May, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (5), 1137—1141 (1977) 1137

Substituent Effects on the Photo-ethoxycarbonylation of Monosubstituted Ferrocenes

Takeo Akiyama, Taro Kitamura, Takao Kato, Haruo Watanabe,
Toshio Serizawa, and Akira Sugimori
*Department of Chemistry, Faculty of Science and Technology, Sophia University,
Kioi-cho 7, Chiyoda-ku, Tokyo 102*

(Received March 17, 1976)

The effect of the substituent in the ferrocene nucleus on the photo-ethoxycarbonylation of monosubstituted ferrocene in carbon tetrachloride–ethanol solution is described. The electron withdrawing substituents, such as chloro, bromo, iodo, cyano, and acetyl, retarded the photo-ethyoxycarbonylation, whereas the electron releasing substituents, such as ethyl accelerated the reaction. The electronic effects which affect the formation of the charge transfer complex and those which affect the reactivity of the cyclopentadienyl ring toward the attack of a trichloromethyl radical can be considered for the photo-ethoxycarbonylation.

In the previous paper,[1a] we reported the photochemical introduction of ethoxycarbonyl, formyl, and ethoxymethyl into the ferrocene nucleus in carbon tetrachloride–, chloroform–, and dichloromethane–ethanol solutions. In the photo-ethoxycarbonylation of ferrocene in the carbon tetrachloride–ethanol system, the excitation of the charge transfer complex of ferrocene with carbon tetrachloride plays an important role in the initial stage of the photo-substitution.[1b] This paper deals with the effect of the substituent in the ferrocene nucleus upon the photo-ethoxycarbonylation of monosubstituted ferrocene in carbon tetrachloride–ethanol solutions.

Experimental

Materials. Ethylferrocene[2] [bp 92 °C/1 Torr, (lit,[3] 93—94 °C/1 Torr)], acetylferrocene[4] [mp 85—86.5 °C(lit,[4] 85—86 °C)], iodoferrocene[5] [mp 48—49 °C (lit,[5] 43—45 °C)], chloroferrocene[6] [mp 59 °C(lit,[7] 59—60 °C)], bromoferrocene[6] [mp 36.1—36.2 °C(lit,[8] 30—31 °C)], cyanoferrocene[6] [mp 103.5 °C(lit,[8] 107—108 °C)], methoxyferrocene[7] [mp 41.5—41.8 °C(lit,[7] 38.5—40 °C)], and phenylferrocene[9] [mp 114 °C(lit,[9] 114—5 °C)] were prepared from ferrocene(Wako Junyaku Co., G. R. grade reagent) by the method given in the literatures. Carbon tetrachloride and ethanol were purified by the method described in the previous paper.[1a]

Irradiation Procedure. General procedure is similar to that described previously.[1a]

Separation of the Photoproducts (General Procedure). After irradiation, the reaction mixture was washed successively with water, aqueous sodium hydrogencarbonate solution and aqueous sodium thiosulfate solution, and then extracted with dichloromethane or ether. The extract was dried over anhydrous sodium sulfate, then the solvent was removed by a rotary evaporator below 30 °C. The residue was subjected to thin layer(Merck, GF-254) or column(Wako Junyaku Co., Wakogel C-200) chromatography in order to separate the photoproducts and the starting material, and then the ethoxycarbonylated compounds were isolated by the second thin layer chromatography(TLC).

Identification of the Photoproducts. The assignments of the chemical shifts of 2-, 3-, 4-, and 5-position were done based on the calculated chemical shifts of those positions. The calculated chemical shifts were obtained by summing the deshielding or the shielding effect of the substituent and the deshielding effect of ethoxycarbonyl to α- and β-positions.[10] The experimentally obtained chemical shifts agreed generally with the calculated ones.

Ethyl 2-Ethylferrocenecarboxylate: A dark red liquid substance. NMR(CCl_4), δ(ppm from TMS) 4.60(t), 1H(H_5); 4.26—4.09, 2H(H_3 and H_4); 4.20(q), 2H($-CH_2-$ of ester); 4.0(s), 5H(C_5H_5); 2.45—2.93(m), 2H($-CH_2-$ of ethyl[11,12]); 1.34(t), 3H($-CH_3$ of ester); 1.13(t), 3H($-CH_3$ of ethyl). IR (direct), 3100, 2960, 2920, 1100, 1000, 920 cm^{-1} (2-substituted ethylferrocene), 1705, 1290 cm^{-1} (ester). MS(70 eV), *m/e*, 286(M^+). Found: C, 62.13; H, 6.35%. Calcd for $C_{15}H_{18}O_2Fe$: C, 62.94; H, 6.29%, Mol wt, 286.

Ethyl 3-Ethylferrocenecarboxylate: A dark red oily substance. NMR(CCl_4), δ(ppm from TMS) 4.62(t), 2H(H_2 and H_5); 4.26—4.2(q and t), 3H($-CH_2-$ of ester and H_4); 4.05(s), 5H(C_5H_5); 2.35(q), 2H($-CH_2-$ of ethyl); 1.32(t), 3H($-CH_3$ of ester); 1.19(t), 3H($-CH_3$ of ethyl). IR(direct), 3100, 2960, 2920, 1100, 1000, 930, 910 cm^{-1} (3-substituted ethylferrocene), 1705, 1285 cm^{-1}(ester). MS(70 eV), *m/e*, 286(M^+). Found: C, 62.29; H, 6.45%. Calcd for $C_{15}H_{18}O_2Fe$: C, 62.94; H, 6.29%, Mol wt, 286.

Ethyl 1′-Ethylferrocenecarboxylate: A red oily substance. NMR(CCl_4), δ(ppm from TMS) 4.61(t), 2H(H_2 and H_5); 4.24—4.15, 4H(H_3 and H_4, and $-CH_2-$ of ester); 3.98(s), 4H($H_{2'}$, $H_{3'}$, $H_{4'}$, $H_{5'}$); 2.30(q), 2H($-CH_2-$ of ethyl); 1.32(t), 3H($-CH_3$ of ester); 1.12(t), 3H($-CH_3$ of ethyl). IR(direct), 3080, 2960, 2920, 900, 890 cm^{-1} (the absence of absorption at 9 and 10 μ indicates 1,1′-disubstituted ferrocene), 1710, 1270 cm^{-1} (ester). MS(70 eV), *m/e*, 286(M^+). Found: C, 62.67; H, 6.60%. Calcd for $C_{15}H_{18}O_2Fe$: C, 62.94; H, 6.60%, Mol wt, 286.

Ethyl 3-Phenylferrocenecarboxylate: A yellow orange solid. NMR(CCl_4), δ(ppm from TMS) 7.50—7.05(m), 5H($-C_6H_5$); 5.18(t), 1H(H_2); 4.83(t), 1H(H_5); 4.74(t), 1H(H_4); 4.24(q), 2H($-CH_2-$ of ester); 4.01(s,) 5H(C_5H_5); 1.36(t), 3H($-CH_3$ of ester). IR(KBr), 3100, 3050, 1600, 1100, 1000, 925, 890 cm^{-1} (3-substituted phenylferrocene), 1705, 1240 cm^{-1} (ester). MS (70 eV), *m/e*, 334(M^+). Found: C, 68.27; H, 5.36%. Calcd for $C_{19}H_{18}O_2Fe$: C, 68.26; H, 5.39%, Mol wt, 334.

Ethyl 2-Phenylferrocenecarboxylate: A yellow oily substance. IR(KBr), 3100, 3050, 1600, 1105, 997, 950 cm^{-1} (2-substituted phenylferrocene), 1705, 1240 cm^{-1} (ester). MS(70 eV), *m/e*, 334(M^+). Found: C, 68.77; H, 5.44%. Calcd for $C_{19}H_{18}O_2Fe$: C, 68.26; H, 5.39%, Mol wt, 334.

Ethyl 1′-Phenylferrocenecarboxylate: A yellow orange solid. NMR(CCl_4), δ(ppm from TMS) 7.5—7.1(m), 5H($-C_6H_5$); 4.55(t), 4H($H_{2'}$, $H_{5'}$ and H_2, H_5); 4.25(t), 2H(H_3 and H_4); 4.14(t), 2H($H_{3'}$ and $H_{4'}$); 4.01(q), 2H($-CH_2-$ of ester); 1.26 (t), 3H($-CH_3$ of ester). IR(KBr), 3090, 3050, 1600, 920, 880 cm^{-1} (1′-substituted phenylferrocene), 1685, 1280 cm^{-1} (ester). MS(70 eV), *m/e*, 334(M^+). Found: C, 68.14; H, 5.38%. Calcd for $C_{19}H_{18}O_2Fe$: C, 68.26; H, 5.39%, Mol wt, 334.

Ethyl p-*Ferrocenylbenzoate*: A yellow orange solid substance. NMR(CCl_4), δ(ppm from TMS) 7.95—7.35(q), 4H (1,4-disubstituted benzene); 4.16(t), 2H(H_2 and H_5); 4.28(t), 2H(H_3 and H_4); 4.35(q), 2H($-CH_2-$ of ester); 3.96(s), 5H(C_5H_5); 1.38(t), 3H($-CH_3$ of ester). IR(KBr), 3070, 3040, 1610, 1100, 1000 cm^{-1} (phenylferrocene), 1705, 1235 cm^{-1}(ester). Found: C, 68.00; H, 5.39%. Calcd for $C_{19}H_{18}O_2Fe$: C, 68.26; H, 5.39%.

Ethyl 3-Methoxyferrocenecarboxylate: A yellow liquid substance. NMR(CCl_4), δ(ppm from TMS) 4.58(t), 1H(H_2); 4.45(q), 1H(H_5); 4.23(q), 1H(H_4); 4.19(q), 2H($-CH_2-$ of ester); 4.10(s), 5H(C_5H_5); 3.60(s), 3H($-OCH_3$); 1.32(t), 3H ($-CH_3$ of ester). IR(KBr), 3100, 2960, 2920, 2860, 1100, 1000(sh), 940, 920 cm^{-1} (3-substituted methoxyferrocene), 1700, 1300 cm^{-1} (ester). MS(70 eV), *m/e*, 288(M^+). Found: C, 57.71; H, 5.51%. Calcd for $C_{14}H_{16}O_3Fe$: C, 58.38; H, 5.55%, Mol wt, 288.

Ethyl 1′-Methoxyferrocenecarboxylate: A yellow oily substance. NMR(CCl_4), δ(ppm from TMS) 4.71(t), 2H(H_2 and H_5); 4.26(t), 2H(H_3 and H_4); 4.19(q), 2H($-CH_2-$ of ester); 3.97 (t), 2H($H_{2'}$ and $H_{5'}$); 3,74(t), 2H($H_{3'}$ and $H_{4'}$); 3.55 (s), 3H($-OCH_3$), 1.33(t), 3H($-CH_3$ of ester). IR(KBr), 3100, 2960, 2920, 2860, 1100, 920, 865 cm^{-1} (1′-substituted methoxyferrocene), 1710, 1280 cm^{-1} (ester). MS (70 eV), *m/e*, 288(M^+).

Ethyl 2-Chloroferrocenecarboxylate: A yellow oily substance. NMR(CCl_4), δ(ppm from TMS) 4.68(t), 1H(H_5); 4.32—4.16, 4H(H_3 and H_4, and $-CH_2-$ of ester); 4.10(s), 5H(C_5H_5); 1.33(t), 3H($-CH_3$ of ester). IR(KBr), 3100, 3020, 1100, 1000, 915 cm^{-1} (2-substituted chloroferrocene), 1710, 1280 cm^{-1} (ester). MS(70 eV), *m/e*, 292(M^+).

Ethyl 3-Chloroferrocenecarboxylate: A yellow oily substance. NMR(CCl_4), δ(ppm from TMS) 4.97(t), 1H(H_2); 4.65(t), 1H(H_5); 4.54(*t*), 1H(H_4); 4.21(q), 2H($-CH_2-$ of ester); 4.23(s), 5H(C_5H_5); 1.31(t), 3H($-CH_3$ of ester). IR(KBr), 3100, 1100, 1000, 905, 900 cm^{-1} (3-substituted chloroferrocence), 1710, 1280 cm^{-1} (ester). MS(70 eV), *m/e*, 292(M^+).

Ethyl 1′-Chloroferrocenecarboxylate: A yellow oily substance. NMR(CCl_4), δ(ppm from TMS) 4.77(t), 2H(H_2 and H_5); 4.35(t), 4H($H_{2'}$, $H_{5'}$, and H_3, H_4); 4.24(q), 2H($-CH_2-$ of ester); 4.03(t), 2H($H_{3'}$ and $H_{4'}$); 1.35(t), 3H($-CH_3$ of ester). IR(KBr), 3120, 1090, 915, 880 cm^{-1} (1′-substituted chloroferrocene), 1710, 1280 cm^{-1}(ester). MS(70 eV), *m/e*, 292(M^+).

Ethyl 2-Bromoferrocenecarboxylate: A yellow oily substance. NMR(CCl_4), δ(ppm from TMS) 4.63(t), 1H(H_5); 4.30—4.15, 4H(H_3, H_4, and $-CH_2-$ of ester); 4.11(s), 5H(C_5H_5); 1.32(t), 3H($-CH_3$ of ester). IR(KBr), 3100, 1095, 1000, 905 cm^{-1} (2-substituted bromoferrocene), 1700, 1265 cm^{-1} (ester). MS(70 eV), *m/e*, 337(M^+).

Ethyl 3-Bromoferrocenecarboxylate: A yellow oily substance. NMR(CCl_4), δ(ppm from TMS) 4.97(t), 1H(H_2); 4.67(t), 1H(H_5); 4.53(t), 1H(H_4); 4.20(s), 5H(C_5H_5); 4.30—4.15(q), 2H($-CH_2-$ of ester); 1.31(t), 3H($-CH_3$ of ester). IR(KBr), 3110, 1100, 1000, 875 cm^{-1} (3-substituted bromoferrocene), 1700, 1275 cm^{-1} (ester). MS(70 eV), *m/e*, 337(M^+).

Ethyl 1′-Bromoferrocenecarboxylate: A yellow oily substance. NMR(CCl_4), δ(ppm from TMS) 4.73(t), 2H(H_2 and H_5); 4.35(t), 4H($H_{2'}$, $H_{5'}$, and H_3, H_4); 4.23(q), 2H($-CH_2-$ of ester); 4.07(t), 2H($H_{3'}$ and $H_{4'}$); 1.38(t), 3H($-CH_3$ of ester). IR(KBr), 3100, 910, 865 cm^{-1} (1′-substituted bromoferrocene), 1705, 1270 cm^{-1} (ester). MS(70 eV), *m/e*, 337(M^+).

Ethyl 2-Iodoferrocenecarboxylate: An orange red oily substance. NMR(CCl_4), δ(ppm from TMS) 4.68(t), 2H(H_3 and H_5); 4.24(t), 1H(H_4); 4.23(q), 2H($-CH_2-$ of ester); 1.33(t), 3H($-CH_3$ of ester). IR(KBr), 3060, 1100, 1000(sh), 960, 930(sh) cm^{-1} (2-substituted iodoferrocene), 1700, 1270 cm^{-1} (ester). MS(70 eV), *m/e*, 384(M^+).

Ethyl 3-Iodoferrocenecarboxylate: An orange red oily substance. NMR(CCl_4), δ(ppm from TMS) 4.98(t), 1H(H_2); 4.68 (t), 1H(H_5); 4.52(t), 1H(H_4); 4.19(q), 2H($-CH_2-$ of ester); 4.12(s), 5H(C_5H_5); 1.24(t), 3H($-CH_3$ of ester). IR(KBr), 3080, 1100, 990, 915, 860 cm^{-1} (3-substituted iodoferrocene), 1710, 1265 cm^{-1} (ester). MS(70 eV), *m/e*, 384(M^+).

Ethyl 1′-Iodoferrocenecarboxylate: An orange red oliy substance. NMR(CCl_4), δ(ppm from TMS) 4.70(t), 2H(H_2 and H_5); 4.34(t), 2H(H_3 and H_4); 4.27(t), 2H($H_{2'}$ and $H_{5'}$); 4.22(q), 2H($-CH_2-$ of ester); 4.12(t), 2H($H_{3'}$ and $H_{4'}$); 1.31 (t), 3H($-CH_3$ of ester). IR(KBr), 3100, 905, 860 cm^{-1} (1′-substituted iodoferrocene), 1700, 1270 cm^{-1} (ester). MS(70 eV), *m/e*, 384(M^+).

Quantitative Analysis: For the photoreaction of phenyl- and haloferrocenes, quantitative analyses were carried out with GLPC(carbowax 20 M, 2 m glass column, column temperature: 170 °C for phenylferrocene and 202—230 °C for haloferrocenes. Ethyl ferrocenecarboxylate was used as an internal standard). For other monosubstituted ferrocenes, quantitative analyses were carried out by gravimetry, after the isolation of the photoproducts by column or thin layer chromatography.

Measurements: UV-spectra were recorded on a Hitachi 124 UV-VS spectrophotometer. IR-spectra were recorded on a Hitachi 215 grating infrared spectrophotometer. NMR spectra were taken with a Hitachi R-22(90 MHz) spectrometer. Mass spectra were recorded on a Hitachi RMU-6 spectrometer. Gas chromatography were performed on a Yanagimoto 550F gas chromatograph equipped with glass column.

Results and Discussion

On the irradiation with 365 nm light, ethyl-, methoxy-, phenyl-, and bromoferrocene in carbon tetrachloride–ethanol (1 : 1, v/v) solutions afforded the corresponding ethoxycarbonylated products, whereas chloro- and iodoferrocene gave only a small amount of ethoxycarbonylated products. No ethoxycarbonylation occurred in the case of cyano- and acetylferrocene. The yields of ethoxycarbonylated products and the yields of isomers are listed in Tables 1 and 2.

Ethylferrocene was effectively ethoxycarbonylated on the irradiation with 365 nm light. Ethyl 2-ethylfer-

Table 1. Photo-ethoxycarbonylation of monosubstituted ferrocenes in carbon tetrachloride–ethanol (1 : 1, v/v) solutions[a)]

Fc–R[b)] R	(mmol)	Irradiation conditions Wave-length (nm)	Time (h)	Conver-sion (%)	Ethoxycabonyl products (%)[c)]
R=$-C_2H_5$	(2.3)	365	42	20.2	88.0
R=$-H$	(1.5)	365	50	17.0	61.0
R=$-OCH_3$	(1.3)	365	42	56.0	32.1
R=$-C_6H_5$	(1.3)	365	42	29.6	42.7
R=$-Cl$	(1.3)	365	42	17.0	4.7
R=$-Br$	(1.3)	365	42	11.0	16.9
R=$-I$	(1.3)	365	42	9.0	7.3
R=$-COCH_3$	(0.5)	365	42	29.0	0.0
R=$-CN$	(1.3)	365	42	39.0	0.0

a) Each reaction was carried out at room temperature under nitrogen atmosphere. The volume of the sample solution is 40 ml. b) Fc- denotes $(C_5H_5)Fe(C_5H_4-)$. c) Yields based on consumed monosubstituted ferrocene.

TABLE 2. YIELDS OF THE ISOMERS OF ETHOXYCARBONYLATED FERROCENE DERIVATIVES[a)]

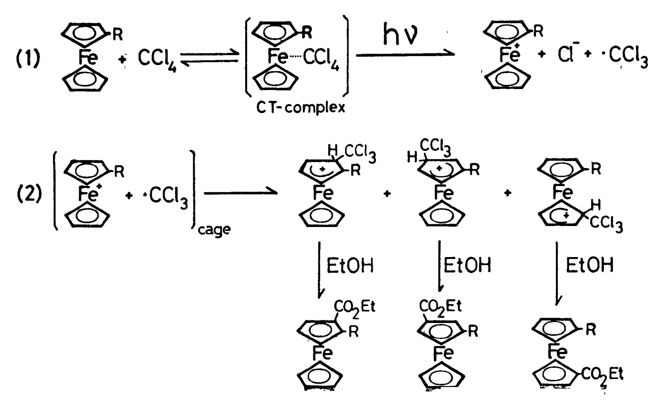
Fc-R[b)] R	Fc-R[b)] (mmol)	Irradiation conditions Wavelength (nm)	Irradiation conditions Time (h)	Products and yields[c)] (%) Disubstituted ferrocene 1,2-	1,3-	1,1'-	Ethyl *p*-ferrocenylbenzoate
R=-C_2H_5	(2.3)	365	42	10.8	35.9	41.3	—
R=-H	(1.5)	365	50	(Ethyl ferrocenecarboxylate, 61.0)		—	—
R=-OCH_3	(1.3)	365	42	0.0	8.6	23.5	—
R=-C_6H_5	(1.3)	365	42	2.1	12.0	20.9	7.7
R=-Cl	(1.3)	365	42	0.2	0.9	3.6	—
R=-Br	(1.3)	365	42	4.0	2.9	11.0	—
R=-I	(1.3)	365	42	1.6	1.4	4.3	—
R=-$COCH_3$	(0.5)	365	42	0.0	0.0	0.0	—
R=-CN	(1.3)	365	42	0.0	0.0	0.0	—

a) Each reaction was carried out at room temperature under nitrogen atmosphere. b) Fc- denotes $(C_5H_5)Fe(C_5H_4-)$. c) Yields were calculated based on consumed monosubstituted ferrocene.

rocenecarboxylate, ethyl 3-ethylferrocenecarboxylate, and ethyl 1'-ethylferrocenecarboxylate were obtained. In phenylferrocene, ethoxycarbonylation occurred not only on the ferrocene ring but also on the *para*-position of the benzene ring. In spite of the high conversion of methoxyferrocene, the yield of ethoxycarbonylated product is low. Among the haloferrocenes, bromoferrocene was most effectively ethoxycarbonylated on the irradiation with 365 nm light, and 1,2- and 1,3-isomer were obtained in addition to 1,1'-isomer. Although the yields were lower, both 1,2- and 1,3-isomer were obtained in the case of iodoferrocene. The 2-position of chloroferrocene was less effectively ethoxycarbonylated than the same position of other haloferrocenes. No ethoxycarbonylation occurred in acetyl- and cyanoferrocene on the irradiation with 365 nm light, and only decomposition of the starting materials was observed. The results listed in Table 1 indicate that the reactivities of the monosubstituted ferrocenes toward photo-ethoxycarbonylation seem to be determined primarily by the electronic character of the substituent. Based on the proposed mechanism of photo-ethoxycarbonylation of ferrocene,[1b)] the effects of the substituent on the photo-ethoxycarbonylation can be considered in the following two separate cases:

(1) The effect of the substituent on the formation of the charge transfer complex of monosubstituted ferrocene with carbon tetrachloride.

(2) The effect of the substituent on the reactivity of the cyclopentadienyl ring of ferrocene toward the attack of a trichloromethyl radical.



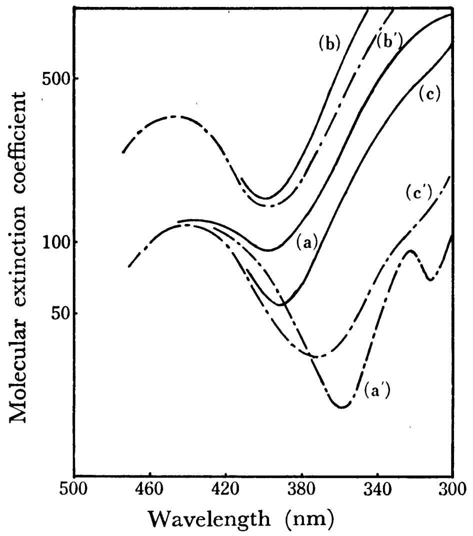


Fig. 1. UV-Spectra of ethylferrocene(2×10^{-3} mol l^{-1}), phenylferrocene(2×10^{-3} mol l^{-1}), and methoxyferrocene (2×10^{-3} mol l^{-1}) in ethanol and in carbon tetrachloride-ethanol(1 : 1, v/v) solutions. (a) Ethylferrocene in carbon tetrachloride-ethanol(1 : 1, v/v) solution. (a') Ethylferrocene in ethanol. (b) phenylferrocene in carbon tetrachloride-ethanol(1 : 1, v/v) solution. (b') Phenylferrocene in ethanol. (c) Methoxyferrocene in carbon tetrachloride-ethanol(1 : 1, v/v) solution. (c') Methoxyferrocene in ethanol.

The contribution of the charge transfer complex to this photo-substitution was examined by the analyses of UV-spectra. The UV-spectra of monosubstituted ferrocenes in ethanol solutions and in carbon tetrachloride–ethanol(1 : 1, v/v) solutions are shown in Figs. 1, 2, and 3. The UV-spectra of methoxy-, ethyl-, phenyl-, chloro-, bromo-, and iodoferrocene in carbon tetrachloride–ethanol solutions show an increment of absorption compared with those in ethanol solutions in 300—360 nm region, whereas only slight enhancements of absorption were observed in the cases of acetyl- and cyanoferrocene. The increment of absorption in this region can be ascribed to the formation of a charge

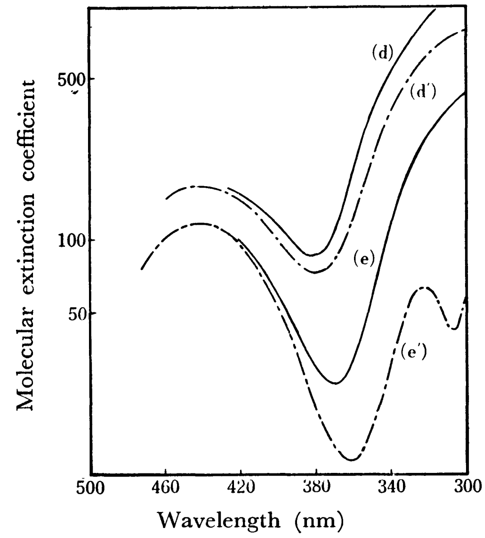


Fig. 2. UV-Spectra of iodoferrocene(2×10^{-3} mol l^{-1}), and chloroferrocene(2×10^{-3} mol l^{-1}) in ethanol and in carbon tetrachloride-ethanol(1 : 1, v/v) solutions. (d) Iodoferrocene in carbon tetrachloride-ethanol(1 : 1, v/v) solution. (d′) Iodoferrocene in ethanol. (e) Chloroferrocene in carbon tetrachloride-ethanol(1 : 1, v/v) solution. (e′) Chloroferrocene in ethanol.

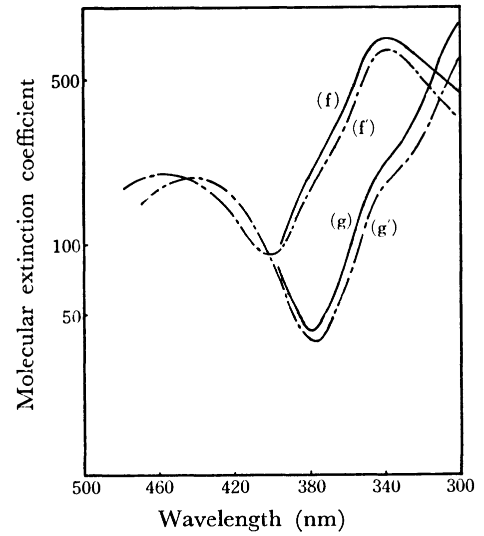


Fig. 3. UV-Spectra of acetylferrocene(2×10^{-3} mol l^{-1}) and cyanoferrocene(2×10^{-3} mol l^{-1}) in ethanol and in carbon tetrachloride-ethanol(1 : 1, v/v) solutions. (f) Acetylferrocene in carbon tetrachloride-ethanol(1 : 1, v/v) solution. (f′) Acetylferrocene in ethanol. (g) Cyanoferrocene in carbon tetrachloride-ethanol (1 : 1, v/v)solution. (g′) Cyanoferrocene in ethanol.

transfer complex between monosubstituted ferrocene and carbon tetrachloride. The increment of absorption, $\Delta\varepsilon$ (expressed in terms of the increase in apparent molar extinction coefficient, therefore, $\Delta\varepsilon=\varepsilon_{\text{app.}}-\varepsilon$) at 300 nm for monosubstituted ferrocenes, was used as a measure of the ability of charge transfer complex formation of monosubstituted ferrocene. Ferrocenes with an electron releasing substituent, such as ethyl and methoxyl, gave higher $\Delta\varepsilon_{300}$ values, whereas those with an electron withdrawing substituent gave lower values

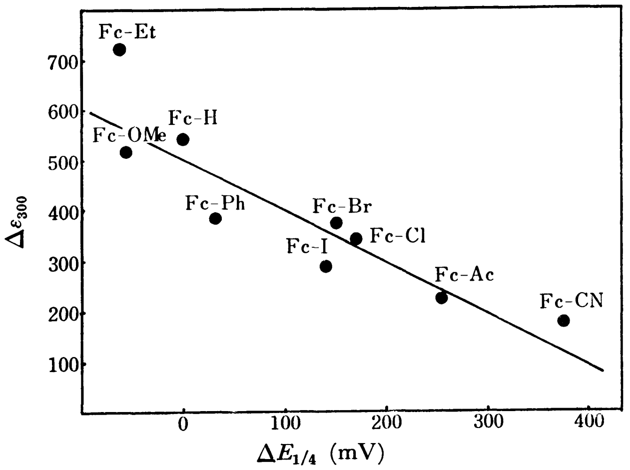


Fig. 4. Plot of the increment of UV-absorption at 300 nm against the oxidation potential, $\Delta E_{1/4}$.

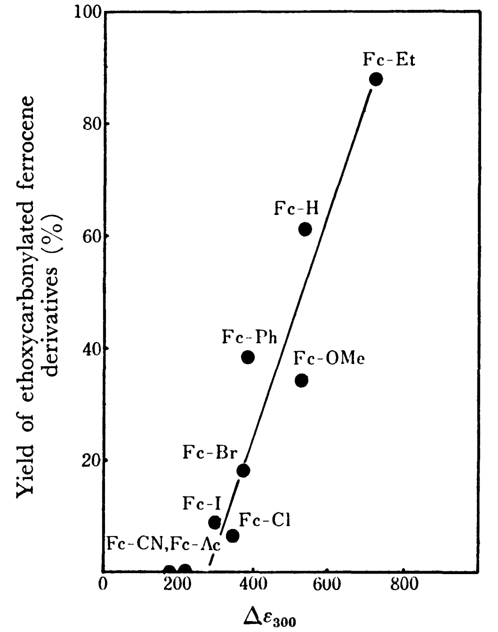


Fig. 5. Plot of the yield of ethoxycarbonylated ferrocene derivative against the increment of UV-absorption at 300 nm.

than ferrocene. These values and the oxidation potentials $\Delta E_{1/4}$(the difference of the chronopotentiometric quarter wave oxidation potentials of substituted ferrocene from that of ferrocene)[13] show a good correlation(Fig. 4). The yields of ethoxycarbonylated products of monosubstituted ferrocenes can also be correlated to $\Delta\varepsilon_{300}$(Fig. 5). These results indicate that the excitation of the charge transfer complex of monosubstituted ferrocene and carbon tetrachloride contribute greatly to the photo-ethoxycarbonylation, as in the case of ferrocene.[1b]

Because of the electrophillic nature of the trichloromethyl radical, the site reactivities of monosubstituted ferrocenes for photo-ethoxycarbonylation can be compared with those for Friedel Crafts' acetylation, which have been extensively investigated by many workers.[14] The site reactivities of monosubstituted ferrocenes for

TABLE 3. SITE REACTIVITIES OF MONOSUBSTITUTED FERROCENES FOR PHOTO-ETHOXYCARBONYLATION AND FOR ACETYLATION[a]

Fc-R[b]	Position		
	2	3	1′
$R=-C_2H_5$	0.65	2.17	1.00
	(1.4)	(4.2)	(1.0)
$R=-OCH_3$	0.00	1.02	1.00
	(3.7)	(2.3)	(1.0)
$R=-C_6H_5$	0.25	1.44	1.00
	(0.7)	(0.4)	(1.0)
R=-Cl	0.02	0.65	1.00
	(0.0)	(0.0)	(1.0)
R=-Br	0.90	0.72	1.00
	(0.0)	(0.0)	(1.0)
R=-I	0.92	0.85	1.00
	(0.0)	(0.0)	(1.0)

a) The values in parentheses are the site reactivities for Friedel Crafts' acetylation taken from references.[14] The reactivity of unsubstituted ring (1′-position) is taken as 1.00. b) Fc- denotes $(C_5H_5)Fe(C_5H_4-)$.

photo-ethoxycarbonylation and those for acetylation are shown in Table 3.

In the case of ethylferrocene, the reactivities of 2- and 3-position for photo-ethoxycarbonylation are lower than those for acetylation, but the relative reactivities of 2-position to 3-position are similar to that of acetylation. The lower reactivity of 2-position than those of 3- and 1′-position indicates that the steric effect is also important in the substitution. In the case of methoxyferrocene, an extremely low reactivity of 2-position can not be explained only by a steric effect, since this position is one and a half times more reactive than 3-position for the electrophillic substitution.[14a] In the case of phenylferrocene, the reactivities of 2- and 3-position seem to be quite different from those for acetylation; although the higher reactivity of 3-position than 2-position for ethoxycarbonylation can be explained by a steric repulsion of a large phenyl group and a bulky trichloromethyl radical, the value 1.44 for 3-position is very high compared to 0.4 for 3-position in acetylation. In the cases of haloferrocenes, this tendency is more obvious; although the homoannular substitution is completely inhibited in acetylation even under drastic conditions,[15] homoannular substitution occurred with nearly the same efficiency as heteroannular substitution in the photo-ethoxycarbonylation. These results indicate that the electrophilicity of the trichloromethyl radical is not so high as to be affected by the electronic nature of the substituents. Therefore, the low yields of ethoxycarbonylated products for haloferrocenes may be due mainly to the efficiency of the formation of the charge transfer complex between monosubstituted ferrocene and carbon tetrachloride.

The authors wish to express their thanks to Mr. Tatsuzo Ishigami of Aoyama Gakuin University for the measurement of mass spectra. The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education.

References

1) a) T. Akiyama, Y. Hoshi, S. Goto, and A. Sugimori, *Bull. Chem. Soc. Jpn.*, **46**, 1851 (1973); b) T. Akiyama, A. Sugimori, and H. Hermann, *Bull. Chem. Soc. Jpn.*, **46**, 1855 (1973).

2) K. Sakai, M. Ishige, H. Kono, I. Motoyama, K. Watanabe, and K. Hata, *Bull. Chem. Soc. Jpn.*, **41**, 1902 (1968).

3) A. N. Nesmeyanov, E. G. Perevalova, and L. S. Shilovtseva, *Izv. Akad. Nauk SSSR*, *Otdel. Khim. Nauk*, **1961**, 1982.

4) P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson, and G. M. Whitman, *J. Am. Chem. Soc.*, **79**, 3416 (1957).

5) H. Shechter and J. F. Helling, *J. Org. Chem.*, **26**, 1035 (1961).

6) M. Sato, T. Ito, I. Motoyama, K. Watanabe, and K. Hata, *Bull. Chem. Soc. Jpn.*, **42**, 1976 (1969).

7) A. N. Nesmeyanov, W. A. Sazonova, and V. N. Drozd, *Chem. Ber.*, **93**, 2717 (1960).

8) A. N. Nesmeyanov, E. G. Perevalova, and L. P. Yur'eva, *Chem. Ber.*, **93**, 2729 (1960).

9) M. Rosenblum, W. G. Howells, A. K. Banerjee, and C. Bennett, *J. Am. Chem. Soc.*, **84**, 2726 (1962).

10) D. W. Slocum and C. R. Ernst, "Advances in Organometallic Chemistry," Vol. 10, ed by F. G. A. Stone and R. West, Academic Press, New York, N. Y. (1972), p. 83.

11) R. Benkaser, Y. Nagai, J. Hooz, *Bull. Chem. Soc. Jpn.*, **36**, 482 (1963).

12) P. L. Pauson, M. A. Sandhu, W. E. Watts, R. C. Haley, and G. R. Knox, *J. Chem. Soc.*, *C*, **1967**, 1851.

13) D. W. Hall and C. D. Russell, *J. Am. Chem. Soc.*, **89**, 2316 (1967), and Ref. 10, p. 98.

14) a) G. R. Knox, I. G. Morrison, P. L. Pauson, M. A. Sandhu, and W. E. Watts, *J. Chem. Soc.*, *C*, **1967**, 1853; b) M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Vol. 1, John Wiley (Interscience), New York, N. Y. (1965), p. 75.

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