

room temperature. Et₂O was added and the supernatant liquid decanted off. The residue was washed with Et₂O (3×10 ml). The combined organic extracts were filtered through a short pad of Florisil and the solvent was removed. The crude product obtained was purified by CC on silica gel (EtOAc-*n*-hexane, 1:15) to produce aldehyde **1e** (1.1 g, 88%) as a oil. IR (neat) $\nu_{\max}$ cm⁻¹: 1719, 1453. ¹H-NMR (CDCl₃): δ 9.76 (1H, t, *J*=0.9 Hz), 5.36 (2H, m), 2.42 (2H, dt, *J*=7.3, 1.2 Hz), 2.01 (4H, m), 1.62 (2H, m), 1.43-1.30 (12H, m), 0.90 (3H, t, *J*=7.4 Hz).

(2E,4E,14Z)-2,4,14-Octadecatrienoic acid ethyl ester (1f). To a solution of lithium diisopropylamide (LDA) which prepared from diisopropylamine (622 mg, 6.2 mmol) and *n*-BuLi in THF was added triethyl phosphonocrotonate (1.4 g, 5.6 mmol) at -10°C. After stirring for 10 min, the mixture was cooled to -78°C. The aldehyde **1e** (980 mg, 4.7 mmol) was then added slowly, the mixture was stirred and allowed to warm to 25°C. This was then poured into saturated Na₂SO₄ solution (25 ml) and extracted with Et₂O. The Et₂O extract was dried and concentrated. The residue was purified by flash column chromatography (EtOAc-*n*-hexane, 1:15) to give trienoic acid ethyl ester **1f** (934 mg, 65%) as a colorless oil. IR (neat) $\nu_{\max}$ cm⁻¹: 1714, 1612, 1441, 1361, 1290, 1252, 1170, 1030, 994; ¹H NMR (CDCl₃): δ 7.20 (1H, m), 6.15 (2H, m), 5.78 (1H, d, *J*=15.4 Hz), 5.35 (2H, m), 4.19 (2H, q, *J*=7.2 Hz), 2.17 (2H, m), 2.01 (4H, m), 1.44-1.26 (17H, m), 0.90 (3H, t, *J*=7.3 Hz).

(2E,4E,14Z)-N-(2,4,14-Octadecatrienyl)piperidine (1). To a cooled solution of piperidine (744 mg, 8.7 mmol) in CH₂Cl₂ at -40°C was added trimethyl aluminum and the mixture was allowed to warm to 0°C during a period of 20 min. A solution of the ester **1f** (535 mg, 1.8 mmol) in CH₂Cl₂ was then added, the mixture was stirred overnight at room temperature. The reaction mixture was poured into saturated

sodium potassium tartrate solution (10 ml) and extracted with CH₂Cl₂ (3×10 ml). The combined extracts were dried over MgSO₄ and filtered. The solvent was evaporated *in vacuo* and the crude product was purified by flash column chromatography (EtOAc-*n*-hexane, 1:4) to give the desired product **1** (332 mg, yield 55%) as a colorless oil, which was identical with the natural product.

Acknowledgments. J. W. A. thanks Prof. I. Kubo (University of California, Berkeley) for providing the sample of the Piper fruits originally from Indonesia and Dr. S. G. Lee (KRICT) for spectral measurements.

References

1. C. K. Atal, K. L. Dhar, and J. Singh, *Lloydia*, **38**, 265 (1975).
2. R. Hanse, D. Wei, and B. Schmidt, *Planta Medica*, **14**, 1 (1966).
3. N. Nakatani, and R. Inatani, *Agric. Biol. Chem.*, **45**, 1473 (1981).
4. E. Wenkert, D. W. Cochran, E. W. Hagaman, R.B. Lewis, and F. M. Schell, *J. Am. Chem. Soc.*, **93**, 6271 (1971).
5. E. J. Corey, H. Niwa, and J. Knolle, *J. Am. Chem. Soc.*, **100**, 1942 (1978).
6. W. S. Wadsworth, *Org. React.*, **25**, 73 (1977).
7. A. Basha, M. Lipton, and S. W. Weinreb, *Tetrahedron Lett.*, 4171 (1977).
8. A. Banerji, M. Sarkar, T. Gahsal, and S. Chandrapal, *Org. Mag. Resonan.*, **22**, 734 (1984).
9. W. Tabuneng, H. Bando, and T. Amiya, *Chem. Pharm. Bull.*, **31**, 3562 (1983).
10. E. J. Corey, and J. W. Suggs, *Tetrahedron Lett.*, 2647 (1975).

Carbonylation of Benzyl Alcohols and Benzyl Bromide to Phenylacetic Acids with Rhodium(I) and Iridium(I) Complexes

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Rhodium(I) and iridium(I) complexes, M(ClO₄)(CO)(PPh₃)₂ and [M(CO)(PPh₃)₃]ClO₄ (M=Rh, Ir), and RhX(CO)(PPh₃)₂ (X=Cl, Br, OH) catalyze the carbonylation of benzyl alcohols to produce phenylacetic acids under 6 atm of CO at 110°C in deuterated chloroform. Benzyl alcohols initially undergo dehydration to give dibenzyl ethers which are then carbonylated to benzyl phenylacetates, and the hydrolysis of benzyl phenylacetate produces phenylacetic acids and benzyl alcohols. The carbonylation is accompanied with dehydrogenation followed by hydrogenolysis of benzyl alcohols giving benzaldehydes and methylbenzenes which are also produced by CO₂ elimination of phenylacetic acids. Phenylacetic acid is also produced in the reactions of benzyl bromide with CO catalytically in the presence of Rh(ClO₄)(CO)(PPh₃)₂ and H₂O, and stoichiometrically with Rh(OH)(CO)(PPh₃)₂ in the absence of H₂O.

Introduction

Catalytic carbonylation of alcohols to produce acids has

been studied with several metal complex catalysts but mostly in the presence of iodide as a promoter in aqueous solution¹ while metal-catalyzed carbonylation of allyl alcohols has been

Table 1. Products of the Reactions of Benzyl Alcohols (2.0 mmol) with CO (6 atm) in the Presence of $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (0.1 mmol) in CDCl_3 (2.0 ml) at 110°C for 20 hours

Substrate	Products (%) ^a			
RCH_2OH	RCH_2COOH	$(\text{RCH}_2)_2\text{O}$	$\text{RCH}_2\text{COOCH}_2\text{R}$	$\text{RCH}_3 + \text{RCHO}$
$\text{R} = \text{C}_6\text{H}_5$	50	10	13	trace
<i>p</i> - $\text{C}_6\text{H}_4(\text{CH}_3)$	84	trace	trace	trace
<i>o</i> - $\text{C}_6\text{H}_4(\text{CH}_3)$	83	trace	trace	trace
<i>p</i> - $\text{C}_6\text{H}_4\text{Cl}$	98	trace	trace	trace
<i>o</i> - $\text{C}_6\text{H}_4\text{Cl}$	98	trace	trace	trace
<i>p</i> - $\text{C}_6\text{H}_4\text{F}$	23	4	16	23

^aAverage values of at least five experiments.

reported to occur in the absence of an iodide promoter.² We have been interested in a new catalytic system that is effective for the carbonylation of alcohols to produce acids in the absence of an iodide promoter. We now wish to report production of phenylacetic acids from the carbonylation of benzyl alcohols catalyzed by rhodium(I) and iridium(I) complexes in the absence of an iodide promoter. The carbonylation of benzyl alcohols in this report occurs through a totally different pathway (*vide infra*) from the well-known one with an iodide promoter.¹

Experimental

Instruments. Varian 60 MHz (EM-360A) (or Bruker WP 80 MHz FT-NMR), Shimadzu IR-440, Shimadzu UV-240, and Varian 3700 gas chromatograph were used for analysis of reactants and products, and for identification of metal complexes.

Materials. All of the metal complexes were prepared by the literature methods.³ Benzyl alcohols, dibenzyl ether and benzyl bromide were purchased from Aldrich and/or Fluka and used without further purification. Benzyl phenylacetate was prepared by the reaction of phenylacetic acid with benzyl alcohol.

Catalytic Reactions. Carbonylation of all the benzyl alcohols in Tables 1 and 2 was carried out in the same manner as described below for benzyl alcohol. Benzyl alcohol (2.0 mmol) was added into a CDCl_3 (2.0 ml) solution of metal complex (0.1 mmol) in a reactor (Parr 1341 bomb reactor, volume = 360 ml) under nitrogen which was immediately flushed with CO before the cap of the reactor was applied. Then CO was introduced into the reactor through the connection tube until the pressure of the reactor reached to 6 atm at room temperature (CO pressure was *ca.* 7.2 atm at 110°C where the catalysis was actually carried out). The reactor was kept in an oven maintained at 110°C for certain period of time and cooled at intervals for product analysis. A part (0.5 ml) of the reaction mixture was taken out of the reactor and analyzed mostly by ^1H -NMR and by GC in some cases (see Figure 1 for analysis of reactants, intermediates and products with ^1H -NMR spectral changes).

Reactions of dibenzyl ether and benzyl bromide with CO in the presence of metal complexes were carried out in the same manner as described above for the carbonylation of

Table 2. Products of the Reactions of Benzyl Alcohols (2.0 mmol) with CO (6 atm) in the Presence of 0.1 mmole of $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**1a**), $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ (**1b**), $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (**1c**), $\text{RhBr}(\text{CO})(\text{PPh}_3)_2$ (**1d**), $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ (**1e**), $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**1f**) and $[\text{Ir}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ (**1g**) in CDCl_3 (2.0 ml) under CO (6 atm) at 110°C for 20 hours

Catalyst	Product (%) ^a			
	PhCH_2COOH	$(\text{PhCH}_2)_2\text{O}$	$\text{PhCH}_2\text{COOCH}_2\text{Ph}$	$\text{PhCH}_3 + \text{PhCHO}$
1a	50	10	33	trace
1b	47	4	13	17
1c	47	5	11	11
1d	55	8	12	1
1e ^b	50	18	11	1
1f	40	8	7	29
1g	7	14	8	35

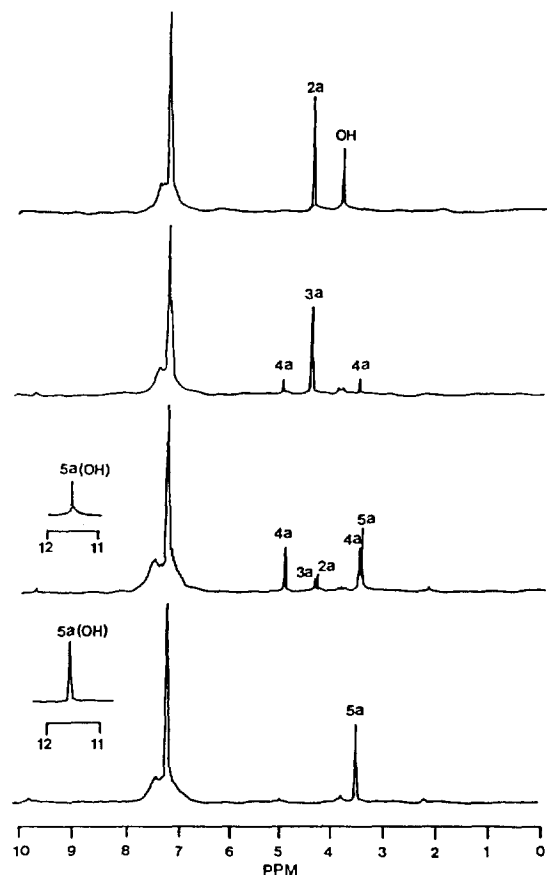
^aAverage values of at least five experiments. ^bIn d_6 -benzene. Practically the same yields were obtained in CDCl_3 .**Figure 1.** ^1H -NMR spectra of the reaction mixture at 60 MHz at 25°C . (a) $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (0.1 mmol) and $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (**2a**, 2.0 mmol) in CDCl_3 (2.0 ml) under N_2 . (b), (c) and (d) were measured after 10, 20, and 25 hours, respectively under CO (6 atm) at 110°C . Signals due to $-\text{CH}_2-$ of $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (**2a**), $(\text{C}_6\text{H}_5)_2\text{CH}_2\text{O}$ (**3a**), $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{C}_6\text{H}_5$ (**4a**), and $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ (**5a**) are indicated by the corresponding numbers. The singlet δ 2.2 ppm is due to $\text{C}_6\text{H}_5\text{CH}_3$ and the signals at δ 3.8 ppm are due to unknown compound(s).

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^aAverage values of at least five experiments.

reported to occur in the absence of an iodide promoter.² We have been interested in a new catalytic system that is effective for the carbonylation of alcohols to produce acids in the absence of an iodide promoter. We now wish to report production of phenylacetic acids from the carbonylation of benzyl alcohols catalyzed by rhodium(I) and iridium(I) complexes in the absence of an iodide promoter. The carbonylation of benzyl alcohols in this report occurs through a totally different pathway (*vide infra*) from the well-known one with an iodide promoter.¹

Experimental

Instruments. Varian 60 MHz (EM-360A) (or Bruker WP 80 MHz FT-NMR), Shimadzu IR-440, Shimadzu UV-240, and Varian 3700 gas chromatograph were used for analysis of reactants and products, and for identification of metal complexes.

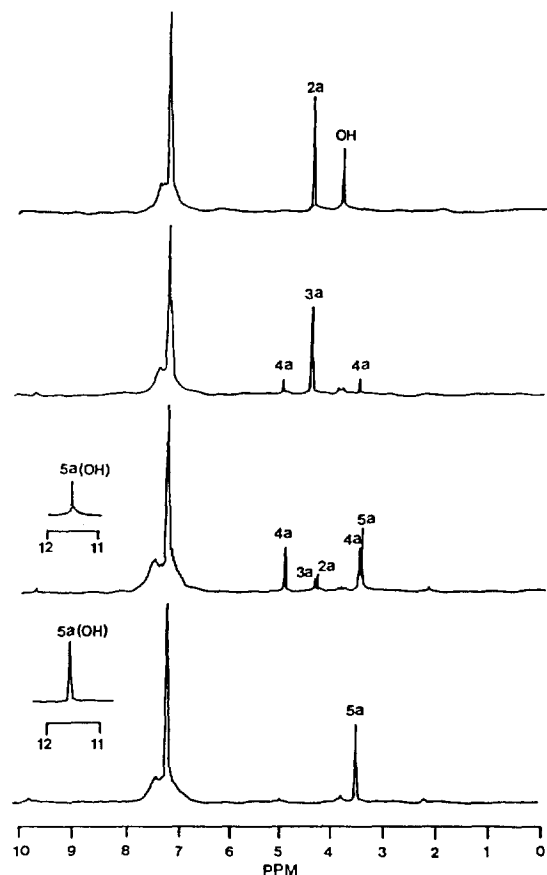
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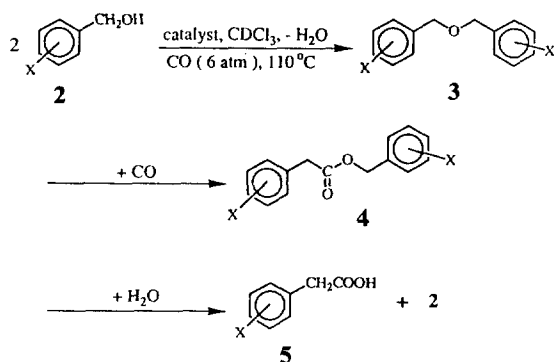
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Catalyst	Product (%) ^a			
	PhCH_2COOH	$(\text{PhCH}_2)_2\text{O}$	$\text{PhCH}_2\text{COOCH}_2\text{Ph}$	$\text{PhCH}_3 + \text{PhCHO}$
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X = H (a), CH₃ (b), Cl (c), F (d)
 catalyst = M(ClO₄)(CO)(PPh₃)₂, [M(CO)(PPh₃)₃]ClO₄ (M = Rh, Ir), RhX(CO)(PPh₃)₂ (X = Cl, Br, OH)

Scheme 1.

benzyl alcohol.

Identification of the product, RhBr(CO)(PPh₃)₂ from the reaction of Rh(OH)(CO)(PPh₃)₂ with benzyl bromide and CO was done by comparison of infrared spectra.

Results and Discussion

Phenylacetic acids are produced in the reactions of benzyl alcohols with CO in the presence of rhodium(I) and iridium(I) complexes (see Scheme 1). Table 1 and 2 summarize the results and Figure 1 shows the spectral changes during the carbonylation of benzyl alcohol (**2a**) with Rh(ClO₄)(CO)(PPh₃)₂ (**1a**). These experimental data unambiguously show that the carbonylation (Scheme 1) occurs *via* dehydration of benzyl alcohols (**2**) to give dibenzyl ethers (**3**) which then undergo the carbonylation to yield benzyl phenylacetates (**4**), and the hydrolysis of **4** produces the final products phenylacetic acids (**5**) and **2**.

The reaction pathway (Scheme 1) is based on the fact that the two intermediates, (C₆H₅CH₂)₂O (**3a**) and C₆H₅CH₂C(O)OCH₂C₆H₅ (**4a**), have been actually identified during the reaction of C₆H₅CH₂OH (**2a**).

Figure 1(b) clearly shows that most benzyl alcohol (**2a**) was converted into the first intermediate, dibenzyl ether (**3a**) within 10 hours by which time only a small amount of the second intermediate, benzyl phenylacetate (**4a**) was produced with a trace amount of the final product, phenylacetic acid (**5a**). Figure 1(c) and (d) confirm the production of **4a** and **5a** at the expenses of **3a** and **4a**, respectively. The two intermediates, **3a** and **4a** and the final product **5a** were identified by measuring ¹H-NMR spectra of the reaction mixtures with the authentic samples of dibenzyl ether (**3a**, -CH₂- at δ 4.41 ppm), benzyl phenylacetate (**4a**, -CH₂- at δ 3.53 and 4.97 ppm) and phenylacetic acid (**5a**, -CH₂- at δ 3.47 ppm).

Dehydration of alcohols to give ethers has been known to occur in the presence of metal complexes.⁴ Dehydrogenation (to give aldehydes) and simultaneous hydrogenolysis (to give hydrocarbons and H₂O) of alcohols are known to be catalyzed by M(ClO₄)(CO)(PPh₃)₂ (M = Rh,⁵ Ir⁶). It is, therefore, not so surprising to see the reaction, **2**→**3** in Scheme 1 in the presence of those metal complexes at elevated temperature. In the absence of CO (under N₂), the reaction of benzyl alcohol (**2a**) with Rh(ClO₄)(CO)(PPh₃)₂ (**1a**) at 110°C

yields mostly C₆H₅CHO and C₆H₅CH₃, the products of dehydrogenation and hydrogenolysis with a very small amount of dibenzyl ether, **3a**. This may be understood in terms of different metal complexes present in the reaction mixtures in the presence and absence of CO, respectively.

While iodide-promoted metal catalyzed CO insertion into C-O bond has been studied,⁷ direct CO insertion into C-O bond with metal complexes has been also reported.⁸ It was found in a separate experiment using dibenzyl ether (**3a**) as the initial reactant that **3a** undergoes carbonylation to give **4a** in the presence of **1a** under the same experimental conditions employed for Scheme 1. The last step of Scheme 1 (**4**→**5**) is a hydrolysis of an ester one may expect to occur in the presence of a metal complex at such high temperature. In another separate experiment, it was also observed that benzyl phenylacetate **4a** readily undergoes the hydrolysis to give **5a** and **2a** in the presence of **1a**.

The fact that the carbonylation of **2a** to **5a** occurs in the presence of Rh(OH)(CO)(PPh₃)₂ in C₆D₆ (see Table 2) excludes the possibility that it is catalyzed by the acid (such as HClO₄ or HCl) produced during the reaction. Under the same experimental conditions given in Table 1 and 2, the reaction of benzyl alcohol (**2a**) with CO in the presence of HClO₄ (**2a**/HClO₄=20) and in the absence of a catalyst did not produce phenylacetic acid at all but the uncharacterized material(s), whereas in the presence of both the catalyst, **1a** and HClO₄ (**2a**: HClO₄: Rh=20:1:1), a small amount (*ca.* 10%) of phenylacetic acid was obtained. These observations support a metal catalyzed pathway (non-acid catalyzed pathway) for the carbonylation (Scheme 1).

Addition of a free radical initiator, benzoyl peroxide never increased the rate of the carbonylation (Scheme 1); addition of a large amount of benzoyl peroxide (**2a**/benzoyl peroxide/**1a**=10/10/1) significantly decreased the yield. The presence of a free radical scavenger, hydrobenzoquinone (**2a**/hydrobenzoquinone/**1a**=10/1/1) slightly reduced the yield by *ca.* 5%. The observations may suggest that the carbonylation (Scheme 1) does not occur through a free radical involved step.

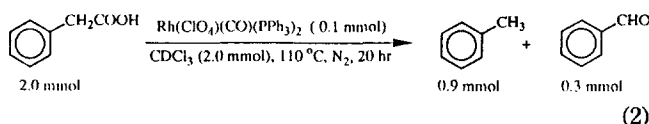
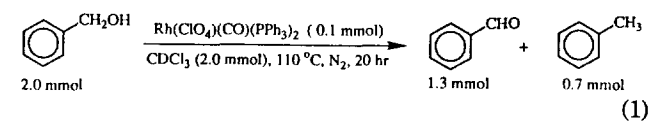
In general, the rhodium(I) complexes give higher yields of acids than do the iridium(I) complexes while no significant differences in the yields were observed between rhodium(I) complexes (see Table 2). Both methyl- and chlorobenzyl alcohols give higher yields of acids while the fluorine substituted alcohol shows considerable amounts of dehydrogenation and hydrogenolysis products (see Table 1).

It should be mentioned here that the reactions of other alcohols such as CH₃OH and *n*-C₃H₇OH with CO in the presence of **1a** in CDCl₃ under the same experimental conditions produced very small amount of ethers ((CH₃)₂O and (*n*-C₃H₇)₂O), esters (CH₃C(O)OCH₃ and CH₃(CH₂)₂C(O)O(CH₂)₂CH₃), acids (CH₃COOH and *n*-C₃H₇COOH) and small amounts of uncharacterized materials while neither (CH₃)₂CHCOOH nor (CH₃)₂CHC(O)O(CH₂)₂CH₃ was observed in the reaction of *n*-C₃H₇OH. These results also support a non-acid catalyzed pathway for the carbonylation (Scheme 1).

Of other products in Table 1 and 2, benzaldehydes seem to be the products of the dehydrogenation of benzyl alcohols and methylbenzenes may be produced both from the hydrogenolysis of benzyl alcohols and the CO₂ elimination of phenylacetic acids (*vide infra*). Metal complex catalyzed dehydro-

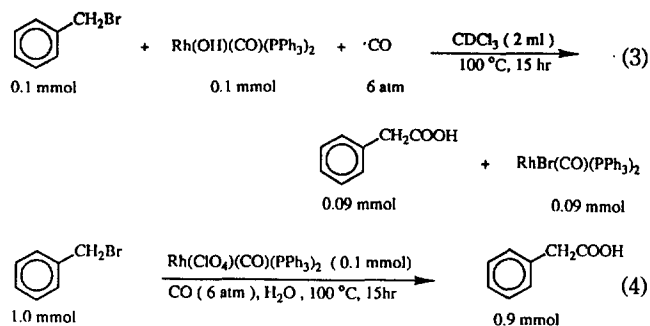
genation of alcohols to give aldehydes is somewhat well-known.^{4,9,10} Rhodium(I) and iridium(I) complexes, $M(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ ($M=\text{Rh}$ (**1a**), Ir (**1f**)) are known to catalyze the dehydrogenation and simultaneous hydrogenolysis of $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{OH}$ to give $\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$ and $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$, respectively.^{5,6} The reaction of **2a** with **1a** under N_2 actually produced benzaldehyde and methylbenzene (see Eq. 1).

Methylbenzene is also produced in the reaction of phenylacetic acid, **5a** with **1a** under N_2 (see Eq. 2). Benzaldehydes in Tables 1 and 2 seem to be the products of the dehydrogenation of benzyl alcohols whereas methylbenzenes could be produced by Eq. (1) (hydrogenolysis of benzyl alcohols by metal hydrides formed in the dehydrogenation of benzyl alcohols as seen before in the reactions of alcohols with **1f**) and Eq. (2).



Carbonylation of benzyl halides to produce phenylacetic acids has been known to occur in the presence of various transition metal compounds under somewhat relatively mild conditions.¹¹

During the investigation for production of phenylacetic acids, we have found that $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ reacts with benzyl bromide and CO to give phenylacetic acid and $\text{RhBr}(\text{CO})(\text{PPh}_3)_2$ (see Eq. 3). Benzyl bromide is also converted to phenylacetic acid by the reaction of CO in the presence of $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ and H_2O (see Eq. 4). Neither dibenzyl ether nor benzyl phenylacetate was observed during the reactions of benzyl bromide with CO in the presence of $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ (Eq. 3) and $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (Eq. 4). Reactions of benzyl bromide (Eq. 3 and 4) evidently do not follow the same reaction pathway of benzyl alcohols (Scheme 1): they may well be initiated by the oxidative addition of benzyl bromide. The reaction with $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ (Eq. 3) may follow the well-known steps: oxidative addition of benzyl bromide, CO insertion into metal-benzyl bond with CO addition, and reductive elimination of phenylacetic acid to yield $\text{RhBr}(\text{CO})(\text{PPh}_3)_2$. The reaction with $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ in the presence of H_2O (Eq. 4) may occur through a very similar pathway with that of $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ with CO except the last step, i.e., the hydrolysis of phenylacetyl bromide, the presumable product of the reductive elimination of $\text{Rh}(\text{Br})(\text{COCH}_2\text{C}_6\text{H}_5)_n$.



Acknowledgement. We wish to thank the Korea Science and Engineering Foundation (87-0304-03) and the Ministry of Education, Korea for their financial supports.

References

- (a) R. W. Wegman, A. G. Abatjoglou, and A. M. Harrison, *Chem. Commun.*, 1891 (1987); (b) T. W. Dekleva and D. Forster, *J. Am. Chem. Soc.*, **107**, 3565, 3568 (1985); (c) A. Masuda, H. Mitani, K. Oku, and Y. Yamazaki, *Nippon Kagaku Kaishi*, **2**, 249 (1982); (d) D. Forster and T. W. Dekleva, *J. Chem. Edu.*, **63**, 204 (1986); (e) Y. Sugi, K. Bando, and Y. Takami, *Chem. Lett.*, 63 (1981); (f) D. Forster, *Adv. Organomet. Chem.*, **17**, 255 (1979); (g) D. Brodzki, B. Denise, and G. Pannetier, *J. Mol. Catal.*, **2**, 149 (1977).
- H. Alper and I. Amer, *J. Mol. Catal.*, **53**, L33 (1989) and references therein.
- (a) D. Evans, J. A. Osborn, and G. Wilkinson, *Inorg. Syn.*, **11**, 99 (1968); (b) L. Vaska and J. Peone, Jr., *Chem. Commun.*, 419 (1971); (c) J. Peone, Jr. and L. Vaska, *Angew. Chem. Internat. Edit.*, **10**, 511 (1971).
- J. Blum, *J. Mol. Catal.*, **3**, 33 (1977).
- J. Park and C. S. Chin, *Bull. Korean Chem. Soc.*, **8**, 324 (1987).
- C. S. Chin, J. H. Shin, and J. B. Kim, *J. Organomet. Chem.*, **356**, 381 (1988).
- Y. Matsui, *Tetrahedron Lett.*, 1107 (1976) and references therein.
- Y. Kamiya, K. Kawato, and H. Ota, *Chem. Lett.*, 1549 (1980).
- T. F. Blackburn and J. Schwartz, *Chem. Commun.*, 157 (1977).
- P. B. Critchlow and S. D. Robinson, *Inorg. Chem.*, **17**, 1902 (1978).
- (a) H. Alper, K. Hashem, and J. Heveling, *Organometallics*, **1**, 775 (1982); (b) H. Alper, *Adv. Organomet. Chem.*, **19**, 183 (1981); (c) M. El-Chahawi and U. Prange, *Chem. Zeit.*, **102**, 1 (1978).