Brief Communications

Effective heterogeneous palladium catalysis of the reactions of organoboron compounds with aryl halides

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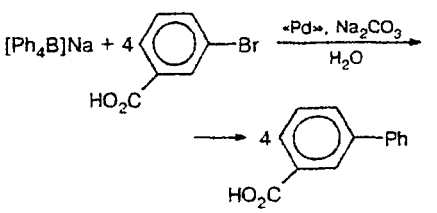
Reactions of $[Ph_4B]Na$ and $ArB(OH)_2$ with aryl halides are effectively catalyzed by heterogeneous palladium catalysts ($PdCl_2/C$, Pd(0)/C, and palladium black) to give cross-coupling products in high yields.

Key words: organoboron compounds; aryl halides; cross-coupling; heterogeneous palladium catalysis.

Palladium catalyzed cross-coupling reactions of organoboron compounds with organic halides are widely used as a method for carbon-carbon bond formation.[1—4] The longstanding interest in these reaction is above all explained by the fact that organoboron compounds make it possible to retain all functional groups in the course of cross-coupling without preliminary protection. The reactions are conventionally carried out in a mixture of an organic solvent and an aqueous solution of a base (Na_2CO_3, NaOH) in the presence of Pd phosphine complexes used as catalysts with prolonged heating. We have reported earlier[5,6] that cross-coupling of organoboron compounds with aryl halides can be easily performed in water or in a water-acetone mixture at room temperature in the presence of "ligandless" palladium. The significant disadvantage of the above mentioned modifications is use of one-time acting catalysts. The development of catalysts for these reactions that can be used many times is a problem of great practical interest.

For this purpose, we studied the catalytic activity of such easily available heterogeneous catalysts as $PdCl_2/C$, Pd(0)/C, and coarsely crystalline palladium black using the reaction of $[Ph_4B]Na$ with *m*-bromobenzoic acid as an example. The Pd(0)/C catalyst was prepared by immobilization of a Pd(0) complex with slightly coordinated ligands on the surface of activated carbon. The reaction was carried out in an aqueous Na_2CO_3 solution at 20—100 °C in the presence of 1 mol % Pd under argon. The results obtained are summarized in Table 1.

Pd(0)/C and $PdCl_2/C$ catalysts are close in their effectiveness: the reaction occurs at room temperature in 24 h to form *m*-phenylbenzoic acid in high yields (entries 1 and 4).



(1)

It is important that all four phenyl groups in $[Ph_4B]Na$ are involved in the reaction.

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Table 1. Reaction of $[Ph_4B]Na$ with *m*-BrC_6H_4COOH under conditions of heterogeneous Pd-catalysis, H_2O, Na_2CO_3, 1 mol % "Pd", argon

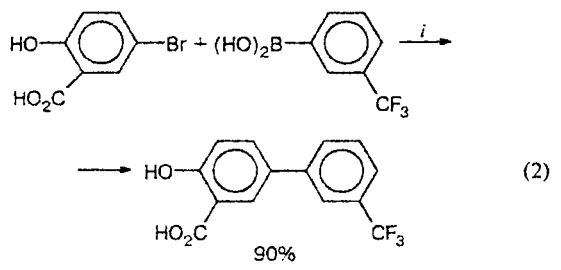
Entry	"Pd"[a]	*T*/°C	Time/h	Yield[b] (%)
1	A (1)	20	24	61
2	A (2)	20	24	31
3	A (3)	100	3	90
4	B (1)	20	24	86
5	B (2)	20	100	85
6	B (3)	20	120	85
7[c]	B (1)	20	6	96
8	C (1)	20	200	85
9[d]	C (1)	20	5	90

[a] "Pd": A — 1% Pd(0)/C, B — 10% $PdCl_2$/C, C—Pd-black. The number of reaction runs is given in parentheses. [b] The preparative yield is given. [c] Reaction of $[Ph_4B]Na$ with *m*-IC_6H_4COOH. [d] Reaction of *m*-$CF_3C_6H_4B(OH)_2$ with 5-bromosalicylic acid.

When these catalysts are re-used, their activity decreases (*cf.* entries 1 and 2). If either the reaction time or the temperature is increased, cross-coupling can be performed in almost quantitative yields (entries 3, 5, and 6). For example, reaction (1) gives *m*-PhC_6H_4COOH in 90% yield when it is carried out at 100 °C for 3 h in the presence of Pd(0)/C that had previously been used twice as a catalyst.

As should be expected, iodoarenes are much more reactive than the corresponding bromo derivatives: the reaction of *m*-iodobenzoic acid with $[Ph_4B]Na$ in the presence of $PdCl_2$/C is complete at 20 °C after 6 h to give *m*-PhC_6H_4COOH in 96% yield (entry 7).

We obtained the most promising and quite unexpected results when we attempted to use coarsely crystalline Pd-black as the catalyst. The aggregation of Pd(0) to Pd-black is generally believed to remove the catalyst from the reaction sphere, and thus block the catalytic process. However, it turned out that although reaction (1) proceeds much more slowly than in the case of Pd(0)/C and $PdCl_2$/C, at room temperature, it is complete after 8 days and gives the cross-coupled product in 85% yield (entry 8). The time of cross-coupling can be decreased to several hours if the reaction is carried out at an elevated temperature (entry 9). For instance, *m*-$CF_3C_6H_4B(OH)_2$ reacts with 5-bromosalicylic acid in the presence of 1 mol % Pd-black at

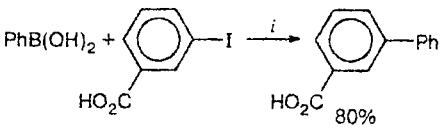


(2)

i. Pd-black, Na_2CO_3, H_2O, 80 °C, 5 h

80 °C for 5 h to form 5-(3-trifluoromethylphenyl)salicylic acid (90%).

If aryl iodides (instead of aryl bromides) are used in the reactions with arylboronic acids, Pd-black is a very effective catalyst even at room temperature.



(3)

i. Pd-black, NaOH, H_2O, 20 °C, 3 h

In conclusion we should note that the procedures for isolation and purification of the end products are the simplest and the most convenient when Pd(0)/C and Pd-black are used as the catalysts, because in these cases the reactions lead only to the cross-coupled products. When $PdCl_2$/C (1 mol % Pd) is used, the corresponding diaryl (to 2%) is obtained in the reaction due to the reduction of $PdCl_2$ to Pd(0) either with arylboronic acid or with $[Ph_4B]Na$.

Experimental

A. *m*-Bromobenzoic acid (0.201 g, 1 mmol), a 1.7 *M* aqueous solution of Na_2CO_3 (1.76 mL, 3 mmol), $[Ph_4B]Na$ (0.0927 g, 0.27 mmol), and water (3.24 mL) were added under argon to 0.106 g of 1% Pd(0)/C (0.01 mmol of Pd), which had been previously used twice as a catalyst. The reaction mixture was boiled for 3 h and cooled. The catalyst was filtered off, and the reaction mixture was diluted with water (200 mL) and acidified with HCl. The precipitate that formed was filtered off, washed with water, and dried *in vacuo* over P_2O_5 to afford *m*-phenylbenzoic acid (0.178 g, 90%), m.p. 164—165 °C (lit.[8]: 166 °C).

B. *m*-Iodobenzoic acid (0.246 g, 1 mmol), 1.76 mL of a 1.7 *M* aqueous solution of Na_2CO_3 (3 mmol), $[Ph_4B]Na$ (0.0927 g, 0.27 mmol), and water (3.24 mL) were added to 0.0176 g of 10% $PdCl_2$/C (0.01 mmol of $PdCl_2$) under argon. The reaction mixture was stirred at 20 °C for 6 h. *m*-Phenylbenzoic acid (0.19 g, 95%, m.p. m.p. 163—165 °C) was isolated (similarly to procedure *A*).

C. A mixture of *m*-(trifluoromethyl)phenylboronic acid (0.308 g, 2 mmol), water 16.5 mL), 3.5 mL of a 1.7 *M* aqueous solution of Na_2CO_3 (6 mmol), 5-bromosalicylic acid (0.434 g, 2 mmol), and Pd-black (0.0022 g, 0.02 mmol) was stirred under argon at 80 °C for 5 h. The reaction mixture was then poured into water (300 mL) and heated at 40 °C with stirring until the precipitate was completely dissolved. The Pd-black was filtered from the solution, and the solution was worked up as described above (procedure *A*) to give 5-(3-trifluoromethylphenyl)salicylic acid (0.51 g, 90%), m.p. 182—183 °C. Found (%): C, 59.69; H, 3.16. $C_{14}H_9F_3O_3$. Calculated (%): C, 59.58; H, 3.18. ^1H NMR (300 MHz, $(CD_3)_2CO$), δ: 7.10 (d, 1 H, J = 6.6); 7.68—7.71 (m, 2 H); 7.90—7.96 (m, 3 H); 8.20—8.21 (m, 1 H).

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Effect of water on the palladium-catalyzed reaction of styrene with iodobenzene

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The effect of the amount of water in the solvent (DMF) on the rate of the reaction of styrene with iodobenzene in the presence of various palladium compounds has been studied. Addition of water to reaction mixture promotes the reaction. The effect of the addition water depends on the nature of the palladium complexes and temperature.

Key words: Heck reaction, catalysis, palladium, water, iodobenzene, styrene.

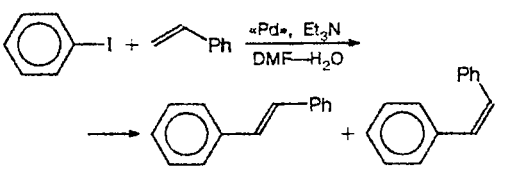
The reaction of organic halides with olefins catalyzed by palladium compounds (Heck reaction) is a widely used method for the formation of a carbon-carbon bond.[1—4] This reaction attracts great interest, because it makes it possible to perform highly regio- and stereoselective syntheses of unsaturated compounds of various types containing almost all functional groups. This reaction is conventionally carried out in an anhydrous organic solvent in the presence of a base. Recently several new modifications of the Heck reaction have been developed that make it possible to carry out the process either in a water-containing organic solvent or in water with both water-soluble and water-insoluble reactants in the presence of conventional palladium catalysts [PdX_2, $PdX_2(PPh_3)_2$, and $PdX_2(P(o\text{-Tol})_3)_2$].[5—11] Palladium complexes with hydrophilic phosphine ligands, $PPh_2(m\text{-}C_6H_4SO_3Na)$[12—13] and $P(m\text{-}C_6H_4SO_3Na)_3$,[14] have been used as the catalysts to carry out the reactions in water-organic solvent media ($MeCN—H_2O$, $EtOH—H_2O$). Additives of water to the catalytic systems DMF/K_2CO_3 and $EtOH/Bu_4NCl/Et_3N/NaHCO_3$ are of crucial importance in these reactions.[5,11]

In this work we have studied the influence of the addition of water on the rate of the Heck reaction in the presence of various palladium compounds. We succeeded in finding new effective reaction conditions ($DMF/H_2O/Et_3N$/"Pd") that allow us to decrease the reaction temperature.

Results and Discussion

As a model, we chose the reaction of styrene with iodobenzene in DMF in the presence of various palladium compounds and triethylamine (as a base). The reaction (Scheme 1) was carried out at 60 °C, and the reaction mixture was analyzed after 1.5 h.

Scheme 1



We chose this reaction primarily because it proceeds without the formation of any by-products to give *trans*-

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