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Hydroesterification of 1-alkenes in Supercritical Carbon dioxide

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Abstract The palladium catalysed hydroesterification of linear alkenes to obtain carboxylic esters in supercritical carbon dioxide is studied for the first time. Palladium complexes with phosphines containing $–CF_3$ groups are used as catalyst precursors. For 1-hexene, conversions into the corresponding methyl esters up to 67% were obtained using $[PdCl_2(PhCN)_2]/P(3,5\text{-}CF_3C_6H_4)_3$.

Keywords Homogeneous catalysis · Hydroesterification · Alcoxycarbonylation · Carbonylation · Palladium · Supercritical carbon dioxide

1 Introduction

Palladium-catalyzed hydroesterification of alkenes (Scheme 1) is a straightforward and environmental friendly method for obtaining carboxylic esters with a selectivity of 100% [1, 2]. In this reaction (Scheme 1), two regioisomers can be formed: the branched (b) and the linear (l). Carboxylic esters have important industrial applications as large volume products, and chemical intermediates such as methyl-propanoate, are used in the methyl metacrylate synthesis. Linear esters are used to synthesize detergents and nylons. Other products of interest include 2-arylpropranoate derivatives, which are transformed to the most important classes of non-steroidal anti-inflammatory drugs [3].

This reaction has been studied in depth in organic solvents. Two mechanisms were proposed for the catalytic cycle (Fig. 1). The first one is the alcoxy-mechanism, in which the initial species is an alcoxy intermediate $[Pd–OR']^+$; it was proposed for the first time by Milstein, in 1988 [4] (Fig. 1a). The second mechanism is the hydride-mechanism, in which the active species is the hydride intermediate $[Pd–H]^+$; this was proposed by Knifton, in 1976 (Fig. 1b) [5–7]. Furthermore, the regiocontrol depends on the ligand used. It was determined that chelated diphosphine ligand leads to a stabilization of the *cis* intermediate to yield the linear ester as a major product [8]. On the other hand, the monophosphine ligand favors the *trans* intermediate species, leading to the formation of branched esters.

The use of supercritical fluid (SCF) is attracting considerable attention as an alternative reaction medium to environmentally hazardous organic solvents in green chemistry and catalysis. SCFs with characteristic properties of both liquid- and gas-phase offer a great opportunity to tune the chemical reactivity and to attain the desired selectivity [9–12]. The supercritical carbon dioxide ($scCO_2$) has been used in a growing number of applications by the end of the last decade [13–15]. Several features of $scCO_2$ make it an interesting solvent. The critical point of CO_2 is easily accessible at a T_c of 31 °C and a P_c of 73 atm. In addition, carbon dioxide is non-toxic, chemically inert towards many substances, non-flammable; furthermore, simple depressurisation results in its removal and by changing pressure and temperature, it can be easily recovered [9, 16].

Nowadays, few examples of hydroesterification of alkenes are known in multiphasic systems [17] and only one example of hydroesterication of norbornene in supercritical carbon dioxide has been described in the literature [18].

Here, we present the first example of hydroesterification of linear alkenes in supercritical carbon dioxide media using the catalytic precursor formed with $[PdCl_2(PhCN)_2]$ and phosphine ligands containing fluorinated groups (**1**–**2**, Fig. 2). In a previous paper, we reported the solubility

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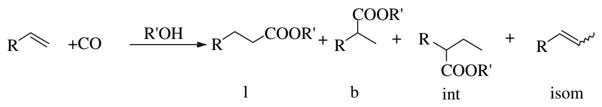


Scheme 1 Hydroesterification reaction of alkenes

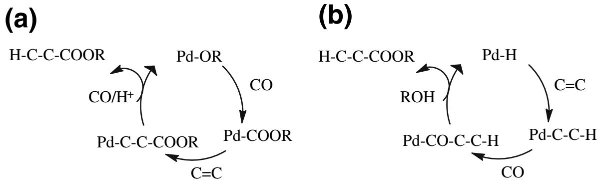


Fig. 1 Catalytic cycles for the hydroesterification reaction with palladium and diphosphine ligand. (**a**) Palladium alcoxy cycle; (**b**) Palladium hydride cycle

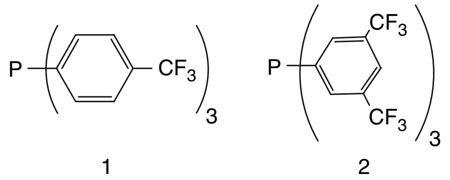


Fig. 2 Phosphines containing fluorine groups (**1**–**2**) used as ligands in the Pd-catalysed hydroesterification of 1-alkenes

studies of the systems [$PdCl_2(PhCN)_2$]/**1**–**2** and the analogous hydrocarboxylation reaction was performed [19]. We observed that the palladium–phosphine **2** system (150 atm., 65 °C) was soluble at milder conditions than was the palladium–phosphine **1** system (175 atm., 75 °C).

2 Experimental

2.1 General Remarks

Compounds **1**–**2** are commercially available and were used without purification. The syntheses of the palladium complex [$PdCl_2(PhCN)_2$] was performed according to previously described procedures [20]. All olefins used as substrates were filtered over alumina before being used. All materials were obtained from Aldrich and Fluorochem. Carbon dioxide (SCF Grade, 99.999%) was obtained from Air Products and Linde) and carbon monoxide (99.99%) was supplied by Air Liquid.

2.1.1 Safety Warning

Experiments involving pressurized gases can be hazardous and must be conducted with suitable equipment and only following appropriate safety conditions.

2.2 Hydroesterification Reaction

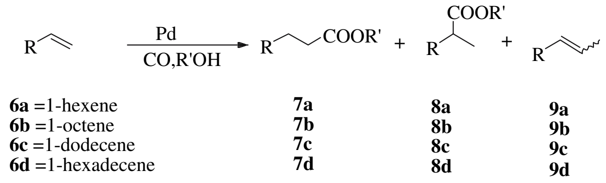
For the catalytic experiments, the palladium precursor [$PdCl_2(PhCN)_2$] (0.025 mmol) with the phosphine (0.1 mmol) were loaded into a 25 mL stainless steel reactor vessel. The system was purged with nitrogen/vacuum. The corresponding amount of degassed alcohol, substrate (1.562 mmol), chlorhidric acid (0.0077 mmol) and undecane (97.5 mg), used as the GC internal standard, were mixed and charged in vacuum. The CO gas was then charged, the reactor pressurized to the desired pressure and the liquid carbon dioxide introduced. The contents were then heated. The compressed carbon dioxide was introduced to attain the desired reaction pressure and magnetically stirred (750 rpm). After the reaction, the vessel was cooled with ice water to 0 °C and slowly depressurized to atmospheric pressure through a cold trap. The reaction mixture was extracted with diethylether and analyzed by gas chromatography.

Dimethoxy ethane (DME) was used as organic solvent in the comparative experiments, which were conducted with a 100 mL autoclave following the preceding procedure, without the CO_2 charge.

3 Results and Discussion

The hydroesterification of higher alkenes **6a**–**d** (Scheme 2) in the presence of an alcohol was studied using a catalyst precursor prepared in situ by the addition of the complex [$PdCl_2(PhCN)_2$], the corresponding ligand **1**–**2** (Pd/**1**–**2** systems), an alcohol and using supercritical carbon dioxide as solvent. The products obtained were the corresponding linear esters (**7a**–**d**) and branched esters (**8a**–**d**). The corresponding isomerised alkenes (**9a**–**d**) were the main by-products of the reaction. For comparative purposes, reactions were also studied using a standard catalyst precursor [$PdCl_2(PPh_3)_2$] in an organic solvent and using reaction conditions selected based on previous studies [21].

The hydroesterification of 1-hexene was first studied using the Pd/**1** and Pd/**2** catalyst precursors in $scCO_2$ at 200 atm and at 150 atm of total pressure. Under these conditions, in which the catalytic systems are soluble, low conversion and selectivity in esters were obtained (entries 1



Scheme 2 Products obtained in alcoxycarbonylation of different linear alkenes

and 2, Table 1). The main by-products were isomerisation products.

Upon decreasing the total pressure to values in which the catalytic systems were not soluble in the reaction media (150 for Pd/**1** and 120 atm. for Pd/**2**), the conversion and selectivity improved. The best results were obtained using the Pd/**2** catalytic system, which provided a 67% of conversion and a 64% of selectivity in esters (entry 4, Table 1). The increase of conversion and selectivity when the catalytic system was not soluble was also observed in the analogous hydrocarboxylation of 1-octene in $scCO_2$ [19]. In fact, in the literature there are many reports on catalytic systems which are insoluble under the conditions used for the carbonylation of alkenes in $scCO_2$. The advantage of these systems is the possibility of recycling of the catalysts after product extraction with $scCO_2$ [22]. A moderated regioselectivity to the branched esters was observed in our case. This was also reported by Guiu et al. in the hydroesterification of styrene using diphosphine modified with CF_3-groups catalyst precursors [23].

The presence of $scCO_2$ was necessary to have catalytic activity of the catalyst since when we performed the reaction in net 1-hexene, no esters were detected and considerable amount of Pd(0) at the end of the reaction was observed.

The alcohol plays an important role in this reaction because it determines the termination step to obtain the carboxylic ester. Thus, the amount and nature of the alcohol was changed to study this effect. Upon increasing the amount of alcohol, the conversion and the selectivity dropped off, regardless of whether the catalytic system was soluble or not (entries 5 and 6, Table 1). This could be because the higher concentration of alcohol might lead to a competition for coordination vacant at the catalyst centre and decreased the conversion. A similar inhibiting effect of water was observed in the hydrocarboxylation of alkenes [24].

Using other alcohols, we observed the formation of oligomers and a low conversion to esters. Using trifluoroethanol, only oligomers were obtained (entry 7, Table 1). Using t-BuOH and EtOH, a decrease in conversion was observed (entries 8 and 9, Table 1), probably due to the higher steric hindrance of these alcohols, which decreases the rate of the nucleophilic attack step, as previously reported [25, 26]. This also agrees with the results reported for monophosphine PPh_3 complexes, in which the chemoselectivity of the reaction was observed to depend on the alcohol used. The relative growth rate versus termination rates was reported to increase in the order $CF_3CH_2OH > t\text{-BuOH} > EtOH > MeOH$ [27–29].

These experiments lead us to conclude that the best conditions of pressure and temperature for hydroesterification of 1-hexene were 30 atm of carbon monoxide pressure, 90 °C and 120 atm of total pressure using Pd/**2** catalytic system. This result was better than the results obtained with the palladium catalytic system with PPh_3 in $scCO_2$ (entry 10, Table 1); however, the conversion and selectivity were lower than obtained in an organic solvent (dimethoxyethane) under conditions similar to $[PdCl_2(PPh_3)_2]/4PPh_3$ catalytic system (entry 11, Table 1). The conversion obtained with other long chain substrates **6b–d** in $scCO_2$ with the best conditions found for 1-hexene decreased as the chain length increased.

In conclusion, hydroesterification reactions can be performed with supercritical carbon dioxide as a solvent and using palladium catalysts with phosphines containing $-CF_3$ groups. Using $[PdCl_2(PhCN)_2]$ and phosphines as catalyst precursors, the conversion in the carbonylation of 1-hexene was better when the catalyst was not soluble in $scCO_2$. Using these systems, the best conversions were up to 67%,

Table 1 Hydroesterification of alkenes 1-hexene (**6a**) with Pd/**L** systems[a]

Entry	L	Substrate	P_T^b	ROH	ROH/Pd	%C[c]	$S^d_{7,8}$	7/8	S^e_9
1	**1**	**6a**	200	MeOH	375	69	0^f	0	44
2	**2**	**6a**	150	MeOH	375	44	20	45/55	80
3	**1**	**6a**	150	MeOH	375	40	18^f	51/49	8
4	**2**	**6a**	120	MeOH	375	67	64^g	$45/46^h$	4
5	**2**	**6a**	120	MeOH	2,470	14	26	50/50	19
6	**2**	**6a**	150	MeOH	2,470	34	14	33/66	86
7	**2**	**6a**	150	TFE	375	0^f	–	–	–
8	**2**	**6a**	120	*t*-BuOH	375	28	100	69/31	–
9	**2**	**6a**	120	EtOH	375	0	–	–	–
10	PPh_3	**6a**	120	MeOH	375	0	–	–	–
11[j]	PPh_3	**6a**	30	MeOH	375	82	99	$46/52^i$	–
12	**2**	**6b**	120	MeOH	375	25	35^k	86/14	36
13	**2**	**6c**	120	MeOH	375	5	98	15/85	2
14	**2**	**6d**	120	MeOH	375	12	8	42/58	92

[a] Pd/L/substrate/HCl(0.1 N) = 1/4/62.5/0.31; $[PdCl_2(PhCN)_2] = 1.10^{-3}$ M; P_{CO}: 30 atm; time: 12 h; T° = 90 °C; [b] Total pressure; [c] Total conversion; [d] Selectivity in carboxylic esters; [e] Selectivity in internal alkenes; [f] oligomers are also formed; [g] oligomers and acids were also formed, [h] 9% of methyl-3-ethylpentanoate; [i] 1% of methyl-3-ethylpentanoate; [j] dimethoxyethane used as a solvent, [k] 29% of aldehydes were also formed

with selectivities in the ester up to 64%. The regioselectivity in the branched ester was moderate, but in the expected range. The conversions obtained for higher alkenes were lower.

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