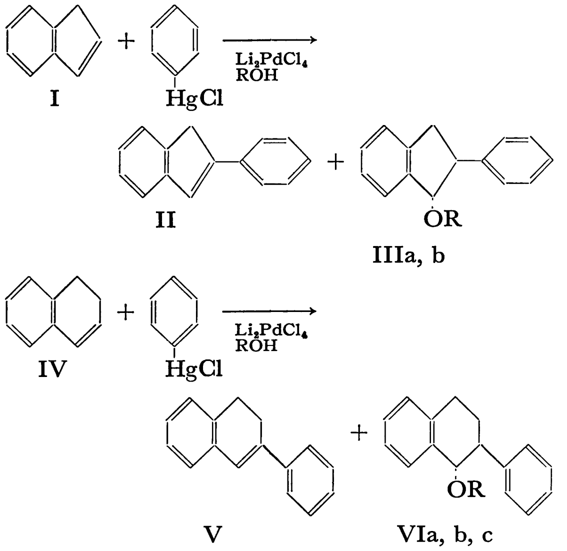
SHORT COMMUNICATIONS

The Oxyphenylation of Olefins

Hiroshi Horino and Naoto Inoue
College of General Education, Tohoku University, Kawauchi, Sendai

(Received May 21, 1971)

A number of papers on the aromatic substitution of olefins by the reaction of palladium compounds have been published in recent years.[1–3] In the course of our studies of the aromatic substitution of olefins according to Heck's arylation, a new addition reaction was found in which a phenyl group and an anion part of the protic solvents were added simultaneously to reactant olefins.



a: R=H, b: R=COCH$_3$, c: R=CH$_3$

Table 1. Results of oxyphenylation of olefins in various solvents

Olefin	Solvent	Product	(yield, %)
I	Dioxane-H$_2$O(1:1)	II(35)[4]	IIIa(50)[a]
I	CH$_3$COCH$_3$-H$_2$O(1:1)	II(28)	IIIa(51)
I	CH$_3$CO$_2$H-H$_2$O(1:1)	II(18)	IIIa(48) IIIb(17)[b]
I	CH$_3$CO$_2$H	II(72)	IIIb(7)
I	CH$_3$COCH$_3$-H$_2$O(1:1) CH$_3$CO$_2$Na(2 mmol)	II(17)	IIIa(61)
IV	Dioxane-H$_2$O(1:1)	V(16)[5]	VIa(72)[6]
IV	CH$_3$CO$_2$H	V(40)	VIb(14)[6]
IV	CH$_3$OH	V(16)	VIc(47)[c]

a) Mp 81—82°C, IR(KBr); ν_{OH}=3300—3150 cm^{-1}, NMR(CCl$_4$); τ 4.95(1H, d, J=6 Hz)

b) Bp 162—165°C/1 mmHg, IR(Neat); $\nu_{C=O}$=1740 cm^{-1}, NMR(CCl$_4$); τ 8.0(3H), 3.75(1H, d, J=5 Hz).

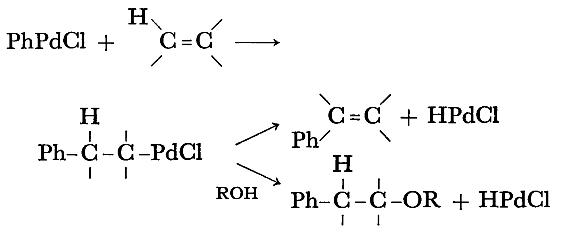
c) Bp 133—136°C/1 mmHg, IR(Neat); ν_{C-O}=1080 cm^{-1}, NMR(CCl$_4$); τ 6.88(3H), 5.6(2H, d, J=8 Hz).

The general procedure of the reaction is as follows. A solution of indene (I) (1.2 mmol) or 1,2-dihydronaphthalene (IV) (1.2 mmol), lithium palladium chloride (1 mmol),[2] and phenylmercuric chloride (1 mmol) in the solvents listed in Table 1 was stirred for more than five hours at room temperature.

The reaction products were then separated by chromatography on a silica-gel column. Compound II (or V) was eluted with *n*-hexane, and III (or VI) was eluted with benzene or a mixture of *n*-hexane and benzene (1:1). The isolated products were identified by elementary analysis and by mixed-melting-point tests with authentic samples.[4–7] The addition of sodium acetate (1 or 2 mmol) to a solution of I (1.2 mmol), lithium palladium chloride (1 mmol), and phenylmercuric chloride (1 mmol) in a mixture of acetone and water gave IIIa in a 50 to 60% yield, as is shown in Table 1. The treatment of II or V with a solution of lithium palladium chloride and mercuric chloride in methanol, or with a solution of hydrochloric acid in a mixture of acetone and water, gave only the starting material. The reaction of IIIa or VIa with lithium palladium chloride and mercuric chloride afforded the starting substance. Therefore, it is clear that the oxy compound (III or VI) was not derived from the arylated olefin (II or V), and that II or V was not formed from III or VI.

According to Heck's mechanism,[2] we suggest the following scheme to illustrate the formation of the oxy compounds as well as the arylated olefins.

$$PhHgCl + PdCl_2 \longrightarrow PhPdCl + HgCl_2$$



$$PhPdCl + \overset{H}{>}C{=}C{<} \longrightarrow$$

$$Ph{-}\overset{H}{\underset{|}{\overset{|}{C}}}{-}\underset{|}{\overset{|}{C}}{-}PdCl \begin{cases} \longrightarrow \ \overset{\diagdown}{\underset{Ph\diagup}{}}C{=}C\overset{\diagup}{\underset{\diagdown}{}} + HPdCl \\ \xrightarrow{ROH} \ Ph{-}\overset{H}{\underset{|}{\overset{|}{C}}}{-}\underset{|}{\overset{|}{C}}{-}OR + HPdCl \end{cases}$$

The configurations of the isolated oxy compounds, IIIa, b, and VIa, b, c, were determined to be *trans*.[7]

The extension of this reaction to other simple olefins is now under investigation.

---

[1] Y. Fujiwara, I. Moritani, S. Danno, R. Asano, and S. Teranishi, *J. Amer. Chem. Soc.*, **91**, 1766 (1969); S. Danno, I. Moritani, and Y. Fujiwara, *Tetrahedron*, **25**, 4809 (1969).

[2] R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968); R. F. Heck, *ibid.*, **91**, 6707 (1969).

[3] K. Garves, *J. Org. Chem.*, **35**, 3273 (1970).

[4] J. von Braun and G. Manz, *Ber.*, **62**, 1062 (1929).

[5] N. Campbell and D. Kidd, *J. Chem. Soc.*, **1954**, 2154.

[6] K. Hanaya, *Nippon Kagaku Zasshi*, **87**, 745 (1966).

[7] The hydroboration and oxidation of 2-phenylindene (II)[4] and 2-phenyl-3,4-dihydronaphthalene (V)[5] gave IIIa and VIa[6] respectively, those substances were then acetylated to IIIb and VIb[6] with acetic anhydride and pyridine. The treatment of VIa with sodium hydride and subsequently with methyl iodide afforded VIc.