Highly Efficient Heck Reactions of Aryl Bromides with *n*-Butyl Acrylate Mediated by a Palladium/ Phosphine-Imidazolium Salt System

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General Information

- All aryl halides (Aldrich), $Pd(dba)_2$ (Strem), $Pd(OAc)_2$ (Strem), N,N-dimethylacetamide (Aldrich) were used as received. Flash chromatography was performed on silical gel 60 (230-400 mesh) (Natland International Corporation). The NMR solvents were dried from activated molecular sieve (4 Å). 1-(mesityl)imidazole was synthesized according to the literature procedure.[1]
- ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded using a Varian 400 MHz spectrometer, and elemental analyses were preformed by Desert Analysis, Tucson, AZ. GC analyses were preformed on a Agilent 6890 GC spectrometer with an FID detector and an HP-5 column.
- All reactions were carried out under an atmosphere of dry argon with standard Schlenk tube techniques or in an MBraun glovebox containing less than 1 ppm of oxygen and water.
- The identity of Heck coupling product was confirmed by comparison with literature spectroscopic data: 3-*p*-tolyl-acrylic acid *n*-butyl ester[2] , 4-methoxy-*trans*-cinnamic acid *n*-butyl ester[2], 3-methoxy-*trans*-cinnamic acid *n*-butyl ester[2], 3-phenyl-acrylic acid *n*-butyl ester[3], 3-*o*-tolyl-acrylic acid *n*-butyl ester[4], 3-(2,6-dimethyl-phenyl)-acrylic acid *n*-butyl ester[2,4], 3-(4-formyl-phenyl)-acrylic acid *n*-butyl ester[4a].

Synthesis of (1-bromoethylene-3-(mesityl))imidazolium bromide. A mixture of 4.0 g 1-(mesityl)imidazole (21.4 mmol) and 8.0 mL 1,2-dibromoethane (94.1 mmol) in 40 mL of THF was stirred for 2 d. During the reaction, a white solid was slowly precipitated. The solid was collected by filtration, washed with THF, and dried under vacuum. Yield: 1.8 g, 23 %. ^{1}H NMR (399.95 MHz, CD_2Cl_2): δ 1.83 (s, 6 H, CH_3), 2.10 (s, 3 H, CH_3), 3.80 (t, *J*(HH) = 5.6 Hz, 2H, CH_2), 4.90 (t, *J*(HH) = 5.6 Hz, 2 H, CH_2), 6.80 (s, 2 H, Ph), 7.00 (d, J(HH)= 1.6 Hz, 1 H, NCHCHN), 7.98 (d, J(HH)= 1.6 Hz, 1 H, NCHCHN), 10.00 (s, 1 H, NCHN). $^{13}C\{^{1}H\}$ NMR (100.57 MHz, CD_2Cl_2): δ 17.95 (*o*-CH_3), 21.38 (*p*-CH_3), 32.28 (CH_2), 51.76 (CH_2), 123.51, 124.43, 130.28, 131.21, 134.96, 138.78, 142.01 (3 CH(imid), *ipso*-, *o*-, *m*-, *p*-C(mes)). Anal. Calcd. for $C_{14}H_{18}N_2Br_2$: C, 44.95; H, 4.85; N, 7.49; Found: C, 44.84; H, 4.80; N, 7.33.

Synthesis of L·HBr (1, L = (1-ethylenediphenylphosphino-3-(mesityl))imidazol-2-ylidene). To a mixture of $KPPh_2$, which was freshly prepared by a mixture of 365 mg $KOBu^t$ (3.25 mmol) and 0.59 mL $HPPh_2$ (3.41 mmol) in 4.0 mL DMSO, was added 1.16 g of (1-bromoethylene-3-(mesityl))imidazolium bromide (3.09 mmol) . The solution was allowed to stir for 1 h at room temperature. The solvent was then removed under vacuum. Methanol (10 mL) was added to quench excess $KPPh_2$. The methanol was then removed under vacuum. Dichloromethane (10 mL) was added and the mixture was filtered to remove any inorganic salts formed. The solvent was then removed completely under vacuum to give a white solid. The solid was washed with diethyl ether to give the product. Yield, 1.35 g, 91 %. ^{1}H NMR (399.95 MHz, CD_2Cl_2): δ 2.04 (s, 6 H, CH_3), 2.31

(s, 3 H, CH_3), 2.88(t, *J*(HH) = 7.2 Hz, 2 H, CH_2), 4.69 (*pseudo* q, ^3J(HH) = ^2J(HH) = 7.2 Hz, 2 H, CH_2), 7.01 (s, 2 H. Ph), 7.13 (d, J(HH) = 1.6 Hz, 1 H, NCHCHN), 7.34 (m, 6 H, Ph), 7.47 (m, 4 H, Ph), 7.67 (d, J(HH) = 1.6 Hz, 1 H, NCHCHN), 10.48 (s, 1 H, NCHN). $^{13}C\{^1H\}$ NMR (100.57 MHz, CD_2Cl_2): δ 18.09 (s, o-CH_3), 21.40 (s, *p*-CH_3), 30.02 (d, *J*(PC) = 16.1 Hz, CH_2), 48.59 (d, *J*(PC) = 23.0 Hz, CH_2), 123.58 (d, *J*(PC) = 13.1 Hz), 129.42 (d, *J*(PC) = 7.6 Hz), 129.86 (s), 130.28 (s), 131.38 (s), 133.46 (d, *J*(PC) = 19.2 Hz), 134.99 (s), 137.04 (d, *J*(PC) = 11.5 Hz), 138.94 (s), 141.92 (s). (3 CH(imid), *ipso*-, *o*-, *m*-, *p*-C (mes), PPh_2) $^{31}P\{^1H\}$ (161.90 MHz, CD_2Cl_2): δ –22.2 (s). Anal. Calcd. for $C_{26}H_{28}N_2BrP$: C, 65.14; H, 5.89; N, 5.84; Found: C, 64.74; H, 5.65; N, 5.54.

Catalytic Heck Reactions. In a typical catalytic run, to a scintillation vial equipped with a cap and a septum was added $Pd(dba)_2$ (0.005 mmol), **1** (0.005 mmol), Cs_2CO_3 (2.0 mmol), and 2.0 mL of N,N-dimethylacetamide in a glovebox. The mixture was stirred for 15 min. Then 1.0 mmol of aryl halide, 1.4 mmol of *n*-butyl acrylate, and 1.0 mmol of diethyleneglycol di-*n*-butyl ether (GC standard) were charged into the vial. The reaction mixture was allowed to stir in an oil bath at 120 °C. The product yields were monitored and determined by GC analyses based on the internal standard (diethyleneglycol di-*n*-butyl ether). In some cases, products were isolated by column chromatography and their identity confirmed by ^1H NMR[2-4] and GC-MS. The workup procedure was as following: Water (50 ml) was added to the reaction mixture, followed by the extraction with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and evaporated under reduced pressure to give a crude product. The pure product was obtained by flash chromatography (1/10 ethyl acetate/hexane). In all cases, only the trans product was obtained as confirmed by GC and ^1H NMR.

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