

vibrational excess energy. This is unusual because in liquid the vibrational relaxation occurs with the comparative time scale of collision process so that the excess energy is distributed *via* intermolecular vibrational relaxation, so excitation energy dependence may not be observed. They conclude that the ionization may compete with the intramolecular vibrational redistribution (IVR) and that the rate may depend on the optically excited vibrational mode. In their experiment, wide excitation wavelengths (270-350 nm) were used and the dependence was remarkable in the absorption edge. It will be interesting to check the dependence of fluorescence lifetimes in water in the absorption edge.

**Acknowledgement.** This work was financially supported by Ministry of Science and Technology and by Korea Science and Engineering Foundation.

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## Cobalt Catalyzed Carbonylation of Benzal Chloride Derivatives to Alkyl Phenylacetates(II)

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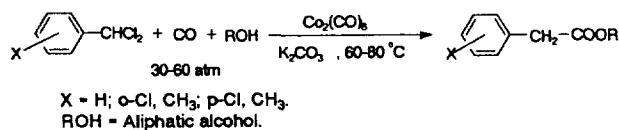
Treatment of benzal chloride, alcohol,  $K_2CO_3$ , and a catalytic amount of  $Co_2(CO)_8$  at  $80^\circ C$  for 24 hours under 30 atm of CO gave the corresponding alkyl phenylacetate in good yield.

### Introduction

The technology of transition metal complexes catalyzed carbonylation reaction is being currently used for the production of large volume chemicals.<sup>1</sup> Many applications were reported on the carbonylation of benzyl halide with carbon monoxide using cobalt,<sup>2</sup> iron,<sup>3</sup> ruthenium,<sup>4</sup> rhodium,<sup>5</sup> and palladium.<sup>6</sup> However, there are few reports on the carbonylation of benzal halides as the geminal dihalide compound to give alkyl phenylacetates<sup>7</sup> and phenylacetic acid.<sup>8</sup> Recently, we reported that carbonylation of benzal bromide by  $Co_2(CO)_8$  gave phenylacetic acid under phase transfer catalysis.<sup>8</sup> Now we wish to report in some details on the carbonylation of benzal chloride under homogeneous catalyst. A preliminary report of this work was published in this journal.<sup>9</sup>

### Results and Discussions

Reaction of benzal chloride with ethanol in the presence of  $K_2CO_3$  and  $Co_2(CO)_8$  as a catalyst at  $80^\circ C$  for 24 hours under 30 atm of carbon monoxide gave ethyl phenylacetate in good yield.



From investigation of base effect,<sup>9</sup> potassium carbonate was superior for the carbonylation to other bases such as calcium hydroxide, triethylamine, potassium hydroxide, and pyridine. Carbon monoxide pressure played a decisive role in the carbonylation of benzal chloride. At the higher carbon monoxide pressure than 30 atm, ethyl phenylacetate was generated in excellent yield. The product yields dropped significantly with

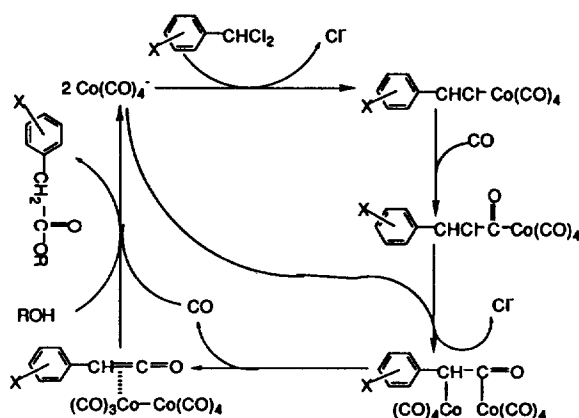
**Table 1.** Carbonylation of Benzal Chloride Derivatives to Alkyl Phenylacetates Using  $\text{Co}_2(\text{CO})_8$ <sup>a</sup>

Run	$\text{XC}_6\text{H}_4\text{CHCl}_2$ X=	ROH	$P_{\text{CO}}$ (atm) <sup>b</sup>	T (°C)	Yield (%) <sup>c</sup>	
					$\text{XC}_6\text{H}_4\text{CH}_2\text{COOR}$	$\text{XC}_6\text{H}_4\text{CHO}$
1	H	$\text{C}_2\text{H}_5\text{OH}$	30	80	85 (92)	( 6)
2	H	$\text{C}_2\text{H}_5\text{OH}$	25	80	(65)	(11)
3	H	$\text{C}_2\text{H}_5\text{OH}$	20	80	(28)	(11)
4	H	$\text{C}_2\text{H}_5\text{OH}$	10	80	(14)	(44)
5 <sup>d</sup>	H	$\text{C}_2\text{H}_5\text{OH}$	30	80	(22)	(18)
6	H	$\text{C}_2\text{H}_5\text{OH}$	30	100	(16)	(82)
7	H	$\text{C}_2\text{H}_5\text{OH}$	30	60	(32)	( 5)
8	<i>p</i> -Cl	$\text{C}_2\text{H}_5\text{OH}$	40	80	84 (90)	( 8)
9	<i>p</i> -Cl	$\text{C}_2\text{H}_5\text{OH}$	30	80	19	(33)
10	<i>p</i> -Cl	$\text{CH}_3\text{OH}$	40	80	50	—
11	<i>p</i> -Cl	$n\text{C}_3\text{H}_7\text{OH}$	40	80	77	—
12	<i>p</i> -Cl	$n\text{C}_4\text{H}_9\text{OH}$	40	80	85	—
13	<i>o</i> -Cl	$\text{C}_2\text{H}_5\text{OH}$	30	80	78	(tr)
14	<i>p</i> -CH <sub>3</sub>	$\text{C}_2\text{H}_5\text{OH}$	60	60	66 (70)	(22)
15	<i>p</i> -CH <sub>3</sub>	$\text{C}_2\text{H}_5\text{OH}$	30	60	(43)	(52)
16	<i>p</i> -CH <sub>3</sub>	$\text{C}_2\text{H}_5\text{OH}$	40	80	(23)	(62)
17	<i>p</i> -CH <sub>3</sub>	$\text{C}_2\text{H}_5\text{OH}$	30	80	(14)	(83)
18	<i>o</i> -CH <sub>3</sub>	$\text{C}_2\text{H}_5\text{OH}$	30	60	86 (91)	( 6)
19	<i>o</i> -CH <sub>3</sub>	$\text{C}_2\text{H}_5\text{OH}$	30	80	63	(31)

<sup>a</sup>  $\text{XC}_6\text{H}_4\text{CHCl}_2$  (2.0 mmol),  $\text{K}_2\text{CO}_3$  (0.345 g, 2.5 mmol), ethanol (10 ml), and  $\text{Co}_2(\text{CO})_8$  (0.034 g, 0.1 mmol) for 24 h under CO. <sup>b</sup> At room temperature. <sup>c</sup> Isolated yield; Parenthesis is GLC yield. <sup>d</sup>  $\text{Co}_2(\text{CO})_8$  (0.01 mmol).

lowering the pressure. These observations might be attributed to the migratory aptitudes of coordinated carbon monoxide on  $\alpha$ -chlorobenzylcobalt tetracarbonyl assumed as an intermediate. It was generally agreed that electron-releasing R groups in  $\text{R-M}(\text{CO})_L$  complex enhance the rate of CO insertion, whereas electron-withdrawing R groups slow it down. Replacement of H in R with F invariably reduces the rate of CO insertion by strengthening the M-R linkage.<sup>10</sup> Accordingly, CO insertion in  $\text{PhCHCl-Co}(\text{CO})_4$  requires higher pressure of CO than CO insertion in  $\text{PhCH}_2\text{-Co}(\text{CO})_4$ .

Increasing the relative ratio of benzal chloride over cobalt carbonyl from 20 to 200, lowered the yield of the carbonylation from 92% to 22%. Turnover number of the present carbonylation reached about 40-50 based on  $\text{Co}_2(\text{CO})_8$  by Run 5. Successive carbonylation of benzal chloride derivatives leading to the formation of alkyl phenylacetates was also observed under different reaction conditions. The yields of these were much dependent on solvent, temperature, and pressure of CO. Benzal chloride was easily carbonylated at 30 atm of CO and 80°C. At higher temperature (100°C), most of the substrate was converted to benzaldehyde. *p*-Chlorobenzal chloride containing an electron-withdrawing group gave bad result at 30 atm of CO and 80°C, but good result at 40 atm of CO and 80°C. *p*-Tolual chloride containing an electron-donating group also gave bad result at 30 atm of CO and 80°C. Enhanced result was obtained at 40 atm of CO and 80°C. The better result than these of run 15, 16, and 17 was obtained at 60 atm of CO and 60°C. But reaction condition was not further optimized. These reaction patterns

**Figure 1.** Proposed mechanism of carbonylation of benzal chlorides catalyzed by cobalt.

were also attributed to the migratory aptitudes of coordinated carbon monoxide. Ortho substituted benzal chlorides showed different reaction pattern compared with the corresponding para-compounds. Ortho substituted benzal chlorides were easily carbonylated at 30 atm of CO and 80°C. In the case of *o*-tolual chloride, the better result than that of run 19 was obtained at 30 atm of CO and 60°C. Methoxybenzal chlorides were quantitatively converted to anisaldehydes under the reaction conditions.

Benzotrichloride,  $\text{PhCCl}_3$ , was carbonylated to alkyl phenylacetate in trace amount at the same condition described here not only at 40 atm of CO and 80°C or 100°C but also at 30 atm of CO and 150°C.

**Mechanism.** In Figure 1 was proposed a possible mechanism for the carbonylation of benzal chlorides by  $\text{Co}_2(\text{CO})_8$ . Cobalt tetracarbonyl anion<sup>11</sup> reacted with benzal chloride to generate (1-chloro-1-phenylmethyl)cobalt tetracarbonyl. Migratory insertion of the coordinated carbon monoxide to the carbon-cobalt bond gave (2-chloro-2-phenylacetyl)cobalt tetracarbonyl absorbing a carbon monoxide. (2-Chloro-2-phenylacetyl)complex was dehalogenated by  $\text{Co}(\text{CO})_4^-$  through single electron transfer (SET)<sup>12</sup> process to form ketene complex,<sup>13</sup> which reacted with alcohol to give the ester.

## Experimental

The procedure was as follows. The mixture of benzal chloride (0.325 g, 2.0 mmol),  $\text{K}_2\text{CO}_3$  (0.345 g, 2.5 mmol),  $\text{Co}_2(\text{CO})_8$  (0.034 g, 0.1 mmol), ethanol (10 ml), and phenyl ether as internal standard was stirred magnetically at 80°C for 24 hours under 30 atm of carbon monoxide in 100 ml stainless steel autoclave. After cooling, gases were vented out in fume hood. The mixture was concentrated, filtered by short column chromatography ( $\text{SiO}_2$ , 3 cm, ether), concentrated and chromatogramed by preparative TLC ( $\text{SiO}_2$ , ethyl acetate: *n*-hexane=1:10) to give ethyl phenylacetate (0.27 g, 85%).

**Acknowledgement.** This work was supported by the Organic Chemistry Research Center-the Korea Science & Engineering Foundation (893-0306-006-2), by NON DIRECTED RESEARCH FUND, and Lucky R & D Center.

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## **$^{13}\text{C}$ and $^{51}\text{V}$ Nuclear Magnetic Resonance Studies of Vanadium (V) Complexes of Iminodiacetate Analogues**

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*Received July 29, 1991*

The solution structures of the vanadium (V) complexes of iminodiacetate analogues, such as iminodiacetate (IDA), methyliminodiacetate (MeIDA), ethyliminodiacetate (EtIDA), benzyliminodiacetate (BzIDA), pyridine-2,6-dicarboxylate (DPA), and 2-hydroxyethyliminodiacetate (HEIDA), have been studied by  $^{13}\text{C}$ - and  $^{51}\text{V}$ -NMR spectroscopy. Assuming that the complexes have a *cis*- $\text{VO}_2$  core, IDA, MeIDA, EtIDA, and BzIDA act as facial tridentate ligands to form octahedral complexes, whereas DPA coordinates to  $\text{VO}_2^+$  as a meridional tridentate. And one water molecule fulfills the remaining site to satisfy the coordination number of six. But HEIDA coordinates to  $\text{VO}_2^+$  through one IDA moiety and one hydroxyl group, acting as a tetradenate.

### **Introduction**

There is increasing evidence that vanadium plays an important role in biological reactions.<sup>1-5</sup> Especially vanadium is an important trace element that has potent biological effects in mammals. But the chemistry of vanadium (V) is not much well known because of the complexity of vanadium (V) species in solution and the strong oxidizing power of the metal ion.

Amos and Sawyer<sup>6</sup> first reported  $^1\text{H}$ -NMR studies of vanadium (V) of aminopolycarboxylates such as ethylenediaminetetraacetate (EDTA), ethylenediaminediacetate (EDDA), and  $\text{N,N}'$ -dimethylethylenediamine- $\text{N,N}'$ -diacetate (DMEDDA). In the previous study<sup>7</sup> we reported the solution structures of vanadium (V) complexes of some aminopolycarboxylates, such as ethylenediaminetetraacetate (EDTA), *trans*-cyclohexanediaminetetraacetate (CDTA), 1,2-propylenediaminetetraacetate (PDTA), ethylenediaminediacetate (EDDA), 2-hydroxyethylthylenediaminetriacetate (HEDTA), diethylenetriaminepentaacetate (DTPA), and nitrilotriacetate (NTA) by  $^{13}\text{C}$ -

and  $^{51}\text{V}$ -NMR spectroscopy. All of these ligands acted as tetradentates to form octahedral complexes containing a *cis*- $\text{VO}_2$  core.

Iminodiacetate (IDA)-type ligands which can act as tridentates have been reported to form 1 : 1 complexes with vanadium (V) in the acidic solution by their kinetic studies,<sup>8-10</sup> but the structures of the complexes have not been studied. It is hoped to obtain more information about the solution structures of the vanadium (V) complexes of IDA-type ligands. In this paper we report the results on  $^{13}\text{C}$ - and  $^{51}\text{V}$ -NMR studies of vanadium (V) complexes of IDA analogues, such as iminodiacetate (IDA), methyliminodiacetate (MeIDA), ethyliminodiacetate (EtIDA), benzyliminodiacetate (BzIDA), pyridine-2,6-dicarboxylate (DPA), and 2-hydroxyethyliminodiacetate (HEIDA), in aqueous solution.

### **Experimental**

All chemicals were of reagent grade (Aldrich etc.) and used without further purification.  $^{13}\text{C}$ -NMR spectra were