

## Chlorocarbonylation of Unsaturated Substrates Catalysed by Palladium Complexes in the Presence of Anhydrous HCl

Nathalie Bénard,<sup>a</sup> Michel C. Bonnet,<sup>a</sup> Serge Lécolier<sup>b</sup> and Igor Tkatchenko\*<sup>a</sup>

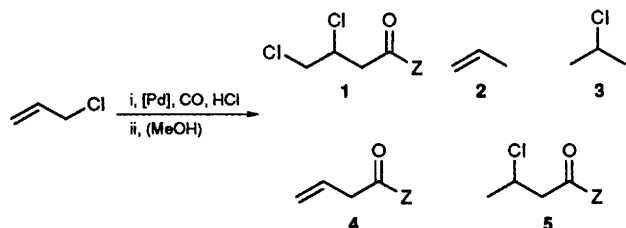
<sup>a</sup> Laboratoire de Chimie Coordination de CNRS, 205 Route de Narbonne, 31077 Toulouse Cedex, France†

<sup>b</sup> Centre de Recherches du Bouchet, SNPE, BP 2, 91710 Vert le Petit, France

Chloroacyl halides are obtained under mild conditions by catalytic carbonylation of allylic halides or ethene and allyl chloride under CO and anhydrous HCl pressure; excellent selectivities for formation of dichloroacyl and chloroacyl derivatives are achieved.

The catalytic carbonylation of allyl halides to give acyl halides or acids and esters is well documented.<sup>1</sup> However, the simultaneous chlorination-carbonylation of such substrates has only been exemplified by the work of Tsuji *et al.*<sup>2</sup> The reaction is stoichiometric and affords only poor yields of the dichlorinated acyl product, based on PdCl<sub>2</sub>. We report a new catalytic system for such a double functionalization reaction leading to chloroacyl and dichloroacyl chlorides (Scheme 1) which uses HCl as a source of chlorine, and CO and Pd compounds.

For example, the reaction with allyl chloride is catalysed by zero- or di-valent Pd compounds, *e.g.* PdCl<sub>2</sub>, PdCl<sub>2</sub>(PhCN)<sub>2</sub>, [Pd(CO)Cl]<sub>n</sub>,<sup>3</sup> Pd(dba)<sub>2</sub> or even 10% Pd/C, under moderate pressures of carbon monoxide and hydrogen chloride. The expected product, 3,4-dichlorobutanoyl chloride **1a**, was recovered from the reaction medium in high purity [>98%; MS (Cl, CH<sub>4</sub>): *m/z* 179 (6.4), 177 (21.8), 175 (22.2), 143 (9.5),



Scheme 1

a; Z = Cl  
b; Z = OMe

141 (61.8) and 139 (100); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 3.3 (dd, <sup>2</sup>J = 17.8, <sup>3</sup>J = 8.5 Hz, 1H), 3.65 (dd, <sup>2</sup>J = 17.8, <sup>3</sup>J = 4.2 Hz, 1H), 3.7 (dd, <sup>2</sup>J = 11.6, <sup>3</sup>J = 8.1 Hz, 1H), 3.86 (dd, <sup>2</sup>J = 11.6, <sup>3</sup>J = 4.5 Hz, 1H) and 4.37–4.49 (m, 1H)]. GC and GC-MS also indicated the formation of hydrogen and phosgene (traces), propene **2**, 2-chloropropane **3**, but-3-enoyl chloride **4a** and 3-chlorobutanoyl chloride **5a** (Table 1). Systematic studies have been carried out with further methanolysis of the reaction mixture in order to simplify GC analysis.‡

A solvent is not necessary, but reactions are best carried out in solution. The best solvents are aprotic ones, such as halogenated hydrocarbons (CH<sub>2</sub>Cl<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> *etc.*). Catalytic runs performed at different temperatures and pressures (total and partial pressures) show that the reaction occurs above 60°C, but that the formation of **1** depends slightly on the total and partial pressures, except for the *p*(HCl)/*p*(CO) = 1. Noteworthy is the increase in the yield of **4** with the amount of HCl present and occurrence of **1** but not **4** at lower temperatures.

The reaction could be extended to other allyl chlorides with different results depending on the nature of the substituents. Methallyl chloride, allylbenzene and cinnamyl chloride are converted with HCl to the addition products 1,2-dichloro-2-methylpropane, 1-chloro- and 2-chloro-propylbenzene, and 1,3-dichloropropylbenzene, respectively. Crotyl chloride and

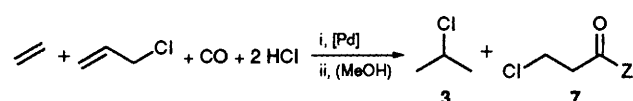
‡ MS (Cl, NH<sub>3</sub>): *m/z* 192 (2.8), 190 (20.4), 188 (29.4), 99 (100%); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 2.75 (dd, <sup>2</sup>J = 16.5, <sup>3</sup>J = 8.5 Hz, 1H), 3.00 (dd, <sup>2</sup>J = 16.5, <sup>3</sup>J = 4.7 Hz, 1H), 3.73 (s, 3H), 3.75 (dd, <sup>2</sup>J = 11.4, <sup>3</sup>J = 7.6 Hz, 1H), 3.85 (dd, <sup>2</sup>J = 11.4, <sup>3</sup>J = 4.8 Hz, 1H) and 4.39–4.52 (m, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (50.3 MHz, CDCl<sub>3</sub>): δ 47.2 (CH<sub>2</sub>), 52.6 (CH), 39.8 (CH<sub>2</sub>), 51.9 (Me) and 170.2 (CO).

† Associated with the Université Paul Sabatier and the Institut National Polytechnique de Toulouse.

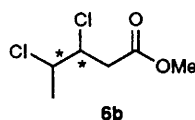
**Table 1** Catalytic carbonylation of allyl chloride<sup>a</sup>

Palladium complex	t/h	p/bar			1a/b (%)	2 (%)	3 (%)	4a/b (%)	5a/b (%)	Selectivity 1 (%)
		CO	HCl	N <sub>2</sub>						
PdCl <sub>2</sub>	16	48	9	—	31	18	27	2	11	70
PdCl <sub>2</sub>	8	48	9	—	30	20	24	2	8	75
PdCl <sub>2</sub>	4	48	9	—	25	19	22	3	5	76
PdCl <sub>2</sub>	2	48	9	—	24	16	22	2	4	80
PdCl <sub>2</sub>	4	24	24	—	29	13	21	36	Tr. <sup>j</sup>	45
PdCl <sub>2</sub>	4	24	9	15	36	15	26	5	2	84
PdCl <sub>2</sub>	4	24	14	10	41	12	27	7	1	84
PdCl <sub>2</sub>	4	24	18	6	42	12	28	9	1	81
PdCl <sub>2</sub>	4	12	9	27	38	18	27	3	5	83
PdCl <sub>2</sub>	4	18	9	21	34	14	25	6	1	83
PdCl <sub>2</sub>	4	36	9	3	39	14	27	3	5	83
PdCl <sub>2</sub>	4	16	6	11	25	28	19	3	1	86
PdCl <sub>2</sub>	4	12	9	12	29	27	23	6	1	81
PdCl <sub>2</sub>	4	24	9	—	26	22	23	3	1	87
PdCl <sub>2</sub> <sup>b</sup>	4	24	9	—	8	8	7	Tr.	Tr.	89
PdCl <sub>2</sub> <sup>c</sup>	4	24	9	—	12	12	9	1	Tr.	92
PdCl <sub>2</sub> <sup>d</sup>	4	24	9	—	41	20	23	12	2	74
PdCl <sub>2</sub> <sup>e</sup>	4	24	9	—	30	15	19	3	1	91
PdCl <sub>2</sub> <sup>f</sup>	4	24	9	—	0	0	0	3	Tr.	0
PdCl <sub>2</sub> <sup>g</sup>	4	24	9	—	23	33	15	4	1	82
Pd/C	4	24	9	—	30	17	29	9	3	71
Pd(acac) <sub>2</sub> <sup>j</sup>	4	24	9	—	30	28	21	4	2	83
[(C <sub>3</sub> H <sub>5</sub> )PdCl] <sub>2</sub>	4	24	9	—	29	22	20	3	1	88
Pd(dba) <sub>2</sub> <sup>j</sup>	4	24	9	—	22	18	18	2	1	88
Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	4	24	9	—	0	2	1	3	Tr.	0
PdCl <sub>2</sub> <sup>h</sup>	4	24	9	—	29	19	19	3	1	88
PdCl <sub>2</sub> <sup>i</sup>	4	24	9	—	25	28	16	2	2	86

<sup>a</sup> Conditions (unless noted otherwise): 100 mmol of C<sub>3</sub>H<sub>5</sub>Cl and 2 mmol of Pd catalyst in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) at 100 °C. <sup>b</sup> 60 °C. <sup>c</sup> 80 °C. <sup>d</sup> 130 °C. <sup>e</sup> C<sub>2</sub>H<sub>5</sub>Cl<sub>2</sub> solvent (10 ml). <sup>f</sup> MeOH solvent (10 ml). <sup>g</sup> No solvent. <sup>h</sup> 1 mmol of PdCl<sub>2</sub>. <sup>i</sup> 0.5 mmol of PdCl<sub>2</sub>. <sup>j</sup> Tr = trace; Hacac = pentan-2,4-dione; dba = dibenzylideneacetone.



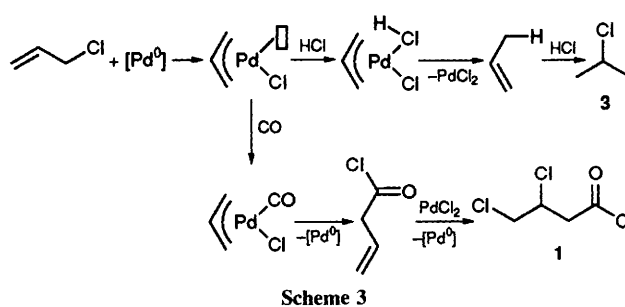
**Scheme 2**  
a; Z = Cl  
b; Z = OMe



3-chlorobut-1-ene gives the same dichloroester **6b** (GC-MS, two diastereoisomers) and products of the addition of HCl to the corresponding allyl halides and unsaturated esters.

This new synthesis of 3,4-dichlorobutanoyl chloride is a considerable improvement on the only method described so far. The halogen source during the catalytic process could be chloride, phosgene, chloride ion or palladium chloride.

The reaction performed under a pressure of chlorine and carbon monoxide (respectively 5 and 24 bar), in the presence of palladium chloride, at 100 °C, for 4 h gives only 1,2,3-trichloropropane. This reaction proceeds easily, even at room temperature and without any metal as catalyst. Blank experiments show that 1,2,3-trichloropropane is not converted to **1**. The reaction run with phosgene does not occur in the absence of carbon monoxide. Compound **1** can be obtained under CO pressure, but in low yield (maximum 3%). Moreover, the IR spectrum of the gaseous products shows the presence of phosgene, carbon monoxide, hydrogen chloride and carbon dioxide, indicating some phosgene hydrolysis. The presence of water in small quantity is an inevitable consequence of the introduction of phosgene. Finally, the carbonylation of allyl



chloride with an equimolar amount of dimethylammonium chloride does not occur. Moreover, the addition of dimethylammonium chloride (2 equiv. with respect to PdCl<sub>2</sub>) to the catalytic system (24 bar CO and 9 bar HCl) completely inhibits the carbonylation. The reaction is also prevented when protic reagents (water, alcohols) are added to the system, even in small quantities. Coordinating ligands, such as phosphines (in the preformed catalyst or in addition to the reaction medium) also inhibit the reaction.

At the end of the reaction, the mixture consists of two phases: a red solution and a green precipitate. Each phase contains a different palladium compound, which has been isolated and reused for the carbonylation of allyl chloride. Both species are active and give identical results. However the yield of 3,4-dichlorobutanoyl chloride is somewhat lower.

Blank experiments indicate that the formation of 2-dichloropropane and propene requires the presence of both CO and HCl. The absence of CO leads mainly to the formation of the adduct of HCl with allyl chloride. Inspection of Table 1 clearly shows that the amount of **1** formed corresponds generally to the amount of propene and 2-chloropropane evolved, therefore suggesting that one-half of the allyl chloride is sacrificed

for the synthesis of **1**. It is noteworthy that the chlorocarbonylation of ethene to give **7** (Scheme 2) occurs only if allyl chloride is added to the reaction medium [conditions:  $p(\text{C}_2\text{H}_4) = 12$  bar,  $p(\text{CO}) = 12$  bar,  $p(\text{HCl}) = 9$  bar;  $\text{C}_3\text{H}_5\text{Cl} = 100$  mmol;  $100^\circ\text{C}$ ; 4 h].

This reaction corresponds to the formal addition of the elements of phosgene to a double bond. However, no phosgene is detected in the reaction medium and, furthermore, phosgene does not react with ethene under the reaction conditions, even in the presence of  $\text{PdCl}_2$ .

Since crotyl chloride and 3-chlorobut-1-ene give rise to the same product distributions, we suggest that the reaction occurs *via* the carbonylation of an allyl complex obtained from the oxidative addition of the allyl chloride to a zerovalent palladium compound. The key steps would be: (i) the generation of  $\text{PdCl}_2$  and, (ii) the chlorination of **4** by  $\text{PdCl}_2$  which should be more rapid than HCl addition to a double bond (Scheme 3). In fact, reaction of allylchloropalladium dimer with an excess of dry HCl in dichloromethane gives quantitative yields of  $\text{PdCl}_2$  and **3**, a process which has some precedent with the recent observation of protonation of allylmolybdenum complexes in the presence of dry HCl.<sup>4</sup> Addition of  $\text{PdCl}_2$  to unsaturated substrates has been studied by several groups<sup>5</sup> and occurs under mild conditions; it could be assisted in the present case by the chelating nature of **4a**.

We are studying the generalisation of these reactions, especially with the objective of replacing allyl chloride by other systems capable of regenerating  $\text{PdCl}_2$ .

N. B. thanks the CNRS and SNPE for a fellowship.

Received, 22nd June 1993; Com. 3/03598K

## References

- 1 W. T. Dent, R. Long and G. H. Whitfield, *J. Chem. Soc.*, 1964, 1588; D. Medema, R. van Helden and C. F. Kohll, *Inorg. Chim. Acta*, 1969, **3**, 255.
- 2 J. Tsuji, M. Morikawa and J. Kiji, *J. Am. Chem. Soc.*, 1964, **86**, 4851.
- 3 W. Schnabel and E. J. Kober, *J. Organomet. Chem.*, 1969, **19**, 455.
- 4 K. E. Oglieve and R. A. Henderson, *J. Chem. Soc., Chem. Commun.*, 1993, 474 and references therein.
- 5 J. Tsuji, M. Morikawa and J. Kiji, *Tetrahedron Lett.*, 1963, 1061; J. Tsuji, M. Morikawa and J. Kiji, *J. Am. Chem. Soc.*, 1964, **86**, 2095; J. Tsuji, J. Kiji, S. Iwamura and M. Morikawa, *J. Am. Chem. Soc.*, 1964, **86**, 4350; J. Tsuji, M. Morikawa and J. Kiji, *Tetrahedron Lett.*, 1965, 817; J. Tsuji, *Acc. Chem. Res.*, 1969, **2**, 144; A. U. Blackham, US Pat. 3,119,861 (1964, National Distillers), *Chem. Abstr.*, 1964, **60**, 9155.