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Evidence for the spontaneous formation of $N$-heterocyclic carbenes in imidazolium based ionic liquids

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Synthesis

1-ethyl-3-methylimidazolium acetate [C$_2$C$_1$im][OAc]

In air, a solution of [C$_2$C$_1$im]Br (94.30 g, 493 mmol) in water (250 mL) was added to a solution of silver acetate (82.38 g, 493 mmol) in water (450 mL) in a round bottom flask covered with aluminium foil. The reaction mixture was then stirred at room temperature for two days and the yellowish precipitate formed was removed by filtration. The solution obtained was then tested for excess bromide (silver nitrate test) and excess silver (hydrochloric acid test) to ensure removal of excess starting material. If excess bromide was present, 0.1 M silver acetate solution was added dropwise until the test showed a negative result. If excess silver was present, 0.1 M [C$_2$C$_1$im]Br solution was added dropwise until the test showed a negative result. The solution was then filtered to remove the yellow precipitate, treated with activated charcoal for 2 hours and then filtered through Celite, a 0.2 µm non-cellulose membrane filter and a C18 column to remove impurities. The water was then removed using a rotary evaporator and the product was dried in vacuo at 50 °C for 48 hours to give a clear viscous solution (76.72 g, 450 mmol, 91% yield).

$\delta_H$ (ppm) (400 MHz, DMSO-d$_6$): 10.36 (1H, s, C$_H$-2), 8.03 (1H, s, C$_H$-4), 7.91 (1H, s, CH-5), 4.22 (2H, q, $^3J_{HH}$ = 7.3Hz, -N-C$_H_2$-), 3.89 (3H, s, N-C$_H_3$), 1.59 (3H, s, H$_3$CCOO), 1.38 (3H, t, $^3J_{HH}$ = 7.3Hz, CH$_2$-CH$_3$) $\delta_C$ (ppm) (101 MHz, DMSO-d$_6$): 173.89 (s, CH$_3$COO$^-$), 138.34 (s, N-C-N), 124.00 (s, N-C-C-N), 122.50 (s, N-C-C-N), 44.27 (s, N-CH$_2$CH$_3$), 35.78 (s, N-CH$_3$), 26.64 (s, CH$_3$COO$^-$), 15.68 (s, N-CH$_2$CH$_3$). $m/z$ (LSIMS$^+$): 111 (100%) [C$_2$C$_1$im]+, no traces of Ag$^+$ detected (107.8), $m/z$ (LSIMS$^-$): 59 (100%) [OAc]$^-$

1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C$_2$C$_1$C$_2$2im][NTf$_2$]

LiNTf$_2$ (150 g, 522 mmol, 1.3 eq) was dissolved in 200 ml water and added to a solution of [C$_2$C$_1$C$_2$2im][Br] (74 g, 387 mmol) in water (100 mL). 50 ml of dichloromethane was then added to ensure separation of ionic liquid and water phase. The mixture was stirred for 48 hours. The mixture was then separated by collecting the lower organic phase. The organic extract was washed with water until the aqueous phase was halide free (silver nitrate test). The solvent was removed using a rotary evaporator. The resulting liquid was stirred with activated charcoal for 24 hours. After removal of the charcoal by filtration through a filter paper and 0.2 µm membrane filter, the IL was dried in vacuo at 50 °C for 48 hours to give a clear liquid (131.66 g, 336 mmol, 86% yield). $\delta_H$ (ppm)
(400 MHz, DMSO-$d_6$) : 7.67 (1H, s, CH-4), 7.62 (1H, s, CH-5), 4.15 (2H, t, $^3J_{HH} = 7.3$Hz, -N-CH$_2$-), 3.75 (3H, s, N-CH$_3$), 2.59 (3H, s, C2-CH$_3$), 1.34 (3H, t, $^3J_{HH} = 7.3$Hz, CH$_2$-CH$_3$) δC (ppm) (101 MHz, DMSO-$d_6$) : 144.49 (s, N-C-N), 122.80 (s, N-C-C-N), 120.74 (s, N-C-C-N), 118.33 (q, $^1J_{CF} = 322$Hz, [N(SO$_2$CF$_3$)$_2$]) 48.99 (s, N-CH$_2$(CH$_2$)$_2$CH$_3$), 36.11 (s, N-CH$_3$), 31.79 (s, N-CH$_2$CH$_2$CH$_2$CH$_3$), 19.19 (s, N-CH$_2$CH$_2$CH$_2$CH$_3$), 13.55 (s, N-CH$_2$CH$_2$CH$_2$CH$_3$).

Deuterated - 1-ethyl-3-methylimidazolium acetate, d-[[C$_2$C$_1$im][OAc]]

[C$_2$C$_1$im][OAc] (1.03 g, 6.01 mmol) was diluted in D$_2$O (11 g, 10 ml, 552 mmol). The mixture then stirred under nitrogen for 3 days with the removal of water every 24 hours and addition of fresh D$_2$O. The final product was a viscous clear liquid (82% exchange at C2 position in imidazolium cation).

The NMR spectrum was shown in Figure S8.

In-situ NMR Procedure

The kinetic study was done using anisaldehyde and [C$_2$C$_1$im][OAc] at 1:2 mol ratio with [C$_2$C$_1$C$_2$1im][NTf$_2$] as solvent. Approximately 2.02 g (0.502 mmol) of [C$_2$C$_1$C$_2$1im][NTf$_2$] was added into a round bottom flask together with 0.50 g (0.370 mmol) of anisaldehyde. The solution was then stirred under vacuum for 1 hour. A normal NMR tube with a suba seal as its cap was prepared and flushed with nitrogen. 0.84 g (0.123 mmol) of the benzaldehyde mixture was added into the NMR tube. The NMR tube was then placed under vacuum and degassed for another 1 hour whilst agitating using an ultrasonic bath. [C$_2$C$_1$im][OAc] was also degassed in the ultrasonic bath under vacuum. The NMR tube was then placed in the spectrometer and the initial measurement was taken. 0.103 g (0.06 mmol) of [C$_2$C$_1$im][OAc] was added and a measurement then taken every 30 seconds for the first 30 minutes followed by every 10 minutes for another 8 hours.
Fig S1: $^3$H NMR of the Breslow Intermediate of 4-methylbenzaldehyde

Fig S2: MS of the Breslow Intermediate of 4-methylbenzaldehyde
Fig S5: MS of [C₃C₅im][OAc]
Fig S6: $^1$H NMR of [C$_2$C$_1$C$_1$im][NTf$_2$]

Fig S7: $^{13}$C NMR of [C$_2$C$_1$C$_1$im][NTf$_2$]
Fig S8: $^1$H NMR of deuterated-[C$_2$C$_1$im][OAc]