Palladium-catalysed Carbonylation of Halogenoalkynes to Alkynylcarboxylic Acid Esters under Mild Conditions

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Palladium-catalysed carbonylation reactions of bromoalkynes and iodoalkynes, as well as the carbonylation reaction of σ-alkynylpalladium(II) complexes under atmospheric pressure of carbon monoxide lead to formation of alkynylcarboxylic acid esters.

Carbonylations of organohalides RX (R = alkyl, alkenyl, aryl, alkoxy; X = Br, I) with carbon monoxide in solutions of Pd or Pt complexes[1–3] are convenient preparative methods for various carboxylic acids and their derivatives. To our knowledge, there is only one example of a palladium-catalysed iodoalkyne carbonylation resulting in the formation of alkynylcarboxylic acid esters RC≡CCOOR′.[3] A triphenylphosphine complex of palladium(II) was used as a catalyst precursor. In general, the presence of triphenylphosphine results in increased solubility of low-valent palladium compounds, which are active catalysts in the reaction. However, the iodoalkyne carbonylation reaction catalysed by $PdCl_2(PPh_3)_2$ in a methanol–dioxane mixture occurred only at a high pressure of carbon monoxide (30 atm) and gave low yield of esters (16% yield of PhC≡CCOOMe). Bromoalkynes were not carboxylated at all under the same conditions.[3]

We have shown that halogenoalkynes RC≡CX (R = Ph, Me; X = Br, I) can be carboxylated in a methanol solution of PdX_2–LiX at 1 atm CO to the corresponding alkynylcarboxylic acid methyl esters. Reaction (1) is an effective preparative synthetic method for these esters because of the high yield of esters and the mild reaction conditions.

$$\mathrm{RC{\equiv}CX + CO + Et_3N + MeOH \xrightarrow[1\ atm,\ 40\,^{\circ}C]{PdX_2,\ LiX} RC{\equiv}CCOOMe + Et_3N{\cdot}HX} \qquad (1)$$

$$\mathrm{R = Ph, Me;\ X = Br, I}$$

RC≡CX (2 mmol) and Et_3N (2 mmol) were added to a mixture of PdX_2 (0.1 mmol) and LiX (0.2 mmol) in methanol (10 ml) under an atmospheric pressure of CO. The reaction was carried out at 40 °C with stirring during 25–30 min. At the beginning of the process, palladium salts were reduced by carbon monoxide, but black dispersed particles of palladium were dissolved in a few minutes and reaction (1) occured in a homogeneous solution. Products were determined by GLC (Table 1).

Table 1 Catalyst precursors and ester yields for some halogenoalkynes.

Halogenoalkyne	Catalyst precursor	Ester yield (%)
PhC≡CBr	$PdBr_2$	70
MeC≡CBr	$PdBr_2$	71
PhC≡CI	PdI_2	45
MeC≡CI	PdI_2	80

Sodium acetate can be used in place of Et_3N, but in this case the ester yield is lower, *e.g.* carbonylation of MeC≡CI in a solution of PdI_2–LiI–NaOAc (with equal molar concentrations of MeC≡CI and NaOAc) gave 54% of MeC≡CCOOMe instead of 80% when Et_3N was used. A higher triethylamine concentration, however, results in a decreased ester formation rate.

The mechanism of some organohalide carbonylation reactions was studied earlier. It was reported that complexes $RPdXL_2$ (R = alkyl,[4] phenyl[5]) were obtained by treatment of RX with zero-valent palladium complex PdL_4 and can be carboxylated with carbon monoxide,[6] so they are the most likely intermediates in carbonylation reactions of organohalides RX. By analogy, one can suppose that ethynyl compounds of palladium are intermediates in the reaction (1). The possibility of formation of a σ-alkynylpalladium(II) complex by oxidative addition of PhC≡CBr to $Pd(PPh_3)_4$ was established.[7] We have now carried out the carbonylation reaction of complex $(PhC{\equiv}C)_2Pd(PPh_3)_2$ prepared by a known method,[8] to ester PhC≡CCOOMe.

$$\mathrm{(PhC{\equiv}C)_2Pd(PPh_3)_2 + CO + MeOH \xrightarrow{1\ atm,\ 30\,^{\circ}C} 2PhC{\equiv}CCOOMe + Pd(PPh_3)_2 + 2[H]} \qquad (2)$$

The palladium complex (0.05 mmol) was carboxylated in a mixture of benzene (2 ml) and methanol (1 ml) during 3.5–4 h. Ester [0.014 mmol; 14% of theoretical yield, reaction (2)] and 1,4-diphenylbuta-1,3-diyne (0.013 mmol; 26% yield) were obtained.

The formation of alkynylcarboxylic acid esters by reaction (2) is in accordance with the suggestion that ethynyl compounds of palladium(II) are the key intermediates of carbonylation reactions resulting in RC≡CCOOR′ formation. Apparently they can be formed by different ways. In the previous paper,[9] we have reported the palladium-catalysed oxidative carbonylation of σ-alkynylcopper(I) complexes, reaction (3), using $CuCl_2$ as an oxidant.

$$\mathrm{RC{\equiv}CCu + CO + Ox + MeOH \xrightarrow{PdX_2,\ 1\ atm} RC{\equiv}CCOOMe + Cu^+ + Red} \qquad (3)$$

It was shown that the reaction intermediate RC≡CPd was formed by a transmetallation reaction of RC≡CCu with palladium(II) salts.[9] We have found that reaction (3) (R = Ph, Me) also occurs when iodine is used instead of $CuCl_2$, but in this case the main pathway for RC≡CPd formation is oxidative addition of RC≡CI to palladium. Iodoalkynes, the intermediate products of reaction (3) in the presence of I_2, are formed by reaction of RC≡CCu with I_2.

Carbonylation of PhC≡CCu or MeC≡CCu (1 mmol) was carried out in a methanol solution (10 ml) of PdI_2 (0.1 mmol)–I_2 (1 mmol)–NaOAc (1 mmol) at 40 °C under an atmospheric pressure of CO during 25 min. At the start of the reaction (time interval of 2–4 min), RC≡CI (R = Ph, Me) was formed in high yield (*ca.* 90%), then its concentration reduced at the same time the ester concentration increased. The yields of PhC≡CCOOMe and MeC≡CCOOMe are 29% and 25%, respectively. In addition, iodo-derivatives RCI=CHI, $RCI{=}CI_2$, dialkyne RC≡CC≡CR and diesters RC(COOMe)=CH(COOMe) (R = Ph, Me) were obtained with a summary yield of all products of *ca.* 65%.

In the presence of excess iodine (using 2 mmol instead of 1 mmol in the experiment described above), the RC≡CCOOMe esters were not obtained at all; this demonstrates the participation of low-valent palladium in this reaction.

We have also obtained PhC≡CCOOMe (26% yield) by carbonylation of PhC≡CH with CO in a PdI_2–I_2–NaOAc methanol solution. (PhCI=CHI was formed as a main product in this solution). PhC≡CCOOMe was obtained after PhC≡CI was formed and palladium(II) salt was reduced. Ester formation must occur from iodoalkyne as an intermediate product.

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