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Carbonylation of (Dichloromethyl)benzene Catalyzed by Cobalt Carbonyl and Iron Carbonyl under Phase Transfer Catalysis

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Treatment of (dichloromethyl)benzenes with CO (1 atm) in the presene of catalytic amount of $Co_2(CO)_8$, $Fe(CO)_5$, and BTEAC under two phase systems with NaOH(aq) and $PhCH_3$ containing small amount of alcohol for 20 hours at 80℃ gives phenylacetic acids in moderate yields.

Introduction

It is only after 1976[1] that organotransition metal anions are first employed in phase transfer catalysis, and since then they have made an exponential growth in this area. One advantage of using these transition metal complexes is that such reactions which would not otherwise occur, can be affected by these complexes under mild reaction conditions. The organotransition metal catalyzed carbonylation is one of such examples.

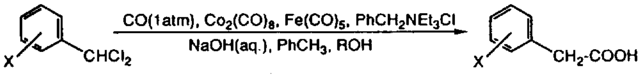
Benzyl halides have been extensively studied using cobalt[2-9], iron[10-12], nickel[13-19] and palladium[20] in phase transfer catalysis. For example, Alper reported that benzyl chlorides and bromides reacted with carbon monoxide in the presence of dicobalt octacarbonyl under phase transfer catalysis at room temperature to give phenylacetic acids in good yields.[21,22] Brunet *et al.*[23,24] reported that the cobalt carbonyl catalyzed carbonylation of aryl and vinyl halides gave benzoic acid and propenoic acid, respectively, in excellent yields in the presence of photostimulated phase transfer catalyst. Recently they also[25] reported that the carbonylation of iodobenzene was catalyzed by bimetallic $Co_2(CO)_8/Fe(CO)_5$ catalysts in the presense of Bu_4NBr in a two phase system to give benzoic acid, benzophenone, and biphenyl. However, bromobenzene did not react with the above bimetallic system.

Despite a great amount of research on the phase transfer catalyzed carbonylation, little attention has been paid to catalytic carbonylation of organic geminal halides by transition metal complexes.[26-29]

In the course of our investigation for the carbonylation of (dibromomethyl)benzenes[30], $YArCHBr_2$ under phase transfer catalysis, we found that carbonylation of (dichloromethyl) benzene did not occur. Accordingly this paper deals with simple and convenient carbonylation of (dichloromethyl) benzenes using bimetallic system of $Co_2(CO)_8$ and $Fe(CO)_5$ under phase transfer catalysis by modification of the reaction conditions.

Results and Discussion

In the case of phase transfer catalysis, the carbonylation of (dibromomethyl)benzenes to phenylacetic acids takes place successfully under the mild conditions (1 atm of CO, r.t.). But, (dichloromethyl) benzene can not be converted to phenylacetic acid and remains as a reactant. Treatment of (dichloromethyl)benzenes with carbon monoxide in the presence of catalytic amounts of $Co_2(CO)_8$, $Fe(CO)_5$, and PTC in a two phase system composed of $NaOH(aq)/C_6H_5CH_3$ containing a small amount of alcohol for 20 hours at 80℃ gives the corresponding carboxylic acids in moderate yields (Eq. 1).



(Eq. 1)

X = H, *o*-Cl, *p*-Cl, *o*-CH_3, *p*-CH_3

After the reaction, organic phase contains unreacted (dichloromethyl)benzene and small amount of 1,2-diphenylethene. But, the focus is paid to the aqueous phase containing carboxylic acids. The optimum yield is pursued under the conditions given at the footnote of Table 1 by controlling the reaction time from 5 to 20 hours; the yields of phenylacetic acid increase gradually wiyh time. But, the longer reaction time than 20 hours does not show change in the yield of the carboxylic acid.

Many alcohols having C_1-C_4 except ^{t}butyl alcohol show similar yields of the carboxylic acids. In the absence of alcohol, the yield of phenylacetic acid is reduced to 30%. Dioxane, di^{n}butyl ether, and ^{i}propyl alcohol as the organic phase gave low yield of phenylacetic acid. The higher pressure of carbon monoxide (10 atm) could not improve the yield of phenylacetic acid compared with 1 atm using benzene-ethyl alcohol

Table 1. Carbonylation of (Dichloromethyl) Benzene to Phenylacetic Acid Mediated by Cobalt Carbonyl and Iron Carbonyl[a]

Org. phase	Yield[b]	Org. phase	Yield[b]
$PhCH_3/{}^{i}PrOH$	45	Dioxane	39
$PhCH_{/3}{}^{i}PrOH$	39[c]	${}^{n}Bu_2O$	33
$PhCH_{/3}{}^{i}PrOH$	30[d]	${}^{i}PrOH$	36
$PhCH_{/3}EtOH$	41	PhH/EtOH	37
$PhCH_{/3}{}^{n}PrOH$	42	PhH/EtOH	38[e]
$PhCH_{/3}{}^{n}Bu_2O$	42	PhH/EtOH	26[f]
$PhCH_{/3}$	30	PhH/EtOH	19[g]

[a](Dichloromethyl)benzene (0.488 g, 3.0 mmol), BTEAC (0.07 g, 0.3 mmol), $Co_2(CO)_8$ (0.03 g, 0.1 mmol), $Fe(CO)_5$ (0.08 g, 0.4 mmol), 5 M-NaOH (10 m*l*), Alcohol (5 m*l*), and Organic solvent (10 m*l*) are stirred at 80℃ for 12 hrs under CO (1 atm) [b]Isolated yield. [c]For 5 hrs. [e]10 atm of CO. [f]At 60℃. [g]At 40℃.

Table 2. Effect of Phase Transfer Catalysts for the Carbonylation of (Dichloromethyl)Benzene to Phenylacetic Acid Catalyzed by Cobalt Carbonyl and Iron Carbonyl[a]

PTC	Yield[b]	PTC	Yield[b]
BTEAC	45	BTEAC	0[c]
Triton-B	44	NH_4Cl	34
18C6	31	PEG-400	28
Et_4NCl	22	CDMEAB	22
TBAH	22	DB18C6	21
CTMAB	19	DDMEAB	19
Aliquat-336	17	…	20

[a](dichloromethyl)benzene (0.49 g, 3.0 mmol), PTC (0.3 mmol), Co_2 $(CO)_8$ (0.03 g, 0.1 mmol), $Fe(CO)_5$ (0.08 g, 0.4 mmol), 5 M-NaOH (10 m*l*), ^{i}propanol (5 m*l*), and tolune (10 m*l*) were stirred at 80℃ for 24 hrs under CO (1 atm) [b]Isolated yield. [c]In the absence of (dichloromethyl)benzene

mixed organic phase. The activity of a catalyst is reduced in the absence of either $Co_2(CO)_8$ or $Fe(CO)_5$. Accordingly, the mixed metal carbonyl catalyst system is more efficient. At this stage, true catalytic species is ambiguous.

In the absence of (dichloromethyl)benzene as the reactant, even in the presence of benzyltriethylammonium chloride (BTEAC), a possible benzyl group donor no trace of phenylacetic acid was detected. Therefore, the carbonylation of the benzyl group of ammonium salts such as BTEAC and benzyltrimethylammonium hydroxide (Triton-B) is not participated in this reaction. BTEAC and Triton-B show the similar activities for carbonylation of (dichloromethyl)benzene. Other phase transfer catalysts listed in Table 2 exhibit inferior activities to benzyltrialkylammonium salts.

Substituted (dichloromethyl)benzenes are carbonylated by uning BTEAC or Triton-B. (Dichloromethyl)-toluenes can be readily carbonylated to tolylacetic acids in moderate yields in the presence of BTEAC or Triton-B. But, chloro group on phenyl ring is dechlorinated noticeably to give phenylacetic acid. Chloro-(dichloromethyl) benzenes are converted to phenylacetic acid, the dechlorinated product, in addition to chlorophenylacetic acids as shown in Table 3. The present reaction system is not recommandable for halogenated (dichloromethyl) benzenes.

Table 3. Carbonylation of (Dichloromethyl)Benzenes Catalyzed by Cobalt Carbonyl and Iron Carbonyl[a]

Reactant	PTC	Product	Yield[b]
$PhCHCl_2$	BTEAC	$PhCH_2COOH$	45
$PhCHCl_2$	Triton-B	$PhCH_2COOH$	44
$2\text{-}ClPhCHCl_2$	BTEAC	$2\text{-}ClPhCH_2COOH$	15
		$PhCH_2COOH$	9
$2\text{-}ClPhCHCl_2$	Triton-B	$2\text{-}ClPhCH_2COOH$	17
		$PhCH_2COOH$	6
$4\text{-}ClPhCHCl_2$	BTEAC	$4\text{-}ClPhCH_2COOH$	36
		$PhCH_2COOH$	8
$4\text{-}ClPhCHCl_2$	Trion-B	$4\text{-}ClPhCH_2COOH$	27
		$PhCH_2COOH$	6
$2\text{-}CH_3PhCHCl_2$	BTEAC	$2\text{-}CH_3PhCH_2COOH$	44
$2\text{-}CH_3PhCHCl_2$	Trion-B	$2\text{-}CH_3PhCH_2COOH$	46
$4\text{-}CH_3PhCHCl_2$	BTEAC	$4\text{-}CH_3PhCH_2COOH$	44
$4\text{-}CH_3PhCHCl_2$	Trion-B	$4\text{-}CH_3PhCH_2COOH$	43
$PhCHBr_2$	BTEAC	$PhCH_2COOH$	24

[a]Substituted (dichloromethy)benzene (3.0 mmol), PTC (0.3 mmol), $Co_2(CO)_8$ (0.034 g, 0.1 mmol), $Fe(CO)_5$ (0.08 g, 0.4 mmol), 5 M-NaOH (10 m*l*), ^{i}propanol (5 m*l*), and toluene (10 m*l*) were stirred at 80℃ for 24 hrs under CO (1 atm). [b]isolated yield.

J. J. Brunet[25,31] studied the similar reaction system, the carbonylation of iodoarenes, and found the following fact. At beginning of the reaction, the carbonyl species present in the reaction mixture were $HFe(CO)_4^-$, $HFe_3(CO)_{11}^-$, and $Co(CO)_4^-$. Unfortunately, we do not know which species, mono nuclear metal carbonyl anion or mixed dinuclear metal carbonyl anion $(FeCo(CO)_8^-)$, is the active catalyst in the carbonylation of (dihalomethyl)benzenes under the reaction conditions used in out present study.

Experimental

A mixture of (dichloromethyl)benzene (0.48 g, 3.0 mmol), 5 M-NaOH(10 m*l*), ^{i}propanol (5 m*l*), toluene (10 m*l*), $Co_2(CO)_8$ (0.034 g, 0.1 mmol), $Fe(CO)_5$ (0.08 g, 0.4 mmol), and benzyltriethylammonium chloride (0.07 g, 0.3 mmol) was stirred under the atmospheric pressure of carbon monoxide at 80℃ for 20 hours. After cooling and purging of carbon monoxide, the two phases were separated and the organic phase was washed with dilute sodium hydroxide solution. The combined aqueous phase was acidified with dilute hydrochloric acid, extracted with ether (3×20 m*l*), and dried over anhydrous $MgSO_4$. The concentrated crude products were purified by a preparative thin layer chromatography (silicagel, ethyl ether: chloroform = 1 : 2) to give phenylacetic acid (15 a) (0.18 g, 45%). The substituted (dichloromethyl)benzenes were also reacted under the same conditions.

Phenylacetic acid. White solid, mp. 77℃ (lit[32] 77-78.5 ℃); ^1H-NMR ($CDCl_3$) δ 3.62 (s, 2H, CH_2), 7.73 (m, 5H, aromatic H), 117.3 (br, 1H, COOH); ^{13}C-NMR ($CDCl_3$) δ 41.4 (CH_2), 127.7 (aromatic C-4), 128.9 (aromatic C-2,6), 129.7 (aromatic C-3,5), 133.5 (aromatic C-1), 178.7 (COOH); mass (m/e)

137 (3), 136 (M^+, 35), 92 (15), 90 (10), 89 (20); IR (ν_{CO}) 1690 cm^{-1}.

2-Chlorophenyl (acetic acid). White solid, mp. 95℃ (lit[32] 95-97℃); ^{1}H-NMR ($CDCl_3$) δ 3.81 (s, 2H, CH_2), 7.30 (m, 4H, aromatic H), 11.30 (br, 1H, COOH); ^{13}C-NMR ($CDCl_3$) δ 38.8 (CH_2), 127.0 (aromatic C-5), 129.0 (aromatic C-4), 129.6 (aromatic C-6), 131.6 (aromatic C-3), 131.7 (aromatic C-1), 134.7 (aromatic C-2) 177.2 (COOH); mass (m/e) 172 (10), 170 (M^+, 30), 135 (40), 127 (30), 125 (100), 91 (35), 90 (10), 89 (20); IR (ν_{CO}) 1700 cm^{-1}.

(4-Chlorophenyl) acetic acid. White solid, mp. 104℃ (lit[32] 105-108.5℃); ^{1}H-NMR ($CDCl_3$) δ 3.60 (s, 2H, CH_2), 7.21 9d, 2H, $J=7$ Hz, aromatic H-2,6), 7.27 (d, 2H, $J=7$ Hz aromatic H-3,5), 11.51 (br, 1H, COOH); ^{13}C-NMR ($CDCl_3$) δ 40.3 (CH_2), 129.0 (aromatic C-2,6), 131.0 (aromatic C-3,5), 132.0 (aromatic C-1), 134.0 (aromatic C-4), 177.5 (COOH); mass (m/e) 172 (10), 170 (M^+, 30), 127 (30), 125 (10), 91 (20); IR (ν_{CO} 1690 cm^{-1}.

2-Methylphenylacetic acid. White solid, mp. 88℃ (lit[32] 88-90℃); ^{1}H-NMR ($CDCl_3$) δ 2.30 (s, 3H, CH_3), 3.64 (s, 2H, CH_2), 7.20 (m, 4H, aromatic H), 11.64 (br 1H, COOH); ^{13}C-NMR ($CDCl_3$) δ 19.5 (CH_3), 38.9 (CH_2), 126.2 (aromatic C-5), 127.7 (aromatic C-4), 130.3 (aromatic C-3), 130.4 (aromatic C-6), 132.0 (aromatic C-1), 137.0 (aromatic C-2), 178.4 (COOH); IR (ν_{CO}) 1695 cm^{-1}.

4-Methylphenylacetic acid. White solid, mp. 91℃ (lit[32] 90-93℃); ^{1}H-NMR ($CDCl_3$) δ 2.31 (s, 3H, CH_3), 3.58 (s, 2H, CH_2), 7.11 (d, 2H, $J=8$ Hz, aromatic H-3,5), 7.15 (d, 2H, $J=8$ Hz aromatic H-2,6), 11.60 (br, 1H, COOH); ^{13}C-NMR ($CDCl_3$) δ 21.1 (CH_3), 40.7 (CH_2), 129.2 (aromatic C2-6), 129.3 (aromatic C-3,5), 130.2 (aromatic C-1), 137.0 (aromatic C-4), 177.6 (COOH); mass (m/e) 172 (10), 170 (M^+, 30), 127 (30), 125 (10), 91 (20); IR (ν_{CO}) 1700 cm^{-1}.

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