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Palladium catalyzed hydrodechlorination of α-chloroacetophenones by hydrogen transfer from the H_2O–CO system

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Abstract

$PdCl_2(PPh_3)_2$, in combination with an extra amount of PPh_3, is an excellent catalyst precursor for the hydrodechlorination of α-chloroacetophenone to acetophenone by hydrogen transfer from the H_2O–CO system. The reaction occurs with concomitant evolution of CO_2. Under typical reaction conditions (50–70°C, 40–80 atm, substrate/Pd/P = 2000/1/50, H_2O/substrate = 8–12/1), the reaction occurs in 70–80% yield in 2 h, using ethanol or dioxane as a solvent ([Pd] = $5 \cdot 10^{-4}$ mol $\cdot$ l^{-1}). When the catalyst precursor is employed without adding an additional amount of PPh_3 extensive decomposition to metallic palladium occurs. Also Pd/C is active in promoting the hydrodechlorination reaction. As expected the reaction rate increases upon increasing concentration of catalyst, carbon monoxide pressure and temperature. The yield is slightly influenced by the concentration of the substrate. The effect of the concentration of H_2O is the most significant. In ethanol as a solvent at low concentration of water the reaction rate increases to reach a plateau above 6–7 $\cdot$ 10^{-2} mol $\cdot$ l^{-1} of water. On the basis of the fact that it is known that (i) the precursor is reduced to a Pd(0) species by the H_2O–CO system, even in the presence of hydrochloric acid, which is freed during the course of the hydrodechlorination reaction and that (ii) the starting α-chloroacetophenone oxidatively adds to Pd(0) to give $Pd(CH_2COPh)Cl(PPh_3)_2$ (I) and that (iii) this complex reacts with hydrochloric acid to give acetophenone and $PdCl_2(PPh_3)_2$ (II), it is proposed that the hydrodechlorination reaction proceeds via the intermediacy of a species analogous to complex (I) and that (II) is reduced to the Pd(0) complex through the intercation of CO and H_2O with the metal center to give a species having a Pd-(COOH) moiety, which after β-hydride abstraction gives a palladium-hydride species with concomitant evolution of CO_2. The hydride gives off a proton and reduces Pd(II) returning a Pd(0) species back to the catalytic cycle. We found also that complex (I) is reduced to a Pd(0) complex with formation of acetophenone through the action of H_2O and CO. It is proposed that this reaction, which may be at the base of a different catalytic path, occurs via the intermediacy of a species having a H-Pd-(CH_2COPh) which, after reductive elimination of acetophenone give the Pd(0) complex starting a new catalytic cycle. In the case of the Pd/C catalyzed hydrodechlorination it is suggested that H_2O and CO interacts on the surface of the metal to give a hydride and evolution of CO_2 and that this hydride displaces a chloride anion from α-chloroacetophenone absorbed on the catalytic surface to give the hydrodechlorination product. © 1997 Elsevier Science B.V.

Keywords: Hydrodechlorination; Palladium; Chloroacetophenones

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1. Introduction

Normally, the palladium catalyzed carbonylation of organic halides, when carried out in the presence of water or of an alkanol, leads to carboxylic acids or esters, respectively, or to products of double carbonylation i.e. α-ketoacids or α-ketoesters [1,2]. To be effective, the catalyst requires the presence of a base, such as a trialkylamine or an alkaly hydroxide, in order to neutralize the halogenidric acid which forms during the course of the reaction. A key step of the catalytic cycle is the oxidative addition of the halide to a Pd(0) complex [3]. In the absence of any base, the halogenidric acid would compete with the organic halide for the addition to Pd(0) thus endarging the catalytic activity.

Recently, we took into consideration the possibility of synthesizing a malonic acid derivative through the carbonylation of an α-chloro-γ-ketoacid derivative, i.e. $PhCOCH_2CHClCOOH$. Rather surprisingly, we found that the reaction took a quite different pathway. First of all, using a palladium catalyst precursor, such as $PdCl_2(PPh_3)_2$ or Pd/C in the presence of a base, no carbonylation occurred. When the reaction was attempted without the addition of a base, it selectively yielded a hydrodechlorination product, i.e. $PhCOCH_2CH_2COOH$, which resulted from the hydrogen transfer from the H_2O–CO system to the starting chloride [4]. The same product was obtained starting from the corresponding α-hydroxy derivative, $PhCOCH_2CHOHCOOH$, or from the α,β-unsaturated-γ-ketoacid, $PhCOCH{=}CHCOOH$, in the presence of hydrochloric acid which reacts in situ with each substrate to give the corresponding chloride $PhCOCH_2CHClCOOH$ [5–7].

We found also that mandelic acid derivatives ArCHOHCOOH having a hydroxy group in p-position yield the corresponding hydrogen transfer product $ArCH_2COOH$ when treated with carbon monoxide in the presence of a palladium catalyst and of hydrochloric acid as cocatalyst [8].

In order to extend the applicability of the hydrodehalogenation reaction by hydrogen transfer from the system H_2O–CO we carried out some preliminary experiments with α-chloroacetophenones. We found that, in the presence of a palladium system, without adding any base, the reaction yielded a hydrodechlorination product i.e. acetophenone. Since it has been reported that, in the presence of a base and of an alkanol, the reaction gives the expected carbonylation product, the β-ketoester $PhCOCH_2COOR$ [9–11], we decided to undertake a full investigation on the reactivity of α-chloroacetophenones with carbon monoxide, hopefully to shed some light on the factors controlling the selectivity towards the hydrochlorination reaction or the carbonylation one.

The results of this study are presented hereafter.

2. Results and discussion

2.1. *The influence of the reaction parameters on the yield of the hydrodechlorination of α-chloroacetophenone*

The hydrodechlorination reaction by hydrogen transfer from the H_2O–CO system leads to acetophenone with concomitant formation of carbon dioxide:

$$PhCOCH_2Cl + H_2O + CO \rightarrow PhCOCH_3 + HCl + CO_2 \qquad (1)$$

$PdCl_2(PPh_3)_2$ is an excellent catalyst precursor when employed in combination with an extra amount of PPh_3. Under typical reaction conditions (50–70°C, 40–80 atm, substrate/Pd/P = 2000/1/30-50, H_2O/substrate = 8–12/1) the reaction occurs in 70–80% yield in 2 h, sing ethanol or dioxane as solvent ($[Pd] = 5 \cdot 10^{-4}$ $mol \cdot l^{-1}$). When the catalyst precursor is employed without adding an additional amount of PPh_3, extensive decomposition to metallic palladium occurs. In order to prevent decomposition to the metal the ratio Pd/P must be at least 1/30, under the reaction conditions above reported. Anyway, Pd/C is also active in promoting reaction Eq. (1).

The influence of the following reaction parameters on the yield of the reaction were studied: pressure of carbon monoxide, temperature, catalyst and substrate concentrations and H_2O/substrate ratio. Most of the experiments were carried out using EtOH as a solvent because the reaction rate was significantly higher than that observed when employing dioxane.

As expected the reaction rate increases upon increasing carbon monoxide pressure and temperature as shown in Figs. 1 and 2. The increasing of the yield upon increasing carbon monoxide pressure slows down above ca. 80 atm. Almost quantitative yields can be reached upon increasing reaction time.

The yield is slightly influenced by the concentration of the substrate as it appears in Fig. 3. In the range 5–10 mol · l^{-1} the yield remains practically constant suggesting that the reaction rate is of zero order with respect to the substrate.

The reaction rate appears to be of first order with respect to the concentration of the catalyst (Fig. 4).

The effect of the concentration of H_2O is the most significant. The yield steeply increases upon increasing water concentration either when

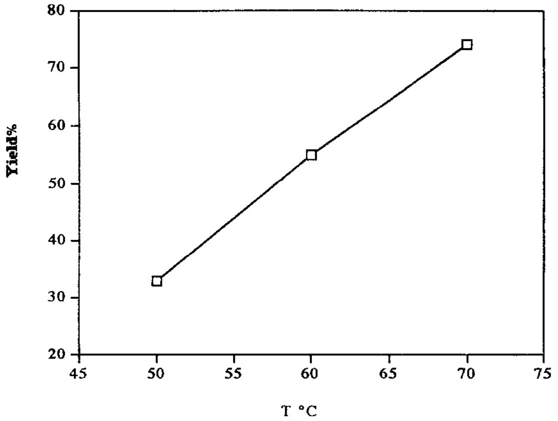


Fig. 2. Run conditions: $PhCOCH_2Cl$ 10 mmol; H_2O 55 mmol; $PdCl_2(PPh_3)_2$ $6.4 \cdot 10^{-3}$ mmol; PPh_3 0.2 mmol; EtOH 7.5 ml (V_{tot} = 10 ml); p_{CO} 50 atm at RT; reaction time 2 h.

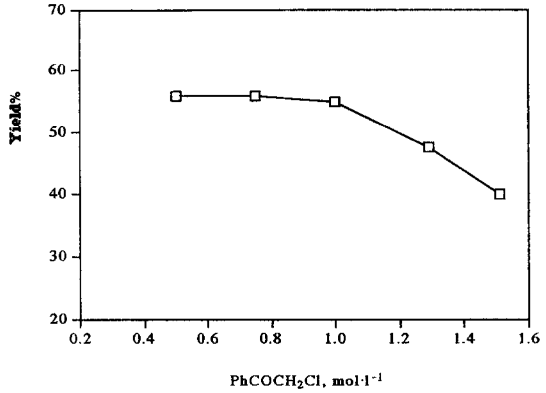
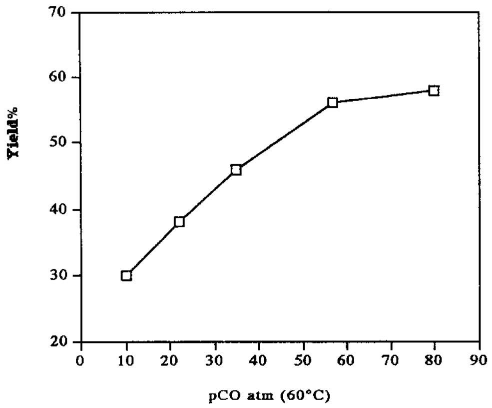


Fig. 3. Run conditions: p_{CO} 50 atm at RT; H_2O 55 mmol; $PdCl_2(PPh_3)_2$ $6.4 \cdot 10^{-3}$ mmol; PPh_3 0.2 mmol; EtOH 7.5 ml (V_{tot} = 10 ml); 60°C; reaction time 2 h.



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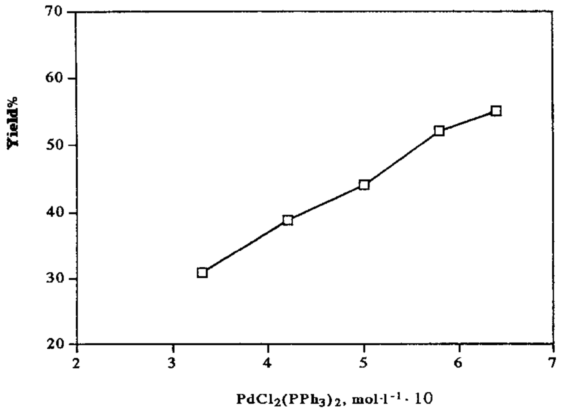

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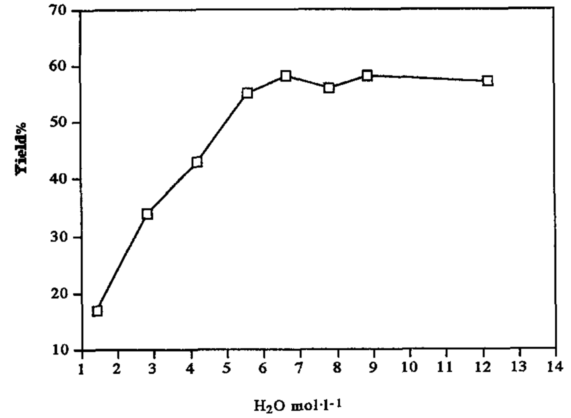


Fig. 5. Run conditions: $PhCOCH_2Cl$ 10 mmol; H_2O 55 mmol; $PdCl_2(PPh_3)_2$ $6.4 \cdot 10^{-3}$ mmol; PPh_3 0.2 mmol; $EtOH+H_2O$ 8.5 ml (V_{tot} = 10 ml); p_{CO} 50 atm at RT; 60°C, reaction time 2 h.

ethanol or dioxane is used as solvent, as shown in Figs. 5 and 6, respectively. At 100°C in dioxane the reaction rate appears to be approximately that of the first order with respect to the concentration of water. In ethanol at low concentration of water the reaction rate regularly increases to reach a plateau above $6–7 \cdot 10^{-2}$ $mol \cdot l^{-1}$ of water.

2.2. The mechanism of the hydrodechlorination of α-chloroacetophenone

In an earlier work we found that the catalyst precursor of Pd(II) is reduced to a Pd(0) species under the action of carbon monoxide and water. For example, in the presence of added PPh_3 the precursor is transformed into $Pd(CO)(PPh_3)_3$ [8] while a molecule of CO is oxidized to CO_2:

$$PdCl_2(PPh_3)_2 + 2CO + H_2O \xrightarrow{CO,\ PPh_3} Pd(CO)(PPh_3)_3 + CO_2 + 2HCl \quad (2)$$

It is noteworthy to observe that Eq. (2) occurs even in the presence of relatively large amounts of hydrochloric acid, even though it has been reported that Pd(0) complexes are reoxidized by the acid to give the dichloride $PdCl_2(PPh_3)2$ [12].

Eq. (2) is closely related to the water gas shift reaction even though it occurs without formation of molecular hydrogen. It has been suggested that it occurs through a carbohydroxy intermediate, for example of type (I), which, after β-hydride abstraction and concomitant evolution of CO_2, leads to a palladium(II)-hydride species (intermediate (II)). Reductive elimination of hydrochloric acid from this hydride leads to the Pd(0) complex [7]:

$$PdCl_2(PPh_3)_2 + CO + H_2O \rightarrow \underset{(I)}{Pd(COOH)Cl(PPh_3)_2} + HCl \quad (3)$$

$$\underset{(I)}{Pd(COOH)Cl(PPh_3)_2} \rightarrow \underset{(II)}{PdClH(PPh_3)_2} + CO_2 \quad (4)$$

$$\begin{tikzcd}
\underset{(II)}{PdClH(PPh_3)_2} \arrow[r, "CO,\ PPh_3"] \arrow[dr, "HCl"'] & Pd(CO)(PPh_3)_3 + HCl \\
& PdCl_2(PPh_3)_2 + H_2
\end{tikzcd} \quad (5)$$

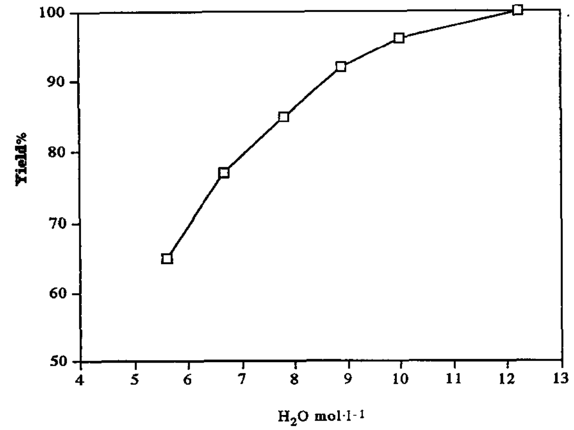


Fig. 6. Run conditions: $PhCOCH_2Cl$ 10 mmol; H_2O 55 mmol; $PdCl_2(PPh_3)_2$ 0.1 mmol; PPh_3 0.2 mmol; $Dioxane+H_2O$ 8.5 ml (V_{tot} = 10 ml); p_{CO} 50 atm at RT; 100°C, reaction time 2 h.

If the acid that forms in Eq. (3) reacted with hydride (II), there would be hydrogen evolution. In this case reactions Eqs. (3)–(5) would be the steps of the water gas shift reaction catalyzed by $PdCl_2(PPh_3)_2$.

It has been reported also that a Pd(0) complex reacts with α-chloroacetophenone to give the product of oxidative addition complex (III) [13,14]:

$$Pd(PPh_3)_3 + PhCOCH_2Cl \rightarrow \underset{(III)}{Pd(CH_2COPh)Cl(PPh_3)_2} + PPh_3 \quad (6)$$

We found that complex (III) reacts with hydrochloric acid, dissolved in ethanol or dioxane, to yield acetophenone and $PdCl_2(PPh_3)_2$:

$$\underset{(III)}{Pd(CH_2COPh)Cl(PPh_3)_2} + HCl \rightarrow PdCl_2(PPh_3)_2 + PhCOCH_3 \quad (7)$$

Eq. (7) is closely related to the protonation of $[(PhCOCH_2)Fe(CO)_4]^-$ which leads to acetophenone [15].

Moreover, we found that complex (III), suspended in aqueous ethanol or dioxane in the presence of an additional amount of PPh_3, when pressurized with CO, is reduced to $Pd(CO)(PPh_3)_3$ and yields acetophenone with evolution of CO_2:

$$\underset{(III)}{Pd(CH_2COPh)Cl(PPh_3)_2} \xrightarrow[-CO_2,-HCl]{CO,H_2O,PPh_3} Pd(CO)(PPh_3)_3 + PhCOCH_3 \quad (8)$$

These experimental evidences suggest that the hydrodechlorination of α-chloroacetophenone may occur through two different mechanisms, both via intermediate (III), which forms through the oxidative addition of the organic chloride to a Pd(0) complex, like in Eq. (6). One mechanism then proceeds through protonolysis of the Pd–C bond of (III) by hydrochloric acid, like in Eq. (7), with formation of the hydrodechlorination product and of a Pd(II) complex, which is then reduced to the starting Pd(0) complex through a sequence of reactions like Eqs. (3)–(5). Following the other mechanism, interaction of carbon monoxide with water on intermediate (III) leads to the formation of a carbohydroxy intermediate like (IV), which evolves carbon dioxide with formation of the hydride intermediate (V). Reductive elimination of $(PhCOCH_2)$ and of the hydride gives acetophenone and the Pd(0) species back to the catalytic cycle:

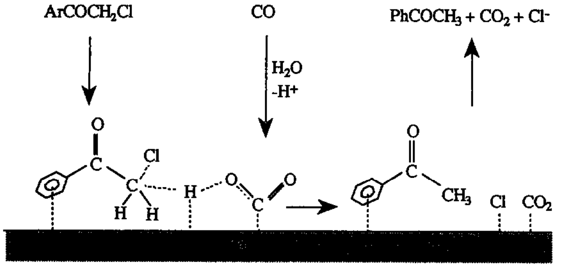
$$\underset{(III)}{Cl\text{–}Pd\text{–}CH_2COPh} \xrightarrow[-H^+]{CO,H_2O} \underset{(IV)}{HOOC\text{–}Pd\text{–}CH_2COPh} \xrightarrow{-CO_2} \underset{(V)}{\text{–}\underset{\underset{H}{|}}{Pd}\text{–}CH_2COPh} \rightarrow Pd(0) + PhCOCH_3 \quad (9)$$

The intermediacy of a Pd–COOH species was proposed also for the hydrogen transfer from CO and H_2O to γ-ketoacid derivatives catalyzed by a $PdCl_2(PPh_3)_2$ precursor in combination with hydrochloric acid [7].

As already mentioned, we found that the hydrodechlorination of α-chloroacetophenone is catalyzed also by Pd/C. In this case a key step of the catalytic cycle can be the displacement of the chloride anion by a hydride anion which is proposed to form after interaction of carbon monoxide and water on the palladium surface with formation of a carbohydroxy intermediate (Scheme 1).

If a palladium atom inserts into a C–Cl bond of the chloride absorbed on the surface the above mechanism is closely related to the one just proposed for the hydrodechlorination reaction when $PdCl_2(PPh_3)_2$ is used as catalyst precursor (Eq. (9)). A similar mechanism has been proposed for the Pd/C–HCl catalyzed hydrogen transfer from H_2O–CO to mandelic acid derivatives which leads to arylacetic acid derivatives [8].

In addition we found that, when complex (III) is allowed to react with carbon monoxide in ethanol and in the presence of a base, such as for example triethylamine, there is formation of the expected carbonylation product, the β-ketoester $PhCOCH_2COOEt$, and of several palladium complexes, $Pd(CO)(PPh_3)_3$, $PdCl(COOEt)(PPh_3)_2$ and $PdCl_2(PPh_3)_2$. This



Scheme 1. Scheme 1Proposed reaction pathway for the hydrodechlorination of $PhCOCH_2Cl$ by hydrogen transfer from H_2O–CO catalyzed by Pd/C.

fact sheds light to the reaction pathway for the carbonylation of α-chloroacetophenone catalyzed by Pd(II) complex in the presence of a base.

For the carbonylation of an organic halide catalyzed by palladium complexes two mechanisms are widely accepted [3]. They have in common the oxidative addition step of the halide to a Pd(0) complex with formation of a Pd-alkyl intermediate (VI) analogous to intermediate (III). One mechanism involves then the insertion of carbon monoxide into the Pd–C bond of the alkyl species with formation of the acyl intermediate (VII). Nucleophilic attack of the alkanol on the carbon atom of the acyl ligand yields the ester and a Pd(0) species back to the catalytic cycle. The presence of a base is required in order to neutralize the acid which forms during the course of the reaction: otherwise it would oxidize the Pd(0) species to a Pd(II) halide thus preventing the oxidative addition step of the organic halide to intermediate (VI):

$$\mathrm{Pd(0)} + \text{R-X} \rightarrow \underset{(\mathrm{VI})}{\text{X-Pd-R}} \xrightarrow{\mathrm{CO}} \underset{(\mathrm{VII})}{\text{X-Pd-COR}} \xrightarrow[\mathrm{B}]{\mathrm{R'OH}} \mathrm{Pd(0)} + \mathrm{RCOOR'} + \mathrm{B}\cdot\mathrm{HX} \qquad (10)$$

Following the other proposed mechanism, intermediate (VI) reacts with carbon monoxide and the alkanol with formation a carboalkoxy intermediate (VIII). Reductive elimination of R and of (COOR′) yields the ester and a Pd(0) complex which starts another catalytic cycle:

$$\text{R-Pd-X} + \mathrm{CO} + \mathrm{R'OH} \xrightarrow[-\mathrm{B}\cdot\mathrm{HX}]{\mathrm{B}} \underset{(\mathrm{VIII})}{\text{R-Pd-COOR}'} \rightarrow \mathrm{Pd(0)} + \mathrm{RCOOR'} \qquad (11)$$

It is known that the formation of the carboalkoxy species is favored when the reaction is carried out in the presence of a base [16,17], whose main role is to neutralize the proton arising in the step forming the carboalkoxy species (VIII), otherwise this step would be reversed [17]:

$$-\mathrm{Pd{-}COOR'} + \mathrm{HX} \rightarrow -\mathrm{Pd{-}CO^{+}X^{-}} + \mathrm{R'OH} \qquad (12)$$

Going back to the hydrodechlorination reaction, this occurs when it is carried out in the absence of any base. The acid that forms during the reaction prevents the formation of any carbohydroxy species and hence that of the ester. On the other hand it splits the Pd–C bond yielding the hydrodechlorination product and a Pd(II) complex, following the proposed mechanism in which Eq. (7) plays a key role. As already pointed out, the acid does not prevent the reduction of the Pd(II) species which likely occurs through the intermediacy of a Pd–(COOH) species, as schematized by Eqs. (3)–(5). Thus the hydrodechlorination reaction may occur also through a mechanism depicted by Eq. (9).

In principle, acetophenone could form also through a carbonylation reaction with formation of a β-ketoacid intermediate (IX), which is unstable and gives off CO_2 [18], with formation of the observed product, acetophenone:

$$\mathrm{PhCOCH_2Cl} + \mathrm{CO} + \mathrm{H_2O} \rightarrow \underset{(\mathrm{IX})}{\mathrm{PhCOCH_2COOH}} + \mathrm{HCl} \qquad (13)$$

$$\mathrm{PhCOCH_2COOH} \rightarrow \mathrm{PhCOCH_3} + \mathrm{CO_2} \qquad (14)$$

However, this is not the case because of the following reasons. First of all, as already pointed out, the carbonylation of organic halides usually requires the presence of a base. Second, palladium catalysts in carbonylation reactions are normally less active then that observed for Eq. (1), which occurs in high yield even when only ca. 0.5‰ of catalyst, with respect to the starting α-chloroacetophenone, is employed at a temperature as low as 60°C. Third, but most importantly, when Eq. (1) is carried out using EtOH as a solvent, if any carbonylation occurred, there would be formation of also of the β-ketoester. In this case, the ester would be detectable in the reaction mixture even though, through hydrolysis, it decomposes to acetophenone. In fact, under the conditions in which a typical hydrodechlorination experiment was carried out, but employing the ester in place of α-chloroacetophenone, we found that the ester only partially decomposes to acetophenone, the remaining being still present after heating the ester in aqueous EtOH in the presence of HCl for 2 h at 60°C (see Section 3).

In conclusion, both the hydrodechlorination and the carbonylation reactions proceed via an intermediate like (III), the latter reaction being favoured by the presence of a base. Otherwise intermediate (III) undergoes protonolysis or reduction by the CO–H_2O system to the hydrodechlorination product.

3. Experimental

3.1. Materials and reagents

Carbon monoxide, quality N 37, was purchased from S.I.O. Company. Solvents and PPh_3 were of commercial grade. α-chloroacetophenone was used without further purification. $PdCl_2(PPh_3)_2$ [19], $Pd(CO)(PPh_3)_3$ [20], $Pd(PPh_3)_4$ [21] and $Pd(CH_2COPh)Cl(PPh_3)_2$ [13,14] were prepared as reported in the literature.

3.2. Product identification and analysis

Products were identified by NMR on a Bruker 200 AC spectrometer, by IR on a Perkin Elmer model 683 spectrometer and by MS-GC on a HP 5890-series II instrument equipped with a HP 5971 A detector. Yields were determined by GC on a HP 5890-series II instrument.

3.3. Hydrodechlorination of α-chloroacetophenone by the system CO–H_2O catalyzed by palladium

In a typical experiment 1.5 g of α-chloroacetophenone (10 mmol) were dissolved in 7.5 ml of EtOH in a Pyrex bottle to which 1 ml of H_2O was added. To this solution 4.5 mg of $PdCl_2(PPh_3)_2$ (0.0065 mmol) and 52 mg of PPh_3 (0.2 mmol) were added. The bottle was placed into an autoclave which was purged with carbon monoxide at room temperature. The autoclave was then pressurized with 50 atm of the same gas and heated to 60°C. This temperature was maintained for 2 h while stirring. After cooling to room temperature, the mixture was analyzed by GC. The yield in acetophenone was 55%.

3.4. Protonolysis of $Pd(CH_2COPh)Cl(PPh_3)_2$ with hydrochloric acid

80 mg of $Pd(CH_2COPh)Cl(PPh_3)_2$ (0.1 mmol) were added under nitrogen to 1 ml of EtOH in which dry HCl was previously dissolved to make a 0.1 M solution. The suspension was heated to 60°C and maintained at this temperature for 2 h. After cooling the suspension was filtered. The solid was identified as $PdCl_2(PPh_3)_2$ by IR. The solution was analyzed by GC. Acetophenone was found to be present in an almost quantitative yield.

3.5. Reaction of $Pd(CH_2COPh)Cl(PPh_3)_2$ with H_2O–CO

80 mg of the complex together with an equimolecular amount of PPh_3, suspended in 1 ml of EtOH to which 0.1 ml of H_2O was added, were pressurized under 50 atm of CO at 60°C for 2 h. After cooling the suspension was filtered. The solid was a mixture of

$Pd(CO)(PPh_3)_3$, $PdCl_2(PPh_3)_2$ and $PdCl(COOEt)(PPh_3)_2$ as shown by IR.

3.6. Carbonylation of $Pd(CH_2COPh)Cl(PPh_3)_2$ in the presence of NEt_3 in EtOH

80 mg of the complex together with an equimolecular amount of PPh_3, were suspended in 5 ml of EtOH in which 0.12 mmol of NEt_3 were added. The mixture was pressurized with 50 atm of CO for 2 h at 60°C. After cooling the suspension was filtered. The solid showed the presence of $Pd(CO)(PPh_3)_3$, $PdCl_2(PPh_3)_2$ and $PdCl(COOEt)(PPh_3)_2$. The solution contained the β-ketoester $PhCOCH_2COOEt$.

3.7. Decomposition of $PhCOCH_2COOEt$ to acetophenone by aqueous hydrochloric acid in EtOH

In a Pyrex bottle, placed into an autoclave, 1.92 g of β-ketoester (10 mmol), 4.5 mg of $PdCl_2(PPh_3)_2$ together with 52 mg of PPh_3 were added to a mixture of EtOH and H_2O (7.5 ml of EtOH and 1 ml, respectively, in which 10 ml mol of HCl were dissolved). The autoclave, after purging with carbon monoxide at room temperature, was pressurized with 50 atm of the same gas and heated to 60°C for 2 h while stirring. After cooling to room temperature, the mixture was analyzed by GC. 37% of the ester decomposed to acetophenone, the remaining fraction being the starting ester.

Acknowledgements

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