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PAPER

Silver-free synthesis of nitrate-containing room-temperature ionic liquids†

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Nitrate-containing 1-alkyl-3-methylimidazolium ionic liquids, [C$_n$-mim]NO$_3$, where n = 4, 6, 8, 12, are synthesized in one step by reacting 1-methylimidazole with alkyl nitrates under various conditions without using AgNO$_3$ and 1-alkyl-3-methylimidazolium halides.

Introduction

Ionic liquids have found numerous applications in various areas of chemistry, physics, biology and engineering.[1] Development of more efficient, facile and greener synthetic approaches to ionic liquids constitutes a significant area of research, which should further increase the utility of ionic liquids.

The majority of ionic liquids feature halogen-containing anions, including $[PF_6]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$ and $[(CF_3SO_2)_2N]^-$.[2] Since some of these anions such as PF_6^-, for example, are prone to hydrolysis, the liberation of HF presents a concern.[3] In this light, the synthesis and applications of several halogen-free ionic liquids were reported.[4]

Among room-temperature ionic liquids, nitrate-containing ionic liquids remained a relatively unexplored class of ionic solvents.[5] Several accounts indicated that nitrate-containing ionic liquids are of interest for potential nuclear waste treatment,[6] co-solvents and promotors for organic and organometallic reactions[7] as well as applications in biological[8] and materials chemistry.[9]

The relatively small number of applications for NO$_3$-ionic liquids, compared to other types of ionic liquids, is likely due to the fact that the reported syntheses of nitrate-containing ionic liquids rely almost exclusively on the conversion of halide-containing ionic liquids, *i.e.*, chloride or bromide, into the nitrate-containing ionic liquids using AgNO$_3$. Preparation of NO$_3$-containing ionic liquids using HNO$_3$ and an ion-exchange resin was recently reported.[10] Arguably, the significant cost of AgNO$_3$[11] coupled with generation of the AgCl or AgBr by-products complicate large-scale preparations of NO$_3$-containing ionic liquids using AgNO$_3$. Thus, the AgNO$_3$-free synthesis of nitrate-containing ionic liquids would be an important addition to the synthetic repertoire of ionic liquids, potentially enhancing and expanding the applications of these solvents.

We envisioned that a nucleophilic substitution of the ONO$_2$ group from an alkyl nitrate by an electron pair of the nitrogen of an amine, a reaction that is similar to the synthesis of halide-containing ionic liquids from an amine and alkyl halide,[12] will yield nitrate-containing ionic liquids in one step. This approach would be more economical than the currently available two-step process, *i.e.*, preparation of a halide-containing ionic liquid precursor followed by a metathesis reaction with AgNO$_3$. Furthermore, halide-free synthesis of ionic liquids will also eliminate problems associated with the presence of halides in ionic liquids, which are known to have a drastic impact on the physical and chemical properties of ionic liquids.[13] To our surprise, a one-step approach to nitrate-containing ionic liquids has not been reported in the literature.

Results and discussion

To test this hypothesis, we used commercially available butyl nitrate and a set of amines, including 1-methylimidazole, pyridine, triethylamine and *N*-methylmorpholine (Scheme 1). This initial reaction was performed under neat conditions at elevated temperatures. Among the tested amines, ionic liquid formation was noted only for 1-methylimidazole and pyridine. In the case of pyridine, however, the conversion was only *ca.* 10%. Neither triethylamine nor *N*-methylmorpholine produced a product: starting materials were recovered in the case of triethylamine,[14] whereas a complex mixture of starting materials and unidentified products was detected in the case of 1-methylmorpholine. Thus, we decided to explore the synthesis of 1-butyl-3-methylimidazolium nitrate, [C$_4$-mim]NO$_3$, in more detail.

We prepared [C$_4$-mim]NO$_3$ ionic liquid using neat conditions (Table 1, entries 1–5). Similarly to halide-containing imidazolium ionic liquids,[15] the efficiency of the synthesis of nitrate-containing ionic liquids was found to be temperature-dependent: the higher the temperature, the higher the conversion. Although temperatures above 120 °C led to even faster

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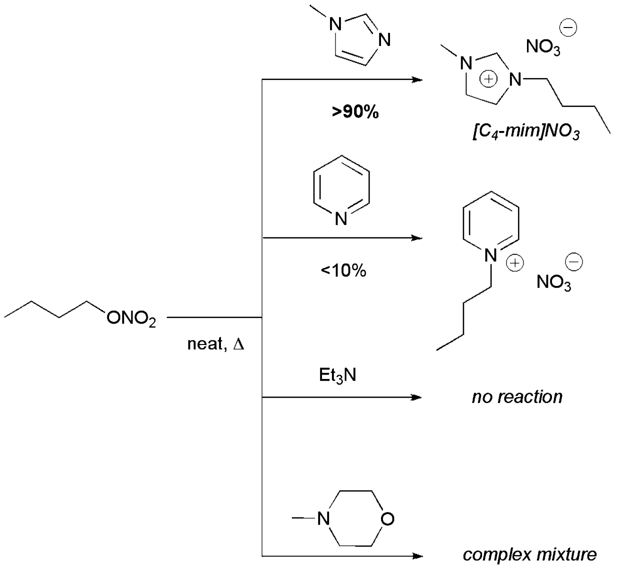


Scheme 1 Initial attempts of the one-step synthesis of nitrate-containing ionic liquids.

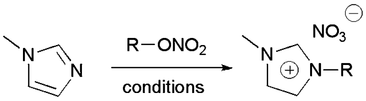
formation of [C_4-mim]NO_3, the ionic liquid was obtained as a dark brown liquid. It appeared that increasing the amount of the butyl nitrate (Table 1, entries 4–5) produced the ionic liquid in high yield in a short period of time as a dark yellow viscous liquid (Fig. S1, ESI†). It is of interest to point out that the increased amounts of butyl nitrate up to 2.0 eq. prevented the formation of dark colored impurities. Notably, the excess of butyl nitrate was recovered by decantation from the [C_4-mim]NO_3, which was obtained in high yield.

Consistent with literature accounts,[16] NMR spectroscopy (Fig. S1, ESI†) is a convenient way of establishing the purity of ionic liquids suitable for the majority of applications, but it is insensitive to minute amounts of impurities that might be significant for spectroscopic studies. In order to remove the colored impurities (Fig. S1, ESI†), the ionic liquid was subjected to several purification protocols according to other reports.[16]

We found that passing the solution of the ionic liquid in a molecular solvent (either acetonitrile or ethanol) through a silica gel/charcoal column produced a light brown liquid, albeit in a very low yield.[16b] Large quantities of eluent were also required to recover the ionic liquid from the column, thus, this procedure was abandoned.

Next, we attempted purification of the [C_4-mim]NO_3 using charcoal/solvent.[16] It appeared that the temperature at which the charcoal treatment was done had a significant impact on the final color of the ionic liquid. Specifically, refluxing the ionic liquid with charcoal in dichloromethane produced a light yellow solution; in refluxing acetonitrile—a yellow solution was obtained; and finally, in refluxing water—a colorless solution was obtained (Fig. S1, ESI†). Notably, repetitive treatment with charcoal appeared to have little impact on

Table 1 Synthesis of [C_n-mim]NO_3 ionic liquids



R	ionic liquid
C_4H_9	[C_4-mim]NO_3
C_6H_{13}	[C_6-mim]NO_3
C_8H_{17}	[C_8-mim]NO_3
$C_{12}H_{25}$	[C_{12}-mim]NO_3

Entry	$RONO_2$/eq.	Conditions[a]	Conversion[b] (%)	Yield[c] (%)
1	$C_4H_9ONO_2$ (1.1)	120 °C, 1 h	89	ND[d]
2	$C_4H_9ONO_2$ (1.1)	120 °C, 3 h	93	ND[d]
3	$C_4H_9ONO_2$ (1.1)	120 °C, 5 h	98	ND[d]
4	$C_4H_9ONO_2$ (2.0)	120 °C, 1 h	93	ND[d]
5	$C_4H_9ONO_2$ (2.0)	120 °C, 2 h	>99	90
6	$C_4H_9ONO_2$ (1.1)	MW, 120 °C, 10 min	80	ND[d]
7	$C_4H_9ONO_2$ (1.1)	MW, 120 °C, 30 min	85	ND[d]
8	$C_4H_9ONO_2$ (2.0)	MW, 120 °C, 10 min	88	ND[d]
9	$C_4H_9ONO_2$ (2.0)	MW, 120 °C, 30 min	>99	96
10	$C_4H_9ONO_2$ (2.0)	H_2O, 120 °C, 20 h	84	ND[d]
11	$C_4H_9ONO_2$ (2.0)	H_2O, 120 °C, 40 h	>99	95
12	$C_4H_9ONO_2$ (2.0)	120 °C, 2 h[e]	ND[d]	99
13	$C_4H_9ONO_2$ (2.0)	H_2O, 120 °C, 40 h[e]	ND[d]	95
14	$C_6H_{13}ONO_2$ (2.0)	120 °C, 6 h	>99	96
15	$C_6H_{13}ONO_2$ (2.0)	H_2O, 120 °C, 20 h	>99	98
16	$C_6H_{13}ONO_2$ (2.0)	MW, 120 °C, 30 min	95	ND[d]
17	$C_6H_{13}ONO_2$ (2.0)	MW, 120 °C, 45 min	>99	99
18	$C_8H_{17}ONO_2$ (2.0)	120 °C, 6 h	>99	95
19	$C_8H_{17}ONO_2$ (2.0)	H_2O, 120 °C, 20 h	>99	96
20	$C_8H_{17}ONO_2$ (2.0)	MW, 120 °C, 30 min	>99	95
21	$C_{12}H_{25}ONO_2$ (2.0)	120 °C, 6 h	>99	79[f]
22	$C_{12}H_{25}ONO_2$ (2.0)	MW, 120 °C, 45 min	>99	94[f]

[a] Unless indicated the reactions were performed on a 12.5 mmol scale (based on 1-methylmidazole) under stirring, exposed to air using the specified set of conditions; H_2O indicates that the reaction was done in the presence of H_2O, MW indicates microwave irradiation. [b] Determined from ^1H NMR of the crude reaction mixture. [c] Isolated yields after purification with charcoal/H_2O. [d] Not determined. [e] 0.188 mol scale based on 1-methylimidazole. [f] Isolated yields after washing with Et_2O.

further decolorization of [C_4-mim]NO_3. It should be pointed out that the same color of the [C_4-mim]NO_3 was obtained when this ionic liquid was prepared from a metathesis reaction of the [C_4-mim]Br with $AgNO_3$. Thus, water/charcoal treatment was chosen as the purification method for all subsequent preparations. Upon removing water under vacuum at 40 °C, the ionic liquid was obtained as a pale yellow viscous liquid. It should also be pointed out, that [C_4-mim]NO_3 can develop a more intense, darker color if exposed to extensive heating.

It has been previously proposed that absorbance and fluorescence spectroscopies could be used to check the purity of ionic liquids.[16] Specifically, transitions above 350 nm in the UV/vis spectrum of an ionic liquid could generally indicate the presence of impurities.[16c]

The presence of the shoulder at 350 nm indicated that the crude [C_4-mim]NO_3 (Fig. 1) contained such impurities. This transition progressively decreased as the color of the ionic liquid changed from dark yellow to pale yellow (Fig. S1, ESI†). The transition at 307 nm is due to the NO_3-anion: we prepared a 0.7 M solution of KNO_3 in water and obtained the absorbance spectra, which also shows a peak at 307 nm (Fig. S2, ESI†).

Emission spectroscopy has also been used as a tool for determining the purity of ionic liquids. However, unlike absorbance, the use of fluorescence is somewhat controversial as it seems to arise not only due to the impurities,[16d] but also due to the nature of the ionic liquid.[16a,b] In the case of [C_4-mim]NO_3, fluorescence spectroscopy appeared to have no correlation with the presence of impurities (Fig. S3, ESI†). The emission of the crude ionic liquid was quite similar to that of the purified ones. Repetitive treatment with charcoal/water did not reduce the emission at *ca.* 430–460 nm. Furthermore, independent preparations of [C_4-mim]NO_3 followed by charcoal treatment exhibited similar emission profiles.

With the purification protocol in hand, we explored the $AgNO_3$-free synthesis of [C_n-mim]NO_3 ionic liquids in more detail (Table 1). Synthesis of ionic liquids using microwave (MW) irradiation is well documented.[17] Not surprisingly, [C_4-mim]NO_3 was efficiently obtained under MW conditions.

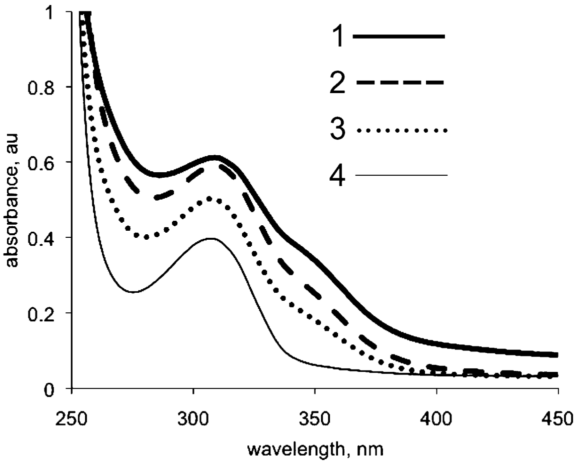


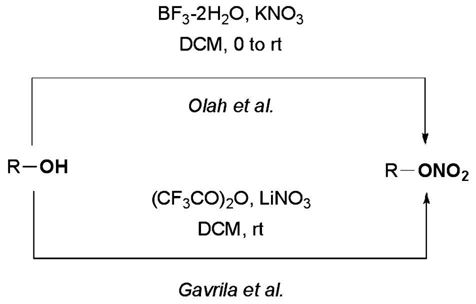
Fig. 1 UV/vis spectra of neat [C_4-mim]NO_3 ionic liquid; 1—crude reaction mixture; 2—1 after charcoal/CH_2Cl_2; 3—1 after charcoal/CH_3CN; 4—1 after charcoal/H_2O (see text for details).

As expected, the conversion of 1-methylimidazole increased with increased temperatures and heating times with 120 °C as the optimum temperature. Temperatures above 120 °C were avoided due to a low boiling/flash point of butyl nitrate. It also appeared (Table 1, entries 6–9) that an excess butyl nitrate was required to achieve complete conversions and high yields of the product. Similar to the neat conditions without MW irradiation, the excess of the butylnitrate was easily recovered by decantation.

We also considered the synthesis of [C_4-mim]NO_3 in a solvent. Our motivation for using the solvent was primarily to decrease/prevent the formation of colored impurities. After screening several solvents, such as ethylacetate, acetonitrile, ethanol and water, we found that water was the most suitable solvent in terms of reaction efficiency and compatability with our purification procedure. It should be pointed out that this list of solvents is not comprehensive, and other solvents might prove to be more efficient.[18] Considering that the reagent concentration plays significant role in the efficiency of the ionic liquid formation, the amount of water was kept to a minimum (*ca.* 24% v/v). Under these conditions, a complete conversion of 1-methylimidazole was noted after about 2 days. The purity of the obtained ionic liquid was identical to that obtained under neat conditions. However, although the resulting [C_4-mim]NO_3 had a less intense color, purification with charcoal was still required.

In addition, we carried out scaled-up syntheses of [C_4-mim]NO_3 using the neat and the water-containing conditions (Table 1, entries 12 and 13, respectively). In both cases, after the specified reaction time, the excess of butyl nitrate was decanted and the ionic liquid was subjected to charcoal purification to give [C_4-mim]NO_3 in high yields; the purity of these ionic liquids was identical to that obtained during small scale preparations. The efficiency of the butyl nitrate's recovery depended on the specific conditions. For the reaction done in the presence of water (Table 1, entry 13), we recovered 70% of butyl nitrate. However, under neat reaction conditions (Table 1, entry 12), only 40% of butyl nitrate was recovered. It appeared that butyl nitrate is partially miscible with [C_4-mim]NO_3, which is responsible for an inefficient recovery. Arguably, the presence of water in the reaction mixture (Table 1, entry 13) reduces the miscibility of butyl nitrate and [C_4-mim]NO_3, thus affording more efficient recovery. If more efficient recovery of butyl nitrate is required, the reaction mixture may be washed with Et_2O, prior to subjecting it to the charcoal/water treatment.

We have also tested all of the above conditions, *i.e.*, neat, MW and water, for the synthesis of *N*-butylpyridinium, butyltriethylammonium and *N*-butyl-*N*-methylmorpholinium nitrates. Neither triethylamine nor *N*-methylmorpholine produced the corresponding ionic liquids. Formation of *N*-butylpyridinium nitrate never proceeded above 30–40% yield. Hence, we decided to focus on the synthesis of imidazolium-based nitrate-containing room-temperature ionic liquids. The survey of the literature indicated that only 1-alkyl-3-methylimidazolium nitrates, [C_n-mim]NO_3, where n = 4, 6 and 8 are room-temperature ionic liquids;[6a,19] other known [C_n-mim]NO_3 ionic liquids, with n = 12, 14, 16, 18 are solids at room temperature.[9a]



Scheme 2 Synthesis of alkyl nitrates.

Even though butyl nitrate is commercially available, other alkyl nitrates are not. Synthesis of alkyl nitrates is well documented, albeit most procedures employ either $AgNO_3$ or highly corrosive mixture of H_2SO_4 and HNO_3 acids.[20] Two procedures reported by Olah *et al.*[21] and Gavrila *et al.*[22] had all the features suitable for convenient, facile, scalable and relatively safe syntheses of alkyl nitrates using inexpensive alkyl alcohols as the starting materials (Scheme 2).

Olah *et al.*[21] procedure worked well for the synthesis of butyl nitrate, which afforded a pure product in 80% yield without any purification. However, hexyl, decyl and dodecyl nitrates were obtained in significantly lower yields, and were contaminated with a BF_3-complexed alcohol, which in the case of dodecyl alcohol was obtained as the major product (the presence of fluorine was confirmed by ^{19}F NMR). All attempts to separate the desired nitrates by distillation and extraction proved ineffective. Upon treatment with ethylene diamine followed by acidic work-up, the BF_3-complex was destroyed liberating the corresponding alcohol. Regretfully, separation of the nitrate from the alcohol by distillation or basic extraction also failed. We found that treating the crude mixture of nitrate and alcohol with phenylisocyanate led to the formation of the nitrate and the corresponding carbamate. From this mixture, the alkyl nitrate could be easily isolated by distillation. However, this lengthy procedure might be of little practical use. In order to increase the conversions, we also increased the amounts of KNO_3 and/or BF_3–$2H_2O$ as well as reaction times, yet neither improved the efficiency of the reaction.

It should be pointed out that the presence of the alcohol does not have a measurable effect on the efficiency of the ionic liquid formation, regardless of the conditions, *i.e.*, neat/heat, water/reflux or MW. Considering that the ratio between the alkyl nitrate and the corresponding alcohol could be easily determined from ^1H NMR spectra (the CH_2 resonance at *ca.* 4.4 ppm for the $NO_3\mathit{CH}_2R$ and 3.6 ppm for $HO\mathit{CH}_2R$), the alcohol–nitrate mixture could, in principle, be directly used for the synthesis of the nitrate-containing ionic liquids. From the ionic liquid, the alkyl alcohol is separated by repetitive washings of the ionic liquid with either ethyl acetate or diethyl ether, and followed by further purification with charcoal in water.

Next, we tested Gavrila *et al.*[22] procedure, which uses a mixture of $(CF_3CO)_2O$ and $LiNO_3$ as the nitrating reagent. It appeared that by directly adopting this protocol, alkyl nitrates were obtained in moderate yields, albeit some unreacted alcohol remained. In order to achieve a complete conversion of the starting alcohol, the amounts of both $(CF_3CO)_2O$ and $LiNO_3$ had to be increased to 2.7 equivalents. Notably, the alkyl trifluoroacetates were obtained as the major by-products. The nitrate and the alkyl trifluoroacetate could not easily be distinguished by ^1H NMR due to resonance overlaps; hence, both ^{13}C and ^{19}F NMR were used for unambiguous identification and purity confirmation. Nonetheless, following this modification, the desired alkyl nitrates were purified by simple distillation from the crude mixture. This procedure was used for the synthesis of the long-chain alkyl nitrates utilized in this work.

Although we have not experienced any safety-related issues during the preparation, purification and handling of alkyl nitrates, care should be exercised when handling alkyl nitrates due to their high flammability.

With the improved procedure in hand, we prepared hexyl, octyl and dodecyl nitrates from the corresponding alcohols. These nitrates were reacted with 1-methylimidazole (Table 1, entries 14–20). The reactions under any given set of conditions appeared to be very efficient and the corresponding nitrate-containing ionic liquids were obtained in high yields. Interestingly, the isolated yields of $[C_n\text{-mim}]NO_3$ are comparable to those obtained *via* a two step procedure that involves $AgNO_3$. Although, the syntheses of $[C_6\text{-mim}]NO_3$ and $[C_8\text{-mim}]NO_3$ followed similar trends as for $[C_4\text{-mim}]NO_3$ syntheses, several minor deviations were noted: (i) longer reaction times under neat conditions were observed; (ii) a longer reaction time for $[C_6\text{-mim}]NO_3$ formation under MW conditions (Table 1, entries 16 and 17); (iii) the reaction times in water (Table 1, entries 15 and 19) were significantly shorter.

In addition to room-temperature ionic liquid nitrates, we also explored the synthesis of $[C_{12}\text{-mim}]NO_3$ as a representative member of solid alkylimidazolium nitrates.[9a] Although the synthesis of $[C_{12}\text{-mim}]NO_3$ appeared to be efficient (Table 1, entries 21 and 22), the purification of this ionic liquid proved to be distinct from other nitrate-containing ionic liquids. Any attempts to utilize charcoal/water treatment failed, due to formation of a soapy composition at the water removal step leading to significant losses of the ionic liquid. Also, dodecylnitrate appeared to be completely miscible with the $[C_{12}\text{-mim}]NO_3$, and no phase separation was noted at the endpoint of the reaction. Therefore, colored impurities and the excess of dodecylnitrate were removed by repetitive washings with Et_2O. The dodecylnitrate was recovered upon removal of Et_2O.

Conclusions

In conclusion, we have developed a facile, $AgNO_3$-free synthesis of $[C_n\text{-mim}]NO_3$ ionic liquids, which does not utilize 1-alkyl-3-methylimidazolium halides as intermediates. Although the reported procedure is limited in scope, the facile nature of this one-step synthesis of $[C_n\text{-mim}]NO_3$ should broaden the range of applications of the nitrate-containing ionic liquids. The green aspect[23] of this one step process should be taken with caution, since the access to many alkyl nitrates is not very efficient at the moment and is currently being explored in our laboratory.

Experimental

Materials and methods

All reagents and solvents were from commercial sources (Sigma-Aldrich, Acros, Alfa Aesar) and were used as received. Butyl nitrate was purchased from Frontier Scientific, Inc. and it was also synthesized according to the reported procedure.[24] 1H NMR spectra were recorded on a Varian (300 MHz) spectrometer. The chemical shifts are reported in ppm (δ) downfield from tetramethylsilane in $CDCl_3$ or residual DMSO in DMSO-d_6. IR spectra of ionic liquid were acquired on a Midac M series instrument, using NaCl pressed windows either as neat [C_n-mim]NO_3 ionic liquid (for $n = 4, 6, 8$) or deposited from a dichloromethane solution for [C_{12}-mim]NO_3. Microwave-based reactions were done using a CEM discovery microwave reactor in manufacturer supplied 10 ml vials. Absorbance measurements were performed on a Agilent 8453 UV-visible instrument with a resolution of 1 nm using 0.1 cm quartz cells for solutions and 0.01 cm cell for neat ionic liquids. Fluorescence measurements were performed using Shimadzu RF-5301PC. Fluorescence measurements were carried out as follows: excitation and emission width slits were 3 mm and 3 mm; intensity—high; using 1 cm quartz cells.

Synthesis of dodecyl nitrate—a representative procedure

$(CF_3CO)_2O$ (30.0 ml, 0.216 mol) was added to a suspension of $LiNO_3$ (14.9 g, 0.216 mol) in acetonitrile (400 ml). The mixture was allowed to be stirred at room temperature until $LiNO_3$ completely dissolved, and the solution was cooled to 0 °C. Na_2CO_3 (22.9 g, 0.216 mol) was added in one portion, followed by the dodecyl alcohol (18.0 ml, 0.080 mol) and the reaction mixture was stirred for 3 h. Subsequently, the reaction mixture was poured into an ice-cold solution of saturated $NaHCO_3$ (500 ml), and extracted with CH_2Cl_2 (2×200 ml). The organic phase was dried ($MgSO_4$) and volatiles were removed *in vacuo*. The residue was subjected to a vacuum distillation (113–115 b.p.; 1 mmHg) to yield 8.62 g (47% yield) of dodecyl nitrate as a colorless liquid.[24]

^{1}H NMR ($CDCl_3$): δ 4.43 (t, J = 6.9 Hz), 1.71 (p, J = 6.9 Hz, 2H), 1.26 (m, 18H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 73.65, 32.14, 29.84 (overlap of 2 peaks; based on signal intensity), 29.73, 29.63, 29.57, 29.34, 26.94, 25.85, 22.91, 14.29.

Hexyl nitrate[21]

Colorless liquid (b.p. 36 °C; 1 mmHg), 30% yield. ^{1}H NMR ($CDCl_3$): δ 4.42 (t, J = 6.8 Hz, 2H), 1.70 (p, J = 6.6 Hz, 2H), 1.32 (m, 6H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 73.67, 31.47, 26.88, 25.50, 22.62, 14.05.

Octyl nitrate[21]

Colorless liquid (b.p. 86 °C; 4 mmHg), 40% yield. ^{1}H NMR ($CDCl_3$): δ 4.43 (t, J = 7.2 Hz, 2H), 1.70 (p, J = 6.6 Hz, 2H), 1.27 (m, 10H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 73.72, 31.92, 29.29, 29.27, 26.94, 25.85, 22.83, 14.29.

Synthesis of [C_4-mim]NO_3—a representative procedure under neat conditions

A 25 ml round bottom flask was charged with a stirring bar, 1-methylimidazole (1.0 ml, 12.5 mmol) and butyl nitrate (2.9 ml, 25.0 mmol) connected to a water condenser and placed into a 120 °C oil bath for 5 h under vigorous stirring. Next, the flask was allowed to cool to room temperature, the excess of butyl nitrate was decanted, and water (24 ml) was added, followed by charcoal (0.73 g). The mixture was refluxed under stirring for 15 min. The reaction mixture was filtered through a double layer of filter paper while hot, the charcoal washed with water (12 ml), and the water was removed *in vacuo* at 40 °C. The residue was redissolved in dichloromethane, filtered to remove any residual charcoal and the volatiles were removed *in vacuo* to give 2.27 g (90% yield) of [C_4-mim]NO_3. ^{1}H NMR (DMSO-d_6): δ 9.18 (s, 1H), 7.78 (s, 1H), 7.70 (s, 1H), 4.15 (t, J = 7.2 Hz, 2H), 3.83 (s, 3H), 1.74 (p, J = 7.4 Hz, 2H), 1.23 (sept, J = 7.4 Hz, 2H), 0.87 (t, J = 6.9 Hz, 3H); IR (neat): 3150, 2964, 2936, 2875, 1652, 1574, 1560, 1351, 1169 cm^{-1}.[3]

[C_6-mim]NO_3[25]

^{1}H NMR (DMSO-d_6): δ 9.14 (s, 1H), 7.77 (t, J = 1.7 Hz, 1H), 7.69 (t, J = 1.7 Hz, 1H), 4.14 (t, J = 7.2 Hz, 2H), 3.83 (s, 3H), 1.75 (m, 2H), 1.23 (m, 6H), 0.84 (t, J = 6.6 Hz, 3H); IR (neat): 3147, 3100, 2961, 2860, 1680, 1652, 1574, 1567, 1560, 1470, 1458, 1349, 1169 cm^{-1}.

[C_8-mim]NO_3[25]

^{1}H NMR (DMSO-d_6): δ 9.14 (s, 1H), 7.77 (s, 1H), 7.70 (s, 1H), 4.13 (t, J = 7.2 Hz, 2H), 3.83 (s, 3H), 1.75 (m, 2H), 1.23 (m, 10H), 0.83 (t, J = 6.6 Hz, 3H); IR (neat): 3148, 2958, 2937, 2857, 1680, 1652, 1575, 1560, 1458, 1363, 1168 cm^{-1}.

[C_{12}-mim]NO_3[9a]

^{1}H NMR (DMSO-d_6): δ 9.11 (s, 1H), 7.76 (s, 1H), 7.69 (s, 1H), 4.13 (t, J = 7.2 Hz, 2H), 3.83 (s, 3H), 1.75 (m, 2H), 1.23 (m, 18H), 0.87 (t, J = 6.6 Hz, 3H); IR (neat): 2924, 2854, 1682, 1652, 1575, 1560, 1460, 1372, 1169 cm^{-1}.

Synthesis of [C_4-mim]NO_3—a representative procedure under MW irradiation

1-Methylimidazole (1.0 ml, 12.5 mmol), butyl nitrate (2.9 ml, 25.0 mmol) and a stirring bar were charged into a 10 ml vial, sealed and MW irradiated at 120 °C. After 30 min, the vial was allowed to cool to room temperature, the excess of butyl nitrate was decanted, and the residue washed with water (24 ml) into a 100 ml round bottom flask containing a stirring bar. Charcoal (0.73 g) was added and the mixture was refluxed under stirring for 15 min. The reaction mixture was filtered through a double layer of filter paper while hot, the charcoal washed with water (12 ml), and the water was removed *in vacuo* at 40 °C. The residue was redissolved in dichloromethane, filtered to remove any residual charcoal and the volatiles were removed *in vacuo* to give 2.41 g (96% yield) of [C_4-mim]NO_3.

Synthesis of [C_4-mim]NO_3—a representative procedure in the presence of water

A 25 ml round bottom flask was charged with a stirring bar, 1-methylimidazole (1.0 ml, 12.5 mmol), butyl nitrate (2.9 ml, 25.0 mmol), water (1.25 ml), connected to a water condenser and placed into a 120 °C oil bath for 40 h under vigorous stirring. Next, the flask was allowed to cool to room temperature, the excess of butyl nitrate was decanted, and water (24 ml) was added, followed by charcoal (0.73 g). The mixture was refluxed under stirring for 15 min. The reaction mixture was filtered through a double layer of filter paper while hot, the charcoal washed with water (12 ml), and the water was removed *in vacuo* at 40 °C. The residue was redissolved in dichloromethane, filtered to remove any residual charcoal and the volatiles were removed *in vacuo* to give 2.4 g (95% yield) of $[C_4\text{-mim}]NO_3$.

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