Efficient Cross-Coupling Reactions of Aryl Chlorides and Bromides with Phenyl or Vinyltrimethoxysilane Mediated by a Palladium/Imidazolium Chloride System

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General Information

- All aryl halides (Aldrich), TBAF (1.0 M in THF, Aldrich), 1,4-Dioxane (anhydrous, Aldrich), $Pd(OAc)_2$ (Strem) and $Pd_2(dba)_3$ (Strem) were used as received. Flash chromatography was performed on silica gel 60 (230-400 mesh) (Natland International Corporation).
- ^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on a Varian-300 MHz or Varian-400 MHz NMR spectrometer at ambient temperature in $CDCl_3$ (Cambridge Isotope Laboratories, Inc.).
- All reactions were carried out under an atmosphere of argon in oven-dried-glassware with magnetic stirring, unless otherwise indicated.
- 1,3-Bis(2,6-diisopropyllphenyl)imidazolium chlorides (**1**) and 1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride (**2**) were prepared according to reported procedures: (a) Arduengo, A. J. III. US patent 5 077 414, 1991; (b) Jafarpour, L.; Stevens, E. D.; Nolan, S. P. manuscript in preparation.
- The identity of every product was confirmed by comparison with literature spectroscopic data: 4-Methylbiphenyl,[1,2] 4-Carbomethoxybiphenyl,[3] 4-Cyanobiphenyl,[4] 4-Methoxybiphenyl,[2] 2-phenylpyridine,[5] biphenyl[6] and 4-acetylstyrene.[7]

Cross-Coupling Reaction of Aryl Halides and Phenyltrimethoxysilane. *General procedure:* Under an atmosphere of argon 1,4-dioxane (3 mL), aryl halide (1.0 mmol), phenyltrimethoxysilane (2.0 mmol) and TBAF (2 mL, 2.00 mmol) were added in turn to a screw-capped vial with a septum charged with $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), **1** (13 mg, 0.03 mmol), and a magnetic stirring bar. The vial was placed in an 80 ˚C oil bath and stirred. The reaction was monitored by GC. In some cases, the yields were determined by GC using biphenyl as internal standard. The mixture was then allowed to cool to room temperature. The reaction was quenched (30 ml H_2O) and extracted (4 x 30 mL Et_2O). The organic layers were dried over $MgSO_4$, concentrated in vacuo and then purified by flash chromatography. All coupling products were found to be identical by ^{1}H NMR with literature data.

Cross-Coupling Reaction of 4-Bromo- or 4-chloroacetophone and Vinyltrimethoxysilane. *General procedure:* A similar procedure as above was used. Vinyltrimethoxysilane (2.0 mmol) was used. The reaction was monitored by GC. After complete consumption of the aryl halide, the mixture was allowed to cool to room temperature. The reaction was quenched (50 ml H_2O) and extracted (4 x 50 mL Et_2O). The organic layers were dried over $MgSO_4$, concentrated in vacuo and then purified by flash chromatography. The coupling product was found to be identical by ^1H NMR with literature data.

References

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6. Spectroscopy compared to that of an authentic sample obtained from Aldrich.
7. Spectroscopy compared to that of an authentic sample obtained from Aldrich.