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Synthesis of Phenylacetic Acid via Carbonylation of Benzyl Chloride in the Presence of a Water-Soluble Complex, $[PdCl_2\{PPh_2(m\text{-}C_6H_4SO_3Na)\}_2]$, and Surfactants under Two-Phase Conditions

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Synopsis. The addition of surfactants such as $n\text{-}C_7H_{15}SO_3Na$ or $n\text{-}C_7H_{15}COONa$ is effective in acceleration of the carboxylation of benzyl chloride using a water-soluble catalyst, $[PdCl_2\{PPh_2(m\text{-}C_6H_4SO_3Na)\}_2]$, in an aqueous NaOH–heptane solution. Phenylacetic acid is easily isolated from the aqueous layer in high yields. However, the addition of $n\text{-}C_7H_{15}SO_3Na$ has no effect on the carboxylation using hydrophobic catalysts, $[PdCl_2(PPh_3)_2]$ and $[Pd(PPh_3)_4]$, under the two phase conditions.

In spite of the importance of the carboxylic acid synthesis from benzylic halides via catalytic carbonylation, it was difficult to construct the proper reaction systems because of the insolubility of alkali metal hydroxides in organic solvents. One solution to this problem is the use of phase transfer catalysts or the use of amphipathic catalysts under two-phase conditions.[1] These methods have the advantage of easy separation of the product. However, the P.T.C. method is ineffective in preventing the nucleophilic substitution of benzyl chloride with hydroxide ion.[2] We have previously reported on the amphipathic catalyst method in which the carboxylation of benzyl choride is selectively achieved by the use of an amphipathic palladium complex, $[PdCl_2\{PPh_2(m\text{-}C_6H_4SO_3Na)\}_2]$, under aqueous NaOH–heptane two-phase conditions.[3] However, as this carboxylation at low temperatures was rather slow and showed quite a long induction period, we could not discuss whether the carboxylation is a counter phase transfer catalytic reaction or not.[4] Therefore, we started to study the carboxylation in order to solve the problem.

$$\underset{Org.}{PhCH_2Cl} + \underset{Gas(1\ atm)}{CO} + \underset{Aq}{NaOH} \xrightarrow[\text{in } H_2O\text{–Heptane}]{[PdCl_2\{PPh(m\text{-}C_6H_4SO_3Na)\}_2]} PhCH_2COOH$$

Results and Discussion

The carboxylation, whose rate can be estimated by the absorption of carbon monoxide,[3] was very slow at 30 °C in the early stage, as shown in Fig. 1. In the latter stage, however, the rather fast absorption of CO was observed. This result implies that the accumulation of sodium phenylacetate in the aqueous phase accelerates the carboxylation. In fact, the addition of a large amount of sodium phenylacetate (10 mmol) greatly improved the absorption rate, and the long induction period almost disappeared. Therefore, various additives were tested; the results are summarized in Table 1. The sodium salts of octanoic and 3-phenylpropionic acids having long hydrocarbon chains were very efficient, and the curves of CO absorption were almost equal to that of the carboxylation using 10 mmol of sodium phenylacetate. On the other hand, the carboxylates having short hydrocarbon chains were less efficient, and in particular, sodium acetate was totally inefficient. These results indicate that the lipophilicity of carboxylates is correlated to the acceleration effect. Sodium sulfonates were also found to be good additives. The effect of sodium heptanesulfonate was almost equivalent to that of sodium octanoate, which has the same alkyl chain as the sulfonate. It is interesting to note that tetrabutylammonium salts and $n\text{-}C_{18}H_{35}(OCH_2CH_2)_nOH$ (n=about 7) were evidently effective in acceleration of the CO absorption, while these are less efficient than the carboxylates and the sulfonates. These compounds typify the cationic and neutral surfactants, whereas sulfonates and carboxylates are anionic surfactants. Consequently, the acceleration effect of these additives is considered to be due to their action as surfactant.

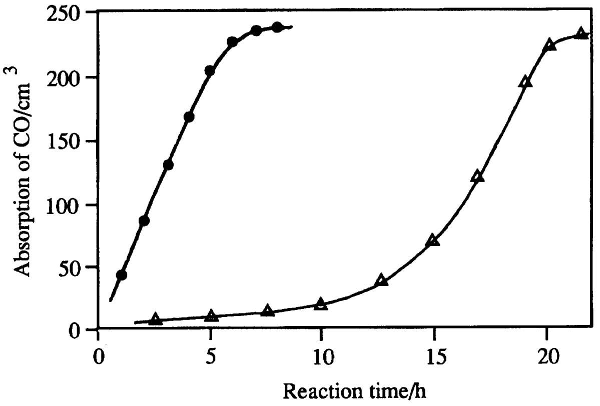

Fig. 1. Carboxylation of $PhCH_2Cl$ catalyzed by $PdCl_2[PPh_2(m\text{-}C_6H_4SO_3Na)]_2$ in the presence (●) or absence (△) of $PhCH_2COONa$ (10 mmol). The reaction conditions are the same as in Table 1.

The amount of additives is also an important factor in accelerating the carboxylation with the water-soluble phosphine complex (see Table 2). When 10 mmol of sodium p-methylbenzoate was used, a very high acceleration effect was observed. However, the efficiency was dramatically reduced by decreasing the amount of the additive. The acceleration effects of heptanesulfonate and octanoate were nearly unchanged in the range of 5

Table 1. Effect of Additives on the Carboxylation of $PhCH_2Cl$ under Heptane–Water Two-Phase Conditions

Additive	Absorption of carbon monoxide/%$^{a,b)}$
n-$C_7H_{15}SO_3Na$	90 (88)
p-$CH_3C_6H_4SO_3Na$	59 (35)
n-$C_7H_{15}COONa$	87 (85)
$PhCH_2CH_2COONa$	86
n-$C_6H_{13}COONa$	80
$PhCH_2COONa$	65
p-$CH_3C_6H_4COONa$	58
n-C_4H_9COONa	43
CH_3COONa	16
$(n$-$C_4H_9)_4NBr$	(53)
$(n$-$C_4H_9)_4NCl$	(47)
n-$C_{18}H_{35}(OCH_2CH_2)_7OH$	(38)
None	14

Reaction conditions; $PhCH_2Cl$ (10 mmol), aq-NaOH (2.5 mol dm^{-3}, 10 cm^3), $PdCl_2[PPh_2(m\text{-}C_6H_4SO_3Na)]_2$ (0.1 mmol), additive (5 mmol), heptane (10 cm^3), CO (1 atm), 30 °C, 6 h. a) Based on $PhCH_2Cl$ used. b) The CO absorptions of the reactions using 2 mmol of the additives are given in parentheses.

Table 2. Effect of the Amount of Additives on the Absorption of Carbon Monoxide

	Absorption of carbon monoxide/%		
Additive/mmol	n-$C_7H_{15}SO_3Na$	n-$C_7H_{15}COONa$	p-$CH_3C_6H_4COONa$
10	82	82	77
5	82	80	44
1	81	79	12
0.5	58	33	
0.2	22	14	
0	10		

The reaction conditions are the same as in Table 1 except for the reaction time (5 h).

Table 3. Effect of the Addition of n-$C_7H_{15}SO_3Na$ on the Carboxylation under Two-Phase Conditions

Organic phase	Catalyst	Absorption of carbon monoxide/%$^{a,b)}$	
Toluene	$Pd(PPh_3)_4$	3	(3)
Toluene	$PdCl_2(PPh_3)_2$	4	(4)
Toluene	$PdCl_2[PPh_2(m\text{-}C_6H_4SO_3Na)]_2$	59	(5)
Heptane	$PdCl_2[PPh_2(m\text{-}C_6H_4SO_3Na)]_2$	100$^{c)}$	(20)

Reaction conditions; $PhCH_2Cl$ (10 mmol), aq-NaOH (2.5 mol dm^{-3}, 10 cm^3), organic solvent (10 cm^3), catalyst (0.1 mmol), n-$C_7H_{15}SO_3Na$ (2 mmol), CO (1 atm), 30 °C, 8 h. a) Based on $PhCH_2Cl$ used. b) The CO absorptions of the reactions without n-$C_7H_{15}SO_3Na$ are shown in parentheses. c) The isolated yield of $PhCH_2COOH$ was 93%, and $PhCH_2OH$ (0.1%) and $PhCH_2Cl$ (3%) were detected by GLC.

mmol to 1 mmol, and were decreased at the lower concentrations. Since at low concentrations the efficiency of sodium heptanesulfonate was higher than that of the octanoate, the sulfonate is considered to be the best additive.

The preparative carbonylation was carried out in the presence of 2 mmol of sodium heptanesulfonate under the aqueous NaOH–heptane two-phase conditions. The almost equimolar absorption of CO was attained after 8 h. The phenylacetic acid, which was easily isolated in a 93% yield as colorless crystals from the aqueous layer by simple extraction after acidification, was very pure without contamination with the additive and catalyst, because the sulfonates are more acidic than phenylacetic acid. The by-product of this reaction was a trace amount of benzyl alcohol, which was detected in the organic layer together with a small amount of the unreacted benzyl chloride.

The carboxylation using heptane as an organic phase was faster than that using toluene (see Table 3). Since this is the inverse of the solvent effect on the normal P.T.C. reactions, the water-soluble complex in this reaction probably acts as counter phase transfer catalyst.[4] Interestingly, the addition of sodium heptanesulfonate to the toluene system improved the catalytic activity of the water-soluble complex, while this additive had no effect on the carboxylations with $[Pd(PPh_3)_4]$ and with $[PdCl_2(PPh_3)_2]$. This fact indicates that the acceleration of the carboxylation is not ascribed to a simple surface activation by the sulfonate but to an activation of the reaction environment of this counter phase transfer catalysis by some mutual interaction between the sulfonate and the water-soluble catalyst. The interaction details are still unclear, and mechanistic studies are in progress.

Experimental

Materials. All chemicals were purchased from chemical sources. Organic solvents, $PhCH_2Cl$ and water were distilled and stored under argon. The sodium salts of carboxylates and sulfonates were purified by recrystallization before use. n-Bu_4NCl, n-Bu_4NBr, and n-$C_{18}H_{35}(OCH_2CH_2)_nOH$ (n=about 7) were used without further purification. Carbon monoxide (99.9%) was obtained from Sumitomo Seiki Co. and used as received. $[PdCl_2(PPh_3)_2]$,5) $[PdCl_2[PPh_2(m\text{-}C_6H_4SO_3Na)]_2]$,6) and $[Pd(PPh_3)_4]$7) were prepared according to literature methods.

Catalytic Carboxylation of Benzyl Chloride. The reactions were carried out in a 50 cm^3 two-necked flask fitted with a threeway stopcock. A gas buret filled with decalin, magnetic stirrer and polyethylene glycol bath thermostatted at 30 °C were used. In the flask, palladium catalyst (0.1 mmol) and a surfactant were placed, and the atmosphere was replaced with carbon monoxide. The flask was then charged with organic solvent (10 cm^3), $PhCH_2Cl$ (1.27 g, 10 mmol) and aqueous NaOH solution (2.5 $mol\,dm^{-3}$, 10 cm^3) by syringes in turn, and the mixture was vigorously stirred (about 1500 rps). After the carboxylation, the reaction mixture was poured into a mixture of ether (10 cm^3) and aqueous NaOH solution (2.5 $mol\,dm^{-3}$, 10 cm^3). The aqueous and organic layers were separated, then the aqueous layer was washed with two 20 cm^3 portions of ether. The ethereal washings and the organic layer were combined, dried over anhydrous Na_2SO_4, and concentrated to about 20 cm^3. After addition of naphthalene as an internal calibrant, the solution was analyzed by means of GLC (PEG-HT, 3 m) to quantify $PhCH_2OH$ and $PhCH_2Cl$. The aqueous layer was acidified with concentrated hydrochloric acid, and $PhCH_2COOH$ was extracted with four 20 cm^3 portions of ether. The ethereal solution was dried over anhydrous Na_2SO_4, and concentrated to dryness to give almost pure phenylacetic acid.

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