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

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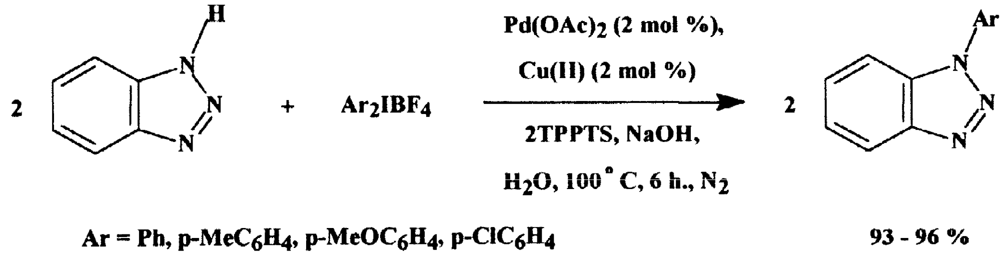
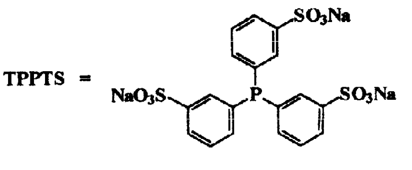
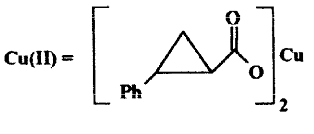
Abstract: Palladium(0)-catalyzed arylation of 1*H*-1,2,3-benzotriazole (BTA) in water at 100° C with diaryliodonium salts proceeds in the presence of copper salt regioselectively at N-1 position. Best result has been obtained with the $Pd(OAc)_2(tppts)_2$ as catalyst and the Cu(II) phenylcyclopropylcarboxylate as co-catalyst. Both aryl groups from diaryliodonium salt participate in the reaction.

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 $PdCl_2$(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 Ar_2IBF_4 in the presence TPPTS[2] and $Pd(OAc)_2$:







As in the case of ArI[1] 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

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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 salts[3] 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_2IBF_4	60	21.5
2	Ph_2IBF_4	96	-
3	$(p\text{-}CH_3C_6H_4)_2IBF_4$	93	-
4	$(p\text{-}CH_3OC_6H_4)_2IBF_4$	93	-
5	$(p\text{-}ClC_6H_4)_2IBF_4$	95	-
6[b]	Ph_2IBF_4	~50	-

[a] Without 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).[6] [d] All products were characterized by NMR, MS and elemental analysis.

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   (d) McKillop, A.; Kobylecki, R. J., *J. Org. Chem.* **1974,** 39, 2710 - 2714.
5. **Synthetic** [illegible] **ocedu** [illegible] mixture of Na-BTA, obtained from 0.002 mol of BTA and 0.002 mol of NaOH, 2 [illegible] ol % [illegible] $Ac)_2$, 4 mol % of TPPTS, 2 mol % of Cu(II)-salt and 0.001 mol of Ar_2IBF_4 [illegible] s hea [illegible] x in 25 ml. of water under N_2 for 6 h. (TLC control). Reaction mixture was ext [illegible] ed by [illegible] Extract was washed by water, dried over $MgSO_4$, passed through layer of sili [illegible] d evap [illegible] The residue was recrystallized from appropriate solvent .
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