Kinetics on the Formylation of Iodobenzene Catalyzed by Palladium(II) Chloride in a Pyridine Solution

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Benzaldehyde was obtained in good yields by the formylation of iodobenzene with carbon monoxide and hydrogen catalyzed by palladium(II) chloride in a pyridine solution. The effect of following variables on the rate of producing benzaldehyde was examined kinetically : initial catalyst and iodobenzene concentrations, partial pressure of carbon monoxide and hydrogen, and temperature. A probable reaction mechanism *via* formyl- and benzoyl-palladium(II) intermediates is discussed on the basis of this kinetic study.

The formylation of halobenzene with carbon monoxide and hydrogen has been recently reported to produce benzaldehyde in the presence of tertiary amine and a catalytic amount of dihalogenobis(triphenylphosphine)palladium(II)[1] or palladium-black.[2] In both reactions, palladium(0) complex was suggested to be the active species. The formylation of halobenzene differs from the earlier hydroformylation of olefin in respect to the applicable substrate, though both reactions react with carbon monoxide and hydrogen to produce aldehyde. As an example of hydroformylation catalyzed by palladium(II) chloride or metallic palladium, the production of propanal from ethylene has been known[3] but the yield was low and a considerable amount of ethane was simultaneously produced. In our previous paper,[4] methyl benzoate has been obtained from iodobenzene, carbon monoxide and methanol in the presence of such a tertiary amine as pyridine and a catalytic amount of palladium(II) chloride. In this reaction, the mechanism *via* methoxycarbonyl-palladium(II) intermediate was proposed on the basis of the kinetic study. The formylation is rather analogous to the methoxycarbonylation although hydrogen is placed of methanol, because both reactions demand the addition of amine capable of removing hydrogen halide generated during the reactions.

The formylation of iodobenzene according to Eq. 1, was examined kinetically in a pyridine solution using palladium(II) chloride as the catalyst. Benzaldehyde was obtained in good yields,

$$\mathrm{PhI + CO + H_2 \longrightarrow PhCHO + HI} \qquad (1)$$

but the reaction mechanism of the formylation differed from that of methoxycarbonylation.

The purpose of this paper is to describe the results on the formylation of iodobenzene and to discuss its mechanism on the basis of the kinetic study.

Results

Preliminary Investigations. The formylations of some halobenzene were attempted under much the same conditions and the results are shown in Table 1. The maximum yield was obtained when iodobenzene was used as the substrate.

The reactivities of some palladium(II) halide were examined under the same conditions and the results are shown in Table 2. The yield increased to some extent in the order $PdCl_2 < PdBr_2 < PdI_2$. If the active species is palladium(0) complex, the difference of reactivities among palladium(II) halides is difficult to be explained.

In addition to benzaldehyde and pyridine hydroiodide salt, traces of benzene, biphenyl and chlorobenzene were detected in the reaction solutions; refer to the footnote of Table 1. But the sum of amounts of remaining iodobenzene and produced benzaldehyde accounted for over 96% of initial iodobenzene at each reaction time. Thus, the amounts of these by-products were neglected in this study.

The reaction proceeded rapidly in the early stage and then progressed linearly as the time went on; refer to Fig. 1 as an example. The equation $Y = At + B$, where Y and t represent respectively the produced benzaldehyde concentration ($\mathrm{mol\cdot l^{-1}}$) and reaction time (min) while A ($\mathrm{mol\cdot l^{-1}\cdot min^{-1}}$) and B ($\mathrm{mol\cdot l^{-1}}$) are constants, can be applied as the empirical equation for expressing the relationship between time and the produced benzaldehyde concentration after 5—10 min.

The effect of stirring speed on the values of A and B in the empirical equation was examined and the

TABLE 1. REACTION OF Ph-X WITH CO AND H_2
$PdCl_2$ 0.5 mmol, C_5H_5N 20 ml, Initial P_{CO} 50 kg·cm^{-2}, Initial P_{H_2} 50 kg·cm^{-2}, 140 °C, 90 min, 750 rpm

Ph-X (mmol)	Yield of PhCHO (%)[a]
-Cl (49.1)	10[b]
-Br (47.6)	4.4[c]
-I (44.7)	99[c]

a) Based on the amount of initial Ph-X. b) Trace of PhH was also produced. c) Traces of PhH, Ph-Ph and PhCl were also produced.

TABLE 2. REACTIVITY OF CATALYST PdX_2
PdX_2 0.40 mmol, PhI 49.4 mmol, C_5H_5N 50 ml, P_{CO} 50 kg·cm^{-2} (const.), P_{H_2} 50 kg·cm^{-2} (const.), 130 °C, 60 min, 750 rpm

Catalyst PdX_2	Yield of PhCHO (%)[a]
$PdCl_2$	43
$PdBr_2$	51
PdI_2	61

a) Based on the amount of initial PhI.

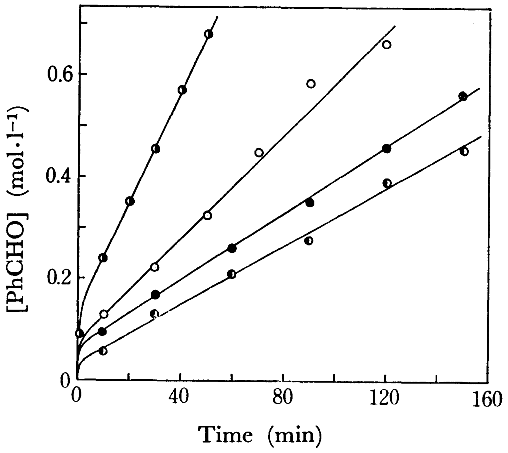

Fig. 1. Relation between time and benzaldehyde concentration.
PhI 0.745 mol·l^{-1}, C_5H_5N 50 ml, P_{CO} 50 kg·cm^{-2} (const.), P_{H_2} 50 kg·cm^{-2}(const.), 130 °C, 750 rpm. Anal. points; ◑ 1.68×10^{-2}, ○ 8.28×10^{-3}, ● 4.49×10^{-3}, ◐ 3.62×10^{-3} mol·l^{-1} initial $PdCl_2$ concn. Curves show the calculated relationships between time and produced benzaldehyde concentration according to Eq. 18.

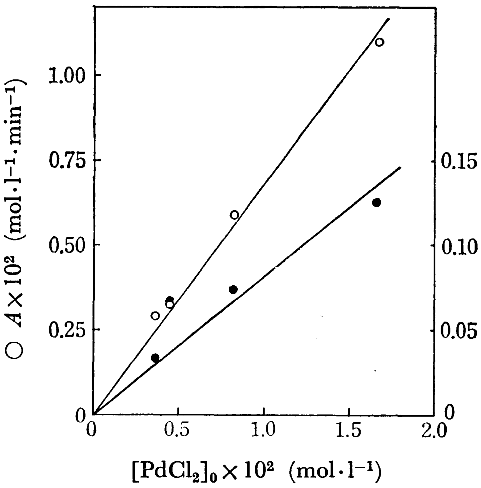

Fig. 2. Relation between $[PdCl_2]_0$ and A or B.
Reaction conditions were shown in the footnote of Fig. 1.

result is shown in Table 3. The value of A was independent of the stirring speeds and the value of B also seemed to be independent of the stirring speeds within an experimental error. Therefore, the reaction may be regarded not to be diffusion-controlled as far as it is carried out under milder conditions than those of Table 3. Henceforwared, the total volume was calculated as the sum of amounts of initial iodobenzene and pyridine.

Kinetic Results. The effects of following variables on the values of A and B in the empirical equation were examined and the results are written in order.

At first, the effect of initial palladium(II) chloride concentration was examined and the result is shown in Fig. 2. Both values of A and B were proportional to the palladium(II) chloride concentration, though the value of B was somewhat insufficient.

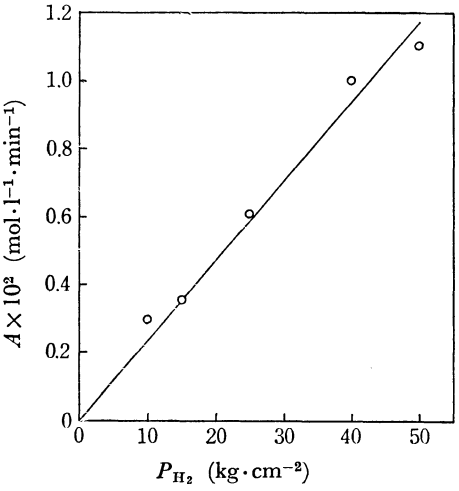

Fig. 3. Relation between P_{H_2} and A.
Reaction conditions were shown in the note of Table 5.

Table 3. Effect of stirring speed
$PdCl_2$ 1.68×10^{-2} mol·l^{-1}, PhI 0.745 mol·l^{-1}, C_5H_5N 50 ml, P_{CO} 50 kg·cm^{-2} (const.), P_{H_2} 50 kg·cm^{-2} (const.), 130 °C

Stirring speed (rpm)	Empirical eq. $Y=At+B$	
	$A\times10^2$ (mol·l^{-1}·min^{-1})	B (mol·l^{-1})
600	1.08	0.140
750	1.09	0.135
750	1.10	0.125
900	1.08	0.113

Table 4. Effect of partial pressure of CO
$PdCl_2$ 1.67×10^{-2} mol·l^{-1}, PhI 0.745 mol·l^{-1}, C_5H_5N 50 ml, P_{H_2} 50 kg·cm^{-2} (const.), 130 °C, 750 rpm

P_{CO} (kg·cm^{-2})	Empirical eq. $Y=At+B$	
	$A\times10^2$ (mol·l^{-1}·min^{-1})	B (mol·l^{-1})
50	1.10	0.125
25	1.18	0.123
10	1.08	0.094

Next, the effect of partial pressure of carbon monoxide was examined and the result is shown in Table 4. The variation in the partial pressure of carbon monoxide did not affect both values of A and B, *i.e.*, the rate is independent of the partial pressure of carbon monoxide. In case of the methoxycarbonylation of iodobenzene the rate was dependent on the carbon monoxide pressure.[4] Thus, this result suggests that the mechanism of formylation is not analogous to that of methoxycarbonylation.

Next, the effect of partial pressure of hydrogen was examined and the result is shown in Fig. 3 and Table 5. The value of A was proportional to the partial pressure of hydrogen irrespective of the other partial pressure of carbon monoxide, as shown in Fig. 3. This result again shows that the rate is independent of the

Table 5. Effect of partial pressure of H_2
$PdCl_2$ 1.68×10^{-2} mol·l^{-1}, PhI 0.745 mol·l^{-1}, C_5H_5N 50 ml, 130 °C, 750 rpm

P_{H_2} (kg·cm^{-2})	P_{CO} (kg·cm^{-2})	Empirical eq. $Y=At+B$ $A\times10^2$ (mol·l^{-1}·min^{-1})	B (mol·l^{-1})
50	50	1.10	0.125
40	20	1.00	0.118
25	50	0.609	0.096
15	45	0.353	0.077
10	50	0.296	0.095

Table 6. Effect of initial PhI concentration
$PdCl_2$ 3.66×10^{-3} mol·l^{-1}, C_5H_5N 50 ml, P_{CO} 50 kg·cm^{-2} (const.), P_{H_2} 50 kg·cm^{-2} (const.), 130 °C, 750 rpm

PhI concn (mol·l^{-1})	Empirical eq. $Y=At+B$ $A\times10^3$ (mol·l^{-1}·min^{-1})	B (mol·l^{-1})
0.745	2.96	0.041
0.447	3.04	0.049
0.303	2.86	0.047

Table 7. Effect of temperature
$PdCl_2$ 1.70×10^{-2} mol·l^{-1}, PhI 0.745 mol·l^{-1}, C_5H_5N 50 ml, P_{CO} 50 kg·cm^{-2} (const), P_{H_2} 50 kg·cm^{-2} (const.), 750 rpm

Temp (°C)	Empirical eq. $Y=At+B$ $A\times10^2$ (mol·l^{-1}·min^{-1})	B (mol·l^{-1})
140[a]	1.77	0.045
130	1.10	0.125
115	0.577	0.076
100	0.290	0.045

a) P_{CO} 100 kg·cm^{-1} (const.).

partial pressure of carbon monoxide. On the other hand, the value of B hardly changed though the partial pressure of hydrogen changed, as seen in Table 5.

As the reaction proceeded linearly as the time went on except for the early stage, the rate is supposed to be independent of remaining iodobenzene concentration; refer to Fig. 1. The effect of initial iodobenzene concentration was examined and the result is shown in Table 6. The rate was remained constant by the change of initial iodobenzene concentration and this result also differed from that in case of the methoxycarbonylation of iodobenzene.[4]

Finally, the effect of temperature was examined and the result is shown in Table 7. The rise in temperature caused the increase in the value of A while little affected the value of B.

Discussion

Reaction Mechanism. The following mechanism is assumed;

$$\underset{\mathbf{1}}{PdCl_2(C_5H_5N)_2} + H_2 \xrightarrow{k_2} \underset{\mathbf{2}}{HPdCl(C_5H_5N)_2} + HCl \tag{2}$$

$$\mathbf{2} + CO \xrightarrow{\text{fast}} \underset{\mathbf{3}}{HCOPdCl(C_5H_5N)_2} \tag{3}$$

$$\mathbf{3} + PhI \xrightarrow{\text{fast}} \underset{\mathbf{4}}{PdClI(C_5H_5N)_2} + PhCHO \tag{4}$$

$$\mathbf{4} + H_2 \xrightarrow{k_5} \mathbf{2} + HI \tag{5}$$

$$\mathbf{4} + H_2 \xrightarrow{k_6} \underset{\mathbf{5}}{HPdI(C_5H_5N)_2} + HCl \tag{6}$$

$$\mathbf{5} + C_5H_5N + CO \xrightarrow{\text{fast}} \underset{\mathbf{6}}{Pd(CO)(C_5H_5)_3} + HI \tag{7}$$

$$\mathbf{6} + PhI \xrightarrow{\text{fast}} \underset{\mathbf{7}}{PhCOPdI(C_5H_5N)_2} + C_5H_5N \tag{8}$$

$$\mathbf{7} + H_2 \xrightarrow{k_9} \mathbf{5} + PhCHO \tag{9}$$

$$HCl \text{ or } HI + C_5H_5N \longrightarrow C_5H_6Cl \text{ or } C_5H_6I \tag{10}$$

where k_2, k_5, k_6 and k_9 represent the rate constants of elementary processes (2), (5), (6) and (9), respectively. The elementary processes (3), (4), (7) and (8) are assumed to proceed rapidly, because the rate was independent of iodobenzene concentration and partial pressure of carbon monoxide. The catalytic cycle from (7) to (9) is the same one proposed by Schoenberg and Heck[1] and Ito *et al.*[2] The reaction (8) is well known[5,6] in case of the analogous triphenylphosphine complexes. However, this catalytic cycle cannot explain the following results mentioned before: the difference of reactivities among palladium(II) halides, the production of chlorobenzene and the rapid reaction in the early stage. Thus, the other catalytic cycle from (3) to (5), which bears a resemblance to the mechanism of methoxycarbonylation of iodobenzene,[4] is assumed to produce benzaldehyde before the catalytic cycle from (7) to (9) proceeds. The existence of complex **2** is known[7] in case of triphenylphosphine being used as a ligand. On the other hand, the formylpalladium(II) complex **3** is unknown but is probably possible to form during the reaction, because acylpalladium(II) complex is well known[8] to be formed by the carbonylation of alkylpalladium(II) complex. The catalytic cycle from (3) to (5) corresponds to the part of rapid reaction in the early stage and the other cycle from (7) to (9) corresponds to the most part of reaction which proceeds linearly as the time goes on. The reaction (8) may proceed essentially *via* phenylpalladium intermediate of short lifetime, because the analogous reaction (triphenylphosphine was used in place of pyridine) has been reported[5] to proceed *via* five co-ordinated phenyl-palladium intermediate. Benzene and biphenyl detected as by-products are probably formed by the attack of hydrogen and iodobenzene on the phenyl-palladium intermediate, respectively. But the reaction (8) is here assumed to be one elementary process, since the amounts of benzene and biphenyl were little enough to be negligiable. Similarly, the reaction (4) too may not always proceed as one elementary process, because detected chlorobenzene is probably formed by the exchange of halides between the chloride in the intermediate **3** and the iodide in iodobenzene.

Rate Equation. From the reaction mechanism proposed above, the rate equation of producing benzaldehyde can be derived in the following way.

The material balance for palladium can be expressed as,

$$C_1 + C_4 + C_7 = [\mathrm{PdCl_2}]_0 \tag{11}$$

where C_n represents the concentration of intermediate ***n*** and $[\mathrm{PdCl_2}]_0$ the initial palladium(II) chloride concentration. The rates of decreasing concentration of intermediates **1** and **4** are respectively expressed as,

$$-\frac{\mathrm{d}C_1}{\mathrm{d}t} = k_2HPC_1 \tag{12}$$

$$-\frac{\mathrm{d}C_4}{\mathrm{d}t} = k_6HPC_4 - k_2HPC_1 \tag{13}$$

where H and P represent the Henry's constant and partial pressure of hydrogen. From Eqs. 12 and 13, C_1 and C_4 can be obtained as,

$$C_1 = [\mathrm{PdCl_2}]_0 \mathrm{e}^{-k_2HPt} \tag{14}$$

$$C_4 = \frac{k_2[\mathrm{PdCl_2}]_0}{k_{2-6}}(\mathrm{e}^{-k_6HPt} - \mathrm{e}^{-k_2HPt})\ (k_{2-6} \equiv k_2 - k_6) \tag{15}$$

and C_7 can also be obtained from Eqs. 11, 14 and 15.

$$C_7 = [\mathrm{PdCl_2}]_0\left(1 + \frac{k_6}{k_{2-6}}\mathrm{e}^{-k_2HPt} - \frac{k_2}{k_{2-6}}\mathrm{e}^{-k_6HPt}\right) \tag{16}$$

The rate equation of producing benzaldehyde can be given from Eqs. 14, 15 and 16 as,

$$\begin{aligned}\frac{\mathrm{d}[\mathrm{PhCHO}]}{\mathrm{d}t} &= k_2HPC_1 + k_5HPC_4 + k_9HPC_7 \\ &= [\mathrm{PdCl_2}]_0HP\left(k_9 - \frac{k_6k_{2-9} - k_2k_{2-5}}{k_{2-6}}\mathrm{e}^{-k_2HPt}\right. \\ &\qquad \left. + \frac{k_2k_{5-9}}{k_{2-6}}\mathrm{e}^{-k_6HPt}\right) \end{aligned} \tag{17}$$

$$(k_{2-9},\ k_{2-5},\ k_{5-9} \equiv k_2 - k_9,\ k_2 - k_5,\ k_5 - k_9)$$

where [PhCHO] represents the produced benzaldehyde concentration. Finally, the relationship between time and the produced benzaldehyde concentration is derived from Eq. 17 as follows.

$$\begin{aligned}[\mathrm{PhCHO}] &= k_9HP[\mathrm{PdCl_2}]_0t \\ &\quad + \frac{k_2k_{5-9} + k_6k_{2-9}}{k_2k_6}[\mathrm{PdCl_2}]_0 \\ &\quad + \frac{k_6k_{2-9} - k_2k_{2-5}}{k_2k_{2-6}}[\mathrm{PdCl_2}]_0\mathrm{e}^{-k_2HPt} \\ &\quad - \frac{k_2k_{5-9}}{k_6k_{2-6}}[\mathrm{PdCl_2}]_0\mathrm{e}^{-k_6HPt} \end{aligned} \tag{18}$$

Analysis of Kinetic Results. The kinetic results are compared with the derived rate equation (18).

Since $\exp(-k_2HPt)$ and $\exp(-k_6HPt)$ in Eq. 18 are quickly drawn close to zero as the time goes on, they are assumed to be zero after about 10 minutes. On this assumption, Eq. 18 can be rewritten as,

$$[\mathrm{PhCHO}] = k_9HP[\mathrm{PdCl_2}]_0t + \frac{k_2k_{5-9} + k_6k_{2-9}}{k_2k_6}[\mathrm{PdCl_2}]_0 \tag{19}$$

and Eq. 19 has the same shape as the empirical equation $Y = At + B$, giving the following relationships.

$$A = k_9HP[\mathrm{PdCl_2}]_0 \tag{20}$$

$$B = \frac{k_2k_{5-9} + k_6k_{2-9}}{k_2k_6}[\mathrm{PdCl_2}]_0 \tag{21}$$

As seen in Eq. 20, the value of A must be of the first order with respect to the palladium(II) chloride concentration and the partial pressure of hydrogen, as shown in Figs. 2 and 3. On the other hand, as seen in Eq. 21, the value of B must be of the first order with respect to the palladium(II) chloride concentration, as shown in Fig. 2. Accordingly, the kinetic results are sufficiently consistent with the relationships of Eq. 19.

Determination of Rate Constants. The value of k_9H is determined as 1.37×10^{-2} kg$^{-1}\cdot$cm$^2\cdot$min^{-1} at 130 °C as the average between 1.35×10^{-2} from the gradient in Fig. 2 and 1.39×10^{-2} in Fig. 3. The value of k_9H at the other temperatures are determined according to Eq. 20 as follows; 2.08×10^{-2}, 6.70×10^{-3} and 3.45×10^{-3} kg$^{-1}\cdot$cm$^2\cdot$min^{-1} at 140, 115 and 100 °C, respectively. The temperature coefficient of k_9H is obtained as 14.4 kcal$\cdot$mol^{-1} from the Arrhenius plot shown in Fig. 4.

The values of other rate constants cannot be determined, but the values of k_2H and k_6H can be estimated roughly in the following way. As the produced benzaldehyde concentration 0.093 mol$\cdot$l^{-1} at 1 min was observed as seen in Fig. 1, the value of 0.093 mol$\cdot$l$^{-1}\cdot$min^{-1} can be regarded to be nearly equal to the initial rate at the palladium(II) chloride concentration 1.7×10^{-2} mol$\cdot$l^{-1}, the partial pressure of hydrogen 50 kg$\cdot$cm^{-2} and 130 °C. On the other hand, the initial rate equation can be given from Eq. 17 as,

$$\left\{\frac{\mathrm{d}[\mathrm{PhCHO}]}{\mathrm{d}t}\right\}_0 = k_2HP[\mathrm{PdCl_2}]_0 \tag{22}$$

and the value of k_2H is estimated as 0.1 kg$^{-1}\cdot$cm$^2\cdot$min^{-1} at 130 °C. Next, the following equation can be

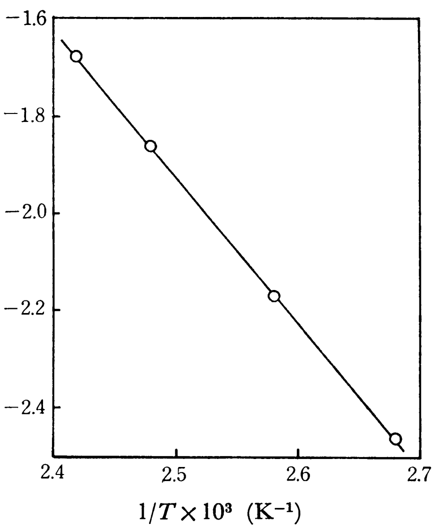

Fig. 4. Arrhenius plot of k_9H.
Reaction conditions were shown in the note of Table 7.

derived from Eq. 21 and the gradient of linear plot between palladium(II) chloride concentration and B in Fig. 2.

$$\left\{\frac{k_2k_{5-9}+k_6k_{2-9}}{k_2k_6}\right\} = 7.4 \qquad (23)$$

By assuming that the value of k_5H is equal to that of k_2H because the reaction (5) has a resemblance to the reaction (2), the value of k_6H is estimated as 0.015 $\mathrm{kg^{-1}\cdot cm^2\cdot min^{-1}}$ at 130 °C.

From the obtained values of k_2H and k_6H, the values of $\exp(-k_2HPt)$ and $\exp(-k_6HPt)$ can be regarded to be nearly equal to zero after about 10 min.

Calculated Relationship between Time and Benzaldehyde Concentration. Finally, the relationships between time and the produced benzaldehyde concentration which are calculated according to the derived rate equation (18), are compared with the observed ones. As an example, Fig. 1 shows that the calculated relationships are consistent with the observed ones including the part of rapid reaction in the early stage.

As discussed above, the proposed mechanism explains sufficiently the experimental results over the range of this study. Thus, the reaction mechanism is supposed to represent one of possible mechanisms.

Experimental

Materials. Palladium(II) chloride, palladium(II) bromide, palladium(II) iodide and biphenyl were commercially obtained and used without further purification. Iodobenzene, bromobenzene, chlorobenzene, benzaldehyde, benzene, pyridine and tetralin were distilled by means of ordinary methods. Hydrogen was commercial material and was over 99.9% pure. Carbon monoxide was prepared by decomposing formic acid in hot sulfuric acid, and was over 98% pure.

Procedure. Reactions were carried out in a glass-tube placed in a stainless-steel autoclave (*ca.* 200 cm^3) equipped with a Teflon stirrer and a Teflon sampling line. Palladium(II) chloride (0.2—1 mmol), iodobenzene(2—5 ml) pyridine (50—53 ml) and tetralin (5 ml) were placed in the autoclave, which was then purged with nitrogen three or four times. The autoclave was heated up to 100—140 °C within 60 min and then maintained over 20 min at the reaction temperature. Immediately after carbon monoxide and hydrogen mixture was added up to 20—100 kg·cm^{-2}, the stirring (750 rpm) was started and this time was marked as zero time. The stirring was stopped from time to time and a sample (*ca.* 1 ml) was withdrawn through the sampling line into a trap chilled in a ice-bath within 30 s. To keep the pressure constant during the reaction, carbon monoxide and hydrogen mixture gas was supplied from the reservoir in which carbon monoxide and hydrogen were mixed beforhand in each fixed ratio.

Analysis. Products were identified by the comparison of their retention times in the gas chromatography with those of authentic samples. An Apiezon Grease L column (2 m, 3 mmϕ) with nitrogen carrier was used at 160 °C for the determination of the amounts of benzaldehyde and iodobenzene with tetralin as an internal standard.

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