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Palladium-catalyzed Reaction of Olefins and Acetylenes with Iodoferrocenes

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Synopsis. Iodoferrocene (**1**) reacts readily with olefinic compounds in the presence of a catalytic amount of palladium(II) acetate to produce alkenylferrocene derivatives. In the presence of a copper(I) iodide and palladium complex, **1** also reacts with acetylene to afford diferrocenylacetylene.

Recently, the palladium-catalyzed reaction of olefin[1—5] with aryl and vinylic halides has received wide attention. Meanwhile, Sonogashira *et al.*[6] have reported the palladium-catalyzed substitution of acetylenic hydrogen with aryl iodide. We are, therefore, intrigued by the palladium-catalyzed reaction of olefins and acetylenes with iodoferrocene (FcI) (**1**) and 1,1′-diiodoferrocene (**2**) and wish to report herein the results of a study of these reactions.

In the presence of triethylamine and catalytic amounts of palladium(II) acetate and triphenylphosphine, **1** and **2** were allowed to react separately with various olefins at 100 °C; the substitution reaction on the double bond has been observed to lead to the formation of 1-alkenylferrocenes and 1,1′-dialkenylferrocenes. The reactions carried out are summarized in Table 1.

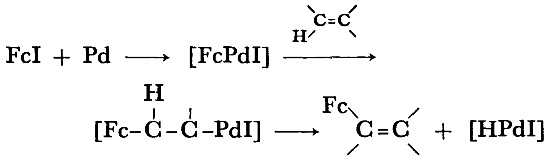
The reaction of **1** with simple olefins, such as styrene and ethyl acrylate, resulted in the formation of strylferrocene (**3**) and ethyl 3-ferrocenylacrylate (**4**) respectively in moderate yields. The mechanism of the

TABLE 1. A PALLADIUM-CATALYZED FERROCENYLATION OF OLEFINS AND ACETYLENES

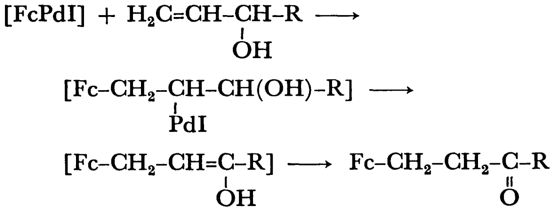
Halide	Olefin or acetylene	Product, mp °C	Yield %[a]
1	Styrene	Styrylferrocene (**3**), 120—121[b]	59
1	Ethyl acrylate	Ethyl 3-ferrocenylacrylate (**4**), 74—75[c]	54
1	Methyl methacrylate	Methyl 3-ferrocenylmethacrylate (**5**), 62—63[d]	64
1	Acrylonitrile	3-Ferrocenylacrylonitrile (**6**), 80—81[d]	60
1	Methyl vinyl ketone	4-Ferrocenyl-3-buten-2-one (**7**), 84—85[e]	52
1	Phenyl vinyl ketone	3-Ferrocenyl-1-phenyl-2-porpen-1-one (**8**), 136—137[f]	70
1	Allyl alcohol	3-Ferrocenylpropanal (**9**), 48—51[g]	48
1	3-Buten-2-ol	4-Ferrocenyl-2-butanone (**10**), 45—46[h]	57
1	Vinyl acetate	1,2-Diferrocenylethylene (**11**), 270—272[i]	38
1	Isopropenyl acetate	1,2-Diferrocenyl-1-propene (**12**), 163—165[j]	32
1	Acetophenone enol acetate	Styrylferrocene (**3**), 120—121[b]	21
		1-Acetoxy-1-phenyl-2-ferrocenylethylene (**13**), 153—154[k]	14
2	Styrene	1,1′-Distyrylferrocene (**14**), 166—167[l]	42
2	Ethyl acrylate	1,1′-Bis(2-ethoxycarbonylvinyl)ferrocene (**15**), 84—85[d]	62
2	Methyl vinyl ketone	1,1′-Bis(2-acetylvinyl)ferrocene (**16**), 112—113[d]	76
2	3-Buten-2-ol	1,1′-Bis(3-oxobutyl)ferrocene (**17**), 153—154[m]	53
1	Acetylene	Diferrocenylacetylene (**18**), 244—246[b]	78
1	Phenylacetylene	Ferrocenylphenylacetylene (**19**), 122—124[b]	85
2	Phenylacetylene	1,1′-Bis(phenylethynyl)ferrocene (**20**), 159—161[n]	46

a) The yields are based upon the iodoferrocene (**1**) or 1,1′-diiodoferrocene (**2**) used. b) P. L. Pauson and E. E. Watts, *J. Chem. Soc.*, **1963**, 2990. c) P. De Re and E. Sianesi, *Experientia*, **21**, 648 (1966). d) A. Kasahara, T. Izumi, G. Saito, M. Yodono, R. Saito, and Y. Goto, *Bull. Chem. Soc. Jpn.*, **45**, 895 (1972). e) J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, **1961**, 4604. f) C. R. Hauser and J. Lindsay, *J. Org. Chem.*, **23**, 906 (1957). g) Compound **9** gave a correct elemental analysis. IR spectrum: 2750, 1725 (C=O), 1104, and 998 cm^{-1}. NMR spectrum (δ, ppm): 2.66 (4H, m, **CH$_2$**), 4.09 and 4.12 (9H, m, ferrocene ring protons), and 9.93 (1H, s, **H**-C=O). Mass spectrum: $M^+=242$. h) J. Decombe, J. P. Ravoux, and A. Dormond, *C. R. Acad. Sci.*, **258**, 2348 (1964). i) K. Schoegel and H. Egger, *Angew. Chem.*, **75**, 1123 (1963). j) Compound **12** gave a correct elemental analysis. IR spectrum: 1620, 1101, 998, and 810 cm^{-1}. NMR spectrum (δ, ppm): 2.13 (3H, d, **CH$_3$**-C=CH), 4.12 and 4.35 (18H, m, ferrocene ring protons), and 6.36 (1H, m, C=CH). Mass spectrum: $M^+=410$. k) Compound **13** gave a correct elemental analysis. IR spectrum: 1760 (O-C=O), 1650 (C=C), 1104, and 998 cm^{-1}. NMR spectrum (δ, ppm): 2.36 (3H, s, O-CO-**CH$_3$**), 4.15 and 4.38 (9H, m, ferrocene ring protons), 6.54 (1H, s, C=**CH**), and 7.32 (5H, m, benzene ring protons). Mass spectrum: $M^+=330$. l) K. Sonogashira and N. Hagihara, *Kogyo Kagaku Zasshi*, **66**, 1090 (1963). m) Compound **17** gave a correct elemental analysis. IR spectrum: 1718 cm^{-1} (C=O). NMR spectrum (δ, ppm): 2.09 (6H, s, **CH$_3$**C=O), 2.55 (4H, m, **CH$_2$**C=O), 2.64 (4H, m, Fc**CH$_2$**-), 4.08 and 4.11 (8H, m, ferrocene ring protons). Mass spectrum: $M^+=310$. n) Compound **20** gave a correct elemental analysis. IR spectrum: 2210 cm^{-1} (C≡C). NMR spectrum (δ, ppm): 4.36 and 4.59 (8H, m, ferrocene ring protons) and 7.33 (10H, m, benzene ring protons). Mass spectrum: $M^+=386$.

reaction involves the formation of ferrocenylpalladium iodide by oxidative addition, followed by addition to the olefin and the elimination of [HPdI], as in the palladium-catalyzed reaction of olefins with aryl halide.[3a)]



The ferrocenylation of allylic alcohols with **1** or **2** led to the formation of the 3-ferrocenyl-aldehyde or -ketone (**9**, **10**, or **17**) in a good yield; neither 2-ferrocenyl-isomer nor 3-ferrocenylated allyl alcohol was observed. The allylic alcohol ferrocenylation can account for the reaction mechanism, which is similar to the one proposed for the allylic alcohol arylation:[4)]



$$[\mathrm{FcPdI}] + \mathrm{H_2C{=}CH{-}\underset{OH}{\underset{|}{CH}}{-}R} \longrightarrow$$
$$[\mathrm{Fc{-}CH_2{-}\underset{PdI}{\underset{|}{CH}}{-}CH(OH){-}R}] \longrightarrow$$
$$[\mathrm{Fc{-}CH_2{-}CH{=}\underset{OH}{\underset{|}{C}}{-}R}] \longrightarrow \mathrm{Fc{-}CH_2{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}R}$$

Vinyl acetate and isopropenyl acetate reacted with **1** to yield differrocenylethylene (**11**) and 1,2-diferrocenyl-1-propene (**12**) respectively. In addition, the reaction of acetophenone enol acetate with **1** afforded a mixture of **3** and 1-acetoxy-1-phenyl-2-ferrocenylethylene (**13**). The formation of **3** suggested that the addition of the ferrocenyl group occurs on the terminal carbon atom, followed by the elimination and a re-addition of palladium hydride in the reverse direction and another elimination of Pd(OAc)I.

$$[\mathrm{FcPdI}] + \mathrm{H_2C{=}C(Ph){-}OAc} \longrightarrow \begin{cases} \mathrm{Fc{-}CH{=}C(Ph){-}OAc}\ (\mathbf{13}) \\ \mathrm{Fc{-}CH{=}CH{-}Ph}\ (\mathbf{3}) \end{cases}$$

In the presence of copper(I) iodide and dichlorobis(triphenylphosphine)palladium(II), **1** reacted with acetylene and phenylacetylene to yield diferrocenylacetylene (**14**) and ferrocenylphenylacetylene (**15**) respectively in good yields.

$$\mathrm{FcI}\ (\mathbf{1}) + \mathrm{H{\equiv}CH} \longrightarrow \mathrm{Fc{-}C{\equiv}C{-}Fc}\ (\mathbf{14})$$
$$\mathrm{FcI}\ (\mathbf{1}) + \mathrm{Ph{-}C{\equiv}C{-}H} \longrightarrow \mathrm{Fc{-}C{\equiv}C{-}Ph}\ (\mathbf{15})$$

Experimental

Materials. All the melting points are uncorrected. Iodoferrocene (**1**) and 1,1′-diiodoferrocene (**2**) were prepared according to the method described by Fish and Rosenblum.[7)] All the olefinic compounds were commercial products and were purified by distillation before use.

General Procedure for the Ferrocenylation of Olefins. A mixture of 1.56 g (5 mmol) of **1**, 0.7 g (7 mmol) of triethylamine, 7 mmol of olefin, 0.026 g (0.1 mmol) of triphenylphosphine, 0.011 g (0.05 mmol) of palladium(II) acetate, and 10 ml of acetonitrile was heated under nitrogen in a sealed tube at 100 °C for 8 h. In the reaction with **2**, 1.08 g (2.5 mmol) of **2** was used. The cooled reaction mixture was diluted with ether and water. The ether phase was separated, washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was then purified by column chromatography (Al_2O_3–benzene or chloroform), followed by recrystallization from ethanol or benzene. The structure of the products was confirmed by a mixed-melting-point determination with an authentic sample and by the observation of the IR and NMR spectra. The results are summarized in Table 1.

General Procedure for the Ferrocenylation of Acetylenes. A mixture of 1.56 g (5 mmol) of **1** (or 2.5 mmol of **2**), 0.61 g (6 mmol) of phenylacetylene, 0.095 g (0.05 mmol) of copper(I) iodide, 0.033 g (0.1 mmol) of dichlorobis(triphenylphosphine)-palladium(II), and 40 ml of diethylamine was heated under nitrogen in a sealed tube at 80 °C for 6 h. In the case of the reaction with acetylene, a slow current of acetylene was passed through the reaction mixture for 6 h at room temperature. After the removal of diethylamine under reduced pressure, ether and water were added to the residue. The ether phase was separated, washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was purified by column chromatography (Al_2O_3–benzene or chloroform), followed by recrystallization from ethanol or benzene. The structure of the products was confirmed by a mixed-melting-point determination with an authentic sample and by the observation of the IR and NMR spectra. The results are summarized in Table 1.

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