

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

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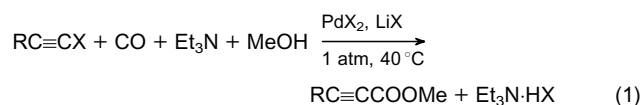
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Palladium-catalysed carbonylation reactions of bromoalkynes and iodoalkynes, as well as the carbonylation reaction of  $\sigma$ -alkynylpalladium(II) complexes under atmospheric pressure of carbon monoxide lead to formation of alkynylcarboxylic acid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

Carbonylations of organohalides RX (R = alkyl, alkenyl, aryl, alkoxy; X = Br, I) with carbon monoxide in solutions of Pd or Pt complexes<sup>1-3</sup> 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  $RC\equiv CCOOR'$ .<sup>3</sup> 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  $PhC\equiv CCOOMe$ ). Bromoalkynes were not carboxylated at all under the same conditions.<sup>3</sup>

We have shown that halogenoalkynes  $RC\equiv CX$  (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.



$RC\equiv CX$  (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  $40^\circ C$  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).

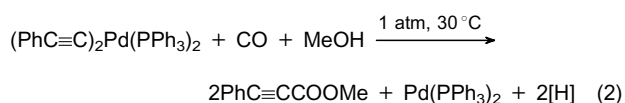
**Table 1** Catalyst precursors and ester yields for some halogenoalkynes.

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

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

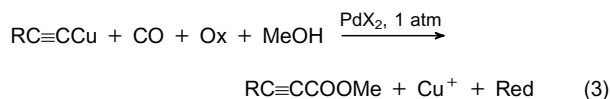
The mechanism of some organohalide carbonylation reactions was studied earlier. It was reported that complexes  $RPdXL_2$  (R = alkyl,<sup>4</sup> phenyl<sup>5</sup>) were obtained by treatment of

RX with zero-valent palladium complex  $PdL_4$  and can be carboxylated with carbon monoxide,<sup>6</sup> 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  $\sigma$ -alkynylpalladium(II) complex by oxidative addition of  $PhC\equiv CBr$  to  $Pd(PPh_3)_4$  was established.<sup>7</sup> We have now carried out the carbonylation reaction of complex  $(PhC\equiv C)_2Pd(PPh_3)_2$  prepared by a known method,<sup>8</sup> to ester  $PhC\equiv CCOOMe$ .



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  $RC\equiv CCOOR'$  formation. Apparently they can be formed by different ways. In the previous paper,<sup>9</sup> we have reported the palladium-catalysed oxidative carbonylation of  $\sigma$ -alkynylcopper(I) complexes, reaction (3), using  $CuCl_2$  as an oxidant.



It was shown that the reaction intermediate  $RC\equiv CPd$  was formed by a transmetallation reaction of  $RC\equiv CCu$  with palladium(II) salts.<sup>9</sup> 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  $RC\equiv CPd$  formation is oxidative addition of  $RC\equiv CI$  to palladium. Iodoalkynes, the intermediate products of reaction (3) in the presence of  $I_2$ , are formed by reaction of  $RC\equiv CCu$  with  $I_2$ .

Carbonylation of  $PhC\equiv CCu$  or  $MeC\equiv CCu$  (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  $40^\circ C$  under an atmospheric pressure of CO during 25 min. At the start of the reaction (time interval of 2–4 min),  $RC\equiv CI$  (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  $PhC\equiv CCOOMe$  and  $MeC\equiv CCOOMe$  are 29% and 25%, respectively. In addition, iodo-derivatives  $RCI=CHI$ ,  $RCI=CI_2$ , dialkyne  $RC\equiv CC\equiv CR$  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  $RC\equiv CCOOMe$  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. ( $\text{PhCI=CHI}$  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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