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Carbonylation reactions
8. Chlorocarbonylation reactions: catalytic formation of chloroacyl chlorides without phosgene and application to the synthesis of 2(H)-5-furanone

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Abstract

Chloroacyl halides are obtained under mild conditions by catalytic carbonylation in halogenated solvents of allylic halides or ethylene and allyl chloride mixtures under pressure of CO and anhydrous HCl in the presence of $PdCl_2$; excellent selectivities for dichloroacyl and chloroacyl derivatives are achieved. Allyl chloride is partly consumed for the regeneration of palladium chloride. The product of oxidative addition of HCl to the oligomeric $[Pd(CO)Cl]_n$ formed in situ by reaction of CO on $PdCl_2$ is proposed as the first step towards the generation of the active species. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Acyl halides and their halogenated derivatives are worthy intermediates for the synthesis of fine chemicals [1,2]. The most attractive way to prepare these compounds could be by transition metal-catalysed carbonylation, either via stepwise incorporation of carbon monoxide and chlorine to an unsaturated substrate or through the formal insertion of carbon monoxide into a C–Cl bond [3]. Indeed, acyl halides are reported as active intermediates in several processes leading to carboxylic acids [4] and esters [5]. Carbonylation of allyl halides is well-documented (Scheme 1) and involves (η^3-allyl) complexes which can generate acyl halides, especially in the case of palladium [6,7] or different families of acids and ketoacids and their esters when further reactions with ethylene or acetylene are possible, as in the case of nickel [8]. The reaction of terminal alkenes (Eq. (1)) is much less facile. Of all the elements of groups 8–10 examined, palladium appears to be the

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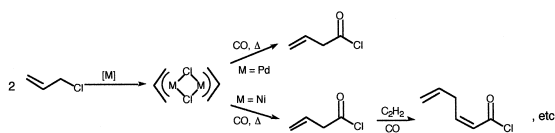
Scheme 1.

most efficient, although the reactions proceed at relatively high pressures [9,10] except in the presence of additional Lewis acids like $GeCl_2$ or $SnCl_2$ [11]. Yet, for all the cases reported, the yields are low, due mostly to a poor selectivity for the chlorocarbonylation process.

$$R\diagup\diagdown + CO + HCl \xrightarrow[\text{5-3000 bar}]{\text{[Pd], 30-250°C}} R\diagup\diagdown\diagup\text{Cl} \qquad (1)$$
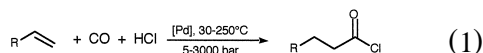
The simultaneous chlorination–carbonylation of olefins has been mostly exemplified by Tsuji et al. β-Chloroacyl chlorides [12] and the corresponding esters [13] are produced from terminal olefins in low yields, based on $PdCl_2$ (Eq. (2)). In addition, some 3,4-dichlorobutanoates are formed when allyl chloride is the starting product [14]. It is noteworthy that the reaction of olefins with CO in the presence of carbon tetrachloride is catalysed by binuclear metal carbonyls and affords β-trichloromethylacyl chlorides in satisfactory yields [15,16]. Therefore, if a halogen source is available, a catalytic process can be achieved. In fact, addition of excess copper(II) chloride [17] or of phosgene [18] favours the catalytic conversion of ethylene into 3-chloropropionyl chloride, albeit under drastic conditions.

$$R\diagup\diagdown + CO + PdCl_2 \longrightarrow R\diagup\diagdown\diagup\text{Cl} + Pd(0) \qquad (2)$$
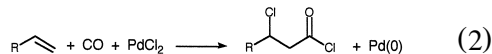
We report herein a new catalytic system for such a double functionalisation reaction leading to chloroacyl and dichloroacyl chlorides which use hydrogen chloride as a source of chlorine, CO, and Pd compounds and the application of these intermediates for the preparation of 2(H)-5-furanone, a useful building-block for bioactive molecules. A preliminary account of part of this work has been given [19].

2. Experimental

2.1. Materials

Chlorine (Air Liquide N27), carbon monoxide (Air Liquide N20 and N60), ethylene (Air Liquide N25), hydrogen chloride (Air Liquide, electronic grade), and phosgene (SNPE) were used as such. Buta-1,3-diene is dried over molecular sieves; allylic halides are distilled under argon over phosphorous anhydride. Acetonitrile, dichloromethane, and dichloro-1,2-ethane are distilled under argon over phosphorous anhydride; methanol is distilled under argon in the presence of magnesium chips; diethyl ether and toluene are distilled under argon over sodium/benzophenone. Anhydrous copper(II) chloride (Janssen, 98%) and palladium chloride (Johnson Matthey) are used as such. 10% Pd/C (Aldrich) has been analysed for palladium (7.98%) and chlorine (1.06%) and is used as such. $PdCl_2(PhCN)_2$, $[(\eta^3-C_3H_5)PdCl]_2$, $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ are prepared according to Refs. [20–23]; $[Pd(MeCN)_4](BF_4)_2$ is obtained by protonation of $Pd(acac)_2$ with $HBF_4 \cdot OEt_2$ in acetonitrile [24].

2.2. Catalytic chlorocarbonylations

Caution! All the following experiments are run in a dedicated facility equipped with efficient fume cupboards, carbon monoxide, chlorine, and phosgene detectors.

All catalytic runs are performed in a 100-ml Hastelloy C276 autoclave equipped with a double envelope for heating with an oil-circulating bath. The cover of the autoclave is supplied with a thermocouple probe; a stopcock for the introduction of the catalyst solution and two valves for introduction of gases and sampling, respectively; a manometer (0–200 bar); and a safety valve adjusted to 100 bar. The agitation is ensured with a magnet bar.

In the standard test, $PdCl_2$ (355 mg, 2 mmol) and allyl chloride (7.65 g, 100 mmol) are placed in a Schlenk tube under argon. The suspension

is introduced in the autoclave and the Schlenk tube rinsed with dichloromethane (2×3 ml, 2×2 ml). The autoclave is pressurised with HCl (9 bar) and CO (24 bar) successively. The autoclave is heated to 100°C for 4 h. The reaction is first quenched by cooling in a water bath (ca. 20°C), then in an acetone bath (-20°C). The remaining gases are vented through a dry ice trap, and methanol (4 ml, 100 mmol) is slowly added to the reaction mixture which is stirred for 20 min until the evolution of HCl stops. Samples can be taken at given intervals, quenched at -20°C with methanol and analysed. Propene is estimated as the difference between the amounts of converted allyl chloride and evolved 2-chloropropane. Each experiment is duplicated and in some cases, triplicated.

GC analysis is performed with a 10% Carbowax on Gas Chrom Q (80–100 mesh) column (2 m $\times 1/8''$; gas vector: nitrogen at 14 ml min^{-1}; injection temperature: 270°C; detection temperature: 250°C; temperature programmation: 60°C during 0.5 min, 8°C min^{-1} up to 160°C) using ethyl crotonate as internal standard.

Hydrogen chloride could be replaced by the appropriate amounts of chlorine or phosgene by weighting the autoclave before and after addition of the reagent. Reactions in the presence of additives are run under the same conditions, the appropriate amount of additive being placed after PdCl$_2$ in the Schlenk tube.

Chlorocarbonylation of ethylene is run under the same conditions, the order of addition of the gases being: (1) HCl (9 bar), (2) ethylene (partial pressure = 12 bar), and (3) carbon monoxide (partial pressure = 12 bar).

2.3. Product identification

2.3.1. *4a*: IR (neat, KBr): 1800 cm^{-1} (ν_{CO})

MS (CI, CH$_4$) m/z: 179 (6.4), 177 (21.8), 175 (22.2) [C$_3$H$_6$Cl$_2$COCl$^+$]; 143 (9.5), 141 (61.8), 139 (100) [C$_3$H$_5$Cl$_2$CO$^+$]; 115 (1.3), 113 (8.9), 111 (13.7) [C$_3$H$_5$Cl$_2^+$]; 105 (4.2), 103 (13.8) [C$_3$H$_4$ClCO$^+$].

MS (EI, 70 eV) m/z: 143 (10), 141 (67), 139 (100) [C$_3$H$_5$Cl$_2$CO$^+$]; 115 (2.6), 113 (15.7), 111 (26.2) [C$_3$H$_5$Cl$_2^+$]; 105 (4.2), 103 (13.8) [C$_3$H$_4$ClCO$^+$]; 77 (32), 75 (95) [C$_3$H$_4$Cl$^+$]; 39 (93) [C$_3$H$_3^+$].

^{1}H NMR (200 MHz, CDCl$_3$): δ 3.3 (dd, $^2J = 17.8$, 3J = 8.5 Hz, 1H), 3.65 (dd, $^2J = 17.8$ $^3J = 4.2$ Hz, 1H), 3.7 (dd, $^2J = 11.6$, $^3J = 8.1$ Hz, 1H), 3.86 (dd, $^2J = 11.6$ $^3J = 4.5$ Hz, 1H), 4.37–4.49 ppm (m, 1H).

^{13}C NMR (50.3 MHz, CDCl$_3$): δ 46.3 ($J_{^{13}C-H} = 154$ Hz, –CH$_2$Cl), 51.5 ($J_{^{13}C-H} = 134$ Hz, –CH2–), 53.5 ($J_{^{13}C-H} = 156$ Hz, –CH–), 170.1 ppm (CO).

2.3.2. *4b*: IR (neat, KBr): 1723 cm^{-1} (ν_{CO})

MS (CI, NH$_3$) m/z: 192 (2.8), 190 (20.4), 188 (29.4) [C$_3$H$_5$Cl$_2$CO$_2$MeNH$_4^+$]; 99 (100) [C$_3$H$_4$CO$_2$Me$^+$].

MS (EI, 70 eV) m/z: 143 (10), 141 (67), 139 (100) [C$_3$H$_5$Cl$_2$CO$^+$]; 137 (15), 135 (48) [C$_3$H$_5$ClCO$_2$Me]; 115 (2.6) C$_3$H$_5$Cl$_2$CO$_2$Me, 113 (15.7), 111 (26.2) [C$_3$H$_5$Cl$_2^+$]; 99 (100) [C$_3$H$_4$CO$_2$Me$^+$]; 77 (32), 75 (95) [C$_3$H$_4$Cl$^+$]; 59 (38) [CO$_2$Me$^+$]; 39 (93) [C$_3$H$_3^+$].

^{1}H NMR (200 MHz, CDCl$_3$): δ 2.75 (dd, $^2J = 16.5$, $^3J = 8.5$ Hz, 1H), 3.00 (dd, $^2J = 16.5$, $^3J = 4.7$ Hz, 1H), 3.73 (s, 3H), 3.75 (dd, $^2J = 11.4$, $^3J = 7.6$ Hz, 1H), 3.85 (dd, $^2J = 11.4$, $^3J = 4.8$ Hz, 1H), 4.39–4.52 ppm (m, 1H).

^{13}C NMR (50.3 MHz, CDCl$_3$): δ 39.8 ($J_{^{13}C-H} = 131$ Hz, –CH$_2$–), 47.2 ($J_{^{13}C-H} = 152$ Hz, –CH$_2$Cl), 51.9 ($J_{^{13}C-H} = 147$ Hz, –OCH$_3$), 52.6 ($J_{^{13}C-H} = 159$ Hz, –CH–), 169.7 ppm (CO).

2.3.3. *20a, c*: IR (neat, KBr): 1800 cm^{-1} (ν_{CO})

MS (CI, CH$_4$) m/z: 223 (6.9), 221 (15.5), 219 (10.5) [C$_3$H$_6$BrCl$_2$CO$^+$]; 187 (26.0), 185 (100), 183 (69.4) [C$_3$H$_5$BrClCO$^+$]; 159 (6.1), 157 (25.1), 155 (19.5) [C$_3$H$_5$BrCl$^+$]; 143 (1.5), 141 (8.6), 139 (13.3) [C$_3$H$_5$Cl$_2$CO$^+$]; 113 (3.7), 111 (6.5) [C$_3$H$_5$Cl$_2^+$]; 105 (4.2), 103 (11.5) [C$_3$H$_4$ClCO$^+$].

2.3.4. *21a, c*: IR (neat, KBr): 1800 cm^{-1} (ν_{CO})

MS (CI, CH$_4$) m/z: 269 (2.3), 267 (9.2), 265 (11.5), 263 (5.3) [C$_3$H$_6$Br$_2$ClCO$^+$]; 231 (48.1), 229 (100), 227 (50.4) [C$_3$H$_5$Br$_2$CO$^+$]; 203 (2.3), 201 (6.1), 199 (6.1) [C$_3$H$_5$Br$_2^+$]; 187 (19.1), 185 (77.9), 183 (77.8) [C$_3$H$_5$BrClCO$^+$]; 159 (7.6), 157 (34.4), 155 (29) [C$_3$H$_5$BrCl$^+$]; 149 (6.1), 147 (6.1) [C$_3$H$_4$BrCO$^+$]; 121 (6.1), 119 (8.4) [C$_3$H$_4$Br$^+$]; 105 (8.4), 103 (6.9) [C$_3$H$_4$ClCO$^+$].

2.3.5. *23b*: IR (neat KBr): 1720 cm^{-1} (ν_{CO})

MS (EI) m/z: 124 (M$^+$), 122, 91, 87 (base peak), 63, 59, 55, 27.

^{1}H NMR (200 MHz, CDCl$_3$): δ 2.77 (2H, t, $^2J = 6.7$ Hz), 3.73 (2H, t, $^2J = 6.7$ Hz), 3.7 ppm (3H, s).

^{13}C NMR (50.32 MHz, CDCl$_3$): δ 37.1, 38.7, 51.7, 170.5 ppm (CO).

2.4. 3,4-Dichlorobutanoic acid

A mixture of **4a** (2.5 g, 14 mmol), potassium carbonate (2 g, 14.5 mmol) and water (5 ml) is heated in dichloromethane (10 ml) for 4 h. The brown solution is cooled down to RT and distilled under reduced pressure (1 Torr) to provide the acid **34** (59% yield).

$F = 62$–$65°C$. Anal.: found (calc.): C 41.6 (40.8), H 4.28 (4.17%). IR (nujol): 3500 (br, ν_{OH}), 1750, 1710 cm^{-1} (ν_{CO}). ^{1}H NMR (200 MHz, CDCl$_3$): δ 4.18 (2H, dd, $^3J = 5.9$, $^4J = 1.7$ Hz), 6.12 (1H, dt, $^3J = 15.3$, $^4J = 1.7$ Hz), 7.08 ppm (1H, dt, $^3J = 15.3$, $^3J = 5.9$ Hz). ^{13}C NMR (50.32 MHz, CDCl$_3$): δ 42.1 (t, $J_{^{13}C-H} = 165.9$ Hz), 123.1 (d, $J_{^{13}C-H} = 151.4$ Hz), 144.3 (d, $J_{^{13}C-H} = 162.3$ Hz), 170.8 ppm.

2.5. 2(H)-5-Furanone

A mixture of **4a** (4.7 g, 27 mmol) and calcium carbonate (2.808 g, 28 mmol) is refluxed in water (20 ml) for 5 h. The clear yellow solution is cooled down to RT and the butenolide **33** is extracted with dichloromethane (10 × 5 ml). The organic layer is dried over MgSO$_4$.

Evaporation of dichloromethane provides 1.579 g (18.8 mmol) of 33 (70% yield).

Bp = 213–214°C. IR (KBr, neat): 1785, 1750 (ν_{CO}), 1600 cm^{-1} ($\nu_{C=C}$). ^{1}H NMR (200 MHz, CDCl$_3$): δ 4.89 (2H, dd, $^3J = 2.2$, $^4J = 1.65$ Hz), 6.17 (1H, dt, $^3J = 2.2$, $^3J = 5.8$ Hz), 7.58 ppm (1H, dt $^3J = 5.8$ Hz, $^4J = 1.65$ Hz).

3. Results and discussion

3.1. Chlorocarbonylation of allyl chloride with homogeneous palladium catalysts

Reaction of allyl chloride with hydrogen chloride and carbon monoxide under moderate pressures is catalysed by molecular Pd compounds as well as 10% Pd/C (Scheme 2). Compounds **1**–**6** are characterised by GC, GC/MS, IR, and ^{1}H and ^{13}C NMR. Trace amounts of hydrogen and phosgene are detected in the gas phase. Running the reaction with high purity carbon monoxide (Air Liquide N60) also leads to the formation of hydrogen, probably via the water–gas shift reaction [25] involving residual water present in the reagents used. Blank experiments indicate that the formation of 2-dichloropropane **5** and propene **6** requires the presence of both CO and HCl; the absence of CO gives mostly rise to the formation of the adduct of HCl on allyl chloride. The expected product, 3,4-dichlorobutanoyl chloride, **4a**, which is only cited by Tsuji et al. [14] has been fully characterised (see Section 2). Systematic studies have been carried out with further methanolysis of the reaction mixture in order to simplify GC analyses.

The best solvents for the reaction are halogenated hydrocarbons (CH$_2$Cl$_2$, C$_2$H$_4$Cl$_2$), but
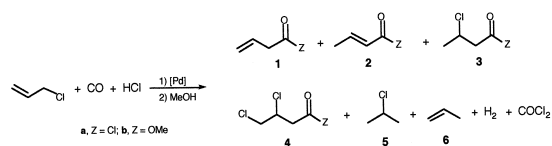
Scheme 2.

the reaction proceeds also in toluene or without solvent, although lower selectivity and yield in **4** are observed (Table 1, entries 1–5). The overlapping of the peaks of toluene and **4b** avoids in this case the determination of yield and selectivity for this compound. The reaction is prevented when protic reagents (e.g., methanol, water) are added to the system, even in small quantities. Although small amounts of **1b** are still produced in addition to **5**, the main compound obtained under these conditions is 3-methoxypropene. The reaction starts only above 60°C. The yield of **4** increases with the

reaction temperature (Table 1, entries 2, 6–8); however, selectivity for this compound decreases sharply above 100°C, owing to an increase in the formation of **1**, as already observed by Tsuji et al. [14]. The conjugated ester **2b** is always detected as traces, even at higher temperatures.

The amount of **4** produced is stable after 8 h reaction as the build-up of **5** which follows a parallel evolution (Table 1, entries 9–15). Nevertheless, the selectivity for **4** decreases with the reaction time due to steady formation of **1** and **3** up to 23 h. Monitoring by GC of the first stages

Table 1
Chlorocarbonylation of allyl chloride: influence of the reaction parameters on yields and product selectivity

Entry	Solvent	Temperature (°C)	Time (h)	CO (bar)	HCl (bar)	N_2 (bar)	Yield (%)					Selectivity
							1a/b	**3a/b**	**4a/b**	**5**	**6**	**4** (%)
1	/	100	4	24	9	/	4	1	23	15	33	82
2	CH_2Cl_2	100	4	24	9	/	3	1	26	23	22	87
3	$C_2H_4Cl_2$	100	4	24	9	/	3	1	30	19	15	91
4	C_6H_5Me	100	4	24	9	/	–	2	24	16	–	–
5	MeOH	100	4	24	9	/	3	traces	0	52	34	0
6	CH_2Cl_2	60	4	24	9	/	traces	traces	8	7	8	89
7	CH_2Cl_2	80	4	24	9	/	1	traces	12	9	12	92
8	CH_2Cl_2	130	4	24	9	/	12	2	41	23	20	74
9	CH_2Cl_2	100	2	48	9	/	2	4	24	22	16	80
10	CH_2Cl_2	100	4	48	9	/	3	5	25	22	19	76
11	CH_2Cl_2	100	8	48	9	/	2	8	30	24	20	75
12	CH_2Cl_2	100	16	48	9	/	2	11	31	27	18	70
13	CH_2Cl_2	100	23	48	9	/	6	13	30	26	16	61
14	CH_2Cl_2	100	32	48	9	/	4	13	30	27	16	64
15	CH_2Cl_2	100	65	48	9	/	6	12	32	28	15	64
16	CH_2Cl_2	100	4	12	9	/	3	traces	18	12	24	86
17	CH_2Cl_2	100	4	18	9	/	2	1	20	14	19	87
18	CH_2Cl_2	100	4	36	9	/	4	2	29	17	25	83
19	CH_2Cl_2	100	4	48	9	/	7	3	34	23	18	77
20	CH_2Cl_2	100	4	48	3	/	4	2	16	11	8	70
21	CH_2Cl_2	100	4	48	6	/	3	4	20	17	11	71
22	CH_2Cl_2	100	4	48	9	/	3	5	25	22	16	76
23	CH_2Cl_2	100	4	24	14	/	10	1	32	18	22	74
24	CH_2Cl_2	100	4	24	18	/	12	1	30	17	24	70
25	CH_2Cl_2	100	4	24	24	/	36	traces	29	21	13	45
26	CH_2Cl_2	100	4	12	9	12	6	1	29	23	27	81
27	CH_2Cl_2	100	4	16	6	11	3	1	25	19	28	86
28	CH_2Cl_2	100	4	18	9	6	5	1	33	22	26	85
29	CH_2Cl_2	100	4	12	9	27	3	5	38	27	18	83
30	CH_2Cl_2	100	4	18	9	21	6	1	34	25	14	83
31	CH_2Cl_2	100	4	24	9	15	5	2	36	26	15	84
32	CH_2Cl_2	100	4	24	14	10	7	1	41	27	12	84
33	CH_2Cl_2	100	4	24	18	6	9	1	42	28	12	81
34	CH_2Cl_2	100	4	36	9	3	3	5	39	27	14	83

Reaction conditions: $[PdCl_2] = 2$ mmol, $[C_3H_5Cl] = 100$ mmol, solvent = 10 ml.

of the reaction indicates this selectivity is the highest after 40 min (Fig. 1). The initial selectivity is 70% suggesting that **4** is the kinetic product of the chlorocarbonylation reaction. This is confirmed by the steady formation of **1** with time (Fig. 1 and Table 1), hence suggesting that this compound is either a decomposition product of **4** or the product of a side reaction involving another, less active, palladium catalyst.

The increase in carbon monoxide pressure from 12 to 48 bar leads to the expected increase in the yields of any carbonylation product (Table 1, entries 2, 16–19). Again, the increase in the formation of **5** follows the increase in the production of **4**. However, at higher pressures, the formation of **1** and **3** occurs more rapidly, therefore leading to a slight decrease in selectivity for **4**. The effect of hydrogen chloride pressure is more contrasted and varies with the partial pressure of carbon monoxide. When p_{CO} = 48 bar, a linear increase in the formation of **3** and **4** is observed (Table 1, entries 20–22). This is further observed up to 14 bars (p_{CO} = 24 bar) where a plateau is reached (Table 1, entries 2, 23–25). However, at that stage, the amount of **1** increases more rapidly, hence lowering the selectivity for the dichloro derivative. A delicate balance dictates the highest yields and selectivities for **4**. Since these values can depend on the total pressure in the autoclave, we examine the

variation of these values at the same initial total pressure by introducing a sufficient amount of nitrogen. Inspection of Table 1 (entries 26–28 for a total pressure of 33 bar, entries 29–34 for a total pressure of 48 bar) indicates that the selectivity for **4** remains practically constant; the lowest ones are observed for the lowest CO/HCl pressure ratio (i.e., 1.33), which corresponds to the optimal ratio for the formation of **1** in both total pressure conditions. The highest yield of **4** is observed at CO/HCl = 2 for a total pressure of 33 bar, but at lower values (i.e., 1.3–1.7) for a total pressure of 48 bar. Due to low amounts of **3** produced (each experiment has been at least duplicated and provides results within ±3%), the trends for its formation with respect to partial and total pressures are less clear.

The chlorocarbonylation reaction proceeds with different types of palladium complexes (Table 2, entries 2, 35–40). There is no influence of the initial oxidation state for neutral complexes; moreover, Pd/C is operative, leading to similar a yield of **4**, albeit with a lower selectivity (Table 2, entry 41); further results with this precursor will be detailed below. However, the catalyst activity seems to be sensitive to the nature of the ligands present on the catalyst precursors. Ligands which are easily protonated such as η^3-allyl [26] and acac [27], or labile like PhCN induce better activities; the lower activity of the dicationic complex $[Pd(MeCN)_4](BF_4)_2$ may result from the stronger retention of the acetonitrile ligands in the coordination sphere of the palladium centre during the formation of the active species.

Noteworthy is the total inhibition by triphenylphosphine (entries 42, 43) which prevents the formation of the catalyst or poisoned it; both reasons may take place. In fact, addition to $PdCl_2$ of 1 equivalent of triphenylphosphine strongly reduce the catalytic activity and product yields (Table 2, entry 44). Addition of ureas which are reported to facilitate the carbonylation of allyl chlorides [28] is also depressing the catalyst performances (Table 2, entries 45–47).
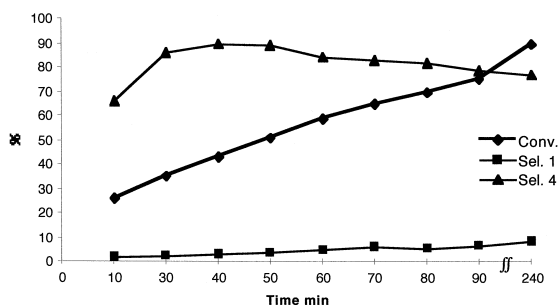

Fig. 1. Evolution of allyl chloride conversion and yield of **4b** in the first stages of the chlorocarbonylation of allyl chloride (reaction conditions: $[PdCl_2]$ = 2 mmol, $[C_3H_5Cl]$ = 100 mmol, CH_2Cl_2 = 10 ml, p_{CO} = 24 bar, p_{HCl} = 9 bar, T = 100°C, t = 4 h).

Table 2

Chlorocarbonylation of allyl chloride: influence of the reaction parameters on yields and product selectivity

Entry	Complex/Additive	S/C	Conversion (%)	Yield (%)					Selectivity
				1a/b	**3a/b**	**4a/b**	**5**	**6**	**4** (%)
2	$PdCl_2$	50	75	3	1	26	23	22	87
35	$Pd(dba)_2$	50	61	2	1	22	9	22	88
36	$PdCl_2(PhCN)_2$	50	75	3	2	31	22	22	86
37	$PdCl_2$ (cod)	50	67	3	1	23	18	22	85
38	$(C_3H_5PdCl)_2$	50	75	3	1	29	20	22	88
39	$Pd(acac)_2$	50	85	4	2	30	21	28	83
40	$[Pd(MeCN)_4](BF_4)_2$	50	54	3	1	12	11	27	75
41	Pd/C	50	88	9	3	30	29	17	71
42	$Pd(PPh_3)_4$	50	5	2	traces	0	2	1	0
43	$PdCl_2(PPh_3)_2$	50	6	3	traces	0	1	2	0
44	$PdCl_2 + PPh_3$	50	17	traces	traces	2	3	12	100
45	$PdCl_2 + TMU$	50	25	2	traces	10	10	3	83
46	$PdCl_2 + TMU^a$	50	17	1	traces	1	3	12	50
47	$PdCl_2 + TMTU$	50	13	1	traces	1	2	9	50
48	$PdCl_2 + SnCl_2$	50	82	8	1	30	24	19	77
49	$PdCl_2 + SnCl_2^b$	50	93	19	traces	22	24	28	54
50	$PdCl_2 + LiCl$	50	59	3	1	25	18	12	86
51	$PdCl_2 + LiCl^b$	50	54	5	1	21	16	11	78
52	$PdCl_2 + CuCl_2$	50	86	4	1	40	30	11	89
53	$PdCl_2 + CuCl_2^c$	50	83	4	1	42	28	8	89
54	$PdCl_2 + CuCl_2^b$	50	85	5	1	42	28	8	89
55	$PdCl_2 + PPNCl^a$	50	18	3	traces	traces	6	9	100
56	$PdCl_2 + Me_2NH \cdot HCl$	50	38	3	traces	16	13	6	84
57	$PdCl_2 + Me_2NH \cdot HCl^b$	50	24	2	traces	traces	7	15	100
58	Bu_4NCl	50	57	5	1	24	18	9	80
59	$PdCl_2$	40	72	3	1	29	18	21	88
60	$PdCl_2$	66	78	3	1	29	23	22	88
61	$PdCl_2$	100	69	3	1	29	22	23	88
62	$PdCl_2$	200	73	2	2	25	21	19	86
63	$PdCl_2$	500	47	2	1	12	16	28	80
64	[Pd], soluble^d	50	63	4	2	20	15	22	77
65	[Pd], insoluble^d	50	54	3	1	19	15	26	83

[a] 2 equiv/Pd.

[b] 5 equiv/Pd.

[c] 2.5 equiv/Pd.

[d] Recycling experiment: see text.

Reaction conditions: [Pd] = 2 mmol, [additive] = 1 equiv with respect to palladium, if not stated, $[C_3H_5Cl]$ = 100 mmol, if not stated, CH_2Cl_2 = 10 ml, p_{CO} = 24 bar, p_{HCl} = 9 bar, T = 100°C, t = 4 h.

On the other hand, chlorides may have a strong effect on activity and yields (Table 2, entries 48–58). Tin(II) chloride increases both conversion and production of chlorocarbonyl products. However, the selectivity for **4** is lower, due to the higher amounts of **1** formed, especially in the presence of an excess of the additive. Ionic chlorides like LiCl are not improving the yields, though the selectivity for the expected **4** is higher. Copper(II) chloride provides the best results, but still with the production of large amounts of **5**, even if the chloride is in excess with respect to palladium chloride. Onium salts are much less effective (Table 2, entries 55–58). Finally, variation of the substrate to catalyst ratio, S/C, has no effect on the catalyst performances up to S/C = 200. For S/C = 500, conversion and yield of **4** decrease, which also leads to a lower selectivity. The lack of response on catalyst concentration may suggest

that under the reaction conditions used, part of the active species precipitates from the solution. This is suggested by the observation at the end of the reaction of a precipitate which corresponds to ca. 50% of the $PdCl_2$ engaged. It is noteworthy that changing $PdCl_2$ to $Pd(dba)_2$, $PdCl_2(cod)$ or $PdCl_2(PhCN)_2$ and running the chlorocarbonylation for two other S/C ratios (100 and 500) does not lead to strong variations of the catalytic performances.

This new synthesis of 3,4-dichlorobutanoyl chloride represents a considerable improvement compared to the only method described so far [14]. The nature of the halogen source during the catalytic process could be chlorine, phosgene, chloride ion or palladium chloride. The reaction performed under a pressure of chlorine and carbon monoxide (5 and 24 bar, respectively), in the presence of palladium chloride, at 100°C, for 4 h only gives 1,2,3-trichloropropane. This reaction proceeds easily, even at room temperature and without any metal as catalyst. Carbonylation of 1,2,3-trichloropropane to **4** does not proceed under the reaction conditions used. The reaction run with phosgene does not occur in the absence of carbon monoxide. In fact, **4** can be obtained under CO pressure, but in poor yield (maximum 3%). Moreover, the infrared spectrum of gases shows the

presence of phosgene, carbon monoxide, hydrogen chloride and carbon dioxide, indicating some phosgene hydrolysis. The presence of water in small quantities is inherent to the introduction of phosgene.

At the end of the reaction, the mixture is made up of two phases: one red solution and one green precipitate. Each phase contains different palladium compounds (vide infra), which have been isolated and re-used for the carbonylation of allyl chloride. Both isolated systems are active and give identical product distributions (Table 2, entries 64 and 65). However, the yield of 3,4-dichlorobutanoyl chloride is somewhat smaller.

3.2. Chlorocarbonylation of allyl chloride with Pd/C

The use of supported palladium catalysts could provide an easier work-up of the reaction mixture and the possibility of recycling the catalyst. Since palladium on charcoal has been found to be active (Table 1, entry 41), we have examined these opportunities. Under the standard conditions used above, the catalytic system is more sensitive to the amount of substrate involved (Table 3, entries 41, 66–68), a maximum being observed for a substrate to catalyst

Table 3
Chlorocarbonylation of allyl chloride: use of 10% Pd/C

Entry	Complex	S/C	Conversion (%)	Yield (%)					Selectivity
				1a/b	**3a/b**	**4a/b**	**5**	**6**	**4** (%)
2	$PdCl_2$	50	75	3	1	26	23	22	87
66	Pd/C	33	78	6	2	28	27	15	78
41	Pd/C	50	88	9	3	30	29	17	71
67	Pd/C	100	58	5	1	18	17	17	75
68	Pd/C	200	35	2	traces	9	9	15	82
69	Pd/C, recycled[a]	100	14	1	traces	traces	1	12	–
70	Pd/C, recycled[b]	100	43	2	traces	7	8	26	78
71	[Pd], soluble[b]	100	48	2	traces	13	9	24	81
72	Pd/C, 5 $CuCl_2$	100	57	2	traces	15	11	29	88
73	Pd–Cu/C, recycled[b]	100	48	2	traces	8	16	22	80

[a] With methanolysis, see text.
[b] Without methanolysis, see text.
Reaction conditions: [Pd] = 2 mmol, [C_3H_5Cl] = 100 mmol, if not stated, CH_2Cl_2 = 10 ml, p_{CO} = 24 bar, p_{HCl} = 9 bar, T = 100°C, t = 4 h.
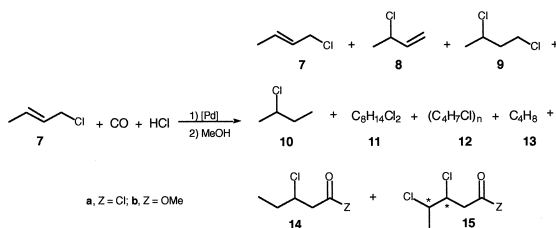
Scheme 3.

ratio of 50. The solid recovered after the reaction with $S/C = 100$ (Table 3, entry 67) performed with methanolysis of the reaction products, when engaged in a new reaction shows no more activity for chlorocarbonylation (Table 3, entry 69). This solid contains palladium, but in an amount smaller than that of the starting catalyst (5.8 instead of 7.98%), and chlorine (11.86 instead of 1.06%). After the attempted reaction, the amounts of palladium and chlorine have decreased again (2.74 and 9.22, respectively). Leaching of palladium from carbon supports is known [29] and is favoured here by the presence of carbon monoxide and hydrogen chloride. The lack of activity of the recycled solid may originate from poisoning during the methanolysis process. In fact, if the methanolysis of the reaction mixture is not carried out, the solid recovered by centrifugation from a standard reaction with $S/C = 100$ is active, but less than the fresh catalyst (Table 3, entry 70). Besides, the recovered red solution freed from the reaction products is also active (Table 3, entry 71), so suggesting the soluble nature of the active species. The effect of additives as reported above is limited to copper(II) chloride (Table 3, entry 72). This effect is lower than in the case of $PdCl_2$ and is not further observed for the recycled solid (Table 3, entry 73).

3.3. Chlorocarbonylation of substituted allyl chlorides

The reaction could be extended to other allyl chlorides with very different results depending on the nature of the substituents. Methallyl chloride and cinnamyl chloride are converted with HCl into the addition products 1,2-dichlorobutane and 1,3-dichloropropylbenzene, respectively.

The chlorocarbonylation of crotyl chloride **7** leads, in addition to the isomeric 3-chloro-but-1-ene **8**, to different types of compounds (Scheme 3, Table 4) which are mostly halogenated hydrocarbons arising from addition of HCl to the double bond, **9**, reduction of the double bond, **10**, dimerisation, **11**, and oligomerisation, **12**, of crotyl chloride. Similarly, in the case of allyl chloride, butenes (but-1-ene and *cis*- and *trans*-but-2-enes) are present in significant amounts. Mono- and dichloroacyl chlorides, **14** and **15**, are minor components which account for 6% of the reaction mixture (Table 4); no unsaturated acyl chlorides are detected by GC/MS. The structure of **15** is ascertained on the basis of the presence of the fragment $m/z = 74$ in the mass spectrum, resulting from a McLafferty rearrangement (Scheme 4) and the occurrence of two peaks in GC corresponding to the expected diastereomers (ratio of 45:55).

Chlorocarbonylation of 3-chloro-but-1-ene **8** gives the same products (Table 4). The conversion of **8** is higher, but the product distribution is very similar, therefore suggesting that the reactions involved during this process occur via

Table 4

Chlorocarbonylation of crotyl chloride and 3-chloro-1-butene: comparison of the product distributions

Entry	Compound	Conversion (%)	Yield (%)								
			7	8	9	10	11	12	13	14	15
74	**7**	78	22	9	29	9	4	1	15	1	5
75	**8**	91	24	9	25	10	2	1	19	1	6
76	**7** + **8** (1:1)	–	28	11	22	7	3	2	18	traces	4
77	Buta-1, 3-diene	–		33	13	13	7	1	1	n.d.[a]	1	4

[a] Not determined.

Reaction conditions: $[PdCl_2] = 2$ mmol, [allyl chloride(s)] = 100 mmol, $CH_2Cl_2 = 10$ ml, $p_{CO} = 24$ bar, $p_{HCl} = 9$ bar, $T = 100°C$, $t = 4$ h.
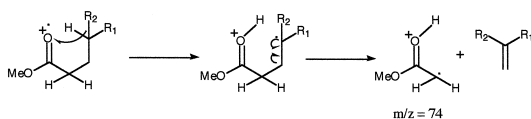
Scheme 4.

the same intermediates and pathways. Further, chlorocarbonylation of a 1:1 mixture of these two allyl chlorides provides the same product distribution.

Finally, it is worthy to note that buta-1,3-diene is converted into the same reaction mixture under the chlorocarbonylation used (Table 4). In fact, addition of HCl to buta-1,3-diene leads to a mixture of **7** and **8** which undergoes the chlorocarbonylation. However, selectivities are poor and this reaction has not been optimised further.

3.4. Extension to allyl bromide

The easier reaction of organic bromides with transition metal complexes than organic chlorides [30] prompts us to examine the chlorocarbonylation of allyl bromide with the anticipation of preparing the corresponding dichloroacyl bromide. Under the standard conditions used, allyl bromide is converted (71%) into a product pattern similar to that of allyl chloride (Scheme 5). Structures **17** and **18** are assigned on the basis of CI (methane) mass spectra, ^{1}H and ^{13}C NMR spectra. The acyl bromide **19** has been identified by comparison with an authentic sample. The MS spectra of the dihaloacyl halides **20** and **21** (see Section 2) are compared to those of **4** and indicate the presence of both acyl chloride and bromide, since peaks corresponding to respective loss of HCl and HBr are observed. However, a comparison of the relative intensities of the peaks at $m/z = 229$ ($C_3H_5Br_2CO^+$), 185 ($C_3H_5BrClCO^+$) and 157 ($C_3H_5BrCO^+$) suggests that the acyl chloride predominates. Moreover, the IR spectra of these two compounds show a strong band attributed to ν_{COCl} centred at 1800 cm^{-1} which fits well with the one attributed to **4**. Hence, the product distribution is unexpectedly different from what is ob-

tained with allyl chloride. Moreover, in the absence of hydrogen chloride, **16** mostly leads to oligomeric materials: only small amounts of **17** and **19c** and the isomeric but-2-enoyl bromide **22c** are detected (4, 1 and 1%, respectively). This could be explained by the occurrence of radical processes. In fact, chlorocarbonylation of **16** is not inhibited by radical scavengers like galvinoxyl, but no more oligomers are formed under these conditions.

3.5. Chlorocarbonylation of ethylene

In its basic work on nickel-catalysed reactions of allyl halides, Chiusoli reported the formation of hexenoic esters by co-reaction of allyl chloride with ethylene, carbon monoxide and methanol [31]. In the present case, the reaction undergoes a completely different pathway, resulting in the formation of 3-chloropropionic derivatives **23**, and **5** and **6** (Eq. (3)).

$$(3)$$
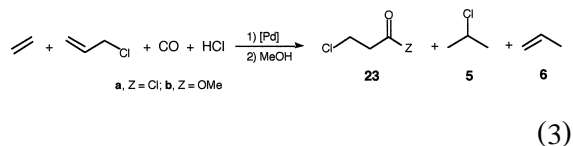
The chlorocarbonylation of ethylene has been reported as a stepwise process in the presence of stoichiometric amounts of palladium dichloride [18]. The formation of **23a** is also achieved by the reaction of phosgene with ethylene, catalysed by Rh/C, Pd/C or Pd(PPh$_3$)Cl$_2$ under high pressures of carbon monoxide [32]. This reaction corresponds to the formal addition of the elements of phosgene on ethylene. However,
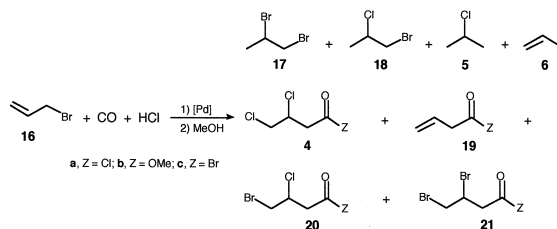
Scheme 5.

no phosgene is detected in the reaction medium and, furthermore, phosgene does not react with ethylene under the reaction conditions used, even in the presence of $PdCl_2$. The other products involving ethylene are obtained in low amounts and were identified by GC/MS as $C_7H_{14}Cl_2$ and $C_6H_{12}ClCO_2Me$. They formally originate from the coupling of (i) allyl chloride, two ethylene and hydrogen chloride, and (ii) three ethylene (the equivalent of phosgene and methanol), with evolution of hydrogen chloride. Allyl chloride is converted into 2-chloropropane and propene. Small amounts of the expected chlorocarbonylation products of allyl chloride **1b**–**4b** are obtained (Table 5). When the reaction is performed without allyl chloride, practically no products are formed: the expected compound 23b is detected in only small amounts (2% yield).

The formation of this compound starts even with small amounts of allyl chloride added to the reaction medium. An optimal quantity of allyl chloride is required for its production (Table 5): the ratio of 2 is presumably associated with a specific reaction pathway (vide infra).

3.6. Reaction mechanism

The formation of **4** and its analogues does not result from chloration of **1** or **2** which are reported to be formed via carbonylation of an allyl intermediate followed by reductive elimination [6,7]. A control experiment with a mixture of these isomers under the standard reaction conditions used gives **3** with only traces of **4**.

The yellow-green solid which is recovered at the end of all chlorocarbonylation reactions display the typical features reported for the oligomeric ill-characterised $[Pd(CO)Cl]_n$ (1975, 616, 444, 246, 217 cm^{-1}) which is best described as an oligomer, **24**, where $Pd_2(CO)_2$ units are bridged by chloro ligands [31–37]. The elemental analysis of this product (C: 7.9, H: 0.4, Cl: 22.9, Pd: 59.9%) fits well with that of the compound obtained by reacting $PdCl_2$ with allyl chloride and carbon monoxide as reported by Schnabel and Kobler (C: 7.8, H: 0.3, Cl: 19.92, Pd: 60.24%) [38,39].


24
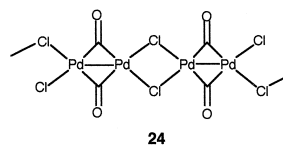
The supernatant deep-red solution consists of a mixture of the organic reaction products and of palladium complexes which cannot be purified. Due to the similar results obtained for both the soluble and insoluble Pd-containing fractions, we assume they are both precursors of the active species which is formed in the presence

Table 5
Chlorocarbonylation of ethylene: influence of the allyl chloride to ethylene ratio on the yield of compound **23b**

Entry	Allyl chloride (mmol)	Ratio	Conversion (%) allyl chloride	Yield (%) 1b–4b[a]	23b[b]	5[a]
76	0					2
77	7	0,11	83	traces	10	71
78	12	0,19	92	traces	26	74
79	25	0,40	99	2	30	70
80	52	0,90	90	3	53	47
81	100	1,61	81	6	68	42
82	117	2,17	68	5	68	31
83	148	2,74	56	5	57	22
84	222	3,96	35	3	16	16

[a] Based on allyl chloride.
[b] Based on ethylene.
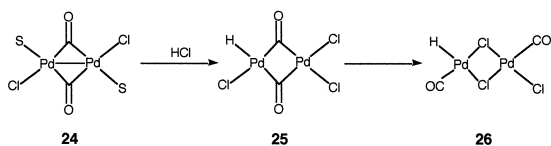
Scheme 6.

of carbon monoxide and hydrogen chloride. This active species may result from first the oxidative addition of HCl on the Pd(I)–Pd(I) bond of **24** leading to **25** which rearranges to the chloro-bridged dimer **26** (Scheme 6).

In the presence of a substrate, this dimer can be split into two different monomers, **27** and **28**, which may react further through migratory insertions. However, migratory insertion within **27** will not provide the expected chloroacyl chloride; in fact, **27** is certainly too unstable and will decompose into palladium and hydrogen chloride. On the other hand, **28** offers two possibilities which depend on the timing of migratory processes involving the substrate and the Cl/CO ligands. If the migratory {Cl, substrate} process is preferred, **29** is formed and will evolve via CO migratory insertion, then reductive elimination to the expected chloroacyl chloride. Conversely, the formation of a chlorocarbonyl complex **30** may occur prior to the migratory insertion involving the substrate which leads to **31** (Scheme 7).

The chlorocarbonylation should be therefore sensitive to the substitution on the substrate

used: the order of reactivity is: ethylene > allyl chloride > 3-chloro-1-butene > crotyl chloride. Methallyl chloride and cinnamyl chloride are not converted into the expected products: the adducts with HCl are exclusively formed instead. Hence, the reaction occurs preferentially on terminal double bonds. In the case of crotyl chloride, the same product distribution as for 3-chloro-1-butene is explained by an interconversion between both substrates which operates via a (η^3-crotyl)palladium intermediate. It should be pointed out that the two reaction pathways starting from **28** take place with opposite regioselectivities, though leading to the same product. To our knowledge, there is no indication in the literature about the regioselectivity of the chlorocarbonylation reaction. In the case of alkoxycarbonylation, regioselectivity of the coupling depends strongly on the nature of the substrate and ligands attached to palladium [40]. In the present case, the absence of bulky ligands, the neutral character of the palladium centre will favour **31** thanks to an intramolecular stabilisation of the intermediate. Moreover, the formation of the acyl chloride in the chlorocarbonylation of allyl bromide speaks for this pathway, since Cl/Br exchange does certainly not take place in the steps preceding **30**.

Inspection of Table 1 clearly shows that the amount of 4 formed corresponds grossly to the amount of propene and 2-chloropropane

a, R = H; **b**, R = CH$_2$Cl; **c**, R = CH$_2$Br **d**, R = CH(Me)Cl
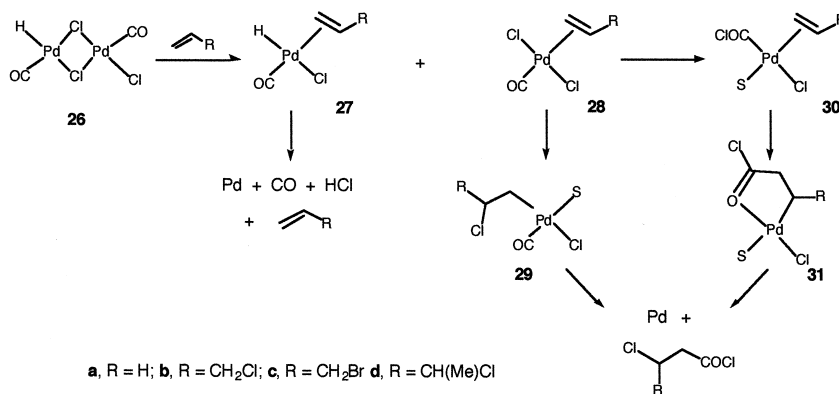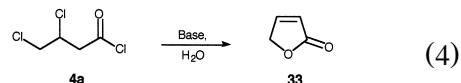
Scheme 7.

evolved, therefore suggesting that part of the allyl chloride is sacrificed during the catalytic process. Scheme 7 proposes the formation of zerovalent palladium species which should be converted back to $PdCl_2$ and then to **24** for further catalytic cycles. Although reoxidation of Pd(0) to Pd(II) is known to be mediated by $CuCl_2$ in aqueous HCl [41], under the reaction conditions used, carbon monoxide and hydrogen chloride are inoperative for this redox process. We suggest that allyl chloride initiate this regeneration which starts with the formation of the (η^3-allyl) species **32** (Scheme 8). We suggest that the next step corresponds to the attack of HCl on this intermediate affording $PdCl_2$ and propene which reacts further with HCl to give **5**. Such a process has been recently reported for allylmolybdenum complexes [26]. In fact, reaction of allylchloropalladium dimer with an excess of dry HCl in dichloromethane gives quantitative yields of $PdCl_2$ and **5**. The amounts of **1**–**3** built during chlorocarbonylation arise from the trapping of **32** with carbon monoxide. Hence, the higher is the CO partial pressure, the higher is the yield in **1**–**3**, as indicated in Table 1. The beneficial effect of the HCl partial pressure for the generation of **1** and, to a lesser extent, of **5** could be explained by the higher availability of zerovalent palladium species obtained according to Scheme 6.

In agreement with Scheme 8, two equivalents of allyl chloride are required to reoxidise the zerovalent palladium built during the conversion of one $[Pd(CO)Cl]_2$ unit into the catalytically

active system. This is in full coherence with the optimal ratio of 2 observed for the chlorocarbonylation of ethylene. Moreover, the involvement of allyl chloride in the reoxidation process of palladium limits the yields in **4** to 36% (taking into account the initial amount of $PdCl_2$), except in the cases where $CuCl_2$ is used. This addition may induce some reoxidation due to the presence of residual water in the autoclave; it is however limited, since no improvement is observed with an excess of this salt (Table 2, entries 53 and 54).

3.7. Synthesis of 2(H)-5-furanone

Reaction of **4a** with bases would provide 2(H)-5-furanone **33** (Eq. (4)) which is an organic intermediate of great potentialities for biologically active molecules (e.g., chrysanthemic acid, cerulenine and staganincine [42], enterolactones [43], prostaglandins [44], soluble polymers [45]). Several bases have been examined for this reaction.
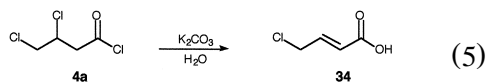
$$(4)$$

Treatment with potassium carbonate in dichloromethane–water mixture gives only 4-chlorobut-2-enoic acid **34** in 59% isolated yield (Eq. (5)), although it has been reported that reaction of 3,4-dichlorobutanoic acid with this
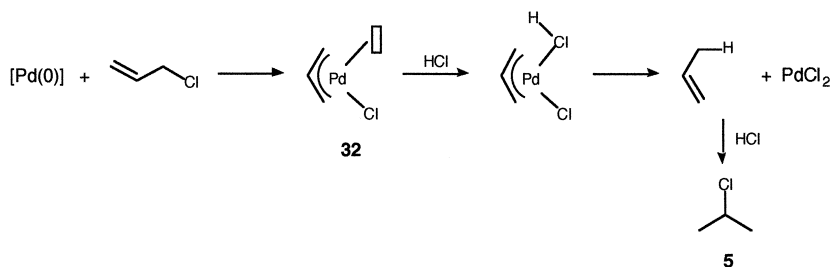
Scheme 8.

base in dichloromethane provides the expected butenolide [46].

$$(5)$$

Examination of different bases (NaOH, KOH, triethylamine, pyridine) has led to poor results. Only the use of calcium carbonate in refluxing water gives a practically quantitative yield (GC) of **33**. The compound is recovered by extraction with dichloromethane due to its high solubility in water and the formation of an azeotrope (see Section 2; 70% isolated yield).

This procedure competes very favourably with the more conventional routes starting from (i) bromation of γ-butyrolactone, followed by dehydrobromation of α-bromo-γ-butyrolactone with triethylamine [47], or (ii) partial sodium borohydride reduction of the Diels–Alder adduct of furane and maleic anhydride, followed by a retro-Diels–Alder reaction [48].

4. Conclusions

Chlorocarbonylation of olefins by a CO + HCl mixture is observed under mild conditions for ethylene and allylic halides. Its extension to other olefins is limited by the competitive addition of the hydracid on the double bond. Chlorocarbonylation of allyl chloride gives dichloro-3,4-butanoyl chloride in good yields and the reaction has been scaled up for its conversion into the valuable 2(H)-5-furanone. All the experimental data are compatible with a process involving $[Pd(CO)Cl]_n$ as a catalyst precursor. We suggest that the active species for this reaction arises from oxidative addition of HCl on the Pd–Pd bond of this oligomer. However, further work is needed for demonstrating this process and also for explaining the discrepancies reported in the literature on the preparation of $[Pd(CO)_xCl_y]_n$ species. Specific oxidants

are required for the regeneration of $PdCl_2$. They are limited to allyl chloride owing to the reaction conditions which forbid the use of well-known systems for zerovalent palladium oxidation; this undoubtedly represents the major drawback of the chlorocarbonylation process described above.

References

[1] S. Patai (Ed.), The Organic Chemistry of Functional Groups, The Chemistry of Acyl Halides, Interscience Publishers, New York, 1972.
[2] R. Sustmann, H.G. Korth, in: J. Falbe (Ed.), Methoden der Organischen Chemie, Vol. E5, Georg Thieme Verlag, Stuttgart, 1985, p. 587.
[3] I. Tkatchenko, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 8, Pergamon, Oxford, 1982, p. 102.
[4] D. Forster, Adv. Organometal. Chem. 17 (1979) 255–267.
[5] M.C. Bonnet, J. Combes, B. Manzano, D. Neibecker, I. Tkatchenko, J. Mol. Catal. 52 (1989) 263–278.
[6] W.T. Dent, R. Long, G.H. Whitfield, J. Chem. Soc. (1964) 1588–1594.
[7] D. Medema, R. van Helden, C.F. Kohll, Inorg. Chim. Acta 3 (1969) 255–265.
[8] G.P. Chiusoli, L. Cassar, Angew. Chem., Int. Ed. Engl. 6 (1967) 124–133.
[9] T. Alderson, V.A. Engelhardt (DuPont), US Pat. 3 065 242 (1962); Chem. Abstr. 58 (1964) 89112.
[10] N. von Kutepow, K. Bittler, D. Neubauer, H. Reis (BASF), German Pat. 1 237 116 (1967); Chem. 68 (1968) 21550.
[11] J.F. Knifton (Texaco), US Pat. 3 880 898 (1975); Chem. Abstr. 83 (1975) 113698.
[12] J. Tsuji, M. Morikawa, J. Kiji, Tetrahedron Lett. (1963) 1061–1064.
[13] J. Tsuji, M. Morikawa, J. Kiji, J. Am. Chem. Soc. 86 (1964) 4851–4853.
[14] J. Tsuji, J. Kiji, S. Imamura, M. Morikawa, J. Am. Chem. Soc. 86 (1964) 4350–4353.

[15] T. Susuki, J. Tsuji, Tetrahedron Lett. (1968) 913–915.

[16] T. Susuki, J. Tsuji, J. Org. Chem. 35 (1970) 2982–2986.

[17] J.A. Scheben, I.L. Mador, in: P.N. Rylander, H. Greenfield (Eds.), Catalysis in Organic Synthesis, Academic Press, New York, 1976, p. 183.

[18] W.W. Pritchard (DuPont), US Pat. 3 681 449 (1972); Chem. Abstr. 77 (1972) 126017.

[19] N. Bénard, M.C. Bonnet, S. Lécolier, I. Tkatchenko, J. Chem. Soc., Chem. Commun. (1993) 1448–1450.

[20] R.F. Heck, Palladium Reagents in Organic Syntheses, Academic Press, New York, 1985, p. 17.

[21] W.T. Dent, R. Long, A.J. Wilkinson, J. Chem. Soc. (1964) 1585.

[22] R.F. Heck, Palladium Reagents in Organic Syntheses, Academic Press, New York, 1985, p. 18.

[23] D. Coulson, Inorg. Synth. 13 (1972) 112.

[24] M.C. Bonnet, L. Carmona, I. Tkatchenko, submitted.

[25] W.A. Herrmann, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, A Comprehensive Handbook, Vol. 2, VCH, Weinheim, 1996, p. 957.

[26] K.E. Oglieve, R.A. Henderson, J. Chem. Soc., Chem. Commun. (1993) 474–478.

[27] I. Guibert, D. Neibecker, I. Tkatchenko, J. Chem. Soc., Chem. Commun. (1989) 1850–1853.

[28] H. Urata, H. Maekawa, S. Takahashi, T. Fuchikami, J. Org. Chem. 56 (1991) 4320–4322.

[29] M.M. Barreto Rosa, M.C. Bonnet, I. Tkatchenko, Heterogeneous catalysis and fine chemicals II, Stud. Surf. Sci. Catal. 59 (1991) 263–268.

[30] J.K. Kochi, Organometallic Mechanisms and Catalysis, Academic Press, New York, 1978, p. 156.

[31] G.P. Chiusoli, Acc. Chem. Res. 6 (1973) 422–427.

[32] A.U. Blackman (National Distillers and Chemical), US Pat. 3 119 861 (1964); Chem. Abstr. 60 (1964) 9155.

[33] E. Fink, Compt. Rend. 126 (1898) 646–648.

[34] W. Manchot, Chem. Ber. 58 (1925) 2518–2521.

[35] E.-O. Fischer, A. Vogler, J. Organometal. Chem. 3 (1965) 161–162.

[36] P.L. Goggin, J. Mink, J. Chem. Soc., Dalton Trans. (1974) 534.

[37] D. Belli dell'Amico, F. Calderazzo, C.A. Veracini, N. Zandona, Inorg. Chem. 23 (1984) 137.

[38] A. Treiber, Tetrahedron Lett. (1966) 2831–2832.

[39] W. Schnabel, E. Kobler, J. Organometal. Chem. 19 (1969) 455–457.

[40] M. Sperrle, G. Consiglio, Chem. Ber./Recueil 130 (1997) 1557–1565.

[41] J. Smidt, W. Hafner, R. Jira, R. Sedlmeier, A. Sabel, Angew. Chem., Int. Ed. Engl. 1 (1962) 80.

[42] T.S. Brima (National Distillers and Chemical), US Pat. 4 356 310 (1982); Chem. Abstr. 98 (1983) 16569.

[43] D.N. Kirk, L.M. McLaughlin, A.M. Lawson, K.D.R. Setchell, S.K. Patel, J. Chem. Soc., Perkin Trans. I (1985) 35–37.

[44] M.R. Binns, R.K. Haynes, D.E. Lambert, P.A. Shober, Tetrahedron Lett. 26 (1985) 3385–3388.

[45] H. Cherdron, H. Ohse, R. Palm, K. Friedhelm (Shell), German Pat. 1 228 065 (1966); Chem. Abstr. 66 (1967) 55994.

[46] A.A. Gevorkyan, A.T. Manukyan, M.S. Sargsyan, Arm. Khim. Zh. 43 (1990) 390–393; Chem. Abstr. 114 (1991) 80993.

[47] C.C. Price, J.M. Judge, Organic Syntheses Coll., Vol. V, Wiley, New York, 1973, pp. 255–258.

[48] S. Takano, K. Ogasawara, Synthesis (1974) 42–43.