Arylation of Olefin with Iodobenzene Catalyzed by Palladium

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Arylation of propylene, ethylene, styrene, and methyl acrylate with iodobenzene was found to be catalyzed by metallic palladium in methanol to give methylstyrene, styrene, *t*-stilbene, and methyl cinnamate, respectively. Their yields and selectivities increased significantly by the addition of excess potassium acetate as an acceptor of hydriodic acid formed. The course of catalytic reaction is discussed in terms of the oxidative addition of iodobenzene to a palladium complex of low oxidation state.

Oxidative addition of organic halides to metal complexes of low oxidation state is well-known a method of σ-organometallic complexes. Before such an addition is made to a catalytic reaction, it should be considered whether the metal complex of low oxidation state specified as a catalyst is regenerated during the course of reaction. In the carbonylation of phenyl halide catalyzed by bis(triphenylphosphine)carbonylchlororhodium(I) in benzene,[1] benzoyl and halogen ligands are reductively eliminated from $C_6H_5CORh(PPh_3)_2(CO)(Cl)(X)$ to give benzoyl halide and $Rh(PPh_3)_2(CO)Cl$, with the result that the rhodium(I) complex works well as the catalyst. Nickel tetracarbonyl is also labile for oxidative addition of organic halides such as phenyl and allyl halides to give acyl nickel carbonyls.[2,3] In this case, however, these nickel complexes decompose into nickel(II) halide to give α-diketones or esters, their formation depending on the solvent used. Accordingly, nickel carbonyl seems to have no catalytic activity for the carbonylation of organic halide except under enforced reaction conditions. It was shown[4] that the carbonylation rate of phenyl halide with nickel carbonyl in methanol increased significantly by the addition of potassium acetate as an acceptor of hydrohalogenic acid formed. It was considered that the acid strongly inhibited the coordination of carbon monoxide to regenerate a nickel carbonyl of low oxidation state. The same effect of potassium acetate is also observed in the palladium black-catalyzed carbonylation of phenyl halide[5] in spite of the fact that metallic palladium has a higher oxidation potential than nickel. These results led us to investigate the effect of potassium acetate on other kinds of catalytic reactions to see whether the inhibition by proton is observed only in carbonylation. It was found that palladium black is highly active and selective for the catalytic arylation of olefin with iodobenzene in the presence of potassium acetate.[6] The present paper deals with the palladium catalyzed arylation of propylene, ethylene, styrene, and methyl cinnamate with phenyl halide to give the corresponding styrene derivatives.

Experimental

A given amount of palladium catalyst ($PdCl_2$ or Pd-black) and a methanol solution (30—35 ml) of phenyl halides and potassium acetate were placed in a titanium-alloy autoclave (100 ml) equipped with a magnetic stirrer (when liquid olefin was used, it was also dissolved in the methanol solution). The autoclave was purged thoroughly with nitrogen and gaseous olefin was then introduced. In the case of liquid olefin, nitrogen gas was charged up to 10 kg/cm^2. The autoclave was heated up to the desired temperature by an electric furnace within 20 min. and the temperature was kept constant for 2—3 hr. It was then cooled rapidly to room temperature with water and gaseous materials were discharged. The products were taken out from the autoclave by using a sufficient amount of methanol or acetone, and they were separated from palladium black before their amounts were quantitatively determined by gas chromatography, using a suitable substance as an internal standard. A DC-550 columun was used for the determination of styrene, α-, β-methylstyrene, methyl cinnamate, and phenyl halides, and a SE-30 columun for 1,1-diphenylethylene and *t*-stilbene with hydrogen as a carrier gas. All materials were commerical products, their purity being checked by gas chromatography before use.

Results

The effect of potassium acetate (pK_a of CH_3COOH=4.7) on the arylation of ethylene with iodobenzene catalyzed by palladium dichloride in methanol was examined. The results are shown in Table 1. The yield of styrene increased with increase in the amount of potassium acetate, no residual iodobenzene being detected when the amount (mole) of potassium acetate added exceeded that of iodobenzene used. Most of the palladium dichloride was reduced to metallic palladium after the reaction. Pyridine (pK_a of $C_5H_5NH^+$=5.4) and sodium benzoate (pK_a of C_6H_5COOH=4.2) showed a similar effect on the arylation of ethylene. No catalytic arylation, however, was observed with potassium trichloroacetate (pK_a of CCl_3COOH=0.7). Palladium black also catalyzed the arylation with high activity as shown in Table 1. There is hardly any difference between palladium dichloride and palladium black in catalytic activity. The effect of acetic acid as a solvent was examined, since hydriodic acid formed by arylation gives potassium iodide and acetic acid during the reaction when potassium acetate is present in the reaction

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TABLE 1. EFFECT OF POTASSIUM ACETATE

Catalyst	C_6H_5I (mmol)	AcOK (mmol)	Styrene (mmol)	Conversion[a] (%)
$PdCl_2$ (0.5 mmol)	50	0	trace	—
	50	15	13	26
	50	30	24	48
	50	60	37	74
	50	(Py) 60	19	36
	50	(CCl_3COOK) 60	trace	—
Pd-black (1 mmol)	30	0	3.3	11
	30	12	9.3	31
	30	20	16	53
	30	30	21	70
	30	40	27	90
	30	50	26	88

CH_3OH, 30 ml; $P_{C_2H_4}$, 8—10 kg/cm²; Temperature 120—125 °C; Time, 3 hr.

a) Based on C_6H_5I employed.

medium. The addition of acetic acid as the solvent considerably decreased the yield of styrene (Table 2).

TABLE 2. EFFECT OF ACETIC ACID AS SOLVENT

Solvent (ml)		Conversion (%)	Selectivity[a] (%)
CH_3OH	AcOH		
0	30	47	57
10	20	70	62
20	10	95	73
30	0	100	87

C_6H_5I, 30 mmol; AcOK, 50 mmol; Pd-black, 1 mmol; $P_{C_2H_4}$, 10 kg/cm²; Temperature 125°C; Time, 3 hr

a) Based on C_6H_5I consumed.

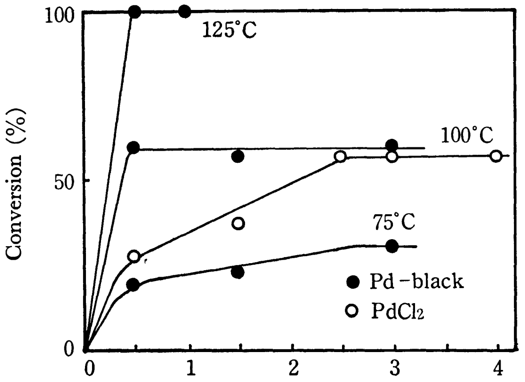

Fig. 1. Effect of the amount of Pd-cat.
C_6H_5I, 30 mmol; AcOK, 50 mmol; CH_3OH, 30 ml; $P_{C_2H_4}$, 10 kg/cm²; Time, 2 hr.

The effects of the amount of palladium black and palladium dichloride on the conversion of iodobenzene were examined at 75 °C, 100 °C, and 125 °C. The degrees of conversion of iodobenzene are plotted against the amount of palladium catalyst in Fig. 1. The conversion at 100 °C becomes nearly constant when the amount of palladium black and palladium dichloride exceeds 0.5 and 2.5 mmol, respectively. Palladium black seems to be more active than palladium dichloride. It is to be noted that a large amount of palladium dichloride gives nearly the same conversion as that obtained from palladium black. The selectivity of styrene formation is 60—90% (Table 1). Even under a higher pressure of ethylene, the selectivity is less than 90%, *t*-stilbene and 1,1-diphenylethylene being always detected. It was found that styrene is also arylated with iodobenzene to give quantitatively *t*-stilbene and 1,1-diphenylethylene (Table 3). This is why the selectivity of styrene from ethylene and iodobenzene is always less than 90%. The results of arylation of propylene, ethylene, styrene, and methyl acrylate are summarized in Table 4. These olefins give almost quantitatively methylstyrene, styrene, *t*-stilbene, and methyl cinnamate, respectively. Propylene gives a considerable amount of α-methylstyrene as well as β-methylstyrene, while methyl acrylate gives exclusively methyl cinnamate. Reactivity of phenyl halide decreases in the order $C_6H_5I > C_6H_5Br \gg C_6H_5Cl$, whereas the arylation of ethylene or propylene with a bromobenzene derivative (Table 5) shows that the reactivity of bromobenzene derivatives decreases in the order *p*-chlorobromobenzene>bromobenzene$\geq$*p*-bromotoluene>*p*-bromoanisole. On the other hand, the yields of arylation product with bro-

TABLE 3. SELECTIVITY OF ARYLATION PRODUCT

Olefin		C_6H_5I (mmol)	Arylation product			Conversion (%)	Selectivity (%)
C_2H_4 (kg/cm²)	Styrene (mmol)		Styrene (mmol)	*t*-Stilbene (mmol)	1,1-Diphenylethylene (mmol)		
5		10	8.4			100	84
10		10	8.2			100	82
20		10	8.8			100	88
10		20	17			100	85
10		40	31			100	78
	10	10		7.3	1.4	87	100
	20	10		7.9	1.5	94	100
	30	10		9.0	1.0	100	100

Pd-black, 1 mmol; AcOK, 50 mmol; CH_3OH, 30 ml; Time, 3 hr; Temperature 125°C.

Table 4. Arylation of substituted olefin

	C_6H_5I (mmol)	AcOK (mmol)	Olefin	Conversion (%)	Arylation product (mmol)		Selectivity (%)	Isomer distribution α/β
1	30	48	C_3H_6 3.5 kg/cm² a)	100	$C_6H_5\overset{CH_3}{C}=CH_2$	8.1	27	2.7
					$C_6H_5CH=CHCH_3$	22	73	
2	50	60	C_2H_4 8.0 kg/cm² a)	100	$C_6H_5CH=CH_2$	37	74	—
3	50	60	$C_6H_5\text{-}CH=CH_2$ 100 mmol	100	$(C_6H_5)_2C=CH_2$	45	10	7.5
					$t\text{-}C_6H_6CH=CHC_6H_5$	6	90	
4	30	48	$CH_2=\underset{COOCH_3}{CH}$ 6.0 mmol	100	$C_6H_6CH=CHCOOCH_3$	29	—	>50
					$C_6H_6\overset{COOCH_3}{C}=CH_2$	—	97	

a) Introduced at room temperature.

Table 5. Reactivity of bromobenzene derivatives

p-Br-C_6H_4-X	Conversion (%)[a]	
	With C_2H_4 (10 kg/cm²)	With C_3H_6 (3.5 kg/cm²)
X=OCH_3	0	—
CH_3	6.7	—
H	6.7	6.7
Cl	10	13

p-Br-C_6H_5-X, 30 mmol; AcOK, 40 mmol; CH_3OH, 30 ml; Pd-black, 1 mmol; Temperature 125°C; Time 3 hr.

a) Calculated from the amount of p-Br-C_6H_5-X consumed.

mobenzene indicate that the reactivity of olefins decreases approximately in the order propylene>ethylene>styrene>methyl acrylate, where no arylation of methyl acrylate with bromobenzene is observed. Addition of triphenylphosphine slightly increased the yield of methylstyrene from propylene and bromobenzene. However, no effect was observed in the isomer distribution of methylstyrene. Triphenylphosphine reacted with iodobenzene to give tetraphenylphosphonium iodide almost quantitatively under the same reaction condition (calcd for $(C_6H_5)_4PI$: H, 4.17%; C, 60.37%; I, 27.23%. Found: H, 4.3%; C, 61.8 %; I, 27.2%).

Discussion

It was reported that ethylene or styrene is arylated with benzene in the presence of palladium(II) diacetate ($C_6H_6+C_6H_5CH=CH_2+Pd(AcO)_2 \rightarrow t\text{-}C_6H_5CH=CH\text{-}C_6H_5+Pd+2AcOH$).[7] The arylation, however, consumes a stoichiometric amount of palladium(II) diacetate, which is reduced to metallic palladium. The arylation is not catalytic with respect to palladium with no simultaneous reoxidation of metallic palladium. Heck found that σ-phenylpalladium(II) acetate prepared from phenylmercuric acetate and palladium diacetate reacts with olefin under mild condition to give styrene derivatives:[8]

$$C_6H_5Hg(AcO) + Pd(AcO)_2 \rightarrow (C_6H_5)Pd(AcO) + Hg(AcO)_2$$

$$C_6H_5Pd(AcO) + CH_2=CH_2 \rightarrow C_6H_5CH=CH_2 + Pd + AcOH$$

In this case, the palladium(II) compound is also reduced into metallic palladium, arylation taking place stoichiometrically. However, arylation of olefin with iodobenzene is effectively catalyzed by metallic palladium, its catalytic efficiency being significantly large.

Palladium(II) dichloride is easily reduced to metallic palladium in a boiling methanol solution. Thus, most of the palladium(II) dichloride we used should be present as metallic palladium during the course of arylation. This may be why practically no difference is observed between palladium dichloride and metallic palladium in their catalytic activities (Table 1). The reaction rate must be determined by some interaction of phenyl halides with palladium catalyst, since their reactivity decreases in the order $C_6H_5I > C_6H_5Br \gg C_6H_5Cl$, which is parallel with the strength of bond energy between carbon and halogen atom. The question is whether the arylation is catalyzed by palladium black suspended in the methanol solution, or by palladium complex dissolved in it. If the suspended palladium black catalyzes the arylation of ethylene, the yield of styrene should increase with the amount of palladium catalyst, since the surface area of palladium black contacting iodobenzene must increase with the amount of palladium black. The yield of styrene, however, does not increase (Fig. 1). This suggests that an active species of the catalyst is some palladium complex dissolved in the methanol solution. Accordingly, the highest rate of arylation of olefin would be obtained with a saturated solution of the palladium complex. Palladium complexes are slightly soluble

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[8] R. F. Heck, *ibid.*, **91**, 6707 (1969).

in methanol, with the result that the conversion of iodobenzene does not increase with the increase in the amount of palladium catalyst (Fig. 1).

Another point to be considered is what kind of palladium complex is supplied from the palladium black suspended during the course of reaction. If the complex were present in the form of palladium(II) compound, arylation with benzene would be expected. This was examined by the arylation of styrene with benzene in the presence of iodobenzene, using a relatively large amount of palladium black. The total amount of arylation product (*t*-stilbene and 1,1-diphenylethylene) is almost equal to that of iodobenzene consumed (Table 6). This supports the view that palladium black supplies no palladium(II) compound which is active for the arylation of styrene with benzene. It can thus be postulated that the oxidation state of the active palladium complex is low, probably zero, in the solution.

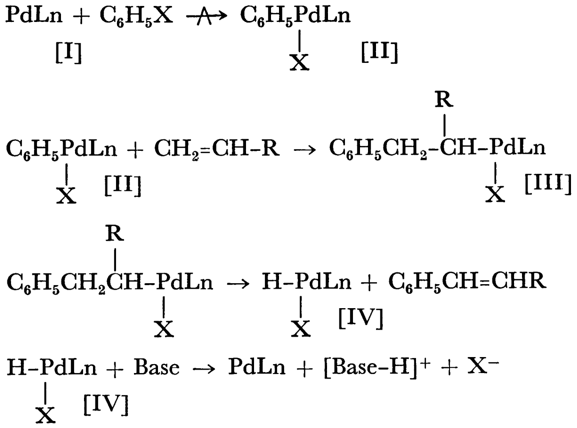
TABLE 6. REACTION OF C_6H_5I WITH STYRENE IN C_6H_6

Time (hr)	Consumed C_6H_5I (mmol)	Arylation product		Selectivity (%)
		t-Stilbene (mmol)	1,1-Diphenyl ethylene (mmol)	
3	1.8	1.6	0.26	100
8	3.2	2.7	0.26	93

C_6H_5I, 10 mmol; C_6H_6, 30 ml; Styrene, 26 mmol; AcOH, 5 ml; AcONa, 15 mmol; Pd-black, 5 mmol; Temperature 125 °C.

a) Based on the amount of C_6H_5I consumed

Taking into account the well-known oxidative addition of phenyl halide to low valent palladium complexes to give σ-aryl palladium(II) halide,[9] the following reaction scheme can be proposed;



$$\underset{[\mathrm{I}]}{\mathrm{PdLn}} + \mathrm{C_6H_5X} \rightarrow \underset{\substack{|\\ \mathrm{X}}}{\mathrm{C_6H_5PdLn}}\ [\mathrm{II}] \qquad (1)$$

$$\underset{\substack{|\\ \mathrm{X}}}{\mathrm{C_6H_5PdLn}}\ [\mathrm{II}] + \mathrm{CH_2{=}CH{-}R} \rightarrow \mathrm{C_6H_5CH_2{-}}\overset{\substack{\mathrm{R}\\ |}}{\mathrm{C}}\mathrm{H{-}}\underset{\substack{|\\ \mathrm{X}}}{\mathrm{PdLn}}\ [\mathrm{III}] \qquad (2)$$

$$\mathrm{C_6H_5CH_2}\overset{\substack{\mathrm{R}\\ |}}{\mathrm{C}}\mathrm{H{-}}\underset{\substack{|\\ \mathrm{X}}}{\mathrm{PdLn}} \rightarrow \mathrm{H{-}}\underset{\substack{|\\ \mathrm{X}}}{\mathrm{PdLn}}\ [\mathrm{IV}] + \mathrm{C_6H_5CH{=}CHR} \qquad (3)$$

$$\mathrm{H{-}}\underset{\substack{|\\ \mathrm{X}}}{\mathrm{PdLn}}\ [\mathrm{IV}] + \mathrm{Base} \rightarrow \mathrm{PdLn} + [\mathrm{Base{-}H}]^+ + \mathrm{X}^- \qquad (4)$$

L=olefin, solvent; X=Br, I; R=H, CH_3, C_6H_5, $COOCH_3$

Phenyl halide is oxidatively added to low valent palladium complex [I] to give σ-phenyl palladium complex[II], to which the olefin is inserted, followed by elimination of β-hydrogen to give [IV] and arylation product. Paths (2) and (3) have been investigated in detail.[8] Arylation with iodobenzene is significantly enhanced in a basic medium. This is in line with the fact that the yield of styrene considerably decreased in acetic acid solvent (Table 2). Such a basic medium should be favorable for paths (3) and (4) to regenerate the low valent palladium complex[10] and also for preventing the decomposition of σ-complex[II]. A stoichiometric reaction of styrene with bis(triphenylphosphine)σ-phenyl(iodo)palladium(II) was examined in methanol at its reflux temperature for the effect of potassium acetate on the reaction paths analogous to (2) and (3). No arylation of styrene was observed even in the presence of a large amount of potassium acetate, probably because triphenylphosphine inhibited the coordination of styrene to the palladium complex. The role of potassium acetate remains unclarified.

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