

Pd- and Cu-catalyzed selective Arylation of Benzotriazole by Diaryliodonium salts in Water.

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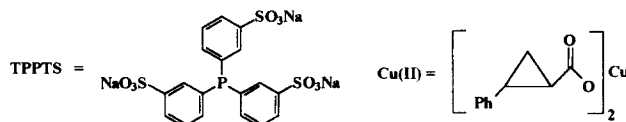
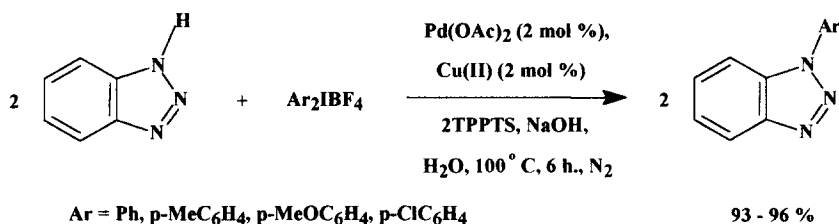
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Abstract: Palladium(0)-catalyzed arylation of 1*H*-1,2,3-benzotriazole (BTA) in water at 100° C with diaryliodonium salts proceeds in the presence of copper salt regioselectively at N-1 position. Best result has been obtained with the Pd(OAc)₂(tppts)₂ as catalyst and the Cu(II) phenylcyclopropylcarboxylate as co-catalyst. Both aryl groups from diaryliodonium salt participate in the reaction.

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Earlier we have carried out the direct regioselective Pd-catalyzed arylation of BTA by ArI in the presence of copper salts and base under solid/liquid phase transfer conditions in reflux DMF using PdCl₂(dppe) as precursor of catalyst.¹ However we failed to perform this reaction in water for PhI in the presence of water soluble ligand and even for water soluble ArI. Herein we have shown that BTA can be arylated in water by Ar₂IBF₄ in the presence TPPTS² and Pd(OAc)₂:



As in the case of ArI¹ the reaction leads to the mixture of N-1 and N-2 isomers (Table, entry 1), but in the presence of Cu(II)-salt (copper phenylcyclopropylcarboxylate) gives only N-1 isomer (entries 2-5) with quantitative yields for both electron-donor and electron-acceptor substituents in aryl groups. This Cu(II)-salt easily decomposes under heating (100°C) and produces low valent Cu-species most likely responsible for the selectivity. Both aryl groups participate into the reaction, although ArI does not react with BTA under these

conditions. This result suggest that ArI does not exist in a free form under such reaction conditions, always remaining in the coordination sphere of palladium.

Earlier diaryliodonium salts³ were used for arylation of N-containing heterocycles in noncatalytic reactions.⁴ However these reactions proceed nonselectively for ambident anions^{4c} and with participation of only one aryl group in all cases.

Table . The Arylation of BTA catalyzed by Pd(OAc)₂(tppts)₂ (2 mol %) and Cu(II)-salt (2 mol %) in Water in the presence of NaOH (2 mol %) at 100 °C. ⁵

NN	Arylation agent	Yield N-1 % ^{c,d}	Yield N-2 % ^{c,d}
1 ^a	Ph ₂ IBF ₄	60	21.5
2	Ph ₂ IBF ₄	96	-
3	(<i>p</i> -CH ₃ C ₆ H ₄) ₂ IBF ₄	93	-
4	(<i>p</i> -CH ₃ OC ₆ H ₄) ₂ IBF ₄	93	-
5	(<i>p</i> -ClC ₆ H ₄) ₂ IBF ₄	95	-
6 ^b	Ph ₂ IBF ₄	~50	-

^aWithout Cu(II)-salt. ^b Without Pd-catalyst. ^c N-1/N-2 ratio and yields of the products were obtained after the separation of the reaction mixture aliquots by TLC spectroscopically (UV-Vis). ^d All products were characterized by NMR, MS and elemental analysis.

References and notes:

- (a) Beletskaya I. P.; Davydov D. V.; Moreno-Mañas, M., *Tetrahedron Lett.* **1998**, 39, 5617-5620.
- (a) Cornils B.; Kuntz E.G., *J. Organometallic Chem.* **1995**, 502 (1-2), 177-186.
(b) Genet J.P.; Blart E.; Savignac, M., *SYNLETT*, **1992**, 9, 715-717.
(c) Safi M.; Sinou D., *Tetrahedron Lett.* **1991**, 32, 2025-2028.
(d) Casalnuovo A.L.; Calabrese J.C. *J. Am. Chem. Soc.* **1990**, 112, 4324-4330.
- (a) Varvoglis, A., *Synthesis*, **1984**, 706 – 726.
(b) Stang, P. J.; Zhdankin, V. V., *Chem. Rev.* **1996**, 96, 1123 - 1178.
- (a) Beringer, F. M.; Forgione, P.S., *J. Am. Chem. Soc.* **1953**, 75, 2708 - 2712.
(b) Nesmeyanov, A. N.; Makarova, L. G.; Tolstaya, T. P., *Tetrahedron*. **1957**, 1, 145 - 148.
(c) Akiyama T.; Imasaki Y.; Kawanisi, M., *Chem. Lett.* **1974**, 229 - 230.
(d) McKillop, A.; Kobylecki, R. J., *J. Org. Chem.* **1974**, 39, 2710 - 2714.
- Synthetic procedure:** The mixture of Na-BTA, obtained from 0.002 mol of BTA and 0.002 mol of NaOH, 2 mol % of Pd(OAc)₂, 4 mol % of TPPTS, 2 mol % of Cu(II)-salt and 0.001 mol of Ar₂IBF₄ was heated at reflux in 25 ml. of water under N₂ for 6 h. (TLC control). Reaction mixture was extracted by CH₂Cl₂. Extract was washed by water, dried over MgSO₄, passed through layer of silica and evaporated. The residue was recrystallized from appropriate solvent.
- Dal Monte, D.; Mangini, A.; Passerini, R.; Zauli, C., *Gazz. Chim. Ital.* **1958**, 88, 977-1034.

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