Designing highly efficient solvents for the Knoevenagel condensation: two novel dicationic dimethyl phosphate ionic liquids

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Abstract

Two novel dicationic dimethyl phosphate ionic liquids have been designed as highly efficient solvents for the Knoevenagel condensation between ethyl cyanoacetate and aldehyde with a decreased reactivity – 4-(dimethylamino)benzaldehyde. A simple synthetic strategy has been demonstrated for obtaining the dicationic dimethyl phosphate ionic liquid bearing both aromatic imidazolium and aliphatic ammonium moieties.

Keywords: Dicationic ionic liquids, dimethyl phosphates, anion metathesis, Knoevenagel condensation

Introduction

The Knoevenagel condensation is a significant C–C bond forming reaction that provides a wide range of key intermediates for the synthesis of pharmaceuticals, polymers, cosmetics and perfumes.[1] This aspect has aroused a particular interest in developing new and advantageous synthetic approaches towards this reaction. Different molecular solvents,[2] catalysts (organic bases,[3,4] heterogeneous catalysts,[5] Lewis acids[6]) and reaction conditions (microwave[7] or ultrasound[8] irradiation) have been applied to ensure sufficiently high yields of the target products. Nevertheless, the utilization of toxic solvents or catalysts and prolonged reaction times are inconsistent with the principles of green and sustainable chemistry[9] and still have to be overcome. Ionic liquids (ILs) – structurally divergent compounds with beneficial and fine-tunable properties[10,11] – have recently been presented as alternative and efficient solvents or catalysts[1,12,13] for environmentally benign Knoevenagel condensations.

As a distinct group, dicationic ionic liquids (DILs) frequently possess enhanced chemical and physical properties,[14,15] as well as decreased toxicity[16] in comparison to the respective monocationic ILs. Several DILs have been successfully applied in the Knoevenagel condensation. Mane and co-workers have performed the DIL mediated synthesis of 5-arylidine-

2,4-thiazolidinediones.[17] Luo and co-workers have exploited PEG bridged tertiary amine functionalized DIL for the condensation between benzaldehyde and ethyl cyanoacetate.[18] Godajdar and co-workers have presented the synthesis of 1*H*-indazolo[2,1-*b*]phthalazinetrione, catalyzed by a magnetic DIL.[19] Our group has recently developed a method for obtaining DILs with a dimethyl phosphate counterion.[20] Several examples of condensation reactions, promoted by imidazolium-based dimethyl phosphates,[21,22] encouraged us to continue our earlier studies and to demonstrate the possibility of designing some dicationic dimethyl phosphate ILs as efficient solvents for the Knoevenagel condensation.

Results and Discussion

Herein, we report the synthesis of two novel DILs – 1,4-bis(3-methylimidazolium-1-yl)butane bis(dimethyl phosphate) (**4**) and 1-[2-(diethylmethylammonium)ethyl]-3-methylimidazolium bis(dimethyl phosphate) (**5**) (Figure 1), as well as their application in the Knoevenagel condensation between 4-(dimethylamino)benzaldehyde (**6**) and ethyl cyanoacetate (**7**) (Scheme 1). To develop a highly efficient solvent, an aldehyde bearing an electron-donating substituent and therefore exhibiting a lower reactivity[23] was selected as the electrophilic reagent for this model reaction and no additional catalyst was used. The impact of ILs was assessed by the conversion of 4-(dimethylamino)benzaldehyde (**6**) and the results obtained *via* gas chromatography were in a full agreement with the respective isolated yields of the product **8**.

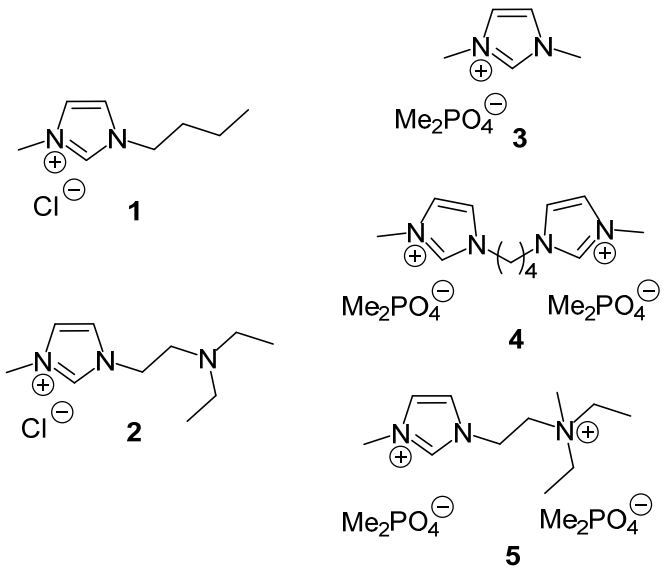
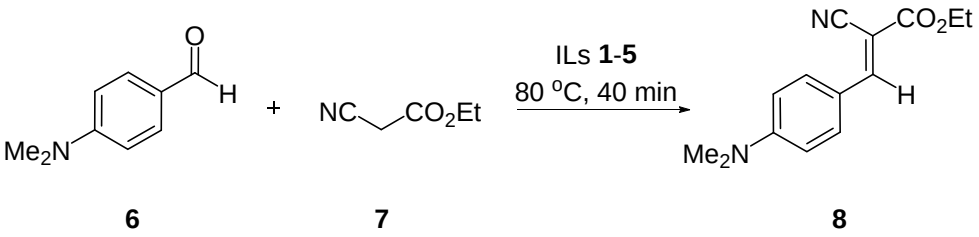


Figure 1. The imidazolium-based ILs **1**-**5** exploited as solvents for the Knoevenagel condensation outlined in Scheme 1.



6 **7** **8**

Scheme 1. The Knoevenagel condensation between 4-(dimethylamino)benzaldehyde (**6**) and ethyl cyanoacetate (**7**) in the medium of ILs **1**-**5**.

We started our investigation using 1-butyl-3-methylimidazolium chloride (**1**), and the conversion of aldehyde **6** after 60 min at 80 °C in this solvent had reached only 17% (Figure 2). Due to the fact that introduction of a basic functionality into the cation of IL may have a significant impact on some base catalyzed reactions,[24,25] IL **2**, having [2-(diethylamino)ethyl]-group in the imidazolium moiety, was evaluated as a potentially more appropriate solvent. Therefore, a simple and mild approach for the synthesis of this salt has been demonstrated (Scheme 2) in the frame of this work. The IL **2** could be easily obtained by the deprotonation of 1-[2-(diethylamino)ethyl]-3-methylimidazolium chloride hydrochloride (**9**) with NaOMe in MeOH at room temperature. However, a slight excess (1.2 equiv) of the dicationic salt **9** was crucial for obtaining a colorless IL **2**, indicating that any residual NaOMe may be responsible for the coloration of the target product. This may be caused by the acidic nature of the imidazolium ring C^2 proton that may lead to the formation of highly reactive *N*-heterocyclic carbene impurities.[26,27]

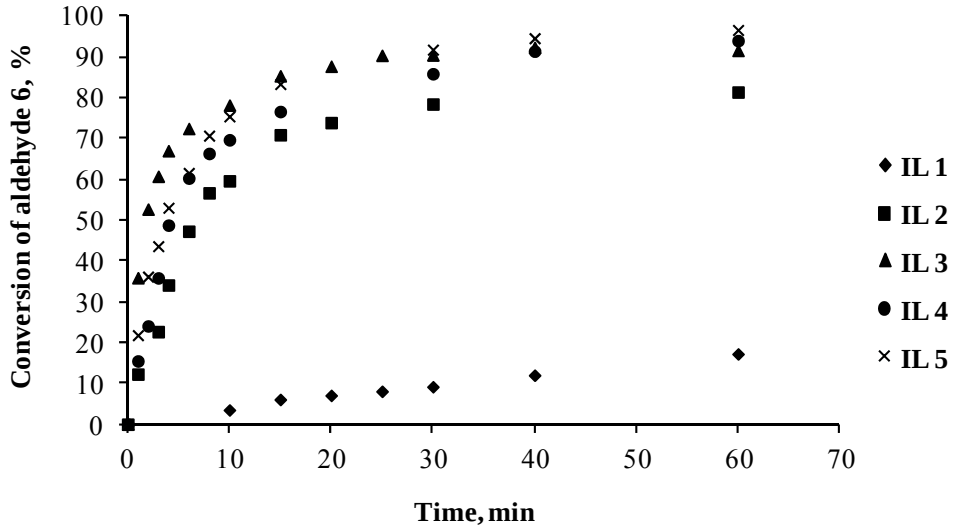
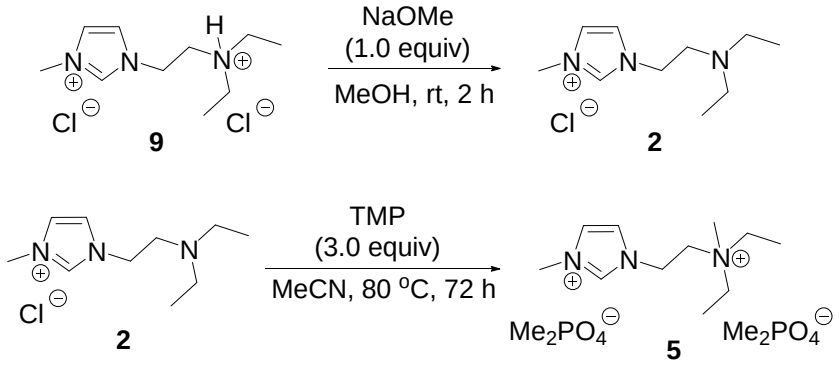


Figure 2. The conversion of 4-(dimethylamino)benzaldehyde (**6**), performing the Knoevenagel condensation in ILs **1**-**5** at 80 °C.



Scheme 2. The synthesis of 1-[2-(diethylmethylammonium)ethyl]-3-methylimidazolium bis(dimethyl phosphate) (**5**).

Hence, the application of 1-[2-(diethylamino)ethyl]-3-methylimidazolium chloride (**2**) allowed improving the conversion (81% after 60 min) of the aldehyde **6**. Nevertheless, 1,3-dimethylimidazolium dimethyl phosphate (**3**)[22] as a solvent provided even higher conversion (92% after 60 min) of the starting material. These aspects clearly showed that structural tuning, with correct selection of the cation and anion of IL, may lead to an efficient solvent for this reaction. Thereby we were encouraged to design two novel DILs with dimethyl phosphate anion. 1,4-Bis-(3-methylimidazolium-1-yl)butane bis(dimethyl phosphate) (**4**) was synthesized according to the procedure reported by our group[20] and provided an excellent conversion (94% after 60 min) of the aldehyde **6**. Furthermore, a synthetic strategy for obtaining 1-[2-(diethylmethylammonium)ethyl]-3-methylimidazolium bis(dimethyl phosphate) (**5**) was developed. A simple procedure, performing a simultaneous metathesis of the chloride ion and alkylation of the tertiary amine in IL **2** with trimethyl phosphate (TMP) (Scheme 2), provided IL **5** in quantitative yield (99%). Despite the lack of a basic site[28] in the cation after quaternization, the DIL **5** consequently provided excellent conversion (97% after 60 min) of the aldehyde **6**. Although the conversion of 4-(dimethylamino)benzaldehyde (**6**) in the medium of ILs **3**-**5** is similar, our attempts to clarify the suitability of dicationic dimethyl phosphate ILs for the Knoevenagel condensation have resulted in the development of two previously unreported compounds. Since DILs usually have enhanced chemical and physical properties[14,15] and decreased toxicity[16] in comparison to monocationic ILs, these new DILs might be a subject of interest in the context of environmentally friendly organic synthesis that benefit from the structural peculiarities of these ILs.

Conclusions

Two novel dicationic ionic liquids (DILs) – 1,4-bis-(3-methylimidazolium-1-yl)butane bis(dimethyl phosphate) (**4**) and 1-[2-(diethylmethylammonium)ethyl]-3-methylimidazolium

bis(dimethyl phosphate) (**5**) – have been designed as highly efficient solvents for the Knoevenagel condensation between 4-(dimethylamino)benzaldehyde (**6**) and ethyl cyanoacetate (**7**). A simple synthetic strategy involving a simultaneous metathesis of the chloride ion and alkylation with trimethyl phosphate (TMP) has been developed for obtaining **5** that possesses both aromatic imidazolium and aliphatic ammonium moieties. Compared with monocationic ILs bearing a chloride anion, dicationic dimethyl phosphate ILs have provided excellent conversion of the aldehyde **6** without exploitation of any additional catalyst. In addition to the successful utilization of DIL **4**, the divergent nature of DIL **5**, having both aromatic imidazolium and aliphatic ammonium moieties and relatively basic anion, suggests that this new compound could also serve as a promising solvent for other reactions that benefit from these particular structural motifs within IL.

Experimental Section

General. All reagents were purchased from Sigma-Aldrich and used as received. Solvents (methanol, acetone, and toluene) were dried and purified according to standard procedures.[29] The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra (in $CDCl_3$ or DMSO-d_6) were recorded on a Varian 400 MR spectrometer (δ in ppm, J in Hz). The chemical shifts were reported relative to a residual solvent peak as an internal reference. The IR spectra were recorded on a PerkinElmer FT-IR/FIR Frontier instrument (ν_{max} in cm^{-1}). The HRMS-ESI analyses were run on an Agilent 6230 TOF LC/MS mass spectrometer. The melting points were recorded on a Stuart SMP3 apparatus. The melting point of IL **5** was determined *via* DTA/TG as the onset temperature of the melting peak. The DTA/TG analysis was performed with a SII NanoTechnology Exstar6000 TG/DTA6300 instrument. Open aluminum pan was used. Sample (~10 mg) was heated from 30 to 300 °C at a heating rate 10 °C/min. The nitrogen flow rate was 300±20 mL/min. The conversion of 4-(dimethylamino)benzaldehyde (**6**) was calculated from the data obtained *via* gas chromatography. The analyses were performed on a YL6100 GC gas chromatograph equipped with a Restek Rtx®-1 MS column (30 m × 0.25 mm × 0.25 μm) and flame ionization detector (FID).

1-Butyl-3-methylimidazolium chloride (**1)** was obtained according to the known procedure.[30] FTIR (ATR film), ν_{max} (cm^{-1}): 1561 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 9.23 (1H, s, NC<u>H</u>N), 7.79 (1H, t, NC<u>H</u>CHN, J 1.8 Hz), 7.72 (1H, t, NCHC<u>H</u>N, J 1.7 Hz), 4.17 (2H, t, NC<u>H</u>$_2$(CH$_2$)$_2$CH$_3$, J 7.2 Hz), 3.85 (3H, s, NC<u>H</u>$_3$), 1.76 (2H, quint, NCH$_2$C<u>H</u>$_2$CH$_2$CH$_3$, J 7.3 Hz), 1.26 (2H, sext, N(CH$_2$)$_2$C<u>H</u>$_2$CH$_3$, J 7.4 Hz), 0.90 (3H, t, N(CH$_2$)$_3$C<u>H</u>$_3$, J 7.3 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 136.7 (N<u>C</u>HN), 123.5 (N<u>C</u>HCHN), 122.2 (NCH<u>C</u>HN), 48.4 (N<u>C</u>H$_2$(CH$_2$)$_2$CH$_3$), 35.7 (N<u>C</u>H$_3$), 31.4 (NCH$_2$<u>C</u>H$_2$CH$_2$CH$_3$), 18.7 (N(CH$_2$)$_2$<u>C</u>H$_2$CH$_3$), 13.3 (N(CH$_2$)$_3$<u>C</u>H$_3$). ESI-HRMS: *m/z* [M]$^+$ calcd for $C_8H_{15}N_2^+$: 139.1230. Found: 139.1216.

1-[2-(Diethylamino)ethyl]-3-methylimidazolium chloride (2). Sodium (0.46 g, 20.0 mmol) was reacted with dry MeOH (20 mL) under vigorous stirring and cooling in an ice bath. After the complete evolution of gas, a solution of 1-[2-(diethylamino)ethyl]-3-methylimidazolium chloride hydrochloride (**9**) (5.13 g, 20.2 mmol) in MeOH (30 mL) was added dropwise and the reaction mixture was stirred at rt for 2 h. The precipitated NaCl was filtered off on Celite® 512 Medium and washed on the filter with MeOH (10 mL). The combined filtrates were concentrated by rotary evaporation (10 mbar, 70 °C) and dry acetone (30 mL) was added to the obtained slurry. The mixture was repeatedly filtered through Celite® 512 Medium and the precipitate was washed on the filter with acetone (20 mL). The combined solutions were filtered through a PTFE filter (0.45 μm) and concentrated by rotary evaporation (10 mbar, 70 °C). The pure product was dried under vacuum (0.6 mbar, 75 °C, 12 h).

IL 2. Colorless, glassy substance, yield 90%, 3.92 g; FTIR (ATR film), ν_{max} (cm^{-1}): 1670 (C=N), 1570 (C=C). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 9.18 (1H, s, NC<u>H</u>N), 7.77 (1H, t, NC<u>H</u>CHN, *J* 1.7 Hz), 7.70 (1H, t, NCHC<u>H</u>N, *J* 1.6 Hz), 4.20 (2H, t, NC<u>H$_2$</u>CH$_2$NEt$_2$, *J* 5.9 Hz), 3.87 (3H, s, NC<u>H$_3$</u>), 2.71 (2H, t, NCH$_2$C<u>H$_2$</u>NEt$_2$, *J* 5.9 Hz), 2.46 (4H, q, NC<u>H$_2$</u>CH$_3$, *J* 7.1), 0.85 (6H, t, NCH$_2$C<u>H$_3$</u>, *J* 7.1 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 136.9 (N<u>C</u>HN), 123.1 (N<u>C</u>HCHN), 122.6 (NCH<u>C</u>HN), 51.8 (NCH$_2$<u>C</u>H$_2$NEt$_2$), 47.3 (N<u>C</u>H$_2$CH$_3$), 46.2 (N<u>C</u>H$_2$CH$_3$), 35.6 (N<u>C</u>H$_3$), 11.6 (NCH$_2$<u>C</u>H$_3$). ESI-HRMS: *m/z* $[M]^+$ calcd for $C_{10}H_{20}N_3^+$: 182.1657. Found: 182.1653.

1,3-Dimethylimidazolium dimethyl phosphate (3) was synthesized in a similar manner as reported previously by our group.[20] FTIR (ATR film), ν_{max} (cm^{-1}): 1577 (C=C), 1242 (P=O), 1040 (P–O). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 9.38 (1H, s, NC<u>H</u>N), 7.73 (2H, d, NC<u>H</u>C<u>H</u>N, *J* 1.5 Hz), 3.85 (6H, s, NC<u>H$_3$</u>), 3.27 (6H, d, OC<u>H$_3$</u>, *J* 10.3 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 137.6 (N<u>C</u>HN), 123.4 (N<u>C</u>H<u>C</u>HN), 51.3 (O<u>C</u>H$_3$), 51.2 (O<u>C</u>H$_3$), 35.6 (N<u>C</u>H$_3$). ESI-HRMS: *m/z* $[M]^+$ calcd for $C_5H_9N_2^+$: 97.0766. Found: 97.0763.

1,4-Bis-(3-methylimidazolium-1-yl)butane bis(dimethyl phosphate) (4) was synthesized in a similar manner as reported previously by our group.[20] FTIR (ATR film), ν_{max} (cm^{-1}): 1579 (C=C), 1241 (P=O), 1037 (P–O). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 9.47 (2H, s, NC<u>H</u>N), 7.82 (2H, s, NC<u>H</u>CHN), 7.72 (2H, s, NCHC<u>H</u>N), 4.24 (4H, s, NC<u>H$_2$</u>(CH$_2$)$_2$C<u>H$_2$</u>N), 3.86 (6H, s, NC<u>H$_3$</u>), 3.28 (12H, d, OC<u>H$_3$</u>, *J* 10.3 Hz), 1.79 (4H, s, NCH$_2$(C<u>H$_2$</u>)$_2$CH$_2$N). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 137.2 (N<u>C</u>HN), 123.6 (N<u>C</u>HCHN), 122.3 (NCH<u>C</u>HN), 51.3 (O<u>C</u>H$_3$), 47.7 (N<u>C</u>H$_2$(CH$_2$)$_2$<u>C</u>H$_2$N), 35.7 (N<u>C</u>H$_3$), 25.9 (NCH$_2$(<u>C</u>H$_2$)$_2$CH$_2$N). ESI-HRMS: *m/z* $[M]^+$ calcd for $C_{12}H_{19}N_4^+$: 219.1604. Found: 219.1603.

1-[2-(Diethylmethylammonium)ethyl]-3-methylimidazolium bis(dimethyl phosphate) (5). A solution of 1-[2-(diethylamino)ethyl]-3-methylimidazolium chloride (**2**) (3.89 g, 17.9 mmol) and TMP (7.51 g, 53.6 mmol) in MeCN (7 mL) was stirred at 80 °C for 72 h. After the completion of the reaction, solvent was removed by rotary evaporation (10 mbar, 70 °C). Diethyl ether (5 mL) was added to the crude product and the mixture was stirred for 5 min. The diethyl ether layer was decanted and the procedure was repeated using toluene (7 × 5 mL) and heating the mixture to reflux. The toluene layer was decanted while hot. Any remaining solvent was then removed by

rotary evaporation (10 mbar, 70 °C). The pure product was dried under vacuum (0.6 mbar, 80 °C, 12 h) and was subjected to $AgNO_3$ test to confirm the absence of starting material.

IL 5. White solid, yield 99%, 7.94 g, mp 79 °C (determined *via* DTA/TG); FTIR (ATR film), ν_{max} (cm^{-1}): 1579 (C=C), 1240 (P=O), 1036 (P–O). ^1H NMR (400 MHz, $CDCl_3$): δ_H 10.67 (1H, s, NCHN), 8.86 (1H, s, NCHCHN), 7.15 (1H, s, NCHCHN), 5.25-5.16 (2H, m, $NCH_2CH_2NCH_3Et_2$), 4.28-4.19 (2H, m, $NCH_2CH_2NCH_3Et_2$), 3.91 (3H, s, NCH_3), 3.79-3.68 (2H, m, NCH_2CH_3), 3.67-3.58 (2H, m, NCH_2CH_3), 3.55 (12H, d, OCH_3, *J* 10.5 Hz), 3.27 (3H, s, $NCH_2CH_2NCH_3Et_2$), 1.36 (6H, t, NCH_2CH_3, *J* 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 139.7 (NCHN), 125.8 (NCHCHN), 122.4 (NCHCHN), 59.7 ($NCH_2CH_2NCH_3Et_2$), 57.2 (NCH_2CH_3), 52.7 (OCH_3), 52.6 (OCH_3), 47.4 ($NCH_2CH_2NCH_3Et_2$), 42.5 ($NCH_2CH_2NCH_3Et_2$), 36.4 (NCH_3), 8.2 (NCH_2CH_3). ESI-HRMS: *m/z* $[M]^+$ calcd for $C_{11}H_{22}N_3^+$: 196.1814. Found: 196.1790.

1-[2-(Diethylamino)ethyl]-3-methylimidazolium chloride hydrochloride (9). 1-Methyl-imidazole (3.98 g, 48.5 mmol) and 2-(diethylamino)ethyl chloride hydrochloride (8.35 g, 48.5 mmol) were dissolved in MeCN (30 mL) and refluxed for 48 h. After cooling to rt, the colorless precipitate was filtered, washed on the filter with EtOAc (15 mL), and recrystallized from EtOH. The pure product was dried under vacuum (0.6 mbar, 100 °C, 5 h).

IL 9. Colorless solid, yield 66%, 8.09 g, mp 197–200 °C (from EtOH); FTIR (ATR film), ν_{max} (cm^{-1}): 3449 (NH), 1641 (C=N), 1576 (C=C). ^1H NMR (400 MHz, DMSO-d_6): δ_H 11.40 (1H, s, NH), 9.45 (1H, s, NCHN), 7.99 (1H, s, NCHCHN), 7.75 (1H, s, NCHCHN), 4.73 (2H, t, $NCH_2CH_2NHEt_2$, *J* 6.6 Hz), 3.85 (3H, s, NCH_3), 3.60 (2H, d, $NCH_2CH_2NHEt_2$, *J* 4.9 Hz,), 3.16 (4H, s, NCH_2CH_3), 1.24 (6H, t, NCH_2CH_3, *J* 7.2 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 137.8 (NCHN), 123.8 (NCHCHN), 122.2 (NCHCHN), 49.5 ($NCH_2CH_2NHEt_2$), 46.6 (NCH_2CH_3), 43.0 ($NCH_2CH_2NHEt_2$), 35.9 (NCH_3), 8.2 (NCH_2CH_3). ESI-HRMS: *m/z* $[M]^+$ calcd for $C_{10}H_{20}N_3^+$: 182.1657. Found: 182.1651.

General procedure for the Knoevenagel condensation in ionic liquids 1-5. 4-(Dimethylamino)benzaldehyde (**6**) (120 mg, 0.80 mmol) was dissolved in the appropriate IL (8.0 mmol) at 80 °C temperature and ethyl cyanoacetate (**7**) (91 mg, 0.80 mmol) was added under vigorous stirring. After specified time (Figure 2), 1-2 drops of the reaction mixture were quenched with EtOAc/brine (1 mL/0.3 mL) mixture at -10 °C. The EtOAc layer was separated and the brine layer was repeatedly extracted with EtOAc (9 × 1 mL) at -10 °C. The combined extracts were concentrated to approximately 1 mL by rotary evaporation (10 mbar, 30 °C) and the conversion of the aldehyde **6** was calculated from the data obtained *via* gas chromatography. To support the results obtained by gas chromatography, the reaction was performed in ILs **2-5** according to the general procedure and product **8** was isolated. After stirring at 80 °C for 40 min, cold distilled water (10 mL) was added to the reaction mixture. The crude product was filtered, washed on the filter with distilled water (10 mL) and recrystallized from $EtOH/H_2O$. The pure product was dried under vacuum (0.6 mbar, 65 °C, 2 h). The isolated yields of **8** were in a full agreement with the results provided by gas chromatography.

In **IL 2**: yield 160 mg (80%); in **IL 3**: yield 186 mg (93%), in **IL 4**, yield 174 mg (87%); in **IL 5**, yield 188 mg (94%). Yellow solid, mp 125–126 °C (from EtOH/H_2O); FTIR (ATR film), ν_{max} (cm^{-1}): 2208 (C≡N), 1701 (C=O), 1610 (C=C). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.07 (1H, s, C<u>H</u>=C), 7.96-7.90 (2H, m, <u>H</u>$_{ar}$), 6.72-6.66 (2H, m, <u>H</u>$_{ar}$), 4.33 (2H, q, OC<u>H</u>$_2$CH$_3$, *J* 7.1 Hz), 3.10 (6H, s, N(C<u>H</u>$_3$)$_2$), 1.37 (3H, t, OCH$_2$C<u>H</u>$_3$, *J* 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 164.4 (<u>C</u>=O), 154.6 (<u>C</u>H=C), 153.7 (N<u>C</u>$_{ar}$), 134.2 (<u>C</u>$_{ar}$), 119.6 (<u>C</u>$_{ar}$CH=C), 117.7 (<u>C</u>N), 111.7 (<u>C</u>$_{ar}$), 94.3 (CH=<u>C</u>), 62.0 (O<u>C</u>H$_2$CH$_3$), 40.2 (N(<u>C</u>H$_3$)$_2$), 14.4 (OCH$_2$<u>C</u>H$_3$). ESI-HRMS: *m/z* $[M+H]^+$ calcd for $C_{14}H_{17}N_2O_2^+$: 245.1285. Found: 245.1286.

Supplementary Material

^{1}H and ^{13}C NMR spectra of ILs **1-5**, salt **9**, and compound **8**.

Acknowledgements

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