Supplementary Material for Chemical Communications

SUPPLEMENTARY INFORMATION

New, Fuctionalized Ionic Liquids from Micheal-type Reactions – a Chance for Combinatorial Ionic Liquid Development

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Synthesis of compunds and spectral data

1-Methyl-3-(3-oxo-butyl)-imidazolium toluene-4-sulfonate

Methylimidazole (4.40 g; 53.6 mmol) was added slowly to a solution of p-toluenesulfonic acid monohydrate (9.51 g; 50.0 mmol) in 10 ml of ethanol. Methylvinylketone (4.5 ml;3.83 g;54.6 mmol) was added and the solution was stirred at 70°C for 1 hour. After removing the volatiles in high vacuum at room temperature, the crude product was dissolved in 15 ml of methylenechloride and precipitated by addition of 250 ml of ethylacetate. Drying in high vacuum yielded 13.60 g (41.9 mmol;84% of theoretic yield) of product as a white solid.

^{1}H-NMR (300 MHz,CD_3CN):
δ = 8.92 (s, 1H, NC<u>H</u>N), 7.64 (d, ^{3}J=7.2 Hz, 2H, C<u>H</u>CSO_3), 7.45/7.36 (2×s, 2H, NC<u>H</u>C<u>H</u>N), 7.18 (d, ^{3}J=8.1 Hz, 2H, C<u>H</u>CCH_3), 4.33 (t, ^{3}J=6.0 Hz, 2H, NC<u>H_2</u>), 3.82 (s, 3H, NC<u>H_3</u>), 3.07 (t, ^{3}J=6.0 Hz, 2H, NCH_2C<u>H_2</u>), 2.36 (s, 3H, C<u>H_3</u>C), 2.11 (s, 3H, COC<u>H_3</u>) ppm.

^{13}C-NMR (75 MHz, CD_3CN):
δ = 205.3, 146.0, 138.4, 136.8, 128.0, 125.3, 122.9, 122.4, 43.6, 41.8, 35.4, 28.7, 19.9 ppm.

SIMS (rel. int.):
calculated values: cation: m/z = 153.10, anion: 171.01.
EI/+VE: m/z = 153.1 (100%); FAB/-VE: m/z = 171.0 (100%), 323.9 (12%), 494.9 (14%).

1-Methyl-3-(3-oxo-butyl)-imidazolium 2-methoxy-ethylsulfate

Pyridine-SO_3-complex (15.92 g; 0.100 mol) was added in small portions to 2-methoxy-ethanol (7.61 g; 0.100 mol). The mixture was stirred at 80°C for 2 hours. After addition of methylimidazole (8.42 g; 0.103 mol) pyridine was removed in high vacuum at room temperature. Methylvinylketone (9.0 ml; 7.65 g; 0.109 mol) was added and the mixture was stirred overnight at room temperature. Drying in high vacuum yielded the product as a yellow liquid.

^{1}H-NMR (300 MHz,CD_3CN):
δ = 8.80 (s, 1H, NC<u>H</u>N), 7.46/7.38 (2×s, 2H, NC<u>H</u>C<u>H</u>N), 4.37 (t, ^{3}J=6.3 Hz, 2H, NC<u>H_2</u>), 3.97-3.94 (m, 2H, C<u>H_2</u>OSO_3), 3.86 (s, 3H, NC<u>H_3</u>), 3.55-3.53 (m, 2H, C<u>H_2</u>CH_2OSO_3), 3.31 (s, 3H, OC<u>H_3</u>), 3.11 (t, ^{3}J=6.3 Hz, 2H, NCH_2C<u>H_2</u>), 2.14 (s, 3H, COC<u>H_3</u>) ppm.

^{13}C-NMR (75 MHz, CD_3CN):
δ = 205.1, 136.8, 122.7, 122.1, 70.5, 64.8, 57.2, 43.4, 41.6, 35.1, 28.4 ppm.

SIMS (rel. int.):
calculated values: cation: m/z = 153.10, anion: 155.00.
EI/+VE: m/z = 153.1 (100%); FAB/-VE: m/z = 96.9 (9%), 154.9 (100%), 462.8 (6%).

1-Methyl-3-(3-oxo-butyl)-imidazolium methanesulfonate

Methanesulfonic acid (9.61 g; 0.100 mol) was dissolved in 6 ml of methanol. Methylimidazole (8.77 g; 0.107 mol) and methylvinylketone (8.00 g; 0.114 mol) were added slowly subsequently. The mixture was stirred in a warm water bath for 1 hour and at room temperature overnight. Drying in high vacuum yielded the product as a yellow liquid.

^{1}H-NMR (300 MHz,CD_3CN):

δ = 9.13 (s, 1H, NC<u>H</u>N), 7.53/7.44 (2×s, 2H, NC<u>H</u>C<u>H</u>N), 4.38 (t, ^{3}J=6.3 Hz, 2H, NC<u>H$_2$</u>), 3.87 (s, 3H, NC<u>H$_3$</u>), 3.14 (t, ^{3}J=6.3 Hz, 2H, NCH$_2$C<u>H$_2$</u>), 2.49 (s, 3H, C<u>H$_3$</u>SO$_3$), 2.13 (s, 3H, COC<u>H$_3$</u>) ppm.

^{13}C-NMR (75 MHz, CD$_3$CN):
δ = 205.5, 137.1, 122.9, 122.4, 43.6, 41.9, 38.7, 35.3, 28.7 ppm.

SIMS (rel. int.):
calculated values: cation: m/z = 153.10, anion: 94.98.
EI/+VE: m/z = 82.0 (8%), 153.1 (100%), 227.1 (8%); FAB/-VE: m/z = 94.9 (100%), 342.9 (19%).

<u>1-Methyl-3-(3-oxo-butyl)-imidazolium trifluoroacetate</u>
Trifluoroacetic acid (34.89 g; 0.305 mol) was added dropwise to methylimidazole (25.12 g; 0.305 g) at 0°C. The resulting solid was recrystallised from acetonitrile to give methylimidazolium trifluoroacetate as a white solid.
Pyridine (0.5 ml), methylvinylketone (4.99 g; 71.2 mmol) and a small amount of hydroquinone were added to 14.03 g (71.2 mmol) of this solid. The mixture was stirred overnight at 40°C and dried in high vacuum at room temperature. The product was obtained as a low viscous, yellow-brownish liquid.

^{1}H-NMR (300 MHz,DMSO):
δ = 9.21 (s, 1H, NC<u>H</u>N), 7.76/7.71 (2×s, 2H, NC<u>H</u>C<u>H</u>N), 4.33 (t, ^{3}J=6.6 Hz, 2H, NC<u>H$_2$</u>), 3.86 (s, 3H, NC<u>H$_3$</u>), 3.16 (t, ^{3}J=6.6 Hz, 2H, NCH$_2$C<u>H$_2$</u>), 2.11 (s, 3H, COC<u>H$_3$</u>) ppm.

^{13}C-NMR (75 MHz, DMSO):
δ = 206.2, 159.0, 158.6, 158.2, 157.8, 137.3, 123.2, 122.8, 44.0, 42.3, 35.9, 30.0 ppm.

SIMS (rel. int.):
calculated values: cation: m/z = 153.10, anion: 112.99.
FAB/+VE: m/z = 153.0 (100%); FAB/-VE: m/z = 112.9 (100%), 378.8 (53%).

<u>1-(3-oxo-butyl)-pyridinium s-butylsulfate</u>
Pyridine-SO$_3$-complex (8.13 g; 51.1 mmol) was added in small portions to 2-butanol (3.79 g; 51.1 mmol) and stirred overnight. The mixture was dissolved in 15 ml of acetonitrile and pyridine (0.5 ml) and methylvinylketone (4.30 g; 61.3 mmol) were added. After stirring overnight at 80°C and drying in high vacuum the product was obtained as a brown liquid.

^{1}H-NMR (300 MHz,CDCl$_3$):
δ = 9.22 (m, 2H, NC<u>H</u>), 8.45 (m, 1H, NCHCHC<u>H</u>), 8.03 (m, 2H, NCHC<u>H</u>), 4.91 (t, ^{3}J=6.0 Hz, 2H, NC<u>H$_2$</u>), 4.28 (sext., ^{3}J=6.0 Hz, 1H, C<u>H</u>OH), 3.38 (t, ^{3}J=6.0 Hz, 2H, NCH$_2$C<u>H$_2$</u>), 2.08 (s, 3H, COC<u>H$_3$</u>), 1.50 (m, 2H, CHOHC<u>H$_2$</u>), 1.39 (d, ^{3}J=6.3 Hz, 3H, CHOHC<u>H$_3$</u>), 0.80 (t, ^{3}J=7.5 Hz, 3H, CHOHCH$_2$C<u>H$_3$</u>) ppm.

^{13}C-NMR (75 MHz, CDCl$_3$):
δ = 206.0, 146.3, 145.9, 128.6, 76.5, 57.0, 43.8, 30.3, 30.1, 20.7, 10.1 ppm.

SIMS (rel. int.):
calculated values: cation: m/z = 150.09, anion: 153.02.
FAB/+VE: m/z = 150.1 (100%), 151.1 (9%), 453.1 (7%); FAB/-VE: m/z = 96.9 (31%), 153.0 (100%), 399.9 (14%), 455.9 (16%).

1-(3-oxo-butyl)-pyridinium i-propylsulfate

Pyridine-SO_3-complex (16.39 g; 0.103 mol) was added in small portions to 2-propanol (6.19 g; 0.103 mol) and stirred for 5 hours at 80°C. The mixture was dissolved in 15 ml of acetonitrile and pyridine (0.5 ml) and methylvinylketone (8.63 g; 0.123 mol) were added. After stirring overnight at 80°C and drying in high vacuum the product was obtained as a brown liquid.

^{1}H-NMR (300 MHz,$CDCl_3$):
δ = 9.03 (m, 2H, NC<u>H</u>), 8.32 (m, 1H, NCHCHC<u>H</u>), 7.85 (m, 2H, NCHC<u>H</u>), 4.71 (t, ^{3}J=6.0 Hz, 2H, NC<u>H</u>$_2$), 4.28 (sept., ^{3}J=6.0 Hz, 1H, C<u>H</u>OH), 3.20 (t, ^{3}J=6.0 Hz, 2H, NCH$_2$C<u>H</u>$_2$), 1.88 (s, 3H, COC<u>H</u>$_3$), 0.96 (d, ^{3}J=6.3 Hz, 6H, CHOH(C<u>H</u>$_3$)$_2$) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$):
δ = 205.8, 146.0, 145.9, 128.5, 71.4, 56.8, 43.6, 30.1, 23.4 ppm.

SIMS (rel. int.):
calculated values: cation: m/z = 150.09, anion: 139.01.
FAB/+VE: m/z = 150.1 (100%), 151.1 (9%), 439.1 (8%); FAB/-VE: m/z = 96.9 (18%), 138.9 (100%), 385.8 (7%), 427.8 (22%).

1-(3-oxo-butyl)-pyridinium 2-ethoxy-ethylsulfate

Pyridine-SO_3-complex (6.38 g; 40.1 mmol) was added in small portions to 2-ethoxy-ethanol (3.61 g; 40.1 mmol). The mixture was stirred overnight at room temperature. Methylvinylketone (6.7 ml; 5.62 g; 80.2 mmol) and pyridine (0.5 ml) were added and the mixture was stirred overnight at 80°C. Drying in high vacuum yielded the product as a brown liquid.

^{1}H-NMR (300 MHz,$CDCl_3$):
δ = 9.10 (m, 2H, NC<u>H</u>), 8.41 (m, 1H, NCHCHC<u>H</u>), 7.99 (m, 2H, NCHC<u>H</u>), 4.85 (t, ^{3}J=6.0 Hz, 2H, NC<u>H</u>$_2$), 4.03-4.00 (m, 2H, C<u>H</u>$_2$OSO$_3$), 3.55-3.52 (m, 2H, C<u>H</u>$_2$CH$_2$OSO$_3$), 3.41-3.34 (m, 4H, OC<u>H</u>$_2$CH$_3$+NCH$_2$C<u>H</u>$_2$), 2.05 (s, 3H, COC<u>H</u>$_3$), 1.00 (t, ^{3}J=6.9 Hz, 3H, OCH$_2$C<u>H</u>$_3$) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$):
δ = 206.1, 146.1, 145.9, 128.6, 69.4, 66.9, 66.6, 56.9, 43.6, 30.2, 15.5 ppm.

SIMS (rel. int.):
calculated values: cation: m/z = 150.09, anion: 169.02.
FAB/+VE: m/z = 150.1 (100%), 151.1 (9%), 469.1 (5%); FAB/-VE: m/z = 96.9 (35%), 169.0 (100%), 415.8 (11%), 487.9 (8%).

1-(2-Butoxycarbonyl-ethyl)-3-methyl-imidazolium tetrafluoroborate

Tetrafluoroboric acid (51 weight% in diethylether) (32.0 ml; 19.42 g; 0.221 mol) was added dropwise to a solution of methylimidazole (18.16 g; 0.221 mol) in 20 ml of diethylether. After removing the solvent in vacuo the crude product was dissolved in methylenechloride, precipitated with diethylether and dried in high vacuum at room temperature.
Pyridine (0.5 ml), butylacrylate (36.8ml; 33.04 g; 0.258 mol) were added to a solution of 17.55 g (0.172 mol) of this solid in 15 ml of acetonitrile. The mixture was stirred overnight at 80°C, dried in high vacuum at room temperature, washed with diethylether several times and again dried in high vacuum at room temperature. The product was obtained as a low viscous, yellow liquid.

^{1}H-NMR (300 MHz,$CDCl_3$):

δ = 8.40 (s, 1H, NC<u>H</u>N), 7.21/7.16 (2×s, 2H, NC<u>H</u>C<u>H</u>N), 4.19 (t, ^{3}J=6.0 Hz, 2H, NC<u>H$_2$</u>), 3.75-3.71 (m, 2H, NCH$_2$C<u>H$_2$</u>), 3.61 (s, 3H, NC<u>H$_3$</u>), 2.66 (t, ^{3}J=6.0 Hz, 2H, COOC<u>H$_2$</u>), 1.20 (pent., ^{3}J=6.6 Hz, 2H, COOCH$_2$C<u>H$_2$</u>), 0.98 (sext., ^{3}J=7.5 Hz, 2H, COO(CH$_2$)$_2$C<u>H$_2$</u>), 0.55 (t, ^{3}J=7.2 Hz, 3H, COO(CH$_2$)$_3$C<u>H$_3$</u>) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$):
δ = 170.4, 136.6, 123.4, 122.3, 64.6, 44.8, 35.6, 33.7, 30.0, 18.6, 13.2 ppm.

SIMS (rel. int.):
calculated values: cation: m/z = 211.14, anion: 87.00.
FAB/+VE: m/z = 155.1 (7%), 211.1 (100%), 212.1 (11%); FAB/-VE: m/z = 85.9 (21%), 86.9 (100%), 383.9 (5%), 384.9 (12%).