PALLADIUM-CATALYZED CROSS-COUPLING OF ARYLDIAZONIUM

SALTS WITH TETRAMETHYLTIN IN AQUEOUS MEDIUM

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Aryldiazonium tetrafluoroborates and hexafluorophosphates react with organotin compounds in an anhydrous organic solvent in the presence of $Pd(OAc)_2$ to give cross-coupling products. Aryldiazonium chlorides do not react under these conditions [1,2].

Aryldiazonium salts react with tetramethyltin in the presence of $Pd(OAc)_2$ in aqueous acetonitrile at about 20°C to give substituted toluenes in high yield.

 $Y + C_6 H_4 N_2^+ X^- + Me_4 S_B \xrightarrow{\text{tmole%} Pd(OAc)_c} Y + C_6 H_4 Me$

The product yields were indicated by gas-liquid chromatography. When $Y = p-NO_2$ and $X = HSO_4^-$, the product yield was 81%. When $Y = p-NO_2$ and $X = Cl^-$, the product yield was 60%. When $Y = o-NO_2$ and $X = HSO_4^-$, the product yield was 84%. When Y = p-I and $X = HSO_4^-$, the product yield was 82%. When Y = p-Br and $X = HSO_4^-$, the product yield was 85%. When Y = p-OCH₃ and $X = HSO_4^-$, the product yield was 80%. When Y = p-CH₃ and $X = Cl^-$, the product yield was 74%. When Y = p-CH₃ and $X = HSO_4^-$, the product yield was 88%.

A sample of 2.5 ml acetonitrile and 0.20 ml (0.264 g, 1.1 mmoles) tetramethyltin, and 0.0022 g (0.01 mmole) $Pd(OAc)_2$ was added to 2.5 ml solution of 1 mmole p-nitrophenyldiazonium salt obtained by the diazotization of 1.72 g (12.5 mmoles) p-nitroaniline using 1 g (14.3 mmoles) sodium nitrite carried out in 7.5 ml 50% sulfuric acid. The reaction mixture was stirred for 2 h at about 20°C until the diazonium salt disappeared. The reaction mixture was diluted with 15 ml water and extracted with four 5-ml portions of ether. The ethereal extracts were combined and ether was distilled off. The residue was subjected to chromatography on alumina using 6:1 hexane-ether as the eluent to give 0.111 g (81%) p-nitrotoluene, mp 53°C [3].

LITERATURE CITED

1. K. Kikukawa, K. Kono, F. Wada, and T. Matsuda, J. Org. Chem., <u>48</u>, No. 8, 1333 (1983).

2. K. Kikukawa, K. Nagira, F. Wada, and T. Matsuda, Tetrahedron, <u>37</u>, 31 (1981).

3. Beilsteins Handbuch der Organischen Chemie, Vol. 5, Berlin, p. 323.

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