Supporting Information

Grignard Reagents in Ionic Liquids.

Man Chun Law,[ab] Kwok-Yin Wong[b] and Tak Hang Chan*[ab]

[a] *Department of Chemistry, McGill University, Montreal, Quebec Canada H3A 2K.;*
[b] *Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Hong Kong SAR, China.*

E-mail: tak-hang.chan@mcgill.ca or <bcchanth@polyu.edu.hk>

Experimental Section

Preparation of ionic liquid 4.

The crude N-butylpyridinium tetrafluoroborate [bpy][BF_4] 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.[1] The mixture was stirred for three days at room temperature and then filtered. The filtrate was evaporated and the residue crude [bpy][BF_4] was vacuum-dried overnight at 70 °C (0.1 mmHg) and stored under nitrogen. Pure [bpy][BF_4] could be obtained by column chromatography of the crude [bpy][BF_4] on silica gel with dichloromethane as eluent.[2] The recovery of [bpy][BF_4] after chromatography was about 60%.

General procedure for the preparation of organomagnesium reagents in [bpy][BF_4]:

To a 50 mL reaction vessel containing the colorless ionic liquid [bpy][BF_4] (1 mL) (Figure 1), metallic magnesium (1.5 mmol) was added. Commercially available magnesium powder (purity 99%; -325mesh) was used without any pre-treatment. Organic iodide (1.5 mmol) was then added and the solution was stirred at r.t. for 1hr, 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. ^1H 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 atthe indicated temperature for the time period (see Tables 1) under inert nitrogen atmosphere. The resulting mixture was extracted with Et_2O (3 x 10 mL).[3] 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**) (1mmol) 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 (1mmol) 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 ^1H NMR spectrum (Figures 5-6) and comparison with known samples previously synthesized[4]. 1-Iodo-1-phenylpropane (**7**): ^1HNMR (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. $CDC1_3$): 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][BF$_4$]: To a 50 mL reaction vessel was charged with [bpy][BF$_4$] (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 (2mmol) 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 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 alcohol **10**. Specific conditions and yields of the alkylation of aldehydes are given in Tables 2.

---

(1) Law, M. C.; Wong, K. Y.; Chan, T. H. *Green Chem.* **2002**, *4*, 328

(2) Park, S.; Kazlauskas, R. J. *J. Org. Chem.* **2001**, *66*(25), 8395.

(3) It is assumed generally that, if necessary, extraction of organic substrates from ionic liquids can be carried out with supercritical carbon dioxide in place of non-polar organic solvents. See: (a) Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. *Nature* **1999**, *399*, 28. (b) Brown, R. A.; Pollet, P.; McKoon, E.; Eckert, C. A.; Liotta, C. L.; Jessop, P. G. *J. Am. Chem. Soc*. **2001**, *123*, 1254.

(4) Stoner, E. J.; Cothron, D. A.; Balmer, M. K.; Roden, B. A. Tetrnhedron, 1995, 51, 11043.

Figure 1. Solution of metallic magnesium in [bpy][BF$_4$]

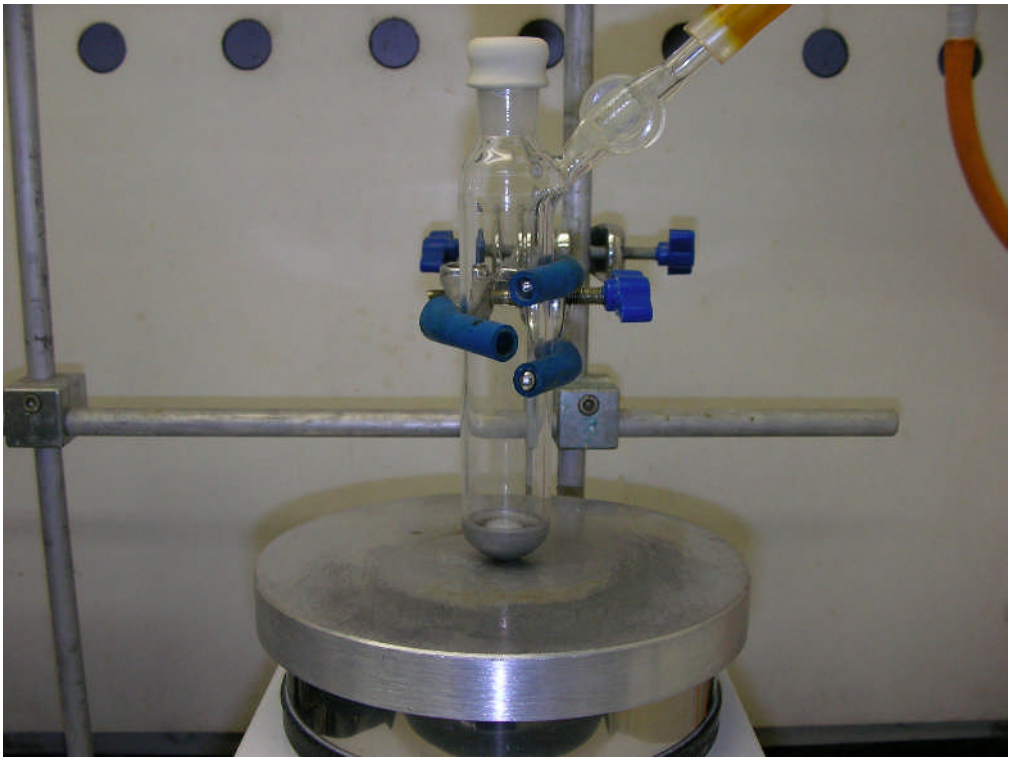


Figure 2. Red color solution of ethylmagnesium species in [bpy][BF_4]

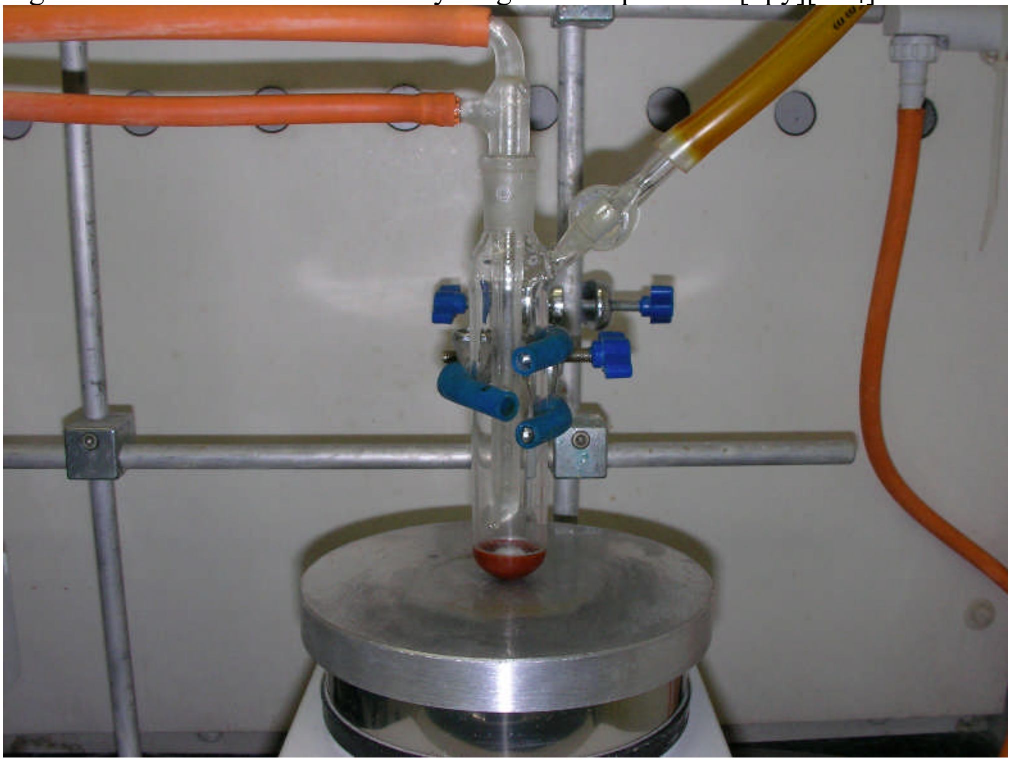


Figure 3. Red color solution of ethylmagnesium species in [bpy][BF_4] with pyridine added

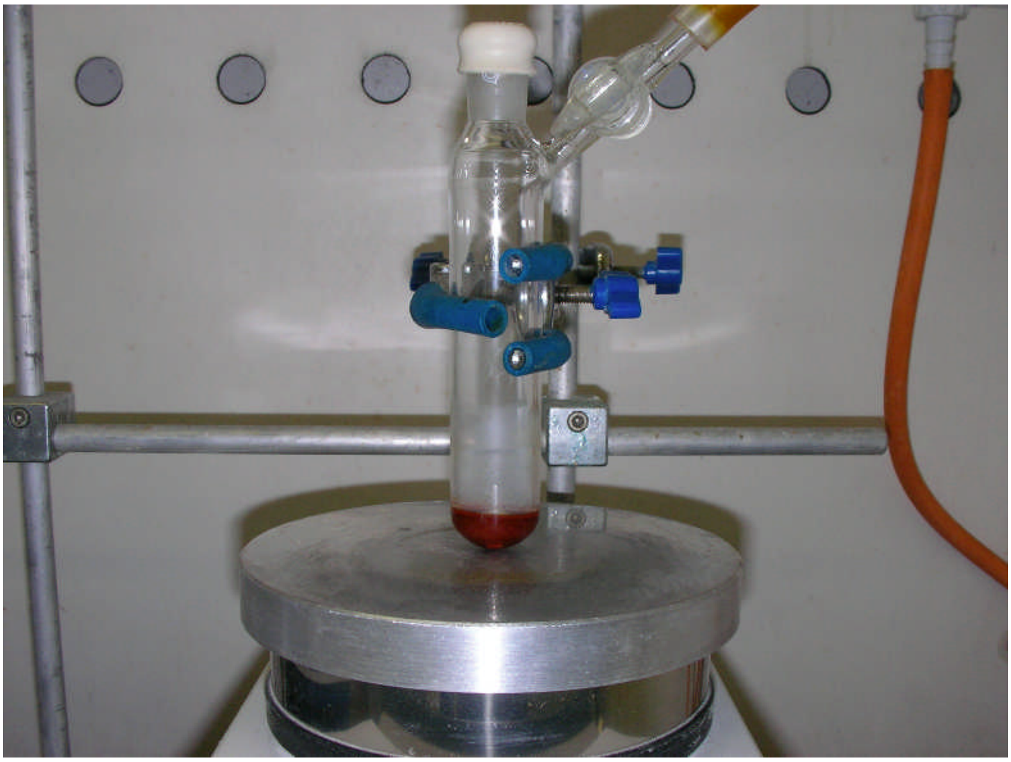


Figure 4. Benzaldehyde added to the ethylmagnesium speces in [bpy][BF_4] after addition of pyridine

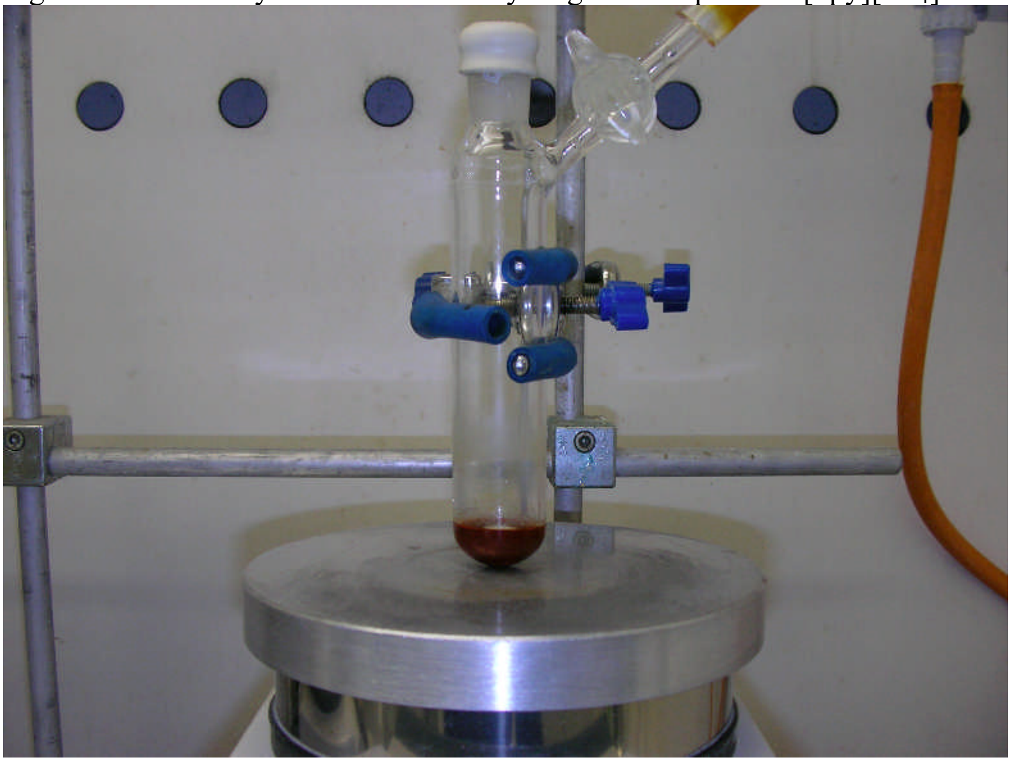
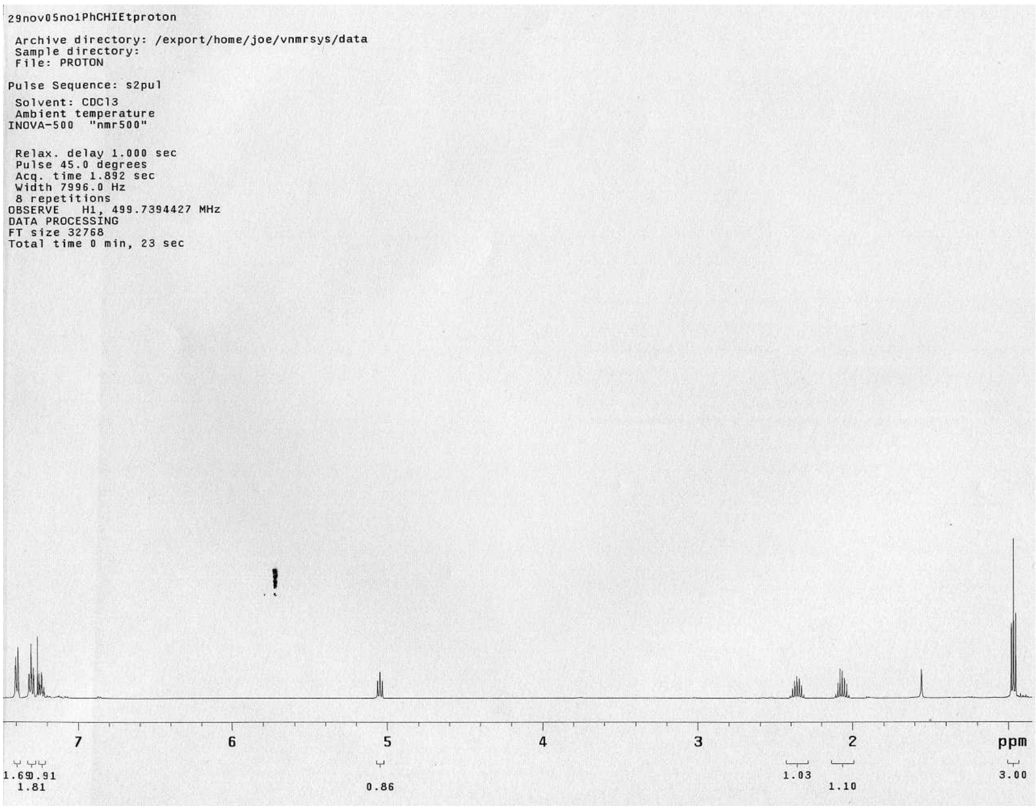


Figure 5: ^{1}H NMR spectrum of 1-Iodo-1-phenylpropane (**7**)



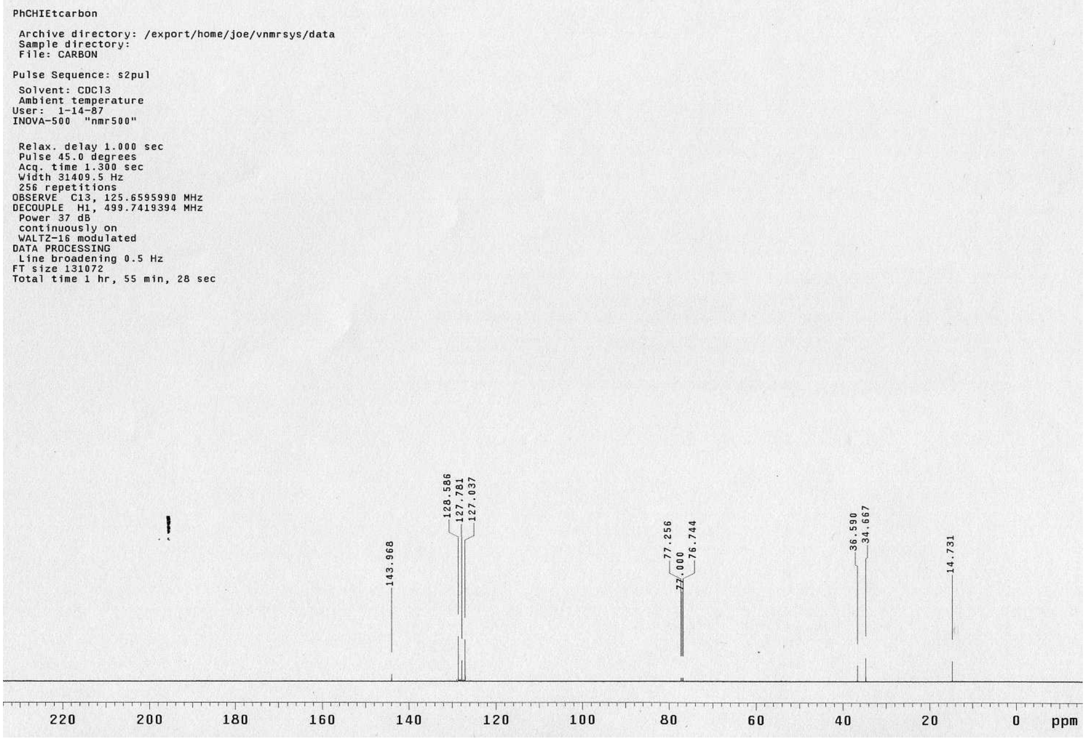
```
29nov05no1PhCHIEtproton

 Archive directory: /export/home/joe/vnmrsys/data
 Sample directory:
 File: PROTON

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
INOVA-500  "nmr500"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.892 sec
 Width 7996.0 Hz
 8 repetitions
OBSERVE   H1, 499.7394427 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec
```

Figure 7: ^{13}C NMR spectrum of 1-Iodo-1-phenylpropane (**7**).



```
PhCHIEtcarbon

 Archive directory: /export/home/joe/vnmrsys/data
 Sample directory:
 File: CARBON

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
User:  1-14-87
INOVA-500  "nmr500"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 31409.5 Hz
 256 repetitions
OBSERVE  C13, 125.6595990 MHz
DECOUPLE  H1, 499.7419394 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 131072
Total time 1 hr, 55 min, 28 sec
```