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Palladium-catalyzed carbonylation of aryl iodides in aqueous media

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Abstract

Carbonylation of ArI in aqueous media under 1 atm CO in the presence of phosphineless palladium complexes and some base leads to aromatic acids.

Carbonylation of aryl iodides, in the presence of various nucleophiles and catalyzed by palladium complexes, is a convenient method for the synthesis of various aromatic carbonyl compounds viz., acids, esters, amides, thioesters, aldehydes and ketones. The reaction conditions, rates, and selectivity are extremely dependent on the nature of both the nucleophile and the ligands of palladium in the catalyst species [1–10]. Here we report on a useful method to obtain aromatic acids bearing different aromatic fragments and having various substituents in the benzene ring:

$$\mathrm{ArI} \xrightarrow[-\mathrm{I}^-]{\mathrm{CO,\ OH^-, \text{“}Pd\text{”}}} \mathrm{Ar{-}COO^-} \xrightarrow{\mathrm{H^+}} \mathrm{Ar{-}COOH}$$

The carbonylation of ArI (Ar = XC_6H_4, Naph, Het (het = heteryl)) has been carried out at room temperature and under 1 atm CO in water/DMF mixture (1/1 or 1/2 v/v) and even in water only, depending on the solubility of substrate. The palladium(II) complexes: $Pd(OAc)_2$, K_2PdCl_4, $PdCl_2(PPh_3)_2$ and $Pd(NH_3)_4Cl_2$ were used as the precursors of the catalyst, with either K_2CO_3 or NaOAc as the base (Table 1). An attempt to use ammonia as the base in water/ethanol solvent was unsuccessful since the reaction of p-IC_6H_4Cl gave three products: acid, ester and amide.

The use of palladium complexes without phosphine ligands allows us to carry out this reaction in water/DMF media at high rates and with good yields for iodoarenes that are either electron-withdrawing (entries 1, 3, 5, 8) or electron-donating (entry 7, 9) groups, and for β-iodonaphthalene (entry 17) and α-iodothiophene (entry 18). The presence of electron-withdrawing substituents such as NO_2, CN or Cl facilitates the reaction. As we have shown, the reaction of p-$O_2NC_6H_4I$ can be accomplished even in the presence of the phosphine palladium complex, and though the reaction

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Table 1

Reactions of ArI ($c_0 = 0.25$ M) with CO and H_2O in the presence of palladium catalyst and base under 1 atm CO at 25 ° C

Run	Aryl	Solvent, H_2O/ DMF	Catalyst, mol.% [a]	Base, equiv.	Reaction time (h)	Yield of ArCOOH (%) [b]	Additional product(s)
1	p-$NO_2C_6H_4$	1/2	A, 1	K_2CO_3,4	1	90	
2	p-$NO_2C_6H_4$	1/0	B, 1	K_2CO_3,2	5 [c]	30	ArI, 70%
3	p-$NO_2C_6H_4$	1/1	A, 1	NaOAc,4	15 [c]	97	
4	p-$NO_2C_6H_4$	1/2	C, 1	K_2CO_3,4	3 [c]	100	
5	p-ClC_6H_4	1/2	A, 1	K_2CO_3,4	2	92	
6	p-ClC_6H_4	1/2 [d]	A, 1	K_2CO_3,4	2	90	
7	p-$CH_3C_6H_4$	1/1	A, 1	K_2CO_3,4	4	100	
8	p-CNC_6H_4	1/2	A, 1	K_2CO_3,4	1.5	98	
9	p-$NH_2C_6H_4$	1/1	A, 1	K_2CO_3,4	4	68	ArI, Pd-black
10	p-$NH_2C_6H_5$	1/1	C, 1	K_2CO_3,4	20	0	ArI, Pd-black
11	p-$NH_2C_6H_4$	1/1	A, 1	NaOAc,4	20	0	ArI
12	p-HOC_6H_4	1/0	D, 1	K_2CO_3,6	6 [c]	92	
13	m-$HOOCC_6H_4$	1/0	B, 0.5	K_2CO_3,4	1	100 [b]	
14	m-$HOOCC_6H_4$	1/0	A, 1	K_2CO_3,6	0.5	80	
15	o-$HOOCC_6H_4$	1/9	B, 1	K_2CO_3,6	5 [c]	0	ArI
16	o-$HOOCC_6H_4$	1/0	B1, 2; NaI, 50	K_2CO_3,6	20 [c]	95	
17	β-$C_{10}H_7$	1/1	A, 1	K_2CO_3,4	5	82 [e]	
18	α-C_4H_9S	1/1	A, 1	K_2CO_3,4	10	85 [e]	
19	2-Pyridyl	1/1	A, 1	K_2CO_3, 4	5	0	2-Pyridone

[a] A = $Pd(OAc)_2$, B = K_2PdCl_4, C = $PdCl_2(PPh_3)_2$, D = $Pd(NH_3)_4Cl_2$. [b] Determined by TLC and UV spectroscopy after acidification of reaction mixture. [c] At 50 ° C. [d] 1,4-Dioxane. [e] Isolated yield.

is slower, the yield is better (entry 4). A weaker base such as NaOAc can be used in this reaction (entry 3). "Ligandless" palladium complex allows carbonylation of p-$O_2NC_6H_4I$ even in water only, though the rate of the reaction is sharply decreased because of the low solubility of substrate (entry 2).

Strong electron-donating substituents, which prevent oxidative addition, thus slow the reaction down. Thus, in the reaction of p-$NH_2C_6H_4I$ the yield falls to 68% and precipitation of Pd-black is observed (entry 9). In the case of p-HOC_6H_4I the negative effects of donor substituent can be overcome by using tetramminpalladium(II) chloride, which effectively catalyzes the reaction even in water only (entry 12). Note, that no carbonylation of the substrates with electron-donating groups takes place in the presence of NaOAc as a base (entry 11).

Carbonylation of m-$HOOCC_6H_4I$, soluble in aqueous K_2CO_3, is rapid with either: K_2PdCl_4 or $Pd(OAc)_2$ (entry 13, 14) as catalyst. Here the amount of palladium complex may be decreased (entry 14). A similar reaction involving the *ortho*-isomer fails to give the carbonylation product (entry 15), probably because of intramolecular coordination between palladium(II) and the *ortho*-carboxylic group in the intermediate arylpalladium complex. We have found that in the presence of iodide the reaction, although slow, gives an excellent yield of acid at elevated temperature (entry 16). This result is probably because of the cleavage of the metallacycle by the iodide.

Unfortunately, 2-iodopyridine is not carbonylated under such conditions, and the compound is readily hydrolyzed (entry 19). It is noteworthy that the hydrolysis proceeds only in the presence of zerovalent palladium generated from palladium(II) complexes and CO in basic media.

References

1 A. Shoenberg, I. Bartoletti and R.F. Heck, J. Org. Chem., 39 (1974) 3318.
2 A. Shoenberg and R.F. Heck, J. Org. Chem., 39 (1974) 3327.
3 J.K. Stille and P.K. Wong, J. Org. Chem., 40 (1975) 532.
4 M. Tanaka, Tetrahedron Lett., 28 (1979) 2601.
5 N.A. Bumagin, I.G. Bumagina, A.N. Kashin and I.P. Beletskaya, Dokl. Akad. Nauk SSSR., 261 (1981) 1141.
6 L. Cassar, M. Foa and A. Gardano, J. Organomet. Chem., 121 (1976) 55.
7 T. Kobayashi and M. Tanaka, J. Organomet. Chem., 205 (1981) 627.
8 N.A. Bumagin, Yu.V. Gulevich and I.P. Beletskaya, Izv. Akad. Nauk SSSR. Ser. Khim., (1986) 1649.
9 N.A. Bumagin, A.B. Ponomaryov and I.P. Beletskaya, Dokl. Akad. Nauk SSSR., 291 (1986) 868.
10 A. Huth, I. Beetz, I. Schumann and K. Thiebert, Tetrahedron., 43 (1987) 1071.