

SHORT COMMUNICATIONS

Photolytic Formation of a Ferrocenyl Radical from Iodoferrocene¹⁾

Takeo SATO, Shigeru SHIMADA and Kazuo HATA

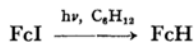
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo

(Received July 11, 1969)

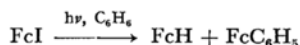
Although a number of studies have been carried out on ferrocene chemistry, not many of them deal with the generation and characterization of a ferrocenyl radical. Existence of the latter as a reactive intermediate in the reactions of metal derivatives, such as lithioferrocenes²⁾ and ferrocenylmercury derivatives³⁾ has been postulated by only a few authors.

We wish to report an attempt to generate the ferrocenyl radical by a photolytic method from iodoferrocene. Dilute solutions of iodoferrocene in appropriate solvents (*ca.* $8.5 \times 10^{-3}M$) were irradiated externally using a 100-W low-pressure (100-L) or 1-kW high-pressure lamp (1000-H). Since the ferrocene nucleus is sensitive to oxygen, especially upon illumination, all reactions have been carried out under nitrogen or using degassed solutions. Analysis of the reaction mixture was performed by gas chromatography using silicone grease on a Daichrom column.

Irradiation in cyclohexane resulted in the reductive deiodination to give ferrocene, which was obtained in 20% yield with 45 hr reaction (1000-H lamp, Pyrex filter):



The rest of the material was recoverable as iodoferrocene. Irradiation in benzene produced phenylferrocene and a small amount of ferrocene:



The representative data are summarized in Table 1. Thus by using 253.7 mμ line (100-L), phenylferrocene was obtained in as high as 89% yield, which is far better than other methods so far described.⁴⁾ It is noteworthy that the reaction does not show any marked dependence on the wavelengths employed. A similar reaction carried out in toluene for 47 hr (1000-H lamp, quartz filter) produced ferrocene (24%) and tolylferrocenes (50%), together with bibenzyl (9%). These results are best interpreted by assuming the intermediacy of the ferrocenyl radical.

TABLE 1. PHOTOLYSES OF IODOFERROCENE IN BENZENE

Lamp	Filter	Irrad. time, hr	Products, %		
			FcH	FcC ₆ H ₅	Recovery
100-L ^{a)}	Vycor	15	6	89	3
1000-H	Quartz	48	3	55	7
1000-H	Pyrex	48	13	54	15
1000-H	Glass	48	10	48	29

a) Irradiation with a 100-L lamp was performed on a degassed solution.

1) Photo-Aryl Coupling and Related Reactions. V.
2) I. J. Spilner and J. P. Pellegrini, Jr., *J. Org. Chem.*, **30**, 3800 (1965); H. Watanabe, I. Motoyama and K. Hata, *This Bulletin*, **39**, 790 (1966).

3) M. D. Rausch, *J. Am. Chem. Soc.*, **82**, 2080 (1960); A. N. Nesmeyanov, E. G. Rerevalova, S. P. Gubin and A. G. Kozlevskii, *J. Organometal. Chem.*, **11**, 577 (1968).

4) M. Rosenblum, "Chemistry of the Iron Group Metalloenes," Part I, John Wiley & Sons, Inc., New York, N. Y. (1965), p. 198.