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The Ferrocenylation of Styrenes-β,β-d_2 with the Ferrocenylpalladium Compound

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Recently, the arylation of olefin with arylpalladium compound (I), formed *in situ* by the exchange of arylmercuric compounds (II) with palladium salts, has been shown to be a useful reaction for the synthesis of various olefinic compounds [Eq. (1)].[1] Moreover, Heck[2] has reported that the reaction of olefin with I was stereospecific with internal olefin, giving products consistent with a *cis* addition of the organopalladium reagent to the olefin, followed by a *cis* elimination of a hydridopalladium(II) species. Henry[3] has also reported that the phenylpalladation of cyclohexene-3,3,6,6-d_4 (III) by phenylmercuric acetate and palladium acetate produces products (IV and V) which are consistent with the *cis* phenylpalladation, followed by *cis* palladium(II) hydride elimination and readdition [Eq. (2)]. On the other hand, Moritani *et al.*[4] have reported that, judging from the deuterium analyses of the *trans* stilbene formed, it seems that the phenylation of styrenes-β,β-d_2 (VI) with benzene in the presence of palladium acetate, without using a phenylmercuric compound, proceeds without any hydride shift. We ourselves have also reported that the reaction of benzo[*b*]furan with I results in the formation of 2-arylbenzo[*b*]furan, and that no hydride shift takes place in the reaction.[5]

Previously, we described the ferrocenylation of olefin with chloromercuriferrocene (VII) in the presence of palladium salts to produce alkenylferrocene derivatives.[6] Therefore, in order to study whether or not the hydride shift also occurs in the reaction of VI with VII, the reaction was performed in the presence of lithium chloropalladite. If the hydride shift occurs in the reaction, the reaction of VI with ferrocenylpalladium chloride (VIII), formed *in situ* from VII and palladium salts, will produce styrylferrocenes (IX) containing two and/or one deuterium as is shown by Eq. (3), and the deuterium content of IX will be 150%. Contrary to this, according to the no hydride shift mechanism,[4,5] the deuterium content of the product should be 100% [Eq. (4)]. The results are summarized in Table 1. Styrene-β,β-d_2, *p*-methylstyrene-β,β-d_2, and *p*-methoxystyrene-β,β-d_2 all resulted in the formation of IX, indicating that the deuterium content is *ca.* 150%, unlike the case of no hydride shift. These results clearly show that the hydride shift occurs in this reaction.

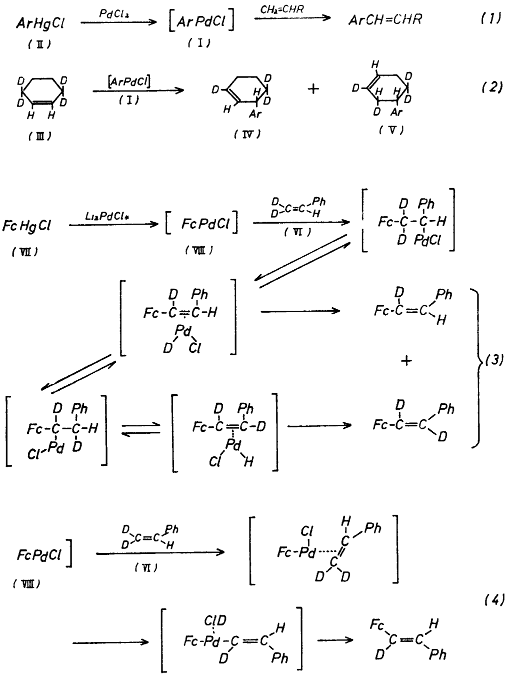

Fig. 1

Experimental

Analysis and Materials. All the melting points are uncorrected. The IR spectra were measured on KBr disks with a Hitachi EPI-S spectrometer, while the NMR spectra were obtained by means of a Hitachi H-60 NMR spectrometer at 60 MHz in $CDCl_3$, using tetramethylsilane as the internal standard. Their chemical shifts are presented in terms of ppm values, together with the splitting pattern and the relative integrated area. The letter designates the multiplicity of the signal: s, singlet; d, doublet; t, triplet; q, quadruplet; *m*, multiplet. The mass spectra were obtained on a Hitachi RMU6E mass spectrometer, using a direct inlet and an ionization energy of 70 eV.

The following compounds were synthesized by the methods described in the literature: chloromercuriferrocene,[7] styrene-β,β-d_2,[8] *p*-methylstyrene-β,β-d_2,[4b] and *p*-methoxystyrene-β,β-d_2.[4b]

General Procedure for the Ferrocenylation of Styrene-β,β-d_2. Lithium chloropalladite solutions were prepared by stirring 0.84 g (20 mmol) of anhydrous lithium chloride and 1.77 g (10 mmol) of palladium chloride overnight at room tempera-

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[1] R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968), and following papers.

[2] R. F. Heck, *ibid.*, **91**, 6707 (1969): *ibid.*, **93**, 6896 (1971).

[3] P. M. Henry and G. A. Ward, *ibid.*, **94**, 673 (1972).

[4] a) S. Danno, I. Moritani, and Y. Fujiwara, *Chem. Commum.*, **1970**, 610; b) S. Danno, I. Moritani, Y. Fujiwara, and S. Teranishi, *J. Chem. Soc.*, *B*, **1971**, 196.

[5] A. Kasahara, T. Izumi, T. Takeda, M. Yodono, R. Saito, and T. Sugawara, This Bulletin, in press.

[6] A. Kasahara, T. Izumi, G. Saito, M. Yodono, R. Saito, and Y. Goto, This Bulletin, **45**, 894 (1972).

[7] R. E. Fish and M. Rosenblum, *J. Org. Chem.*, **30**, 1253 (1965).

[8] W. M. Schubert and Bo Lamm, *J. Amer. Chem. Soc.*, **88**, 120 (1966).

TABLE 1. THE REACTION OF STYRENES-β,β-d_2 WITH FERROCENYLPALLADIUM CHLORIDE

Olefin	Product	Mp °C	Yield %	D-content[a]	Chemical shift
Ph-CH=CD_2[b]	X	228—229	5		
	Styrylferrocene[e]	120—121	55	148±2	$\left.\begin{array}{l}4.17\ s\ 5\\4.32\ q\ 2\\4.50\ q\ 2\end{array}\right\}$ –Fc 6.74s 0.5 -**CH**=CFc 7.37 m 5 Ph
p-$MeC_6H_4CH=CD_2$[c]	X	228—229	3		
	p-Methylstyrylferrocene[f]	130—131	48	145±2	2.32 s 3 -$\mathbf{CH_3}$ $\left.\begin{array}{l}4.09\ s\ 5\\4.24\ q\ 2\\4.43\ q\ 2\end{array}\right\}$ –Fc 6.64 s 0.5 -**CH**=CFc $\left.\begin{array}{l}7.08\ d\ 2\\7.31\ d\ 2\end{array}\right\}$ $C_6\mathbf{H}_4$–
p-$MeOC_6H_4CH=CD_2$[d]	X	228—229	9		
	p-Methoxystyrylferrocene	125—126	43	142±2	3.68 s 3 -O$\mathbf{CH_3}$ $\left.\begin{array}{l}4.10\ s\ 5\\4.24\ q\ 2\\4.41\ q\ 2\end{array}\right\}$ –Fc 6.67 s 0.5 -**CH**=CFc $\left.\begin{array}{l}6.82\ d\ 2\\7.32\ d\ 2\end{array}\right\}$ $C_6\mathbf{H}_4$–

a) Calculated on the basis that D-content of product containing one olefinic deuterium is 100%, and by the comparison of the ratio of integrated area of olefinic proton with that of other protons in the 60 MHz spectrum. b) The mass spectrum showed this to be 98% deuteriated. c) The mass spectrum showed this to be 95% deuteriated. d) The mass spectrum showed this to be 96% deuteriated. e) Mp of an undeuteriated sample, 121—122°C. (P. L. Pauson and E. E. Watts, *J. Chem. Soc.*, **1963**, 2990). f) Mp of an undeuteriated sample, 131°C. (G. Drefahl, G. Ploctner, and I. Winnefeld, *Chem. Ber.*, **95**, 2788 (1962)). g) Mp of an undeuteriated sample, 125—126°C. (A. Kasahara and T. Izumi, unpublished work).

ture in 100 ml of ethanol. To these lithium chloropalladite solutions, mixtures of 4.20 g (10 mmol) of I and twice as much VI were added, after which the mixtures were stirred at room temperature for 12 hr. The products were isolated by filtering to remove a precipitated palladium, and by distilling under reduced pressure to remove the solvent. The residue was dissolved in benzene and chromatographed on alumina. The first elution with benzene and subsequent recrystallization from ethanol afforded deep yellow crystals (mp 228—229°C, 3—9% yields) which were identified as biferrocenyl (X)[9] by a comparison of the IR spectra and by a mixed-melting-point determination with an authentic sample. Further elution with benzene and recrystallization from ethanol afforded the respective ferrocenylation product (IX). The structures of the products were confirmed by the observation of the IR and NMR spectra. The deuterium-content of the products was also calculated from the NMR results (see Table).

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[9] H. Shechter and J. H. Helling, *J. Org. Chem.*, **26**, 1034 (1961).