

## Dehydrogenation, hydrogenolysis, isomerization and hydrogenation of 3-phenylprop-2-en-1-ol with carbonylperchloratobis(triphenylphosphine)iridium(I) and carbonyldihydridoperchloratobis(triphenylphosphine)-iridium(III)

Chong Shik Chin \*, Jun Ho Shin, and Joong Bae Kim

*Department of Chemistry, Sogang University, Mapoku, Seoul 121 (Korea)*

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### Abstract

Reaction of 3-phenylprop-2-en-1-ol (**1**) with  $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$  (**2**) under nitrogen at 25 °C gives 3-phenylprop-2-enal (**4**), 3-phenylprop-2-ene (**5**), and 3-phenylpropanal (**6**). Dehydrogenation of **1** by **2** gives  $\text{Ir}(\text{H})_2(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$  (**3**) which reacts with another molecule of **1** to give **5**, **2** and  $\text{H}_2\text{O}$ . Isomerization of **1** to **6** rapidly occurs and hydrogenation of **6** to 3-phenylpropan-1-ol (**12**) slowly follows in the presence of **2** under hydrogen at 25 °C. The catalytically active species for the isomerization under nitrogen seems to be **3**.

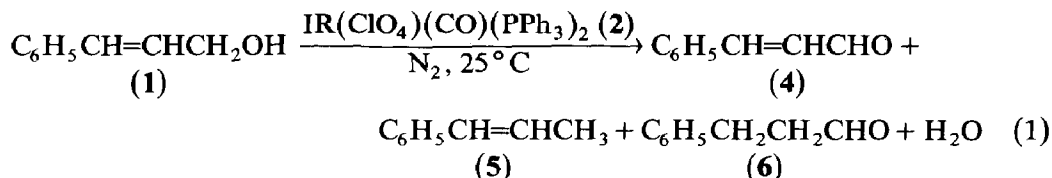
### Introduction

Metal-catalyzed reactions of alcohols are diverse. Hydroxyl group-directed hydrogenation of unsaturated alcohols to give saturated alcohols has long been of interest in the field of stereoselective organic synthesis [1]. Various isomerizations of unsaturated alcohols, to produce carbonyl compounds have been studied [2]. The dehydrogenation of alcohols has provided valuable information on the production of hydrogen from alcohols [3]. Conversion of alcohols into the corresponding hydrocarbons has been reported and can be utilized in a variety of organic syntheses [4]. Here, we report on the catalytic reactions, dehydrogenation, hydrogenolysis, isomerization, and hydrogenation of 3-phenylprop-2-en-1-ol (**1**) with  $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$  (**2**) and  $\text{Ir}(\text{H})_2(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$  (**3**) (along with detailed experimental results).

## Results and discussion

*Dehydrogenation and hydrogenolysis of 3-phenylprop-2-en-1-ol (1) with Ir(ClO<sub>4</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (2) and Ir(H)<sub>2</sub>(ClO<sub>4</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (3)*

The reaction of **1** with **2** under different conditions yields dehydrogenation, hydrogenolysis and isomerization products under nitrogen at 25°C (eq. 1) (see Table 1). The dehydrogenation of alcohols, to give the corresponding carbonyl compounds, is known to be initiated by the formation of alkoxometal species in the presence of base (A<sup>-</sup>) which is originally coordinated to the metal [5] or to the



non-coordinated anion (eq. 2) [3a,6]. Dehydrogenation may also be initiated by the formation of hydridoalkoxometal species in the absence of base (eq. 3) [3c,4a]. One may expect the dehydrogenation of **1** by **2** to occur via alkoxometal species rather



than through hydridoalkoxometal since it is well-known that complex **2** readily releases ClO<sub>4</sub><sup>-</sup> ligand in alcohol solution to give the complex, [Ir(alcohol)(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> [7]. The reactions of **1** with **2**, which yield **4** and **5** however, seem to proceed according to eq. 4 (via hydridoalkoxoiridium(III) (**9**)) and eq. 5 for the following reasons. (1) Addition of ClO<sub>4</sub><sup>-</sup> to the reaction mixture actually suppresses the production of **4** (Table 1), which excludes the OH hydrogen abstraction by the ClO<sub>4</sub><sup>-</sup> group. (2) The dihydrido-iridium(III) complex **3** is very stable [8]. (3) Most of hydrogen abstracted from **1** to yield **4** is used in the production of **5** and H<sub>2</sub>O (see

Table 1

Catalytic reactions of 3-phenylprop-2-en-1-ol (**1**) with Ir(ClO<sub>4</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (**2**), [Ir(CO)(PPh<sub>3</sub>)<sub>3</sub>]ClO<sub>4</sub> (**7**) and [Ir(CO)(PPh<sub>3</sub>)<sub>3</sub>]BF<sub>4</sub> (**8**) in CDCl<sub>3</sub> under nitrogen for 5 h

Catalyst	Temp. (°C)	Product (%) <sup>a</sup>			Unreacted <b>1</b>
		<b>4</b> <sup>b</sup>	<b>5</b> <sup>c</sup>	<b>6</b> <sup>d</sup>	
<b>2</b> <sup>e</sup>	25	40	40	3	17
<b>2</b> <sup>e,f</sup>	25	34	32	2	32
<b>2</b> <sup>e,g</sup>	60	40	36	7	17
<b>7</b> <sup>h</sup>	60	45	43	6	6
<b>8</b> <sup>h</sup>	60	46	43	6	5

<sup>a</sup> H<sub>2</sub>O was also detected in all experiments (H<sub>2</sub>O/5 = 1.0). <sup>b</sup> C<sub>6</sub>H<sub>5</sub>CH=CHCHO. <sup>c</sup> C<sub>6</sub>H<sub>5</sub>CH=CHCH<sub>3</sub>. <sup>d</sup> C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>CHO. <sup>e</sup> 6.0 mmol of **1** and 0.2 mmol of **2** were used in 5.0 ml of CDCl<sub>3</sub>. <sup>f</sup> In NaClO<sub>4</sub> saturated solution. <sup>g</sup> Data obtained after 2 h of reaction. <sup>h</sup> 2.0 mmol of **1** and 0.2 mmol of **7** (or **8**) were used in 5.0 ml of CDCl<sub>3</sub>.

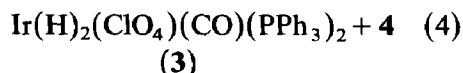
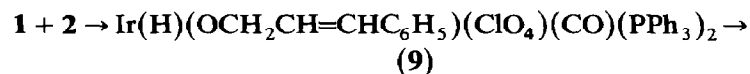
Table 2

Catalytic reactions of 3-phenylprop-2-en-1-ol (**1**) (0.1–1.0 mmol) with  $\text{Ir}(\text{H})_2(\text{ClO}_4)_4(\text{CO})(\text{PPh}_3)_2$  (**3**) (0.1 mmol) in  $\text{CDCl}_3$  (2.0 ml) under nitrogen at 25 °C

Mole ratio ( <b>1</b> / <b>3</b> )	Product (%) <sup>a</sup>			Time (h) <sup>e</sup>
	<b>4</b> <sup>b</sup>	<b>5</b> <sup>c</sup>	<b>6</b> <sup>d</sup>	
1		36	64	10
2		44	56	13
4	31	53	16	19
10	38	51	11	24

<sup>a</sup>  $\text{H}_2\text{O}$  was also detected in all experiments. <sup>b</sup>  $\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$ . <sup>c</sup>  $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$ .  
<sup>d</sup>  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CHO}$ . <sup>e</sup> Elapsed time until all **1** had disappeared.

Table 1). (**4**) **5** is produced in large amount in the reaction of **3** with **1** (see Table 2) in which no dehydrogenation product (**4**) is formed.

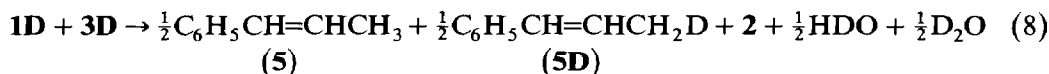
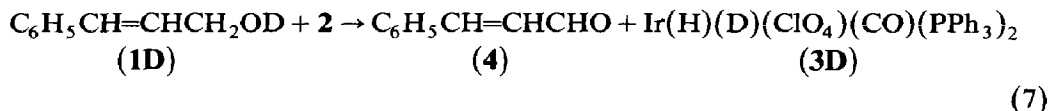
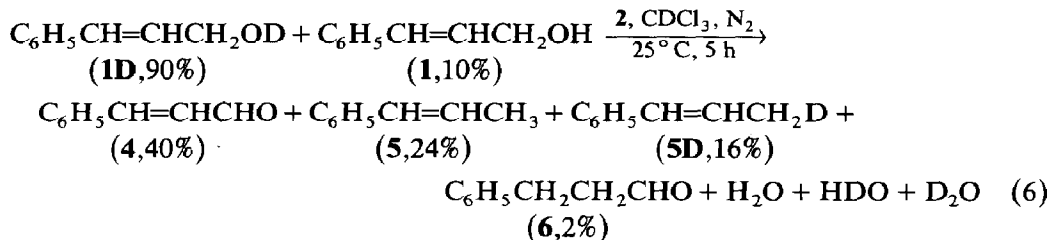


The reactions of  $[\text{Ir}(\text{CO})(\text{PPh}_3)_3]^+$  do furnish some useful information on the dehydrogenation and hydrogenolysis of **1** with **2** on the assumption that  $[\text{Ir}(\text{CO})(\text{PPh}_3)_3]^+$  and **2** follow the similar pathways upon reaction with **1**. The reactions of **1** with  $[\text{Ir}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$  (**7**) and  $[\text{Ir}(\text{CO})(\text{PPh}_3)_3]\text{BF}_4$  (**8**) are much slower than those with **2** (Table 1), to be discussed later. Almost the same results were obtained in the reactions of **1** with **7** and **8** (Table 1), which suggests that the role of the anions  $\text{ClO}_4^-$  and  $\text{BF}_4^-$  of the hydroxyl hydrogen abstraction is negligible and that the hydridoalkoxoiridium(III) species ( $[\text{Ir}(\text{H})(\text{OCH}_2\text{CH}=\text{CH}-\text{C}_6\text{H}_5)(\text{CO})(\text{PPh}_3)_3]^+$ ) is the intermediate.

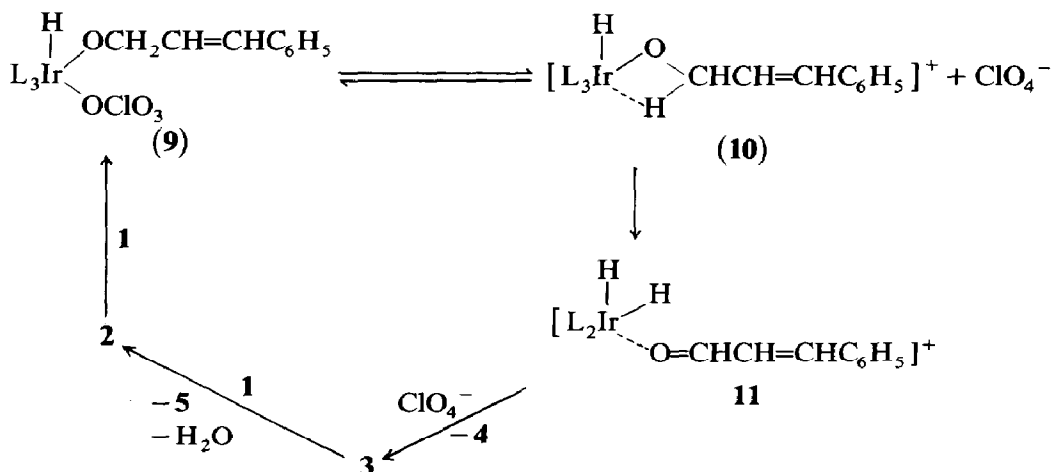
An intermolecular hydrogen transfer between alcohol molecules has been suggested for various reactions of alcohols with metal complexes [4a,9–12]. Dehydrogenation and hydrogenolysis of **1** with **2** do not seem to involve direct intermolecular hydrogen transfer between molecules of **1**. The yield of the dehydrogenation product is significantly higher than that of the hydrogenolysis product at high temperature (Table 1). Some of the  $\text{H}_2$  generated from **3** (the dehydrogenation product of **1**) is lost presumably by the well-known reductive elimination,  $\mathbf{3} \rightarrow \mathbf{2} + \text{H}_2$  [**8**], a reaction which should be significant at elevated temperature.

Reaction of a mixture of **1** and hydroxyl-hydrogen-deuterated 3-phenylprop-2-en-1-ol,  $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{OD}$  (**1D**) [13\*] provided interesting results (eq. 6) in support of eqs. 4 and 5, and is accordingly outlined in eqs. 7 and 8.

\* Reference number with asterisk indicates a note in the list of references.



The lower yield of products obtained from the reaction of **1** with **2** in the presence of an excess of  $\text{ClO}_4^-$  (Table 1) can be as proposed in Scheme 1. An excess of  $\text{ClO}_4^-$  suppresses the formation of **10**. The  $\text{ClO}_4^-$  group in **2** is readily replaced by **4** to give  $[\text{Ir}(\text{trans-C}_6\text{H}_5\text{CH}=\text{CHCHO})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$  (**4** is then coordinated through the oxygen atom but not through the olefinic  $\pi$ -system) [14], whereas the  $\text{ClO}_4^-$  group in **3** can not simply be replaced by **4** [15\*]. Thus **4** in **11** can readily be replaced by the  $\text{ClO}_4^-$  group to give **3**. A dihydridometal complex,  $\text{LnM}(\text{H})_2(\text{O}=\text{CR}_2)$ , analogous to **11** was also suggested as the intermediate in the hydrogenation of carbonyl compounds to alcohols [16]. The reaction rates with  $[\text{Ir}(\text{CO})(\text{PPh}_3)_3]^+$  (**7** and **8**) were lower than those with **2** (Table 1) are probably due to the relative ease of formation of **10** since the  $\text{ClO}_4^-$  in **2** is more labile than  $\text{PPh}_3$  in  $[\text{Ir}(\text{CO})(\text{PPh}_3)_3]^+$  [14,17,18].



Scheme 1.  $\text{L}_3 = (\text{CO})(\text{PPh}_3)_2$ .

*Isomerization and hydrogenation of 3-phenylprop-2-en-1-ol (1) with  $\text{Ir}[\text{ClO}_4](\text{CO})(\text{PPh}_3)_2$  (2) and  $\text{Ir}(\text{H})_2(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$  (3) under nitrogen and hydrogen at 25°C.*

Complex **2** catalyzes the hydrogenation of **1** to give 3-phenylpropan-1-ol (**12**) at room temperature under an atmospheric pressure of hydrogen. The data in Table 3 unambiguously suggest that the hydrogenation proceeds by rapid formation of the



Table 3

Isomerization and hydrogenation of 3-phenylprop-2-en-1-ol (**1**) (6.0 mmol) with  $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$  (**2**) (0.2 mmol) in  $\text{CDCl}_3$  (5.0 ml) at  $25^\circ\text{C}$  under hydrogen ( $P_{\text{H}_2}$ ) + vapor pressure of the solution = 1 atm).

Time (h)	Product (%)	
	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CHO}$ ( <b>6</b> )	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ( <b>12</b> )
3	100	0
10	75	25
28	15	85

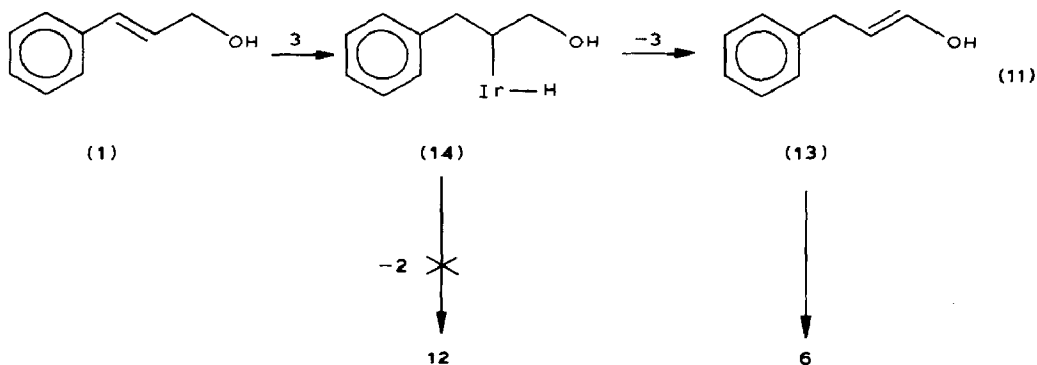
complex, **14** (eq. 11). Thus it was somewhat unexpected not to find the hydrogenation product (**12**) during the isomerization of **1** to **6** (Table 3). This may be due to the fact that the  $\beta$ -hydrogen elimination (**14**  $\rightarrow$  **3** + **13**) is much faster than the reductive elimination (**14**  $\rightarrow$  **2** + **12**). Similar results have been obtained in the catalytic reactions of 3-phenylprop-1-ene (**15**) with **3** under hydrogen, that is, the double bond migration (**15**  $\rightarrow$  3-phenylprop-2-ene) is faster than the hydrogenation (**15**  $\rightarrow$  3-phenylpropane).

## Experimental

**Caution.** Perchlorate salts of transition metal complexes containing organic ligands are potentially explosive [20].

The  $^1\text{H}$  NMR spectra were measured on a Varian 60 MHz (EM-360A) or Bruker WP 80 MHz spectrometer. IR spectra were recorded on a Shimadzu IR-440 and mass spectra were recorded on a JEOL JMS-DX303 spectrometer (70 eV). All manipulations were carried out by use of Schlenk type glassware under nitrogen or hydrogen.

3-Phenylprop-2-en-1-ol (**1**), 3-phenylprop-2-enal (**4**), 3-phenylprop-2-ene (**5**), 3-phenylpropanal (**6**), 3-phenylpropan-1-ol (**12**) and  $\text{CD}_3\text{OD}$  were purchased from Aldrich and used without further purification.  $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$  (**2**),  $\text{Ir}(\text{H})_2(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$  (**3**),  $[\text{Ir}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$  (**7**) and  $[\text{Ir}(\text{CO})(\text{PPh}_3)_3]\text{BF}_4$  (**8**) were prepared by published procedures [7,8,18].



**Preparation of 3-phenylprop-2-en-1-ol-OD (1D).** A solution of 3-phenylprop-2-en-1-ol (**1**, 5.0 g) in CD<sub>3</sub>OD (99.8%, 5.0 ml) was stirred for 30 min under nitrogen at 25 °C, and volatile materials (CD<sub>3</sub>OD and CD<sub>3</sub>OH) were removed by vacuum distillation to yield pale-yellow crystals whose <sup>1</sup>H NMR spectrum showed that ca. 80% of the hydroxyl hydrogen of **1** had been replaced by deuterium to give **1D** (C<sub>6</sub>H<sub>5</sub>CH=CHCH<sub>2</sub>OD). The above H–D exchange procedure was repeated another two times using 1.0 ml of CD<sub>3</sub>OD. The <sup>1</sup>H NMR spectrum of the final product (m.p. 35 °C) in CDCl<sub>3</sub> showed that the product contains 90% of **1D**.

**Isolation of [Ir(trans-C<sub>6</sub>H<sub>5</sub>CH=CHCHO)(CO)(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> from the reaction of 3-phenylprop-2-en-1-ol (1) with Ir(ClO<sub>4</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (2).** A solution of **1** (0.6 g, 4.5 mmol) and **2** (0.12 g, 0.15 mmol) in benzene (30 ml) was stirred under nitrogen at 25 °C. Light yellow microcrystals began to separate within 30 min. The crystals were collected by filtration, washed with benzene (20 ml) and dried in vacuum (0.08 g, 60%). The product was identified as [Ir(trans-C<sub>6</sub>H<sub>5</sub>CH=CHCHO)(CO)(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> by comparison of its spectral (<sup>1</sup>H NMR, IR, electronic absorption) data and molar conductance with those previously reported [14].

**Analyses of products, 3-phenylprop-2-enal (4), 3-phenylprop-2-ene (5), 3-phenylpropanal (6), 3-phenylpropan-1-ol (12), H<sub>2</sub>O, HDO and D<sub>2</sub>O.** The identity of **4**, **5**, **6** and **12** was established by comparison of the <sup>1</sup>H NMR spectra with those of authentic samples. Yields of the products were determined by comparing the signals in the <sup>1</sup>H NMR of the product mixtures. The presence of H<sub>2</sub>O was indicated by use of Karl Fischer reagent. HDO and D<sub>2</sub>O were detected by mass spectroscopy.

**Reaction of 3-phenylprop-2-en-1-ol (1) with Ir(ClO<sub>4</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (2) under nitrogen.** A solution of **1** (0.8 g, 6.0 mmol) and **2** (0.16 g, 0.2 mmol) in CDCl<sub>3</sub> (5.0 ml) was stirred under nitrogen at 25 °C. A 0.5 ml portion of the reaction mixture was removed from the reaction vessel and <sup>1</sup>H NMR measurements were carried out at intervals to find out when most of **1** had disappeared. H<sub>2</sub>O analysis was carried out as soon as the reaction was complete.

**Reactions of 3-phenylprop-2-en-1-ol (1) with Ir(H)<sub>2</sub>(ClO<sub>4</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (3), [Ir(CO)(PPh<sub>3</sub>)<sub>3</sub>]ClO<sub>4</sub> (7), and [Ir(CO)(PPh<sub>3</sub>)<sub>3</sub>]BF<sub>4</sub> (8) under nitrogen.** These reactions were carried out in the same manner as that described for the reaction of **1** with **2**.

**Reaction of 3-phenylprop-2-en-1-ol-OD (1D) with Ir(ClO<sub>4</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (2) under nitrogen.** This reaction was carried out in the same manner as that described for the reaction of **1** with **2**.

**Reaction of 3-phenylprop-2-en-1-ol (1) with Ir(ClO<sub>4</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (2) in the presence of excess ClO<sub>4</sub><sup>-</sup>.** To a solution of **1** (0.8 g, 6.0 mmol) in CDCl<sub>3</sub> (5.0 ml) was added NaClO<sub>4</sub> (ca. 1.0 g) and the mixture was stirred for 10 min. Undissolved NaClO<sub>4</sub> was removed by filtration before complex **2** (0.16 g, 0.2 mmol) was added to the solution, which was then stirred under nitrogen at 25 °C. Products were analyzed by <sup>1</sup>H NMR measurements.

**Reaction of 3-phenylprop-2-en-1-ol (1) with Ir(ClO<sub>4</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (2) under hydrogen.** This reaction was carried out under hydrogen (P(H<sub>2</sub>)) + vapor pressure of the solution = 1 atm) in the same manner as that described for the reaction of **1** with **2**.

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