

Note

Palladium-Catalyzed Addition of Carbon Monoxide and Carbon Tetrachloride to 1-Octene in Supercritical Carbon Dioxide

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The Pd-catalyzed addition of carbon monoxide and carbon tetrachloride to 1-octene gave coadduct [alkyl 2-(2,2,2-trichloroethyl)octanoate] as the major product in supercritical carbon dioxide by using pyridine as the base. It was found that the selectivity and the yield of coadduct were greatly affected by the pressure of carbon dioxide, the reaction temperature and the amounts of alcohol and base used.

Keywords Pd-catalyzed, addition reaction, coadduct, supercritical carbon dioxide

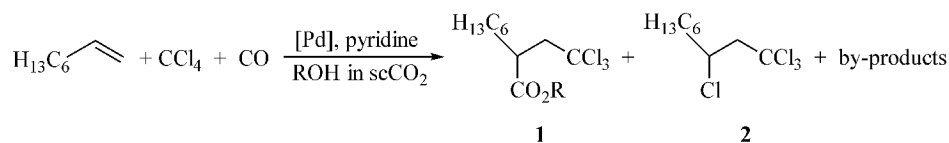
Supercritical carbon dioxide (scCO₂), as a green reaction medium with a lot of favorable features, has received increasing attention in recent years.^{1,2} Carbon dioxide is cheaper, nonflammable, nontoxic and chemically inert under various reaction conditions. In addition, scCO₂ possesses hybrid properties of both liquid and gas, and separation of carbon dioxide from the reaction system is easy. Due to the higher solubility of reaction gas, rapid diffusion of solute and weak solvation around reacting species, scCO₂ could increase the reaction rate and/or improve the selectivity to some extent.^{3,4} Radical reaction in scCO₂ is one of the successful examples to employ scCO₂ as the reaction medium,^{5,6} which requires neither nucleophile nor electrophile and proceeds well in nonpolar solvent.^{7,8}

Recently, our previous paper⁹ found that palladium-catalyzed coaddition reaction of carbon monoxide and car-

bon tetrachloride to 1-octene could be proceeded smoothly in alcohols by using pyridine as the base. This is a radical reaction¹⁰ and the selectivity of coaddition product [alkyl 2-(2,2,2-trichloroethyl)octanoate] is about 62%. There are several advantages in this reaction, such as free of phosphoric ligands, homogeneous status and extensive broad of reactants. But the problem of the low selectivity of coadduct has not been well solved. By considering that the good solubility and diffusion of carbon monoxide in scCO₂ might favor the coaddition reaction and improve the selectivity of coadduct, this paper reported our preliminary results of palladium-catalyzed coaddition reaction of carbon monoxide and carbon tetrachloride to 1-octene in scCO₂ (Scheme 1).

The initial studies were mainly focused on suitable pressure of carbon dioxide and reaction temperature. The most satisfied results were obtained at 10 MPa of CO₂ (Table 1, Entries 1—4). Due to the effect of temperature on the reaction, it was found that at higher temperature (80 °C or 100 °C), the selectivity of product **1** dropped down to 35% (or 34%), although the conversion rose to 90% (or 91%) (Table 1, Entries 3, 6 and 7). It was evident that the pressure of carbon dioxide and reaction temperature were key factors to influence the selectivity and conversion.

Scheme 1



1a (R = Me), **1b** (R = Et), **1c** (R = *i*-Pr)

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Besides pressure and temperature, the amounts of pyridine and alcohol also affected this radical reaction greatly. When more amounts of pyridine and alcohol were added, the conversion was improved obviously, and the selectivity of coadduct kept unchanged (Entries 8–10). In order to achieve higher conversion, it is necessary to add 2 equiv. of pyridine and 1 mL of EtOH in this reaction. Therefore, the final optimum reaction conditions consisted of 1-octene (2 mmol), CCl_4 (1 mL), EtOH (1 mL), pyridine (4 mmol) and $\text{Pd}(\text{OAc})_2$ (0.02 mmol) under 10 MPa pressure of carbon dioxide at 60 °C. However, when MeOH or *i*-PrOH was used instead of EtOH, the reaction also afforded attractive results (Entries 12, 13).

Comparing the results in $\text{scCO}_2 + \text{ROH}$ with those in alcohols alone, the selectivity of coadduct in $\text{scCO}_2 + \text{ROH}$

was significantly improved. A possible mechanism for the reaction is shown in Scheme 2.^{10,11}

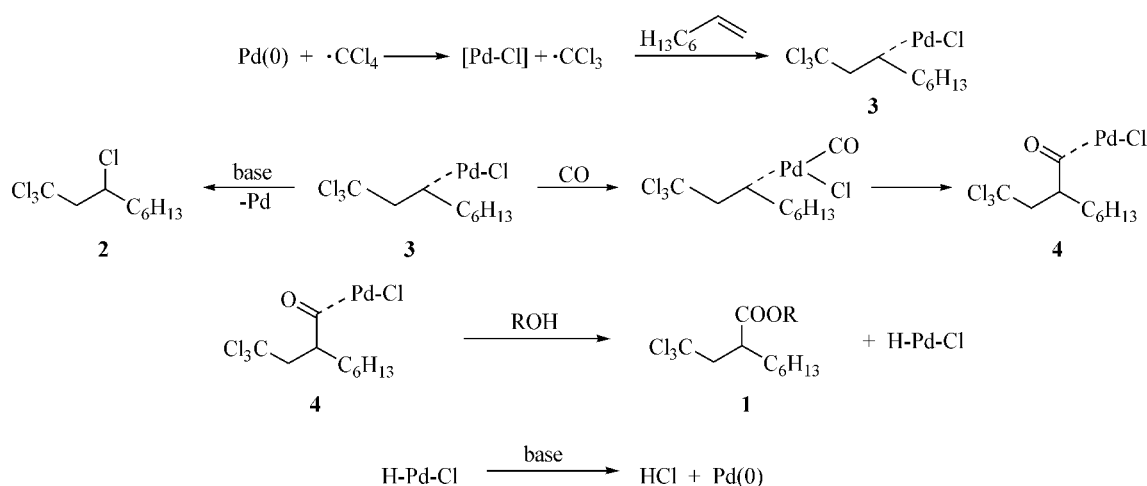
The reactants such as carbon tetrachloride, 1-octene, pyridine and alcohol were all miscible in scCO_2 .¹² In the presence of reductive reagent and base, $\text{Pd}(\text{OAc})_2$ was converted to $\text{Pd}(0)$ immediately. Trichloromethyl radical was then produced by transferring one chlorine atom to $\text{Pd}(0)$, added to 1-octene to form radical species **3**. It has been reported that the nonpolarity of scCO_2 could facilitate the radical initiation and radical addition.^{5,6} After the radical species **3** was formed, there were two competitive reactions as the key steps, one was coaddition reaction and the other was simple addition. Using scCO_2 as the solvent could increase the concentration of carbon monoxide because of its high solubility in scCO_2 , which was

Table 1 Addition reaction of carbon tetrachloride and carbon monoxide to 1-octene^a

Entry	P_{CO_2} (MPa)	Pyridine (eq.)	EtOH (mL)	Conv. ^b (%)	Yield ^c (%)		Select. (%) [1/1+2]
					1	2	
1	6.5	1	0.5	52	30	16	65
2	8	1	0.5	48	32	13	71
3	10	1	0.5	60	46	10	82
4	12	1	0.5	50	32	14	70
5 ^c	10	1	0.5	65	47	12	80
6 ^d	10	1	0.5	90	30	55	35
7 ^e	10	1	0.5	91	29	57	34
8	10	1	1	76	58	13	82
9	10	2	0.5	72	57	12	83
10	10	2	1	100	78	16	83
11 ^f	10	2	1	96	60	32	65
12 ^g	10	2	1	100	79	15	84
13 ^h	10	2	1	92	68	20	71
14	—	2	4	100	59	36	62

^a Reaction conditions: 1-octene (2 mmol), CCl_4 (1 mL), CO (4.0 MPa) and $\text{Pd}(\text{OAc})_2$ (1 mol%) at 60 °C for 24 h in a 10 mL-stainless steel autoclave. ^b Determined by GC analysis. ^c Reacted for 48 h. ^d Reacted at 80 °C. ^e Reacted at 100 °C. ^f Reacted under 2 MPa of CO . ^g MeOH was used instead of EtOH. ^h *i*-PrOH was used instead of EtOH.

Scheme 2



favorable to form carbonyl-palladium species **4**. This hypothesis can be confirmed by the present study. For example, a higher selectivity of coadduct (65%) was obtained under lower pressure of CO (2 MPa) in $\text{scCO}_2 + \text{ROH}$ as compared with the selectivity (62%) in EtOH alone (Entries 11 and 14). Therefore, it is proposed that scCO_2 is the more suitable solvent for the carbonylation than alcohols. The products were formed by the alcoholysis of carbonyl-palladium species or by the reduction-elimination of **3**. When more amount of EtOH was added, the alcoholysis rate became faster and the conversion was increased consequently. Furthermore, more amount of pyridine could also accelerate the production of active palladium species through neutralizing HCl produced in the reaction.

In summary, scCO_2 was successfully used as the solvent for the palladium-catalyzed addition reaction of carbon monoxide and carbon tetrachloride to 1-octene. Regulating the pressure of carbon monoxide and reaction temperature to a good extent, adding suitable amounts of pyridine and alcohol could improve the selectivity and conversion obviously. Of particular note is the fact that this addition reaction is more environmentally friendly than the traditional way and shows potential utility in organic synthesis and industrial application.

Experimental

GC data were obtained by a VARIAN 3700 GC. ^1H NMR spectra were taken on a 400 MHz spectrometer with tetramethylsilane as the internal standard and CDCl_3 as the solvent. IR spectra were obtained with a WQF-410 FTIR spectrometer. MS spectra were recorded on an HP 6890-5937 MS spectrometer. Microanalysis was carried out on a Carlo-Erba 1106 instrument. The reagents employed were of analytical grade and commercially available.

General procedure

1-Octene (2 mmol), carbon tetrachloride (1 mL), pyridine (2 mmol), EtOH (4 mL) and $\text{Pa}(\text{OAc})_2$ (1 mol%) were added to a 10 mL-stainless steel autoclave. The reaction was carried out at appointed temperature and under pressure for 24 h. After venting of carbon monoxide and removing the metal species and solvent, the products were purified by column chromatography on silica gel (10:1 hexane-ether) and then were determined by GC (quantitative analysis) and ^1H NMR (400 MHz).

Methyl 2-(2,2,2-trichloroethyl)octanoate (**1a**)

^1H NMR (CDCl_3 , 400 MHz) δ : 3.69 (s, 3H, CHCOOCH_3), 2.82—2.88 (m, 1H, CHCOOCH_3), 2.65—2.69 (d, $J = 16.8$ Hz, 1H, $\text{CHCH}_2\text{CCl}_3$), 3.35—3.40 (dd, $J = 24$ Hz, 1H, $\text{CHCH}_2\text{CCl}_3$), 1.25—1.67 (m, 10H), 0.85 [t, $J = 8.4$ Hz, 3H, $(\text{CH}_2)_3\text{CH}_3$]; IR (film) ν : 1746 (C=O), 1175 (C—O—C), 785 (C—Cl) cm^{-1} ; MS (70 eV) m/z (%): 288, 257, 193, 87, 74. Anal. calcd for $\text{C}_{11}\text{H}_{19}\text{Cl}_3\text{O}_2$: C 45.83, H 6.60, Cl 36.46; found C 45.77, H 6.65, Cl

36.42.

Ethyl 2-(2,2,2-trichloroethyl)octanoate (**1b**)

^1H NMR (CDCl_3 , 400 MHz) δ : 4.14 (q, $J = 9.0$ Hz, 2H, $\text{CHCOOCH}_2\text{CH}_3$), 2.78—2.84 (m, 1H, $\text{CHCOOCH}_2\text{CH}_3$), 2.63—2.67 (d, $J = 16.4$ Hz, 1H, $\text{CHCH}_2\text{CCl}_3$), 3.35—3.41 (dd, $J = 24$ Hz, 1H, $\text{CHCH}_2\text{CCl}_3$), 1.22—1.69 (m, 13H), 0.85 [t, $J = 8.0$ Hz, 3H, $(\text{CH}_2)_3\text{CH}_3$]; IR (film) ν : 1739 (C=O), 1171 (C—O—C), 782 (C—Cl) cm^{-1} ; MS (70 eV) m/z (%): 302, 257, 193, 88, 29. Anal. calcd for $\text{C}_{12}\text{H}_{21}\text{Cl}_3\text{O}_2$: C 47.68, H 6.95, Cl 34.77; found C 47.61, H 6.99, Cl 34.74.

i-Propyl 2-(2,2,2-trichloroethyl)octanoate (**1c**)

^1H NMR (CDCl_3 , 400 MHz) δ : 4.99—5.05 (m, 1H, $\text{CHCOOCH}_2\text{CH}_2\text{CH}_3$), 2.75—3.81 (m, 1H, $\text{CHCOOCH}_2\text{CH}_2\text{CH}_3$), 2.62—2.66 (d, $J = 16.8$ Hz, 1H, $\text{CHCH}_2\text{CCl}_3$), 3.36—3.42 (dd, $J = 24$ Hz, 1H, $\text{CHCH}_2\text{CCl}_3$), 1.20—1.63 (m, 16H), 0.87 [t, $J = 8.2$ Hz, 3H, $(\text{CH}_2)_3\text{CH}_3$]; IR (film) ν : 1735 (C=O), 1170 (C—O—C), 780 (C—Cl) cm^{-1} ; MS (70 eV) m/z (%): 316, 257, 193, 60, 43. Anal. calcd for $\text{C}_{13}\text{H}_{23}\text{Cl}_3\text{O}_2$: C 49.37, H 7.28, Cl 33.23; found C 49.32, H 7.34, Cl 33.18.

1,1,1- β -Tetrachlorononane (**2**)

^1H NMR (CDCl_3 , 400 MHz) δ : 4.21—4.27 (m, 1H, $\text{C}_6\text{H}_{13}\text{CHClCH}_2\text{CCl}_3$), 3.08—3.28 (m, 2H, $\text{C}_6\text{H}_{13}\text{CHClCH}_2\text{CCl}_3$), 1.28—1.92 (m, 10H), 0.87 [t, $J = 8.6$ Hz, 3H, $(\text{CH}_2)_3\text{CH}_3$]; IR (film) ν : 775 (C—Cl), 735 (CH—Cl) cm^{-1} ; MS (70 eV) m/z (%): 264, 229. Anal. calcd for $\text{C}_9\text{H}_{16}\text{Cl}_4$: C 40.91, H 6.06; found C 40.85, H 6.15.

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