCH_2OEt$ $(C_5H_4CH_2OEt)_2Fe$	53 12

a) Fc: $C_5H_5FeC_5H_4$–.
b) Yield based on unrecovered ferrocene.
c) LP: Low pressure mercury lamp.
d) HP: High pressure mercury lamp.
e) HPpy: High pressure mercury lamp with a Pyrex filter.
f) Formylferrocene is sensitive to 313 nm light.
g) 1,1′-Diethoxymethylferrocene.

TABLE 2. PHOTOCHEMICAL REACTIONS OF FERROCENE IN HALOGENATED HYDROCARBON–ETHANOL SOLUTIONS

Run	FcH[a)] (g)	R–Cl (ml)	Light (W)	Time (hr)	FcH reacted (%)	Product	Yield[b)] (%)
8	1.9	*n*-BuCl (10)	LP[c)] (16)	9	—	$Fc(CH_2)_3CH_3$	trace
9	1.0	*t*-BuCl (15)	HP[d)] (100)	40	7	none	
10	1.9	PhCl (10)	LP (120)	8	—	FcC_6H_5	trace
11	1.0	PhCl (10)	HPpy[e)] (100)	20	35	FcC_6H_5	3.0
12	2.0	$PhCH_2Cl$ (20)	LP (16)	20	65	$FcCH_2C_6H_5$ Disubstituted	6.4 1.2
13	1.0	$PhCH_2Cl$ (20)	HPpy (100)	20	42	$FcCH_2C_6H_5$ Disubstituted	25.6 6.0
14	1.0	$PhCHCl_2$ (20)	LP (16)	45	67.5	$FcCH_2C_6H_5$	trace
15	1.0	$PhCHCl_2$ (10)	HPpy (100)	20	34	$FcCH_2C_6H_5$	trace
16	2.0	$PhCHCl_2$ (20)	HP (150)	16	45.5	$FcCH_2C_6H_5$	4.4
17	2.0	$PhCCl_3$ (20)	LP (120)	5	60.5	none	
18	2.0	$PhCCl_3$ (20)	HP (150)	16	65.0	none	
19	2.0	*p*-$NO_2C_6H_4CH_2Cl$ (3g)	LP (120)	6	6.5	*p*-$NO_2C_6H_4CH_2Fc$	1.2
20	2.0	*p*-$NO_2C_6H_4CH_2Cl$ (5g)	HP (150)	16	4.5	none	
21	2.6	$CH_2=CHCH_2Br$ (30)	LP (16)	14.5	72.5	$FcCH_2CH=CH_2$	39.1
22	2.0	$CH_2=CHCH_2Br$ (80)	HPpy (100)	20	21	$FcCH_2CH=CH_2$	45
23	1.3	$CH_2=CHCH_2Cl$ (30)	HP (150)	40	—	$FcCH_2CH=CH_2$	trace

a) Fc: $C_5H_5FeC_5H_4$–. b) Yield based on unrecovered ferrocene. c) LP: Low pressure mercury lamp. d) HP: High pressure mercury lamp. e) HPpy: High pressure mercury lamp with a Pyrex filter.

benzyl chloride gave photoproducts in considerable yields in the photoreaction with ferrocene, but benzal chloride and benzotrichloride gave only a trace of the substitution products. The results of the photoreactions of ferrocene with chlorides other than chloromethanes are listed in Table 2.

In the photoreactions of ferrocene with halides listed in Table 2, the yields of the photoproducts are lower than those shown in Table 1, except for allyl bromide.

In ferrocene–dichloromethane–ethanol system and ferrocene–benzyl chloride–ethanol system, disubstituted ferrocenes were obtained. However, the yields of the substitution products were lower in the latter system. This type of photoreaction is closely related to the formation of charge transfer complexes between ferrocene and halogenated hydrocarbons.

Brand and Snedden reported that the charge transfer absorption of ferrocene at 300—340 nm in several halogenated hydrocarbon solvents can be attributed to the electron transfer from ferrocene to the solvents.[3)] The UV-spectra of ferrocene in ethanol and halogenated hydrocarbon–ethanol solutions are shown in Figs. 1 and 2. The UV-spectra of ferrocene in carbon tetrachloride, chloroform, dichloromethane, allyl bromide, ben-

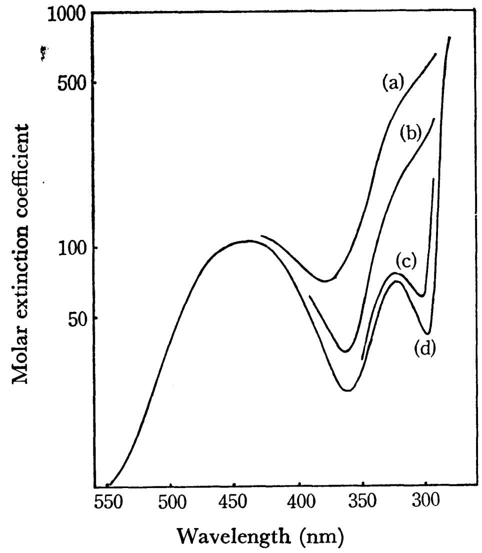

Fig. 1. UV-Spectra of ferrocene in halogenated hydrocarbon–ethanol solutions

(a) Ferrocene (5×10^{-3}mol/l) in carbon tetrachloride–ethanol (1: 1 v/v) solution.

(b) Ferrocene (5×10^{-3}mol/l) in allyl bromide–ethanol (1: 1 v/v) solution.

(c) Ferrocene (5×10^{-3}mol/l) in dichloromethane.

(d) Ferrocene (5×10^{-3}mol/l) in ethanol.

* The UV-spectra of ferrocene (5×10^{-3}mol/l) in chloroform–ethanol (1: 1 v/v) solution was nearly the same as those shown in (b). The UV-spectra of ferrocene (5×10^{-3}mol/l) in allyl chloride–ethanol (3.5×10^{-2}mol/l in ethanol) solution was nearly the same as those shown in (d).

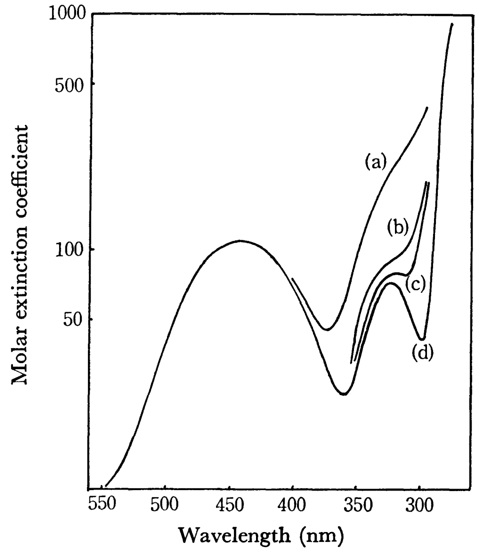

Fig. 2. UV-Spectra of ferrocene in halogenated hydrocarbon–ethanol solutions.

(a) Ferrocene (5×10^{-3}mol/l) in benzyl chloride–ethanol (7.0×10^{-1}mol/l in ethanol) solution.

(b) Ferrocene (5×10^{-3}mol/l) in benzal chloride–ethanol (5.5×10^{-1}mol/l in ethanol) solution.

(c) Ferrocene (5×10^{-3}mol/l) in benzotrichloride–ethanol (6.8×10^{-1}mol/l) solution.

(d) Ferrocene (5×10^{-3}mol/l) in ethanol.

* The UV-spectra of ferrocene (5×10^{-3}mol/l) in *n*-butyl chloride– and *t*-butyl chloride–ethanol solutions (1: 1 v/v) were nearly the same as those shown in (d). In chlorobenzene–ethanol (3.5×10^{-2}mol/l), it is similar to that in ethanol.

zyl chloride, benzal chloride, benzotrichloride and *p*-nitrobenzyl chloride showed the charge transfer absorption at 300—380 nm, but other chlorides, such as *n*-butyl chloride, *t*-butyl chloride, allyl chloride and chlorobenzene showed no charge transfer absorption.

As seen from Tables 1 and 2 and Fig. 1, the system showing charge transfer absorption afforded the photoproducts in higher yields in the irradiation with a high pressure mercury lamp (runs 1—7, Table 1, and runs 12—16, 21, 22, Table 2) than in that with a low pressure mercury lamp. Therefore, the charge transfer complex between ferrocene and halogenated hydrocarbons thus plays an important role.

In the ferrocene–chloroform–ethanol system, the low yield of the photoproducts is due to its sensitivity to 313 nm light which causes secondary decomposition.

In the ferrocene–*p*-nitrobenzyl chloride–ethanol system, the observed charge transfer absorption might be due to the interaction between ferrocene and nitro group, since the formation of ferrocenium ion was not observed and the percentage of loss of ferrocene and that of the product yield were extremely low. In the ferrocene–benzotrichloride–ethanol system, despite the high percentage of loss of ferrocene in irradiation with both high and low pressure mercury lamps, absence of the photoproduct might be due to the photo-sensitivity of benzotrichloride itself. The absorption of incident light by benzyl chloride, benzal chloride and benzotrichloride in the 300—340 nm region causes decomposition of the chlorides in irradiation with a high pressure mercury lamp. The high percentage of loss of ferrocene (runs 12—18, Table 2) might be due to the decomposition of ferrocene by the attack of chlorine atom produced by direct decomposition of the chlorides.