

# Palladium-Catalyzed Addition Reaction of 1-Octene, Carbon Tetrachloride and Carbon Monoxide in Alcohols

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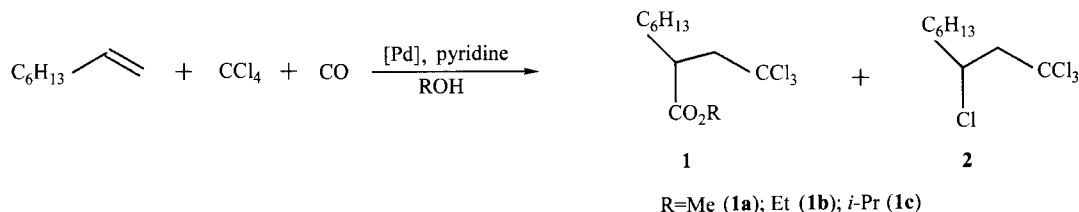
In the presence of pyridine, the Pd-catalyzed addition reaction of CO and CCl<sub>4</sub> to 1-octene could be carried out smoothly under mild conditions. In this reaction, the satisfactory results were afforded when different alcohols and palladium catalysts were used.

**Keywords** Addition reaction, Pd-catalyzed, pyridine, carbon monoxide

## Introduction

Radical addition reaction is a widely used typical method for elongating carbon chain, introducing new functional groups, constructing ring skeleton, etc.<sup>1-3</sup>

### Scheme 1



## Results and discussion

Our investigation began with an effort to optimize reaction conditions for the coaddition reaction of CO and

Using peroxide as an initiator, Foster and co-workers reported the radical addition reaction of ethylene, CO and CCl<sub>4</sub> in methanol to give trichloro esters in 40% conversion under very high pressure (1000 atm).<sup>4</sup> Afterwards, Tsuji group reported that the coaddition of CO and CCl<sub>4</sub> to olefins catalyzed by Pd(OAc)<sub>2</sub> could be carried out smoothly in the presence of phosphine ligand and base at 40–50°C under 40 atm of CO pressure in EtOH.<sup>5-6</sup> However, this reaction did not give satisfactory results when one of phosphine ligand and base was absent or when MeOH or *i*-PrOH was used as reactant and solvent. Here we wish to report the Pd-catalyzed coaddition reaction of CO and CCl<sub>4</sub> to 1-octene in the presence of pyridine in different alcohols (Scheme 1).

CCl<sub>4</sub> to 1-octene using palladium black and pyridine. The final optimized reaction condition for coaddition reaction consisted of CCl<sub>4</sub> (1 mL), Pd black (0.06 mmol), 1-octene (2 mmol), pyridine (2 mmol), ROH

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(4 mL) and CO (40 atm) at 60°C for 24 h. The obtained results were summarized in Table 1.

**Table 1** Addition reaction of 1-octene, carbon tetrachloride and carbon monoxide in different conditions<sup>a</sup>

Entry	Temp. (°C)	$P_{CO}$ (MPa)	Base	ROH	Conv. <sup>b</sup> (%)	Yield (%) <sup>b</sup>		Select. (%) [1/1+2]
						1	2	
1	60	20	pyridine	EtOH	100	41	53	44
2	60	40	pyridine	EtOH	100	58	36	62
3	70	40	pyridine	EtOH	100	54	40	57
4	50	40	pyridine	EtOH	85	45	32	58
5 <sup>c</sup>	60	40	pyridine	EtOH	80	45	30	60
6 <sup>d</sup>	60	40	pyridine	EtOH	100	58	36	62
7 <sup>e</sup>	60	40	pyridine	EtOH	100	58	36	62
8 <sup>f</sup>	60	40	pyridine	EtOH	96	52	40	56
9 <sup>e</sup>	60	40	NEt <sub>3</sub>	EtOH	20	10	9	52
10 <sup>e</sup>	60	40	NEt <sub>2</sub> H	EtOH	15	7	6	54
11 <sup>e</sup>	60	40	none	EtOH	90	16	28	36
12 <sup>e</sup>	60	40	K <sub>2</sub> CO <sub>3</sub>	EtOH	62	31	25	55
13	60	40	K <sub>2</sub> CO <sub>3</sub>	EtOH	26	13	10	57
14 <sup>e</sup>	50	40	KOAc	EtOH	96	22	68	24
15 <sup>e</sup>	50	40	PhCOOK	EtOH	92	18	70	20
16	60	40	pyridine	MeOH	100	62	32	66
17	60	40	pyridine	<i>i</i> -PrOH	94	38	52	42

<sup>a</sup>General procedure for the addition of CO and CCl<sub>4</sub> to 1-octene: In a 10 mL stainless steel autoclave were added 2 mmol of 1-octene, 2 mmol of pyridine, 1 mL of CCl<sub>4</sub>, 4 mL of EtOH and 3 mol% of palladium black, the reactions were carried out under appointed temperature and pressure for 24 h; <sup>b</sup> GC yield; <sup>c</sup> 0.02 mmol of Pd black was used; <sup>d</sup> 4 mmol of pyridine was used; <sup>e</sup> 0.12 mmol of PPh<sub>3</sub> was added; <sup>f</sup> 2 mL of EtOH was used.

From the results shown in Table 1, the presence and choice of bases are quite important. Six bases or salts were used in this reaction, but only pyridine gave the satisfactory result. Although K<sub>2</sub>CO<sub>3</sub> is an acceptable reagent for the selectivity, the conversion is low (Table 1, Entry 12) and the ligands such as PPh<sub>3</sub> are indispensable (Entries 12–13 in Table 1). To our surprise, while pyridine was added in the reaction, PPh<sub>3</sub> became not necessary (Table 1, Entry 7). It is suggested that pyridine is not only an effective base in the reaction but also the ligand of palladium.

The ratio of coadduct/adduct increased with the increase of CO pressure and decreased with the reaction temperature increasing (Table 1, Entries 1–3). Besides EtOH, MeOH and *i*-PrOH were also used as the solvents and reactants, and the satisfactory results were afforded separately (Table 1, Entries 15 and 16).

Besides palladium black, Pd(OAc)<sub>2</sub> and PdCl<sub>2</sub> could also be used as the catalysts (Table 2). In order to obtain satisfactory yields of different coadducts, the amount of pyridine is different in different alcohols. In

EtOH, 1 eq. of pyridine is sufficient (Table 2, Entries 1 and 9), but 2 eq. of pyridine is necessary in MeOH (Table 2, Entries 4 and 10) and 3 eq. of pyridine in *i*-PrOH (Table 2, Entries 8 and 11).

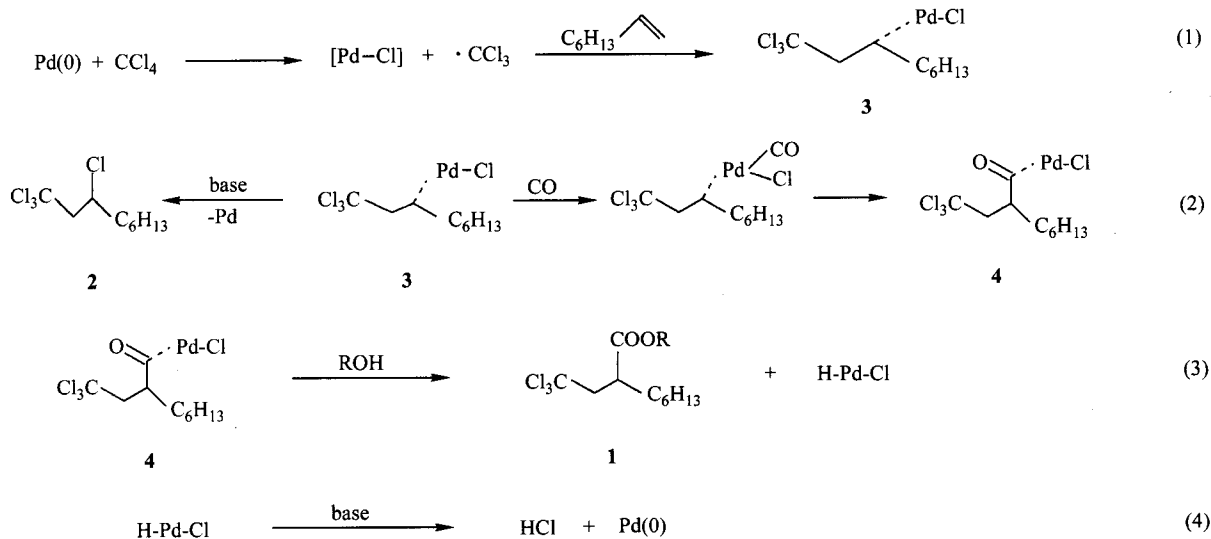
A proposed mechanism involving radical specials is illustrated in Scheme 2. One electron transfer from Pd to CCl<sub>4</sub> produces trichloromethyl radical. The radical species **3** is formed by the addition of trichloromethyl radical to olefin, then reacts with CO to give the trichloro ester after alcoholysis.

In conclusion, the Pd-catalyzed coaddition reaction of CO and CCl<sub>4</sub> to 1-octene give 2-(2,2,2-trichloroethyl) octanoates smoothly under mild reaction conditions. Compared with the literature methods, several outstanding advantages were achieved. First, pyridine might play important role of both base and ligand in the reactions and make the reaction homogeneous. Second, both the extensive application scopes of reactants and catalysts are favour for the synthesis of 2-alkyl-4,4,4-trichlorobutanoates in modern organic chemistry.

**Table 2** Pd(OAc)<sub>2</sub> or PdCl<sub>2</sub>-catalyzed coaddition of 1-octene, carbon tetrachloride and carbon monoxide<sup>a</sup>

Entry	Catalyst	ROH	Pyridine (eq.)	Yield (%)		Select. (%)
				1	2	1/1 + 2
1	Pd(OAc) <sub>2</sub>	EtOH	1	58	35	62
2	Pd(OAc) <sub>2</sub>	EtOH	2	59	36	62
3	Pd(OAc) <sub>2</sub>	MeOH	1	32	60	35
4	Pd(OAc) <sub>2</sub>	MeOH	2	64	32	67
5	Pd(OAc) <sub>2</sub>	MeOH	3	64	32	67
6	Pd(OAc) <sub>2</sub>	<i>i</i> -PrOH	1	25	64	28
7	Pd(OAc) <sub>2</sub>	<i>i</i> -PrOH	2	38	51	43
8	Pd(OAc) <sub>2</sub>	<i>i</i> -PrOH	3	50	42	54
9	PdCl <sub>2</sub>	EtOH	1	57	37	61
10	PdCl <sub>2</sub>	MeOH	2	60	34	64
11	PdCl <sub>2</sub>	<i>i</i> -PrOH	3	48	44	52

<sup>a</sup> All reactions were carried out under the pressure of CO (40 atm) and 60°C for 24 h, 1 mol% of Pd(OAc)<sub>2</sub> and 3 mol% of PdCl<sub>2</sub> were used separately.

**Scheme 2****Experimental**

<sup>1</sup>H NMR spectra were taken at 400 MHz with CD-Cl<sub>3</sub> as solvent. GC data were obtained by VARIAN3700 GC and the reagents were used as commercially received.

*General procedure for the addition of CO and CCl<sub>4</sub> to 1-octene*

In a 10 mL stainless steel autoclave were added 2 mmol of 1-octene, 2 mmol of pyridine, 1 mL of CCl<sub>4</sub>, 4

mL of EtOH and 3 mol% of palladium black. The reactions were carried out under appointed temperature and pressure for 24 h. After venting of CO and removing the metal species and solvent, the products were determined using GC (quantitative analysis) and then <sup>1</sup>H NMR (400 MHz) after the products were purified by column chromatography (silica gel, hexane-ether).

*Methyl 2-(2,2,2-trichloroethyl) octanoate (1a)*<sup>7</sup>

<sup>1</sup>H NMR δ: 3.71 (s, 3H, CHCOOCH<sub>3</sub>), 3.35 (q, *J* = 9.2 Hz, 1H, CHCOOCH<sub>3</sub>), 2.62–2.91 (m, 2H, CHCH<sub>2</sub>CCl<sub>3</sub>), 1.18–1.72 (m, 10H), 0.87 (t,

$J = 6.4$  Hz, 3H).

*Ethyl 2-(2,2,2-trichloroethyl) octanoate (1b)*<sup>7</sup>

<sup>1</sup>H NMR  $\delta$ : 4.14 (q,  $J = 7.2$  Hz, 2H, CHCOOCH<sub>2</sub>-CH<sub>3</sub>), 3.35 (q,  $J = 9.2$  Hz, 1H, CHCOOCH<sub>2</sub>CH<sub>3</sub>), 2.62—2.88 (m, 2H, CHCH<sub>2</sub>CCl<sub>3</sub>), 1.20—1.73 (m, 13H), 0.85 (t,  $J = 6.0$  Hz, 3H).

*i-Propyl 2-(2,2,2-trichloroethyl) octanoate (1c)*<sup>7</sup>

<sup>1</sup>H NMR  $\delta$ : 4.99—5.05 (m, 1H, CHCOOCH-C<sub>2</sub>H<sub>6</sub>), 3.38 (q,  $J = 9.2$  Hz, 1H, CHCOOCHC<sub>2</sub>H<sub>6</sub>), 2.60—2.83 (m, 2H, CHCH<sub>2</sub>CCl<sub>3</sub>), 1.17—1.71 (m, 16H), 0.87 (t,  $J = 6.4$  Hz, 3H).

*1,1,1,3-Tetrachlorononane (2)*<sup>7</sup> <sup>1</sup>H NMR  $\delta$ :

4.20—4.27 (m, 1H, C<sub>6</sub>H<sub>13</sub>CHClCH<sub>2</sub>CCl<sub>3</sub>), 3.08—3.28 (m, 2H, C<sub>6</sub>H<sub>13</sub>CHClCH<sub>2</sub>CCl<sub>3</sub>), 1.20—1.91 (m, 10H), 0.85 (t,  $J = 6.8$  Hz, 3H).

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