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Carbonylation of Benzyl Halides Using bis (Triphenylphosphine)cobalt Dichloride Under Phase Transfer Catalysis

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CARBONYLATION OF BENZYL HALIDES USING BIS(TRIPHENYLPHOSPHINE)COBALT DICHLORIDE UNDER PHASE TRANSFER CATALYSIS

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ABSTRACT: Using $Co(PPh_3)_2Cl_2$ as catalyst, the carbonylation of benzyl halide with CO (1 atm) in a binary system (aq.NaOH/C_6H_6) in the presence of tetrabutylammonium bromide as phase transfer catalyst for 10 h gives the corresponding carboxylic acid in good to excellent yields. The effects of phase transfer catalyst and reaction temperature on the reactions have been investigated. The reaction mechanism is briefly discussed.

Since the first publication on organometallic phase transfer catalysis [1], the field has developed sufficiently rapidly to justify an account at this time. Several similar articles have been published [2-6].

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The carbonylation of benzyl halide under phase transfer catalysis, which gives the corresponding carboxylic acid, has been widely investigated recently [7–10]. Several catalysts such as $Co_2(CO)_8$ [7–8,11–14], $Pd(PPh_3)_2Cl_2$[15], $Fe(CO)_5$[10] , $CoCl_2$ /$NaBH_4$ [16], $CoCl_2/Mn–Fe$ [17], $Co(NO_3)_2/KCN$ [18], $Co(CO)_3NO$ [19], $RhCl_3$ [20], $RhCl(CO)(PPh_3)_2$ [21] etc., have been used in the field. Despite the good yields of carboxylic acid, the catalysts are very expensive and difficult to obtain because of harsh reaction conditions. In the course of searching for cheaper effective catalysts, we have found that $Co(PPh_3)_2Cl_2$ can be used as an effective catalyst for the carbonylation of benzyl halides under phase transfer catalysis. Here, we report the synthesis of corresponding carboxylic acids by carbonylation of benzyl halides using $Co(PPh_3)_2Cl_2/CO/Bu_4N^+Br^-$ /$NaOH/C_6H_6$ system.

Results and discussion

Treatment of benzyl halides with CO (1 atm) in the presence of catalytic amounts of $Co(PPh_3)_2Cl_2$ and $Bu_4N^+Br^-$ in a binary system (aq.$NaOH/C_6H_6$) for 10 h gives the corresponding carboxylic acid. The reactions are shown in Scheme 1 and the results are summarized in Table 1

$$RCH_2X + CO \xrightarrow[C_6H_6/aq.NaOH,10\ h]{Co(PPh_3)_2Cl_2/PTC} RCH_2COOH$$

$$R=C_6H_5,\quad \alpha\text{-}C_{10}H_7,\quad \beta\text{-}C_{10}H_7;\quad X=Cl,\quad Br$$

Scheme 1

Table 1. $Co(PPh_3)_2Cl_2$–Phase transfer catalyzed carbonylation of benzyl halides[a]

Entry No.	Substrate	PTC	T. (℃)	Product[b]	Yield[c] (%)
1	$C_6H_5CH_2Cl$	Bu_4NBr	55	$C_6H_5CH_2COOH$	88
2	$C_6H_5CH_2Cl$	$C_{16}H_{33}N(CH_3)_3Br$	55	$C_6H_5CH_2COOH$	12
3	$C_6H_5CH_2Cl$	$C_6N_5CH_2N(C_2H_5)_3Cl$	55	$C_6H_5CH_2COOH$	38
4	$C_6H_5CH_2Cl$	PEG-400	55	$C_6H_5CH_2COOH$	27
5	$C_6H_5CH_2Cl$	Bu_4NBr	25	$C_6H_5CH_2COOH$	29
6	$C_6H_5CH_2Cl$	Bu_4NBr	40	$C_6H_5CH_2COOH$	47
7	$C_6H_5CH_2Cl$	Bu_4NBr	65	$C_6H_5CH_2COOH$	38
8	α-$C_{10}H_7CH_2Br$	Bu_4NBr	55	$C_6H_5CH_2COOH$	44
9	β-$C_{10}H_7CH_2Br$	Bu_4NBr	55	$C_6H_5CH_2COOH$	50

[a] Molar ratio: Substrate/$Co(PPh_3)_2Cl_2$/PTC = 25/1.25/1.

[b] Products were identified by IR, NMR, and elemental analysis.

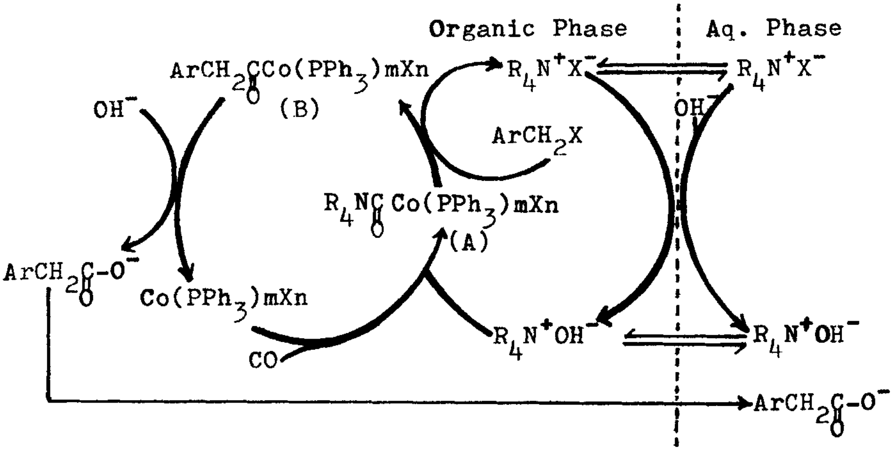
[c] Yield are of isolated, Pure Products and are based on benzyl halide.

Experiments show that the phase transfer catalyst and the temperature greatly affect the reaction. Taking the carbonylation of benzyl chloride for an example, the experiments for the selection of phase transfer catalysts indicate that $Bu_4N^+Br^-$, of all phase transfer catalysts examined, is the best one. The catalytic effectiveness of different phase transfer catalysts was compared. It is found that the activities of the catalysts are in the following sequence.

$Bu_4N^+Br^- > C_6H_5\text{-}CH_2N(CH_3)_3Cl > \text{PEG-400} > C_{16}H_{33}N(CH_3)_3Br$

The carboxylic acid can not be obtained in the absence of phase transfer catalyst. The experiments also show that the yield of phenylacetic acid will increase with the elevation of temperature below 55℃ (entry 5,6,1) and will decrease above 55℃. Thus the optimum temperature is 55 ℃ . Under the optimal condition, i. e., $Bu_4N^+Br^-$ as phase transfer catalyst at 55℃, the reuse of cobalt catalyst has been carried out.

The results show that the yield of phenylacetic acid will decrease from 80% to 6% after three times using of the cobalt catalyst. In view of the fact, we replenished some of cobalt catalyst into organic phase after the reaction and continued the reaction. The experiments have it that 28 % additional cobalt catalyst, which base on the amount of initial cobalt catalyst, is enough to maintain 77 % yield of phenylacetic acid. According to a previous report by H.Alper [1] and our experiments, we tentatively propose a mechanism for the reaction (Scheme 2). The combination of $Co(PPh_3)_2Cl_2$, CO and $R_4N^+OH^-$ gives the complex (A), which reacts with $ArCH_2X$ generating the main intermediate complex(B) . Then, the carboxylic acid is obtained from the reaction between OH^- and(B).



Scheme 2

Experiment

The following typical procedure is as follows: The mixture of cobalt catalyst (1.25 mmol), $Bu_4N^+OH^-$ (1 mmol),benzene (20ml) and catalytic amount of reductive reagent was stirred under CO atmosphere (1 atm) at room temperature for 3- 4 h. After vigorous stirring for one hours at 55℃, benzyl chloride in benzene solution (10 ml) was added drop wise to the above mixture in about 2.5 h and stirring was continued for 8 h. The layers were separated, the aqueous phase was acidified with hydrogen chloride,and extracted with diethyl ether(3×10ml). The ethereal extract was dried($MgSO_4$), and concentrated. The pure product (yield 88%) was obtained after recrystallization from diethyl ether.

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