Supporting Information

Grignard Reagents in Ionic Liquids.

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Experimental Section

Preparation of ionic liquid 4.

The crude N-butylpyridinium tetrafluoroborate [bpy][BF₄] was prepared by metathesis reaction in acetonitrile (300 mL) from sodium tetrafluoroborate (121 g, 1.1 mol) (purchased commercially with 98% purity in fine powder form) and its bromide precursor [bpy][Br] (216 g, 1.0 mol) which was in turn prepared from the microwave-assisted method. The mixture was stirred for three days at room temperature and then filtered. The filtrate was evaporated and the residue crude [bpy][BF₄] was vacuum-dried overnight at 70 °C (0.1 mmHg) and stored under nitrogen. Pure [bpy][BF₄] could be obtained by column chromatography of the crude [bpy][BF₄] on silica gel with dichloromethane as eluent. The recovery of [bpy][BF₄] after chromatography was about 60%.

General procedure for the preparation of organomagnesium reagents in [bpy][BF₄]:

To a 50 mL reaction vessel containing the colorless ionic liquid [bpy][BF₄] (1 mL) (Figure 1), metallic magnesium (1.5 mmol) was added. Commercially available magnesium powder (purity 99%; -325 mesh) was used without any pre-treatment. Organic iodide (1.5 mmol) was then added and the
solution was stirred at r.t. for 1 hr, and the solution turned green and finally red (Figure 2) indicating the formation of the organomagnesium intermediate.

**NMR observation of ethylmagnesium iodide in ionic liquid**

Ethylmagnesium iodide in [bpy][BF$_4$] was prepared according to the procedures described above using ethyl iodide. $^1$H NMR was then examined by adding pyridine (2 mmol) to the reaction mixture (Figure 3) and a few drops of the reaction mixture was added to d$_3$-acetonitrile in a NMR tube. One set of ethyl group absorption (one triplet at $^\delta$CH$_3$ = 0.59 ppm and one quartet at $^\delta$CH$_2$ = 0.45 ppm) was observed with $J_{AB}$ (Hz) = 7.5 (see Tables 3). The measurement was performed on a Varian AS 500 NMR spectrometer.

**General procedure for the preparation of 1-iodo-1-phenylpropane (7) in ionic liquid:**

To a 50 mL reaction vessel was charged with [bpy][BF$_4$] (2 mL), powdered metallic magnesium (3 mmol) and ethyl iodide (3 mmol) under inert nitrogen atmosphere. The reaction mixture was stirred at r.t. for 1 h followed by the addition of benzaldehyde (1 mmol). The mixture was stirred at the indicated temperature for the time period (see Tables 1) under inert nitrogen atmosphere. The resulting mixture was extracted with Et$_2$O (3 x 10 mL). After removal of the ether solvent *in vacuo*, the residue was purified by flash chromatography on silica gel to yield the pure adduct 7. 1-Iodo-1-phenylpropane could also be obtained by addition of 1-phenyl-1-propanol (10a) (1 mmol) to a reaction mixture of the preformed ethylmagnesium species (from 1 mmol of ethyl iodide and 1 mmol of magnesium) in [bpy][BF$_4$] (1 mL) as described above. Magnesium(II) iodide (1 mmol) was then added to the reaction mixture. The mixture was worked-up as described above to give compound 7. Compound 7 is a known compound. Its structure and purity were confirmed by the $^1$H NMR spectrum (Figures 5-6) and comparison with known samples previously synthesized. 1-Iodo-1-phenylpropane (7): $^1$HNMR (500 MHz, CDCl$_3$): 7.40-7.38 (m, 2H), 7.32-7.29 (m, 1H), 7.25-7.22 (m, 2H), 5.05 (t, 1H, J=8Hz), 2.40-2.31 (m, lH), 2.11-2.02 (m, lH), 0.97 (t, 3H, J=7Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): 143.97, 128.59, 127.78, 127.04, 36.59, 34.67, 14.73.
General procedure for the alkylation of aldehydes with organomagnesium reagents in [bpy][BF₄]:

To a 50 mL reaction vessel was charged with [bpy][BF₄] (1 mL), powdered metallic magnesium (1.5 mmol) and alkyl iodide (1.5 mmol) under inert nitrogen atmosphere. The reaction mixture was stirred at r.t. for 1 h followed by the addition of pyridine (2 mmol) and then the carbonyl compound (1 mmol). The mixture was stirred at the indicated temperature for the time period (see Tables 2) under inert nitrogen atmosphere (Figure 4). The resulting mixture was quenched with a few drops of water followed by extraction with Et₂O (3 x 10 mL). After removal of the ether solvent in vacuo, the residue was purified by flash chromatography on silica gel to yield the pure adduct alcohol 10. Specific conditions and yields of the alkylation of aldehydes are given in Tables 2.


Figure 1. Solution of metallic magnesium in [bpy][BF₄]
Figure 2. Red color solution of ethylmagnesium species in [bpy][BF$_4$]

Figure 3. Red color solution of ethylmagnesium species in [bpy][BF$_4$] with pyridine added
Figure 4. Benzaldehyde added to the ethylmagnesium species in [bpy][BF4] after addition of pyridine.

Figure 5: $^1$H NMR spectrum of 1-Iodo-1-phenylpropane (7)
Figure 7. $^{13}$C NMR spectrum of 1-iodo-1-phenylpropane (7).