Journal of Organometallic Chemistry, 285 (1985) 415–418
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PALLADIUM-CATALYZED SYNTHESIS OF AROMATIC ACID DERIVATIVES BY CARBONYLATION OF ARYL IODIDES AND Alk_3SnNu (Nu = MeO, Et_2N, PhS, EtS)

N.A. BUMAGIN, Yu.V. GULEVICH, I.P. BELETSKAYA*

Moscow State University, 119899 GSP Moscow B-234 (U.S.S.R.) and Karpov' Institute of Physical Chemistry, 107120 Moscow (U.S.S.R.)

(Received December 11th, 1984)

Summary

Carbonylation of the ArI/Alk_3SnNu system (Nu = MeO, Et_2N), leading to esters and amides of substituted benzoic acids, occurs readily in the presence of phosphinepalladium complexes. When Nu = PhS and EtS either a cross-coupling product (Ar = p-$NO_2C_6H_4$) or a carbonylation product (Ar = Ph) is formed predominantly, depending on the nature of ArI. Stoichiometric reactions of $ArPdI(PPh_3)_2$ with carbon monoxide, resulting in acylpalladium complexes, and reactions of $ArCOPdI(PPh_3)_2$ with Alk_3SnNu have been studied. Some mechanistic aspects are discussed.

Recently we have shown [1] that carbon monoxide reacts with organotins and aryl iodides in the presence of "ligandless" palladium under very mild conditions, giving unsymmetrical ketones in high yields. In the present paper we report carbonylation of aryl iodides-tin nucleophiles (ArI/Alk_3SnNu).

$$\mathrm{ArI + Alk_3SnNu + CO \xrightarrow[\text{Solv., 20°C, 1 atm CO}]{\text{"Pd"}} ArCONu + Alk_3SnI} \tag{1}$$

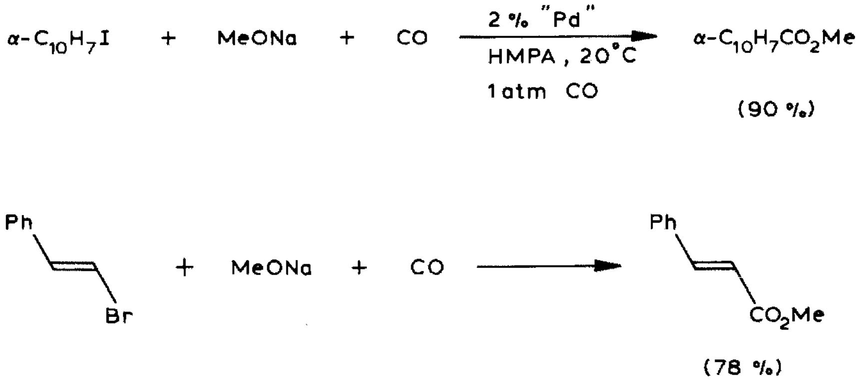
We found that, contrary to carbonylation of the $ArI/RSnMe_3$ system [1], the most efficient catalyst for reaction 1 (Nu = MeO) was the phosphinepalladium complex $PhPdI(PPh_3)_2$.

The influence of the solvent on the yield of the carbonylated product and the reaction rate were studied using the interaction of p-$NO_2C_6H_4I$ and Et_3SnOMe with CO. The highest rate and selectivity was found in HMPA; switching over to other solvents diminishes the reaction rate considerably, possibly due to decrease of nucleophilicity in less electron-donating solvents.

Palladium-catalyzed carboalkoxylation of aryl halides was carried out in the presence of metal alcoholates (eq. 2). Mg and Al alcoholates as well as the

$$\mathrm{ArI + (R'O)_nM + CO \xrightarrow[\text{Solv., 20°C, 1 atm CO}]{\text{2\% PhPdIL}_2} RCO_2R'} \tag{2}$$

corresponding alcohols were actually unreactive under the conditions studied (HMPA, 20°C, 1 atm CO). However, sodium methylate did react in HMPA with aryl iodides containing electron-withdrawing groups; a nucleophilic substitution product was formed together with a carbonylation product. In methanol nucleophilic substitution can be suppressed entirely. Sodium methylate can be used successfully in the carbonylation of α-iodonaphthalene and (E)-β-bromostyrene (eq. 3).



(3)

In the presence of Me_3SnNEt_2 as the nucleophile amidation of aryl iodides proceeds readily (eq. 4).

$$\underset{1.5\text{ eqv.}}{ArI + Me_3SnNEt_2} + CO \xrightarrow[\text{HMPA, 20°C, 1 atm CO}]{2\%\text{ “Pd”}} \underset{(82\text{–}90\%)}{ArCONEt_2} \tag{4}$$

($Ar = Ph$, p-$NO_2C_6H_4$)

When Et_2NH was used as the nucleophile carbonylation occurred to a minor extent and was selective (eq. 5).

$$p\text{-}NO_2C_6H_4I + Et_2NH + CO \xrightarrow[\text{HMPA, 20°C, 5 h, 1 atm CO}]{2\%\text{ “Pd”}} \underset{(23\%)}{p\text{-}NO_2C_6H_4CONEt_2} \tag{5}$$

In competing reactions of carbonylation of p-$NO_2C_6H_4I$ the reactivity ratio of Me_3SnNEt_2 to Et_3SnOMe was found to be 2.7/1.

The nature of aryl iodides had a crucial influence on the direction of reactions with Et_3SnSR' and carbon monoxide. Strong electron-withdrawing groups (e.g. O_2N) in the aryl iodides led to the formation of the corresponding sulphides as major products arising from cross-coupling. Increase of CO pressure up to 6 atm had only little influence on the relative yields of carbonylation and cross-coupling products. Only corresponding thio esters were formed in the reactions of aryl iodides without electron-withdrawing substituents. Tin sulphides were more advantageous than sodium sulphides as illustrated by eq. 6.

$$\underset{(96\%)}{p\text{-}ClC_6H_4COSPh} \xleftarrow[\text{“Pd”, HMPA, 20°C, 4 h, 1 atm CO}]{Et_3SnSPh} p\text{-}ClC_6H_4I \xrightarrow[\text{“Pd”, HMPA, 20°C, 4 h, 1 atm CO}]{PhSNa} \underset{(0\%)}{p\text{-}ClC_6H_4COSPh} \tag{6}$$

A catalytic cycle, involving oxidative addition, CO insertion, *trans*-metalation and reductive elimination, can be suggested for palladium-catalyzed carbonylation of the ArI/Alk$_3$SnNu system [2,3]. Separate catalytic steps were simulated by stoichiometric reactions. The results are presented in equations 7–13.

$$p\text{-}\mathrm{NO_2C_6H_4PdIL_2} \xrightarrow[\text{HMPA , 20°C, 5 h}]{\text{1 atm CO}} p\text{-}\mathrm{NO_2C_6H_4COPdIL_2} \longrightarrow$$

$$\xrightarrow[\text{HMPA , 20°C}]{\text{Argon}} \xrightarrow[\text{2 h}]{\mathrm{Et_3SnOMe}} p\text{-}\mathrm{NO_2C_6H_4CO_2Me}\ (60\%) \tag{7}$$

$$\xrightarrow[\text{HMPA , 20°C}]{\text{Argon}} \xrightarrow[\text{2 h}]{\mathrm{Me_3SnNEt_2}} p\text{-}\mathrm{NO_2C_6H_4CONEt_2}\ (0\%) \tag{8}$$

$$\xrightarrow[\text{HMPA , 20°C}]{\text{Argon}} \xrightarrow[\text{0.5 h}]{\mathrm{Et_3SnSPh_2 4L}} p\text{-}\mathrm{NO_2C_6H_4COSPh}\ (67\%) \tag{9}$$

$$p\text{-}\mathrm{NO_2C_6H_4PdIL_2} \xrightarrow[\text{HMPA , 20°C, 5h}]{\text{1 atm CO, }\mathrm{Me_3SnNEt_2}} p\text{-}\mathrm{NO_2C_6H_4CONEt_2}\ (43\%) \tag{10}$$

$$\mathrm{PhPdIL_2} \xrightarrow[\text{HMPA , 20°C , 1.5 h}]{\text{1 atm CO}} \mathrm{PhCOPdIL_2} \xrightarrow[\text{20°C , 4 h}]{\mathrm{Et_3SnSPh}} \mathrm{PhCOSPh}\ (61\%) \tag{11}$$

$$p\text{-}\mathrm{NO_2C_6H_4PdIL_2} \xrightarrow[\text{HMPA , 20°C, 1 h}]{\mathrm{Et_3SnSPh}} p\text{-}\mathrm{NO_2C_6H_4SPh}\ (68\%) \tag{12}$$

$$\mathrm{PhPdIL_2} \xrightarrow[\text{HMPA , 20°C, 48 h}]{\mathrm{Et_3SnSPh}} \mathrm{Ph_2S}\ (88\%) \tag{13}$$

$(\mathrm{L} = \mathrm{PPh_3})$

The data obtained suggest that CO insertion into C–Pd bonds in arylpalladium(II) complexes is slowed down when electron-withdrawing substituents are introduced into the aromatic ring, and the *trans*-metalation stage is made easier (see eq. 7–9 and 11; 12 and 13). That is why in the reaction of p-$NO_2C_6H_4I$ with Et_3SnSPh and CO, catalyzed by $PhPdIL_2$, p-$NO_2C_6H_4SPh$ is the main product, and in the reaction of PhI, PhCOPh.

Unexpected results were obtained in the reaction of an acylpalladium(II) complex with Me_3SnNEt_2. Not even traces of $ArCONEt_2$ were found (eq. 9). However, when a stoichiometric reaction was performed as shown in eq. 10, 43% of the corresponding amide was formed. These results indicate a different reaction mechanism for trialkyltin amides involving coordination of CO and Et_2N addition to CO in carbonylpalladium(II) complexes and subsequent reductive elimination.

$$ArPdIL_2 + CO \rightleftarrows ArPdI(CO)L_2 \xrightarrow[-Alk_3SnI]{Alk_3SnNEt_2} \qquad (14)$$

$$ArPd(CONEt_2)L_2 \rightarrow ArCONEt_2 + PdL_2$$

A similar mechanism was suggested in ref. 4 for the reaction of double carbonylations of organic halides.

References

1 N.A. Bumagin, I.G. Bumagina, A.N. Kashin and I.P. Beletskaya, Dokl. Akad. Nauk SSSR, 261 (1981) 1141.

2 I.P. Beletskaya, J. Organomet. Chem., 250 (1983) 551.

3 M. Tanaka, Bull. Chem. Soc. Jpn., 54 (1981) 637.

4 F. Ozawa, H. Soyoma, T. Yamamoto and A. Yamamoto, Tetrahedron Lett., 23 (1982) 3383.