SUPPORTING INFORMATION

BMIm HCO_3: an Ionic Liquid with Carboxylating Properties. Synthesis of Carbamate Esters from Amines.

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Experimental

General. All commercially available reagents were used without further purification unless otherwise stated. Reactions were monitored by analytical thin-layer chromatography (TLC) using silica gel 60 F254 precoated glass plates (0.25 mm thickness) and visualized using UV light, iodide, and molibdic reagent.

Flash column chromatography was performed on silica gel (230-400 mesh). ^{1}H NMR and ^{13}C NMR were recorded on a 400 MHz nuclear magnetic resonance spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR).

Synthesis of BMIm HCO_3: A 8%$_{w/w}$ solution of sodium hydroxide (200 ml) was percolated trough a column filled in with DOWEX™ MONOSPHERE™ 550A (OH) (60 g; capacity 1.1 eq/L). The resin was then washed with water until neutrality. Then a 1.0 M solution of sodium hydrogen carbonate (300 ml) was passed through the column, till exchange of ions OH^- to HCO_3^- (pH was monitored during the switch). The column was then washed throughly with anhydrous methanol to remove any traces of water. An anhydrous methanol solution of 1-buthyl-3-methyl imidazolium chloride (5.0 g; 29 mmol) was passed through the column to exchange the chloride ions with hydrogen carbonate ions. The solvent was then evaporated under reduced pressure and the product was collected and dried in vacuo for 3 hours at room temperature.

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J = 7.3 Hz*, 3H); 1.34–1.41 (m, 2H); 1.83–1.90 (m, 2H); 4.12 (s, 3H); 4.29 (t, *J = 7.4 Hz*, 2H); 7.28 (s, 1H); 7.54 (s, 1H); 10.52 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 13.4; 19.4; 32.1; 36.4; 49.8; 121.5; 123.2; 137.3[11]

General procedure for the synthesis of carbamates 3: A solution of amine **1** (1.0 mmol) and BMIm HCO_3 (0.5 ml) was stirred at 55° C for 5 hours, then an alkyl halide **2** was added (3.0 mmol) at room temperature for 2 hours. The crude reaction mixture was then extracted with diethyl ether (5 x 5 ml) and dried under reduced pressure. The residue was, in case, purified by flash column cromatography.

Ethyl cyclohexyl carbamate (3a):[1] white solid (139 mg, 81%, mp 53–55 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06-1.16 (m, 3H); 1.21 (t, *J*= 7.0 Hz, 3H); 1.27-1.37(m, 2H); 1.54-1.61(m, 1H); 1.63-1.73(m, 2H) 1.89-1.91(m, 2H); 3.45 (s, 1H, C*H*NH); 4.07 (d, *J* =7.0 Hz, *2H*, OCH_2CH$_3$); 4.65 (br s,1H, N*H*). ^{13}C (100 MHz, $CDCl_3$): δ 155.9; 60.4; 49.7; 33.4; 25.5; 24.8; 14.6. MS *m/z* 56, 128, 142, 171 (M^+); IR (neat) 3332, 1700, 1536 cm^{-1}.

Ethyl cyclopentyl carbamate (3b):[2] colorless oil (127 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (t, *J* = 7.0 Hz, 3H, CH_3); 1.33-1.41(m, 2H); 1.49-1.67 (m, 4H); 1.87-1.99 (m, 2H); 3.92-3.99

(m, 1H, C*H*); 4.08 (q, *J*=7.0 Hz, 2H, CH_2CH$_3$); 4.72 (br, s, 1H, N*H*). ^{13}C (100 MHz, $CDCl_3$): δ 156.1; 60.4; 52.6; 33.2; 23.5; 14.6. MS m/z 56, 84, 100, 128, 157(M^+); IR: 3325,2967, 1700, 1530 cm^{-1}

Ethyl cycloheptyl carbamate (3c):[2] pale yellow oil (153 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12-1.21(m, 3H, OCH$_2$CH_3); 1.30-1.59 (m, 8H); 1.81-1.92 (m, 4H); 3.61 (s,1H, C*H*N); 4.02 (q, *J*=6.9 Hz, 2H, OCH_2CH$_3$); 4.81 (br,s, 1H, N*H*). ^{13}C (100 MHz, $CDCl_3$): δ 155.6; 60.3; 51.9; 35.3; 28.0; 23.9; 14.6. MS m/z 90, 128, 142, 156, 185(M^+); IR (neat) 3327, 1693 cm^{-1}.

Ethyl benzyl carbamate (3d):[2] colorless solid (129 mg; 72%, mp 43–45 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (t, *J*= 7.0 Hz,3H, CH_3); 4.16 (q, *J*= 7.1 Hz,2H, CH_2CH$_3$); 4.37 (d, *J*=7.0 Hz, 2H, CH_2NH); 5.16 (br, s, 1H, NH); 7.28-7.35 (m, 5H); ^{13}C (100.6 MHz, $CDCl_3$): 156.7; 138.7; 128.6; 127.5; 127.4; 60.9; 45.0; 14.6. MS m/z 91, 106, 150, 179,180(M+); IR (neat) 3326, 1693, 1517 cm^{-1}.

Ethyl (1-cyclohexylethyl) carbamate (3e):[3] white solid (145 mg, 73%, mp 49-50° C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89-1.27 (m, 12H); 1.51-1.82(m, 5H); 3.54 (q, *J*= 7.0 Hz, 1H, C*H*N); 4.07 (q, *J*=7.0 Hz, 2H, OCH_2CH$_3$); 4.59 (d, *J*=7.0 Hz, 1H, N*H*). ^{13}C (100 MHz, $CDCl_3$): δ 156.2; 60.4; 51.1; 43.3; 28.8; 26.4; 26.1; 18.0; 14.6. MS: 44, 55, 116,2 00(M+); IR (KBr): 3312, 2990, 1690, 1546 cm^{-1}

Ethyl (1-phenylethyl) carbamate (3f):[4] colorless oil (135 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (t, *J*=6.8 Hz, 3H, OCH$_2$CH_3); 1.49 (d, *J*=6.9 Hz,3H, CCH_3); 4.06-4.18 (m, 2H, OCH_2CH$_3$); 4.87 (q, *J*= 6.9 Hz, 1H, C*H*CH$_3$); 5.11 (br,s, 1H, N*H*); 7.25-7.38 (m, 5H). ^{13}C (100 MHz, $CDCl_3$): δ 155.8; 143.7; 128.6; 127.2; 125.9; 60.8; 50.5; 22.5; 14.6. MS m/z 91, 106, 164, 178, 193(M^+); IR (neat) 3319, 2972, 1705 cm^{-1}.

Ethyl dibenzylcarbamate (3g):[5] pale yellow oil (220 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (t, *J*=7.1 Hz, 3H, OCH$_2$CH_3); 4.31 (q, *J*=7.1 Hz, 2H, OCH_2CH$_3$); 4.48 (d, *J*= 7.1 Hz, 4H, NCH_2CH); 7.20-7.42(m, 10H). ^{13}C (100 MHz, $CDCl_3$): δ 157.0; 137.6; 128.6; 127.6; 127.4; 61.8; 49.3; 48.9; 14.8. MS m/z 65, 91, 106, 178, 270(M+); IR (neat): 3028, 2982, 2931, 1700, 1428.

Ethyl cyclohexyl(methyl)carbamate (3h):[6] pale yellow oil (35 mg, 20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (t, *J*=7.1Hz, 3H, OCH$_2$CH_3); 1.33-1.45 (m, 4H); 1.60-1.73 (m, 3H); 1.78-1.84 (m, 3H); 2.77 (s, 3H, NCH_3); 3.49 (q, *J*=7.0 Hz, 1H, C*H*N); 4.14 (q, *J*=7.1 Hz, 2H, OCH_2CH$_3$). ^{13}C (100 MHz, $CDCl_3$): δ 156.4; 61.0; 54.6; 30.2; 28.1; 25.7;25.5, 14.7. MS m/z 104, 114, 142, 156, 185(M+); IR: 2930,2859,1695,1454 cm^{-1}.

Ethyl phenylcarbamate (3i):[2] Pale green solid (28 mg, 17%; 49-50° C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (t, *J*=7.1 Hz, 3H, CH_3); 4.25 (q, *J*=7.1 Hz, 2H); 6.65 (b, 1H, NH); 7.08 (t, *J*=7.3 Hz,1H); 7.28-7.42 (m,4H); ^{13}C (100 MHz, $CDCl_3$): δ 153.7; 137.9 129.0; 123.3; 118.7; 61.2; 14.6. MS m/z 106, 137, 165(M^+); IR (neat) 3290, 2947, 1724, 1671, 1513 cm^{-1}.

Ethyl 4-chlorophenylcarbamate (3j):[2] white solid (52 mg, 26%; mp 66-67° C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (t, *J*=7.1 Hz, 3H, OCH_2CH_3); 4.24 (q, *J*=7.1 Hz, 2H, OCH_2CH_3); 6.68 (br,s, 1H, N*H*); 7.26-7.36 (m, 4H); ^{13}C (100 MHz, $CDCl_3$): δ 153.5; 136.6; 129.0; 128.3; 119.8; 61.4; 14.5. MS m/z 127, 140, 153, 171, 199(M^+); IR (KBr): 3300, 1690 cm^{-1}

Benzyl cyclohexylcarbamate (3k):[7] white solid (112 mg, 48%; mp 82-84° C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10-1.25 (m, 3H); 1.27-1.44 (m, 2H); 1.57-1.66 (m, 1H); 1.69-1.77 (m, 2H); 1.87-2.01 (m, 2H); 3.49-3.57 (m, 1H, C*H*NH); 4.84 (br, s, 1H, N*H*); 5.10 (s, 2H, OCH_2); 7.28-7.38 (m, 5H); ^{13}C (100 MHz, $CDCl_3$): δ 155.6; 136.8; 128.5; 128.1; 128.0; 66.4; 49.9; 33.4; 25.5; 24.8. MS m/z 41, 65, 91, 108, 234(M^+); IR (neat): 3320, 2931, 2855, 1699, 1684 cm^{-1}.

3-Phenylpropyl cycloehylcarbamate (3l): white solid (183 mg, 70%; mp 57–59° C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.11-1.25 (m, 4H); 1.33-1.42 (m, 2H); 1.60-1.76 (m, 4H) ;1.90-2.00 (m, 2H, $OCH_2CH_2CH_2$); 2.71(t, *J*=7.0 Hz, 2H, $OCH_2CH_2CH_2$); 3.50-3.53 (m, 1H, C*H*NH); 4.11 (t, *J*=6.9 Hz, 2H, OCH_2CH_2); 4.72 (br, s, 1H, N*H*); 7.20-7.33 (m, 5H). ^{13}C (100 MHz, $CDCl_3$): δ 155.9; 141.5; 128.4;128.3; 125.9; 64.0; 49.8; 33.5; 32.2; 30.8; 25.5; 24.9. MS m/z 41, 65, 91, 118, 261(M+); IR (KBr): 3326, 2936, 2854, 1685, 1536 cm^{-1}.

Anal. Calcd for $C_{16}H_{23}NO_2$: C, 75.53; H, 8.87; N, 5.36. Found: C, 75.35; H, 8.81; N 5.35.

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