

## Reaction of Elemental Chalcogens with Imidazolium Acetates to Yield Imidazole-2-chalcogenones: Direct Evidence for Ionic Liquids as Proto-Carbenes

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### **Supporting Information** **Experimental details**

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#### Materials

Sulfur, as a pale yellow powder, and selenium, as a black powder, were purchased from Fluka and Aldrich respectively, with a nominal purity of 99.5 %. Both elements were used as received. Palladium acetate (99.9 %) and benzaldehyde (>99.5 %) were purchased from Aldrich and used as received.

The ionic liquids 1-butyl-3-methylimidazolium hydrogensulfate ([C<sub>4</sub>mim][HSO<sub>4</sub>]), 1-butyl-3-methylimidazolium thiocyanate ([C<sub>4</sub>mim][SCN]), and 1-butyl-3-methylimidazolium acetate ([C<sub>4</sub>mim][OAc]) were produced by BASF and purchased from Fluka with a nominal purity higher than 95 %. The ionic liquid 1-butyl-3-methylimidazolium chloride ([C<sub>4</sub>mim]Cl) was synthesized by direct alkylation of 1-methylimidazole (Aldrich, 99 %) with 1-chlorobutane (Aldrich, 99 %), following a recipe analogous to that described elsewhere.<sup>1</sup> Similarly, the ionic liquid 1,3-dimethylimidazolium methylsulfate ([C<sub>1</sub>mim][CH<sub>3</sub>SO<sub>4</sub>]) was synthesized by direct alkylation of 1-methylimidazole with dimethylsulfate (Aldrich, 99 %) and the ionic liquid 1-ethyl-3-methylimidazolium tosylate ([C<sub>2</sub>mim][CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>]) was synthesized by direct alkylation of 1-methylimidazole with ethyl tosylate (*p*-toluenesulfonate); as described elsewhere.<sup>2</sup> The ionic liquids 1-hexyl-3-methylimidazolium trifluorosulfonate ([C<sub>6</sub>mim][CF<sub>3</sub>SO<sub>3</sub>]) and 1-hexyl-3-methylimidazolium trifluoroacetate ([C<sub>6</sub>mim][CF<sub>3</sub>COO]) were synthesized by metathetic reactions of 1-hexyl-3-methylimidazolium chloride with sodium

trifluorosulfonate and trifluoroacetate respectively in water, followed by solvent extraction of the ionic liquid with dichloromethane.

All the ionic liquids were dried prior to use, under high vacuum (ca. 0.5 mbar) at ca. 60 °C, for at least 24 h. The chemical structures of the desired products, as well as the substantial absence of organic impurities, were checked by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. The water content of all samples was found to be lower than 600 ppm by Karl-Fischer titration, and the chloride content of the 1-hexyl-3-methylimidazolium-based ionic liquids synthesized by metathesis was measured by ion chromatography (Dionex) and found to be in the range 0.40-0.55 %.

Formaldehyde solution (37 wt% in water) was purchased from Fluka. Ethylamine solution (70 wt% in water), methylamine solution (40 wt% in water), glyoxal solution (40 wt% in water), and glacial acetic acid were purchased from Sigma-Aldrich. These reagents were used as received.

#### Synthesis of a 2:1:1 statistical mixture of 1-ethyl-3-methyl-, 1,3-diethyl-, and 1,3-dimethylimidazolium acetate

Aqueous formaldehyde (37 %) (49.80 mL, 0.60 mol) was cooled in a 500 mL round bottom flask in an ice-salt bath. Aqueous ethylamine (70 %) (57.70 mL, 0.60 mol) was added dropwise. The mixture was stirred for 30 min, followed by the addition of aqueous methylamine (40 %) (53.50 mL, 0.60 mol), while maintaining the temperature below 5 °C. Glacial acetic acid (99-100 %) (38.10 mL, 0.60 mol) was added in small portions while keeping the reaction temperature below 0 °C. After the addition was complete, aqueous glyoxal (40 %) (76.10 mL, 0.60 mol) was added dropwise and the resulting mixture was allowed to reach room temperature and stir for 1.5 days. The mixture was extracted with ethyl acetate to remove any unreacted starting materials, and the water was removed under reduced pressure yielding a light orange solution, which was purified as described in the literature.<sup>3</sup> After purification 80 g (70 % yield) of a faint yellow liquid was obtained (98 % purity by NMR). The <sup>1</sup>H, <sup>13</sup>C NMR confirmed the presence of a 2:1:1 mixture of 1-ethyl-3-methylimidazolium acetate, 1,3-diethylimidazolium acetate, and 1,3-dimethylimidazolium acetate, respectively. The reaction time can be reduced by increasing the temperature of the process, even though this will yield a darker mixture which will require successive purification. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) = 10.11 (s, 0.5H), 10.02 (s, 1H), 9.91 (s, 0.5H), 7.91-7.78 (m, 4H), 4.24 (q, *J* = 7.31 Hz, 2H), 4.23 (q, *J* = 7.31 Hz, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 1.58 (s, 6H), 1.43 (t, *J* = 7.31 Hz, 3H), 1.42 (t, *J* = 7.31 Hz, 3H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) = 174.2, 138.3, 137.6, 136.8, 123.9, 123.7, 122.4, 122.3, 44.4, 44.3, 35.9, 35.8, 26.1, 15.6, 15.5.

#### Reaction of sulfur and 1-ethyl-3-methylimidazolium acetate

Approximately stoichiometric amounts of [C<sub>2</sub>mim][OAc] (2.021 g, 11.88 mmol) and sulfur (0.374 g, 1.46 mmol, equivalent to 11.68 mmol of sulfur atoms) were placed in a two-neck round-bottomed flask. A reflux condenser was attached to the main neck, whereas the auxiliary neck was simply stoppered and used for taking samples from the reaction medium. The flask was partially immersed in a silicon oil bath with a controlled temperature of 25 °C. An evident darkening of the mixture, from pale yellow to dark orange/brown, could be observed within the first minutes. Samples of the reaction medium were withdrawn for <sup>1</sup>H NMR analysis at different times over a period of 5 days. The signals were consistent with the formation of 1-ethyl-3-methylimidazole-2-thione, as reported in the literature.<sup>4</sup> The integration of the spectra indicated

that the reaction initially progresses fast, reaching ca. 22 % conversion of ionic liquid to thione after 15 min; but then slows down, reaching a maximum conversion of ca. 47 % within the first 24 h. For isolation of the thione formed, acetonitrile was added to the reacted medium. The unreacted sulfur did not dissolve, and it was filtered off. Then, the acetonitrile was removed, and water and dichloromethane were added. The organic phase was washed several times with fresh water, and finally the dichloromethane was removed under vacuum. The final sample was further purified under high vacuum, and it was characterized by gas chromatography coupled with mass spectroscopy (GC-MS), by electrospray ionization mass spectroscopy (ESI-MS), and by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR, all of the results indicating that the product was 1-ethyl-3-methylimidazole-2-thione.  $^1\text{H}$  NMR, (300 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) = 7.14 (dd,  $J$  = 14.9 Hz,  $2 \times 1\text{H}$ ), 3.95 (q,  $J$  = 7.2 Hz, 2H), 3.46 (s, 3H), 1.22 (t,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR, (75 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) = 161.3, 118.7, 116.9, 42.3, 34.7, 14.5. GC/MS, single peak: 142 [100%,  $[\text{C}_6\text{H}_{10}\text{N}_2\text{S}]$ ].

In a separate experiment, again stoichiometric amounts of  $[\text{C}_2\text{mim}][\text{OAc}]$  (2.012 g, 11.83 mmol) and sulfur (0.379 g, 1.48 mmol, equivalent to 11.84 mmol of sulfur atoms) were placed in a two-neck round-bottomed flask partially immersed in a silicon oil bath with a controlled temperature of 25 °C. Rubber stoppers were put in both necks, and through one of them, a needle connected to the in-house supply of nitrogen gas was introduced, so that the nitrogen was bubbling through the reacting mixture. A simple needle was used to pierce the other rubber stopper, to allow exhaustion of the gases and equilibration of the pressure in the flask. The mixture was magnetically stirred under these conditions, and small samples were taken at different times. Relative compositional analysis of the formed thione and the unreacted ionic liquid was carried out by  $^1\text{H}$  NMR. A 57 mol% conversion was determined after 24 h, which increased up to 67 mol% after 72 h. After that, a slight decrease was observed in subsequent samples, probably due to significant stripping of the thione as well at prolonged times.

#### Reaction of selenium and 1-ethyl-3-methylimidazolium acetate

Approximately stoichiometric amounts of  $[\text{C}_2\text{mim}][\text{OAc}]$  (2.100 g, 12.30 mmol) and selenium powder (0.935 g, 11.8 mmol) were placed in a two-neck round-bottomed flask equipped with a reflux condenser. The mixture was stirred at a controlled temperature of 75 °C. An aliquot of the liquid reaction medium was withdrawn for  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and  $^{77}\text{Se}$  NMR analysis after several days. The signals were consistent with the formation of 1-ethyl-3-methylimidazole-2-selone, with a conversion of ca. 91 %, according to integration of areas under the peaks in the  $^1\text{H}$  NMR spectrum. For isolation of the selone formed, acetonitrile was added to the reacted medium. The unreacted selenium did not dissolve, and it was filtered off. Then, the acetonitrile was removed, and water and dichloromethane were added. The organic phase was washed several times with fresh water, and finally the dichloromethane was removed under vacuum. The final sample was further purified under high vacuum, and it was characterized by GC-MS, by ESI-MS, and by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and  $^{77}\text{Se}$  NMR, all of the results indicating that the product was 1-ethyl-3-methylimidazole-2-selone.  $^1\text{H}$  NMR, (300 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) = 7.35 (dd,  $J$  = 8.1 Hz,  $2 \times 1\text{H}$ ), 4.05 (q,  $J$  = 7.2 Hz, 2H), 3.56 (s, 3H), 1.25 (t,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR, (75 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) = 154.3, 121.0, 119.1, 44.2, 36.6, 14.7.  $^{77}\text{Se}$  NMR, (57.25 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (ppm) = 7.9. GC/MS, single peak: 190 [100%,  $[\text{C}_6\text{H}_{10}\text{N}_2\text{Se}]$ ; 162  $[\text{M-C}_2\text{H}_4]$ , isotope patterns consistent with one Se atom.

### Screening of 1-alkyl-3-methylimidazolium-based ionic liquids with different anions, for potential reaction with sulfur

Besides the already described reaction of [C<sub>2</sub>mim][OAc] and sulfur, a series of other 1-alkyl-3-methylimidazolium-based ionic liquids were tested for a potential reaction with sulfur. Specifically, the following ionic liquids were used: [C<sub>4</sub>mim]Cl, [C<sub>4</sub>mim][HSO<sub>4</sub>], [C<sub>4</sub>mim][SCN], [C<sub>4</sub>mim][OAc], [C<sub>1</sub>mim][CH<sub>3</sub>SO<sub>4</sub>], [C<sub>2</sub>mim][CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>], [C<sub>6</sub>mim][CF<sub>3</sub>SO<sub>3</sub>], and [C<sub>6</sub>mim][CF<sub>3</sub>COO].

In a typical test, 0.100 g of sulfur and 2.000 g of the ionic liquid were mixed in a vial or a flask, and were magnetically stirred for ca. 8 h at 75 °C. Samples from the vials were then taken and filtered, and <sup>1</sup>H and <sup>13</sup>C NMR analyses were carried out.

The NMR spectra indicated that no reaction occurred, except in the case of [C<sub>4</sub>mim][OAc], for which the NMR spectra of the sample were consistent with the formation of the thione via reaction with sulfur, in an analogous manner to the above reported reaction of [C<sub>2</sub>mim][OAc] and sulfur.

### Reaction of palladium(II) acetate and 1-ethyl-3-methylimidazolium acetate

Pd(OAc)<sub>2</sub> (0.074 g, 0.33 mmol) was added as a single portion to [C<sub>2</sub>mim][OAc] (0.112 g, 0.66 mmol). After stirring at room temperature for 1 h, acetonitrile (5 mL) was added and the resulting mixture was stirred for additional 24 h. The solid was filtered and the solution concentrated, to yield a light brown residue. Although the identity of the Pd-bis(carbene) was confirmed (in the <sup>1</sup>H NMR the imidazole ring protons were shifted upfield, and in the <sup>13</sup>C NMR the characteristic C(2)-Pd shift was observed at 158 ppm), this reaction also yielded other byproducts that we were unable to unambiguously identify. Further study is under way to more fully understand this reaction and will be reported subsequently.

### Reaction of benzaldehyde and 1-ethyl-3-methylimidazolium acetate

Stoichiometric amounts of [C<sub>2</sub>mim][OAc] (2.622 g, 15.43 mmol) and benzaldehyde (1.637 g, 15.43 mmol) were placed in a 20 mL scintillation vial. The reaction was found to be exothermic, yielding a very viscous liquid within 10 min. ESI-MS and NMR spectra showed a carbene-benzaldehyde adduct as the major product, and unreacted starting materials (21 % [C<sub>2</sub>mim][OAc] and 5 % benzaldehyde, determined by <sup>1</sup>H NMR integration). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) = 10.03 (s, 0.05H PhCHO), 9.56 (s, 1H, NCHN), 7.83-7.30 (m, 7.8H, PhCHO, NCHCHN from starting material and adduct, PhCHOH), 6.73 (s, 1H, PhCHOH), 4.25-4.17 (m, 2.41H, NCH<sub>2</sub> from starting material and adduct), 3.87 (s, 3.63H, NCH<sub>3</sub> from starting material and adduct), 1.62 (s, 3.64H, CH<sub>3</sub>COO from starting material and adduct), 1.41 (t, 0.65H, NCH<sub>2</sub>CH<sub>3</sub> from starting material), 1.15 (t, 3H, NCH<sub>2</sub>CH<sub>3</sub> from adduct). ESI-MS *m/z*: 111 ([C<sub>2</sub>mim]<sup>+</sup>), 217 ([C<sub>2</sub>mim-benzaldehyde]<sup>+</sup>).

### Reaction of sulfur and a 2:1:1 statistical mixture of 1-ethyl-3-methyl-, 1,3-diethyl-, and 1,3-dimethylimidazolium acetate

This reaction was performed at 25 °C in a completely analogous way to that of sulfur and the 'pure' [C<sub>2</sub>mim][OAc], but now using a 2:1:1 statistical mixture of 1-ethyl-3-methyl-, 1,3-diethyl-, and 1,3-dimethylimidazolium acetate as reactant. The initial amounts were: 0.379 g of sulfur (1.48 mmol, equivalent to 11.84 mmol of sulfur atoms), and 2.087 g of the statistical mixture (12.26 mmol). Samples of the reaction medium were withdrawn for <sup>1</sup>H NMR analysis at different times over a period of 5 days. The resulting spectra were consistent with the formation

of 1-ethyl-3-methylimidazole-2-thione, 1,3-dimethylimidazole-2-thione, and 1,3-diethylimidazole-2-thione. By integration of the spectra, it was concluded that the reaction progressed to a significant extent within the first hours, achieving a thiones/ionic liquids ratio of 0.64 (in a molar basis) after 24 h.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (ppm) = 7.18-7.13 (m, 4H), 3.96 (m, 4H), 3.46 (s, 6H), 1.23 (m, 6H).

Attempt to react sulfur with 1-ethyl-3-methylimidazolium acetate in the presence of an excess of acetic acid

Acetic acid (0.544 g, 9.07 mmol), supplied by Riedel-de Haën with a nominal purity of 99 %, and  $[\text{C}_2\text{mim}][\text{OAc}]$  (0.768 g, 4.51 mmol) were mixed in a round-bottomed flask, and sulfur (0.145 g, 0.57 mmol, equivalent to 4.540 mmol of sulfur atoms) was added. A reflux condenser was attached to the neck of the flask, and the mixture was magnetically stirred at a constant temperature of 25 °C. A sample was taken after 42 h, and dissolved in  $\text{DMSO}-d_6$  to be analyzed by  $^1\text{H}$  NMR spectroscopy. The resulting spectrum showed the peaks of the starting materials, with no sign of thione formation.

Attempt to react sulfur with 1-ethyl-3-methylimidazolium acetate in the presence of an equivalent mass of water

A 50:50 wt/wt mixture of deionized water (0.526 g) and  $[\text{C}_2\text{mim}][\text{OAc}]$  (0.522 g, 3.07 mmol) was prepared in a round-bottomed flask, and sulfur (0.194 g, 0.76 mmol, equivalent to 6.07 mmol of sulfur atoms) was added. A reflux condenser was attached to the neck of the flask, and the mixture was magnetically stirred at a constant temperature of 25 °C. A sample was taken after 42 h, and dissolved in  $\text{DMSO}-d_6$  to be analyzed by  $^1\text{H}$  NMR spectroscopy. The resulting spectrum was consistent with that of  $[\text{C}_2\text{mim}][\text{OAc}]$  in water, with no sign of thione formation.

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