Arylation of Olefin with Aryl Iodide Catalyzed by Palladium

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(Received October 20, 1970)

The arylation of olefin with aromatic hydrocarbon[1] or arylmercuric compound[2] by the reaction with palladium(II) compound has been reported, where the reaction consumes almost stoichiometric amount of the palladium(II) compound, forming metallic palladium. In this communication we wish to report that the arylation of olefin with iodobenzene in the presence of a catalytic amount of palladium(II) dichloride takes place smoothly when potassium acetate is added as an acceptor of hydrogen iodide formed. A characteristic feature of this reaction is that the arylation of olefin is effectively catalyzed by palladium or palladium(II) compounds without accompanying polymerization of the corresponding styrene derivatives formed, as long as the amount of potassium acetate added is greater than that of iodobenzene used. The reaction can be represented as follows:

$$C_6H_5I + CH_2{=}CHX + CH_3COOK \longrightarrow C_6H_5CH{=}CHX + CH_3COOH + KI$$
(X=H, C_6H_5, CH_3, and $COOCH_3$)

This can be compared with the carbonylation of aryl halide with carbon monoxide catalyzed by nickel carbonyl in the presence of sufficient amount of potassium acetate in methanol ($C_6H_5X + CO + CH_3OH + CH_3COOK \longrightarrow C_6H_5COOCH_3 + CH_3COOH + KX$, X=I, Br).[3]

The catalyst in the present case was initially palladium dichloride, but most of the palladium was found to be reduced to metal in the course of the reaction. As shown in Table 1, metallic palladium has also high catalytic activity for the arylation of olefin (No. 5). This differs considerably from the stoichiometric arylation of olefin with palladium(II) compounds. Pyridine, triethylamine, or potassium benzoate was also used as the acceptor of hydrogen iodide formed, potassium acetate being the most effective. Ethylene, propylene, styrene, and methyl acrylate were used as olefin. The corresponding styrene derivatives (styrene, α- or β-methylstyrene, *trans*-stilbene and methyl cinnamate, respectively) were produced in high yields. The results are summarized in Table 1.

The experimental procedure is illustrated by the arylation of ethylene with iodobenzene. Iodobenzene (50 mmol), potassium acetate (60 mmol), palladium dichloride (0.5 mmol), and methanol (1.0 mol) were placed in a titanium-alloy autoclave (100 m*l*) equipped with a magnetic stirrer. The gas phase in the autoclave was displaced by nitrogen stream, and ethylene from commercial sources was then introduced up to 8 kg/cm² at room temperature. The autoclave was heated up to 120—125°C within 1 hr and kept at this temperature for 3 hr. The decrease in pressure was observed during the first 1 hr (from 16 to 9 kg/cm²). After the reaction, all materials were taken out from the autoclave by using methanol and acetone and the products were quantitatively determined by gas chromatography.

Table 1. Arylation of olefin with iodobenzene

$PdCl_2$ 0.50 mmol, CH_3OH 0.8—1.0 mol, Temp. 120°C

No.	C_6H_5I (mmol)	CH_3COOK (mmol)	Olefin introduced	React. time (hr)	Arylation product (mmol) (%)[e]	
1	50	0	C_2H_4, 8 kg/cm² [b]	3	$C_6H_5CH{=}CH_2$	trace(0)
2	50	15	C_2H_4, 8 kg/cm²	3	$C_6H_5CH{=}CH_2$	13 (26)
3	50	30	C_2H_4, 8 kg/cm²	3	$C_6H_5CH{=}CH_2$	24 (48)
4	50	60	C_2H_4, 8 kg/cm²	3	$C_6H_5CH{=}CH_2$	37 (74)[d]
5[a]	50	60	C_2H_4, 8 kg/cm²	3	$C_6H_5CH{=}CH_2$	36 (72)[d]
6	50	60	$C_6H_5CH{=}CH_2$ 100 mmol	2	*trans*-Stilbene 1,1-Diphenylethylene	45 (90) 6.0 (12)
7	30	48	C_3H_6, 3.5 kg/cm² [b]	2	α-Methylstyrene β-Methylstyrene	8.1 (27) 22 (73)
8	30	48	$CH_2{=}CHCOOCH_3$ 60 mmol	2	Methyl cinnamate	29 (97)[e]

a) Palladium black (54 mg) obtained by reducing $PdCl_2$ was used as a catalyst.
b) The methanol solution was saturated with the olefin at room temperature.
c) Based on the amount of iodobenzene used.
d) *trans*-Stilbene and 1,1-diphenylethylene were detected in the product.
e) No methyl atropate was detected.

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