Letters to the Editor

Pd black in water as an efficient catalyst of the Suzuki reaction

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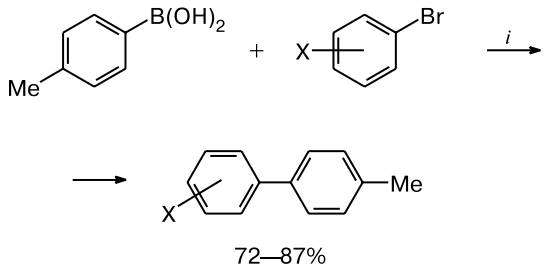
Cross-coupling of organoboron compounds with organic halides (the Suzuki reaction) is widely used in modern organic synthesis as a convenient method for the formation of new carbon—carbon bonds[1] with almost complete retention of functional groups in the reactants. The use of nonrecoverable Pd catalysts is a disadvantage of the presently known versions of the Suzuki reaction.[2] Therefore, the development of catalytic systems that could be used multiply is of great practical interest. Evidently, Pd black, being accessible and easily recoverable, is most attractive for this purpose. We have previously shown[3] that Pd black (1 mol.%) is an efficient catalyst in the Suzuki reaction at room temperature with water-soluble aryl iodides and water as a solvent. Cross-coupling of arylboronic acids with aryl iodides in methanol occurs on boiling of the reaction mixture in the presence of 50 mol.% of Pd black.[4] Under these conditions, aryl bromides do not react.

In the present work, we showed that Pd black is an efficient and easily recoverable catalyst in the cross-coupling of *p*-tolylboronic acid with *p*-bromoanisole, *m*-bromoaniline, and bromomesitylene, *i.e.*, the most inert substrates in the Suzuki reaction (Scheme 1).

After completion of the reaction, Pd black is separated by decantation and can be used repeatedly. In the case of aryl bromides containing electron-withdrawing substituents, the amount of the catalyst and duration of the reaction can be decreased (Scheme 2).

Scheme 1



X = 3-NH_2, 4-MeO, 2,4,6-Me_3
i. 50 mol.% of Pd black, Na_2CO_3, H_2O, 100 °C, 6—8 h

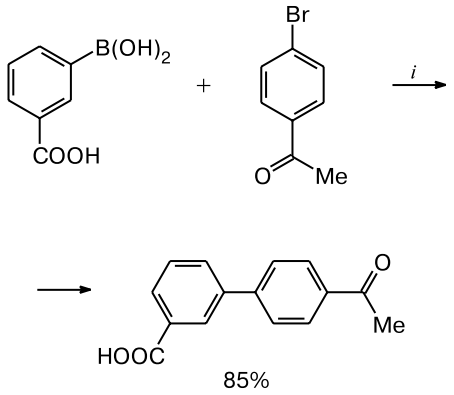
This catalytic system is so efficient that water-soluble aryl halides react in 5—10 min even in the presence of 1 mol.% of the catalyst (Scheme 3).

Pd black. A 0.1 *M* solution of $PdCl_2$ (100 mL) and HCO_2H (99%, 5 mL) were refluxed for 30 min. Pd black was separated by decantation, washed with water (5×10 mL), and dried for 2 h at 120 °C. The yield was 1.02 g (96%).

4-Methoxy-4′-methylbiphenyl. A mixture of *p*-bromoanisole (0.187 g, 1 mmol), *p*-tolylboronic acid (0.15 g, 1.1 mmol), Na_2CO_3 (0.212 g, 2 mmol), Bu_4NBr (0.003 g, 0.01 mmol), and Pd black (0.053 g, 0.5 mmol) in water (3 mL) was refluxed in a

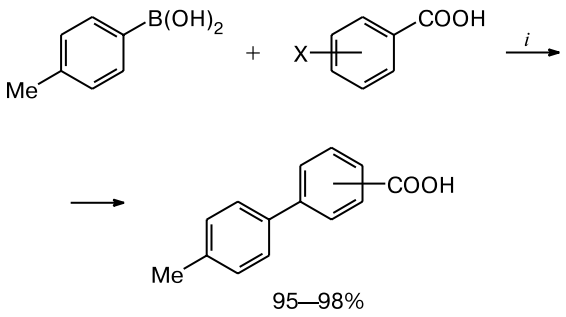
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1783—1784, August, 2003.

Scheme 2



i. 25 mol.% of Pd black, Na_2CO_3, H_2O, 100 °C, 2.5 h

Scheme 3



X = *m*-Br, *p*-I
i. 1 mol.% of Pd black, Na_2CO_3, H_2O, 100 °C, 5—10 min

Schlenk apparatus with vigorous stirring for 8 h under argon. After cooling, Pd black was separated by decantation, washed with water (3×5 mL), and dried for 2 h at 120 °C. The regenerated Pd black (0.052 g, 98%) was repeatedly used in cross-coupling reactions. The reaction product was extracted with ether. The combined ethereal extracts were dried with Na_2SO_4 and passed through a pad of silica gel. After removal of ether, 4-methoxy-4′-methylbiphenyl was obtained in 75% yield (0.148 g), m.p. 110 °C (*cf*. Ref. 5: 109 °C). ^{1}H NMR (DMSO-d_6, 300 MHz), δ: 2.33 (s, 3 H, MeAr); 3.79 (s, 3 H, MeOAr); 6.98 (d, 2 H, MeOCCH, J = 8.6 Hz); 7.24 (d, 2 H, MeAr, J = 8.0 Hz); 7.50 (d, 2 H, MeAr, J = 8.04 Hz); 7.57 (d, 2 H, MeOCCHCH, J = 8.0 Hz).

3-(4-Acetylphenyl)benzoic acid. The reaction of *p*-bromoacetophenone (0.199 g, 1 mmol) with *m*-carboxyphenylboronic acid (0.183 g, 1.1 mmol) in the presence of Pd black (0.027 g, 0.25 mmol), Na_2CO_3 (0.318 g, 3 mmol), and Bu_4NBr (0.003 g, 0.01 mmol) was carried out similarly for 2.5 h. This Pd black (0.027 g, 0.25 mmol) has been used in the previous experiment and in reactions of *p*-tolylboronic acid with *m*-bromoaniline and bromomesitylene. After Pd black was separated (0.025 g, 92%) and the reaction mixture was acidified with HCl, 3-(4-acetylphenyl)benzoic acid was obtained (0.405 g, 85%), m.p. 194 °C. ^{1}H NMR (DMSO-d_6, 300 MHz), δ: 2.62 (s, 3 H, MeCO); 7.64 (t, 1 H, C(5)H, J = 7.7 Hz); 7.89 (d, 2 H, C(2′)H, C(6′)H, J = 8.4 Hz), 7.98—8.02 (m, 2 H, C(4)H, C(6)H); 8.09 (d, 2 H, C(3′)H, J = 8.3 Hz); 8.24 (br.s, 1 H, C(2)H).

References

1. A. Suzuki, *J. Organomet. Chem.*, 1999, **576**, 147; N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.
2. S. Kotha, K. Lahiri, and D. Kashinath, *Tetrahedron*, 2002, **58**, 9633.
3. V. V. Bykov and N. A. Bumagin, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1399 [*Russ. Chem. Bull.*, 1997, **46**, 1344 (Engl. Transl.)].
4. W. Kabalka, V. Namboodiri, and L. Wang, *Chem. Commun.*, 2001, 775.
5. N. Kruber, *Ber.*, 1932, **65**, 1382.

Received April 22, 2003;
in revised form July 21, 2003