Tetrahedron Letters No. 18, pp. 1485-1488, 1970. Pergamon Press. Printed in Great Britain.

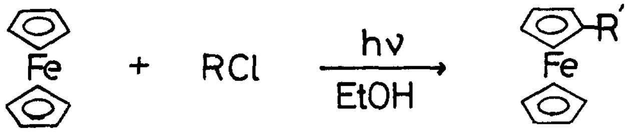
PHOTOCHEMICAL SUBSTITUTION OF FERROCENE IN HALOALKANE-ETHANOL SOLUTIONS

Y. Hoshi, T. Akiyama and A. Sugimori
Department of Chemistry, Faculty of Science and Technology
Sophia University
Kioi-cho 7, Chiyoda-ku, Tokyo, Japan

(Received in Japan 9 March 1970; received in UK for publication 18 March 1970)

Photochemical introduction of functional groups has been an interesting problem from the view point of preparative organic photochemistry. This report deals with the photochemical introduction of ethoxycarbonyl, formyl and ethoxymethyl groups into a ferrocene nucleus by the ultraviolet irradiation of ferrocene in carbon tetrachloride-, chloroform- and dichloromethane-ethanol solutions, respectively.

Brand and Snedden observed spectra of electron transfer to solvent in ferrocene-haloalkane systems(1). This suggests an interaction between ferrocene-haloalkanes under irradiation, and possibility of photochemical introduction of halogenated alkyl groups into a ferrocene nucleus. However, ultraviolet irradiation of ferrocene in carbon tetrachloride did not give the expected substitution product, but an oxidized product, ferricinium tetrachloroferrate(III)$[C_{10}H_{10}Fe]^+FeCl_4^-$(2). On the other hand, ultraviolet irradiation of ferrocene in haloalkane (CCl_4, $CHCl_3$ and CH_2Cl_2)-ethanol solvents gave substitution products.



Ia R = $-CCl_3$
Ib R = $-CHCl_2$
Ic R = $-CH_2Cl$

IIa R' = $-COOEt$
IIb R' = $-CHO$
IIc R' = $-CH_2OEt$

The preparative procedure is as follows: Ferrocene is irradiated in haloalkane-ethanol (1:1) solvents with a low pressure or medium pressure mercury lamp under nitrogen at 0-10^{o}C. After irradiation, the products are extracted with n-hexane, and the extract is washed with water several times. The products are then separated with silica gel chromatography. The results are shown in Table 1.

Table 1. Photochemical Reaction of Ferrocene in Halogenated Hydrocarbon-Ethanol Solvents on Preparative Scale.

	FcH^{a} (g)	Solvent (ml)	Irradiation Source	Time (hr)	FcH reacted (%)	Product	Yield^{b} (%)
CCl_4	3.7	280	LP^{c}(15W)	48	57	FcCOOEt	20
	3.0	140	HP^{d}(150W)	8	35	FcCOOEt	38
	1.9	400	HP (100W) pyrex filter	7	34	FcCOOEt	32
$CHCl_3$	3.0	220	LP (120W)	7	84	FcCHO	42
	2.0	140	HP (150W)	5	35	FcCHO	trace^{e}
CH_2Cl_2	4.0	220	LP (120W)	7	72	$FcCH_2OEt$ $Fc(CH_2OEt)_2$^{f}	43 36
	1.0	140	HP (150W)	3	90	$FcCH_2OEt$ $Fc(CH_2OEt)_2$	53 12
n-BuCl	1.9	220	LP (120W)	9	0	$Fc(CH_2)_3CH_3$	trace
PhCl	1.9	220	LP (120W)	8	—	FcC_6H_5	trace

[a] Ferrocene. [b] Yield of the product are based on ferrocene which reacted. [c] Low pressure mercury lamp. [d] High pressure mercury lamp. [e] Formylferrocene is sensitive to 313nm light. [f] 1,1'-Bis(ethoxymethyl)ferrocene.

It is known that ferricinium ions are reactive toward free radicals(3). The photo-substitution of ferrocene might proceed via photo chemically produced ferricinium and free radicals. However, ultraviolet irradiation of ferricinium ions in carbon tetrachloride-ethanol solvent gave ferrocene, and hexachloroethane instead of ethoxycarbonylferrocene. This fact indicates that the attack of trichloromethyl radicals to ferricinium ions is not involved in the reaction. The wave-length dependence of the reaction in carbon tetrachloride-ethanol solution was studied with monochromatic light in well degassed solutions. The results are shown in Table 2.

Table 2. Quantum Yield in the Photoreaction of Ferrocene in CCl_4-EtOH at Various Wave Lengthes

Wave length nm	Quantum yield of FcH which reacted	Quantum yield of FcCOOEt
254	0.28	0.13
313	0.18	0.13
366	0.14	0.11
436	0.00	0.00

The ultraviolet absorption spectra of ferrocene in ethanol and carbon tetrachloride are shown in Fig.1.

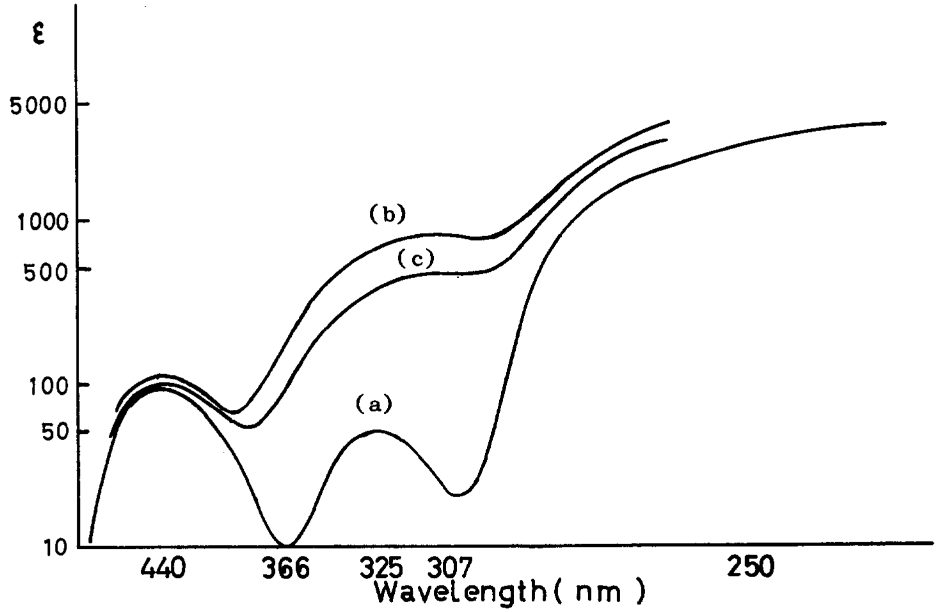


Fig.1 The Absorption Spectra of Ferrocene in Ethanol (a), Carbon tetrachloride (b), and Carbon tetrachloride-Ethanol(1:1) (c)

The band at 440nm is assigned to d-d transition(4). The band at 307nm in carbon tetrachloride is attributed to charge transfer to solvent(1).

The excited state formed by d-d absorption led to no reaction. While charge transfer excitation gave effectively ethoxycarbonylferrocene. The excitation by the light of a shorter wave length brought about an increase in side reactions (presumably oxidation). These facts suggest that the electron transfer is important for the photochemical substitution.

The comparison of Table 1 and Table 2, shows that a small amount of oxygen increases side reactions.

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