

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

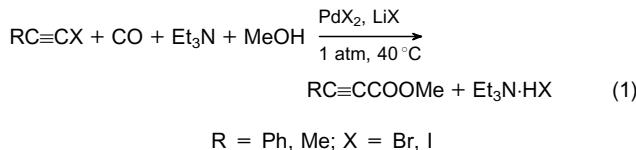
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Palladium-catalysed carbonylation reactions of bromoalkynes and iodoalkynes, as well as the carbonylation reaction of σ -alkynylpalladium(II) complexes under atmospheric pressure of carbon monoxide lead to formation of alkynylcarboxylic acid esters.

Carbonylations of organohalides RX ($R = \text{alkyl, alkenyl, aryl, alkoxy}; X = \text{Br, I}$) 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 $\text{RC}\equiv\text{CCOOR}'$.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 $\text{PdCl}_2(\text{PPh}_3)_2$ 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 $\text{PhC}\equiv\text{CCOOMe}$). Bromoalkynes were not carboxylated at all under the same conditions.³

We have shown that halogenoalkynes $\text{RC}\equiv\text{CX}$ ($R = \text{Ph, Me}; X = \text{Br, I}$) can be carboxylated in a methanol solution of $\text{PdX}_2\text{-LiX}$ 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.



$\text{RC}\equiv\text{CX}$ (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) occurred in a homogeneous solution. Products were determined by GLC (Table 1).

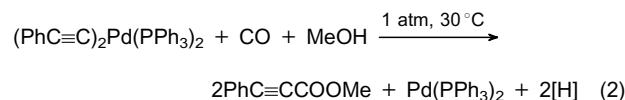
Table 1 Catalyst precursors and ester yields for some halogenoalkynes.

Halogenoalkyne	Catalyst precursor	Ester yield (%)
$\text{PhC}\equiv\text{CBr}$	PdBr_2	70
$\text{MeC}\equiv\text{CBr}$	PdBr_2	71
$\text{PhC}\equiv\text{CI}$	PdI_2	45
$\text{MeC}\equiv\text{CI}$	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 $\text{MeC}\equiv\text{CI}$ in a solution of $\text{PdI}_2\text{-LiI-NaOAc}$ (with equal molar concentrations of $\text{MeC}\equiv\text{CI}$ and NaOAc) gave 54% of $\text{MeC}\equiv\text{CCOOME}$ instead of 80% when Et_3N was used. A higher triethylamine concentration, however, results in a decreased ester formation rate.

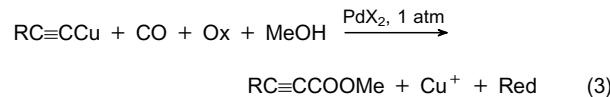
The mechanism of some organohalide carbonylation reactions was studied earlier. It was reported that complexes RPdXL_2 ($R = \text{alkyl, }^4 \text{phenyl}^5$) were obtained by treatment of

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 $\text{PhC}\equiv\text{CBr}$ to $\text{Pd}(\text{PPh}_3)_4$ was established.⁷ We have now carried out the carbonylation reaction of complex $(\text{PhC}\equiv\text{C})_2\text{Pd}(\text{PPh}_3)_2$ prepared by a known method,⁸ to ester $\text{PhC}\equiv\text{CCOOMe}$.



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 $\text{RC}\equiv\text{CCOOR}'$ 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.



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

Carbonylation of $\text{PhC}\equiv\text{CCu}$ or $\text{MeC}\equiv\text{CCu}$ (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), $\text{RC}\equiv\text{CI}$ ($R = \text{Ph, Me}$) was formed in high yield (ca. 90%), then its concentration reduced at the same time the ester concentration increased. The yields of $\text{PhC}\equiv\text{CCOOMe}$ and $\text{MeC}\equiv\text{CCOOMe}$ are 29% and 25%, respectively. In addition, iodo-derivatives RCI=CHI , RCI=CI_2 , dialkyne $\text{RC}\equiv\text{CC}\equiv\text{CR}$ and diesters $\text{RC(COOMe)=CH(COOMe)}$ ($R = \text{Ph, Me}$) 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 $\text{RC}\equiv\text{CCOOMe}$ esters were not obtained at all; this demonstrates the participation of low-valent palladium in this

reaction.

We have also obtained $\text{PhC}\equiv\text{CCOOMe}$ (26% yield) by carbonylation of $\text{PhC}\equiv\text{CH}$ with CO in a $\text{PdI}_2\text{--I}_2\text{--NaOAc}$ methanol solution. (PhCl=CHI was formed as a main product in this solution). $\text{PhC}\equiv\text{CCOOMe}$ was obtained after $\text{PhC}\equiv\text{CI}$ was formed and palladium(II) salt was reduced. Ester formation must occur from iodoalkyne as an intermediate product.

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