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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 [C₂C₁im][OAc]

In air, a solution of $[C_2C_1im]Br$ (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 $[C_2C_1]m]Br$ 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) $\delta_{\rm H}$ (ppm) (400 MHz, DMSO**d**₆) : 10.36 (1H, s, CH-2), 8.03 (1H, s, CH-4), 7.91 (1H, s, CH-5), 4.22 (2H, q, ³J_{HH} = 7.3Hz, -N-CH₂-), 3.89 (3H, s, N-CH₃), 1.59 (3H, s, H₃CCOO⁻) 1.38 (3H, t, ${}^{3}J_{HH} = 7.3$ Hz, CH₂-CH₃) δ_{c} (ppm) (101 MHz, DMSOd₆): 173.89 (s, CH₃COO⁻), 138.34 (s, N-C-N), 124.00 (s, N-C-C-N), 122.50 (s, N-C-C-N), 44.27 (s, N-CH₂CH₃), 35.78 (s, N-CH₃), 26.64 (s, CH₃COO⁻), 15.68 (s, N-CH₂CH₃). m/z (LSIMS+) : 111 (100%) [C₂C₁im]+, no traces of Ag⁺ detected (107.8), m/z (LSIMS-) : 59 (100%) [OAc]-

1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C₂C₁C₁²im][NTf₂]

LiNTf₂ (150 g, 522 mmol, 1.3 eq) was dissolved in 200 ml water and added to a solution of $[C_2C_1C_1^{2}im][Br]$ (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). $\delta_{\rm H}$ (ppm)

(400 MHz, DMSO- d_6) : 7.67 (1H, s, CH-4), 7.62 (1H, s, CH-5), 4.15 (2H, t, ${}^{3}J_{HH} = 7.3Hz$, -N-CH₂-), 3.75 (3H, s, N-CH₃), 2.59 (3H, s, C2-CH₃), 1.34 (3H, t, ${}^{3}J_{HH} = 7.3Hz$, CH₂-CH₃) δ_c (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, ${}^{1}J_{CF} = 322Hz$, [N(SO₂CF₃)₂]⁻),48.99 (s, N-CH₂(CH₂)₂CH₃), 36.11 (s, N-CH₃), 31.79 (s, N-CH₂CH₂CH₂CH₃), 19.19 (s, N-CH₂CH₂CH₂CH₃), 13.55 (s, N-CH₂CH₂CH₂CH₂CH₃).

Deuterated - 1-ethyl-3-methylimidazolium acetate, d-[C₂C₁im][OAc]

 $[C_2C_1\text{im}][OAc]$ (1.03 g, 6.01 mmol) was diluted in D₂O (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 D₂O. 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 $[C_2C_1im][OAc]$ at 1:2 mol ratio with $[C_2C_1C_1^2im][NTf_2]$ as solvent. Approximately 2.02 g (0.502 mmol) of $[C_2C_1C_1^2im][NTf_2]$ 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. $[C_2C_1im][OAc]$ 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 $[C_2C_1im][OAc]$ 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 : ¹H NMR of the Breslow Intermediate of 4-methylbenzaldehyde





Fig S4 : ${}^{13}C$ NMR of [C₂C₁im][OAc]



Fig S5 : MS of $[C_2C_1im][OAc]$



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Fig S7 : 13 C NMR of [C₂C₁C₁²im][NTf₂]



Fig S8 : ${}^{1}H$ NMR of deuterated-[C₂C₁im][OAc]