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Preliminary communication

THE PALLADIUM-CATALYZED CROSS-COUPLING REACTIONS OF MESITYLCOPPER WITH ARYL IODIDES

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Summary

Mesitylcopper reacts with aryl iodides containing both electron-withdrawing and electron-donating groups in the presence of 1 equivalent Bu_4NX (X = Br, I) and 1 mol.% of $PhPdI(PPh_3)_2$ to give cross-coupling products in high yields.

Organocopper compounds are widely used in organic syntheses due to their availability, relative stability and inertness towards active functional groups. Reactions of organocopper compounds with organic halides are utilised for the synthesis of different cross-coupling products [1]. However, these reactions often require rather rigid conditions [2,3] or are accompanied with the formation of by-products [4].

Recently we reported that $PhC{\equiv}CCu$ reacts with organic halides, RX (R = aryl, substituted aryl, vinyl, allyl), under mild conditions in the presence of palladium complexes and tetraalkylammonium or alkaline metal halides, MX (M = Alk_4N, Li, Na; X = Cl, Br, I), to give the corresponding acetylenic derivatives in high yields [5]. Now we report the successful application of this approach in the arylation of mesitylcopper.

We have found that mesitylcopper reacts with p-$NO_2C_6H_4I$ in a mixture of HMPA and THF (1/1) in the presence of 1 mol.% of $PhPdI(PPh_3)_2$ (I) at room temperature under argon to yield 2,4,6-tri-methyl-4′-nitrodiphenyl (61% in 17 h). In the presence of Bu_4NI (1 equiv.), the reaction is completed in 15 min, giving the cross-coupling product in a quantitative yield.

In THF the effect of halide-ion additives is more vivid: the yield of $MesC_6H_4X$-p is 13% (in 42 h) without Bu_4NBr and 90% (in 10 min) in the presence of Bu_4NBr (1 equiv.).

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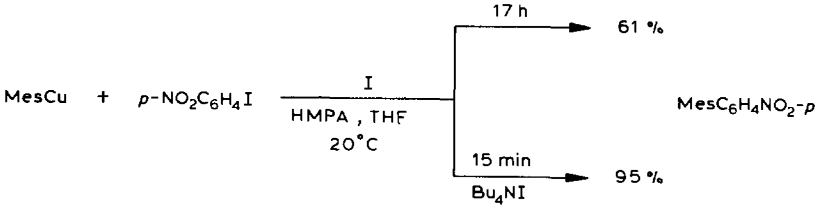
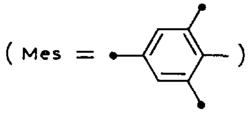
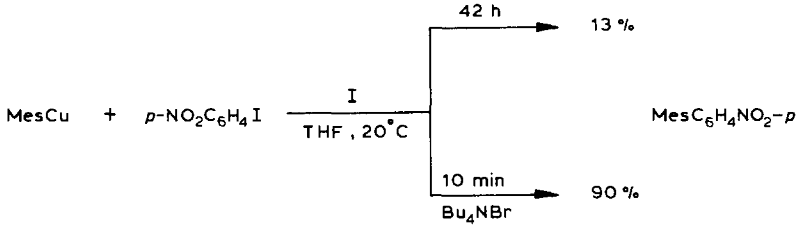


(1)





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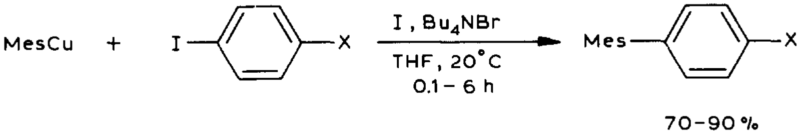
Aryl iodides containing both electron-withdrawing and electron-donating groups are easily involved in cross-coupling with MesCu under these conditions.

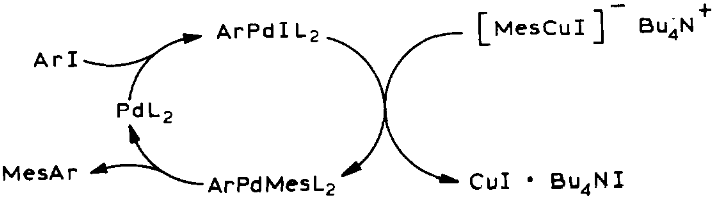


(3)

(X = NO_2 , CN , MeCO , Cl , OMe)

However, the reaction rate decreases markedly for aryl iodides which contain electron-donating substituents.

Typical procedure: 0.123 g (5×10^{-4} mol) of *p*-iodoacetophenone, 0.161 g (5×10^{-4} mol) of Bu_4NBr and 0.0042 g (5×10^{-6} mol) of I were added to 0.137 g (7.5×10^{-4} mol) of MesCu [6] in 2 ml of THF at room temperature under argon. It was found in 1.3 h by TLC on Silufole-UV254 and UV-spectroscopy that the reaction mixture contained 0.102 g (86%) of 2′,4′,6′-trimethylphenyl-4-acetophenone. The reaction mixture was diluted with 20 ml of ether and washed with a saturated solution of NH_4Cl. The organic layer was dried with anhydrous $MgSO_4$. 0.095 g (80%) of the product was isolated by TLC on silica gel, m.p. 96—97°C. IR (Nujol): ν(C=O) 1683 cm^{-1}. ^1H NMR (CCl_4): δ 1.96 (s, 6H), 2.30 (s, 3H), 2.63 (s, 3H), 6.84 (s, 2H), 7.17 (d, *J* 5 Hz,



(4)

2H), 7.95 (d, *J* 5 Hz, 2H). Analysis: found: C, 85.78; H, 7.56. $C_{17}H_{18}O$ calcd.: C, 85.67; H, 7.61%.

The halide ion acts as a nucleophilic catalyst [7] at the transmetallation stage through the formation of an ate-complex, $[MesCuI]^- Bu_4N^+$ having a higher nucleophilicity than MesCu (eq. 4).

A study of the cross-coupling reactions of other organocopper compounds with organic halides is now in progress.

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