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Effect of Co-solvent on the Palladium Catalyzed Alkoxycarbonylation of Allyl Bromide in Supercritical CO_2

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Abstract: The effect of cosolvent on the palladium catalyst which catalyze alkoxycarbonylation of allyl bromide in supercritical CO_2 has been investigated. It was found that a small amount of cosolvent such as ethanol, CH_2Cl_2 and cyclohexane can affect both reaction yields and selectivities largely. Ethanol was the most favorable cosolvent for increasing the total yield of unsaturated esters and the selectivity of 3-butenoic acid ester. Using cosolvent ethanol and cocatalyst $FeCl_2$ simultaneously can lead to better reaction results.

Keywords: Supercritical CO_2, cosolvent, alkoxycarbonylation, palladium, cocatalyst, $FeCl_2$.

We have studied the palladium-catalyzed alkoxycarbonylation of allyl bromide in supercritical (sc) CO_2 and found the reaction rate in sc CO_2 was lower than those in some organic solvents[1]. The possible reason was the lower solubility of sc CO_2 for the palladium catalyst.

As an effective approach to improve the solubility of varieties of solutes, cosolvent such as ethanol has been widely used in the sc CO_2 extraction[2,3]. Based on the above consideration, we chose several organic reagents as cosolvent to explore if the reaction can be tuned by small amount of cosolvent in sc CO_2. The experimental procedures was similar to that reported previously[1].

Table 1 shows the effects of several cosolvents on the palladium catalyzed alkoxycarbonylation of allyl bromide in sc CO_2. First, we investigated the effect of cosolvent ethanol on the total yield and selectivity of 3-butenoic acid ethyl ester (I) and 2-butenoic acid ethyl ester (II) at 50°C. For the $PdCl_2$+2PPh_3 catalytic system, the total yields of I and II were improved dramatically with increasing the amount of cosolvent ethanol, accompanied by slight increases in the selectivity of I. When the molar percentage of cosolvent ethanol was increased to 16.9%, the total yield of I and II can be tuned to nearly four times over that in the pure sc CO_2 solvent. Next, the effect of cosolvents ethanol, cyclohexane, toluene and CH_2Cl_2 has been compared. The result showed that cyclohexane raised the total yield of I and II in a modest way, while toluene

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gave an almost identical result with that in pure sc CO_2. CH_2Cl_2 has the significant cosolvent effect on the total yield of I and II, but it is weaker than ethanol and decreased the selectivity of I. A large disadvantage exist for CH_2Cl_2 concerning clean chemistry.

In another series of experiments to investigate the effects of various transition metallic compounds on the reaction, $FeCl_2$, as a cocatalyst, was found to have a promoting effect on the reaction activity in sc CO_2 and the optimum result was obtained at 70°C. In this paper, the effect of cosolvent ethanol on the reaction with the $PdCl_2$+$FeCl_2$+$2PPh_3$ catalytic system was also investigated. As shown in **Table 1**, increasing the amount of cosolvent ethanol led to higher total yield and higher selectivity of I in the presence of $FeCl_2$. On the other hand, compared with increasing reaction temperature and using $FeCl_2$, increasing the concentration of cosolvent ethanol is a quite mild and more effective approach to improving the reaction total yield and selectivity of I.

Table 1 Effect of cosolvent on the alkoxycarbonylation of allyl bromide in sc CO_2

Catalyst	Temperature (°C)	Reaction Medium	Cosolvent /Cosolvent+ CO_2 (mol %)	Y (I+II) (%)	I / II
$PdCl_2$+$2PPh_3$	50	CO_2	0	12.1	8.1
$PdCl_2$+$2PPh_3$	50	CO_2+ethanol	5.5	15.1	12.5
$PdCl_2$+$2PPh_3$	50	CO_2+ethanol	10.4	32.2	14.2
$PdCl_2$+$2PPh_3$	50	CO_2+ethanol	16.9	45.9	12.2
$PdCl_2$+$2PPh_3$	50	CO_2+cyclohexane	16.9	19.8	10.0
$PdCl_2$+$2PPh_3$	50	CO_2+toluene	16.9	12.4	13.9
$PdCl_2$+$2PPh_3$	50	CO_2+CH_2Cl_2	16.9	42.3	4.7
$PdCl_2$+$2PPh_3$	70	CO_2	0	26.5	9.6
[a] $PdCl_2$+ $FeCl_2$+$2PPh_3$	50	CO_2	0	23.6	10.4
[a] $PdCl_2$+ $FeCl_2$+$2PPh_3$	70	CO_2	0	30.8	10.9
[a] $PdCl_2$+ $FeCl_2$+$2PPh_3$	70	CO_2+ethanol	10.4	34.0	11.0
[a] $PdCl_2$+ $FeCl_2$+$2PPh_3$	70	CO_2+ethanol	16.9	49.0	12.2

Conditions: $PdCl_2$, 0.125 mmol; PPh_3, 0.25 mmol; allyl bromide, 1.25 mmol; ethanol, 0.5 mL; Et_3N, 1.25 mL; CO 1.0 MPa, CO_2 7.5 MPa, 4 h. [a] $FeCl_2$, 0.125 mmol.

In conclusion, the palladium catalyzed alkoxycarbonylation in sc CO_2 can be well tuned by the addition of small amount of cosolvents.

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