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Synthesis, characterization and spectroscopic studies of two new 1-acetyl-3-alkylimidazolium ionic liquids

Abstract: Two new functionalized ionic liquids, 1-acetyl-3-alkylimidazolium iodides, were synthesized by the reactions of 1-acetylimidazole with alkyl iodides under solvent-free condition. Their structures were confirmed by ^{1}H NMR, ESI-MS, IR, UV-Vis and elemental analysis. The 1-acetyl-3-ethylimidazolium iodide (**3a**) is a solid and 1-acetyl-3-hexylimidazolium iodide (**3b**) is a viscous liquid at room temperature.

Keywords: 1-acetylimidazole; iodides; ionic liquids; synthesis.

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Introduction

Ionic liquids have been attracting extraordinary attention for their unique properties, such as high ionic conductivity, negligible vapor pressure, and high thermal and electrochemical stability, which have made their varied applications in organic chemistry [1–6], material science [7], chemical engineering [8], physical chemistry [9], analytical chemistry [10] and biotechnology [11]. To date, a large number of ionic liquids have been reported with diverse structures and properties [12–14]. In particular, imidazolium ionic liquids have become the hot topic in the past years because of their extensive applications. The 1-acetyl-3-alkylimidazolium-based ionic liquids can be used as acetyl-transfer reagents in organic synthesis [15] and other applications [16, 17].

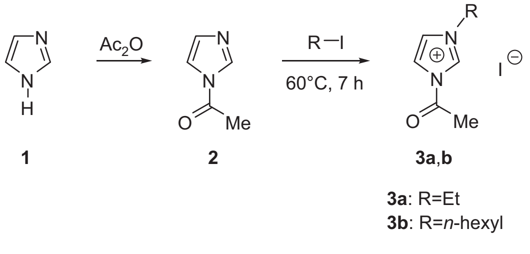
Acetylation on imidazole has been used to prepare a series of neutral compounds such as 1-acetylimidazole and its derivatives [12]. As early as in 1982, Iizuka and coworkers prepared 1-acetyl-3-substituted imidazolium salts by the reaction of 1-acetylimidazole and benzyl halides [16]. Then, Kim and coworkers reported acetyl imidazolium iodide salts and their application as electrolytes in dye-sensitized solar cells [17]. In this paper, we report details of syntheses and structural characterization of two new functionalized ionic liquids, 1-acetyl-3-ethylimidazolium iodide (**3a**) and 1-acetyl-3-hexylimidazolium iodide (**3b**). These compounds were characterized by ^{1}H NMR, ESI-MS, IR, UV-Vis spectroscopy and elemental analysis.

Results and discussion

The synthesis of 1-acetyl-3-alkylimidazolium-based ionic liquids is outlined in Scheme 1.

It should be noted that only the use of iodoalkanes provided the final products **3**. Owing to the presence of an electron-withdrawing acetyl group in **2**, the attempted reactions with less reactive bromides and chlorides were not successful [18]. Compared with previous methods in the literatures [16, 17], this new synthetic route appears to be more convenient, is faster and is more efficient.

The structures of these new 1-acetyl-3-alkylimidazolium compounds were confirmed by IR, UV-Vis, ^{1}H NMR, ESI-MS and elemental analysis. Figure 1 shows the UV-Vis absorption spectra of **3a** and **3b** compared with that of 1-acetylimidazole. The lowest energy electronic transition at 247 nm for **3a** and 248 nm for **3b**, which is



Scheme 1

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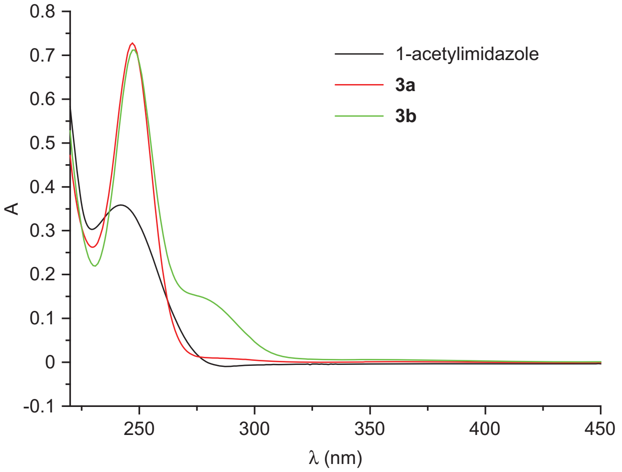

Figure 1 UV-Vis spectra (MeCN) of 1-acetylimidazole, **3a** and **3b**.

a π-π^* electron transition, is bathochromically shifted by 5–6 nm in comparison with 242 nm for 1-acetylimidazole. The bathochromic shift is in agreement with the electron-donating nature of alkyl groups attached to the imidazole ring. The ^{1}H NMR spectra and ESI-MS spectra of compounds **3a** and **3b** are also fully consistent with the assigned structures.

Conclusion

Two 1-acetyl-3-alkylimidazolium ionic liquids were prepared in high purity and moderate yields. Compared with literature methods, this new method allows the reaction to be carried out under solvent-free conditions.

Experimental

The melting point was obtained on a Laboratory Devices XT4 A melting apparatus and is uncorrected. IR spectra were determined in KBr disks with a Thermo Nicolet AVATAR 330 FT-IR spectrometer. ^{1}H NMR spectra were recorded in DMSO-d_6 on a Joel A600 (600 MHz) spectrometer. ESI-MS spectra were obtained by using a Finnigan LCQ Deca XP Plus ion trap mass spectrometer (San Jose, CA, USA). UV-Vis spectra were measured on an Analytikjena Specord 210 Plus instrument. Elemental analysis was performed on a Vario EL analysis system.

1-Acetyl-3-ethylimidazolium iodide (3a)

A mixture of 1-acetylimidazole (11.0 g, 0.1 mol) and iodoethane (32.7 g, 0.3 mol) was heated under reflux for approximately 7 h at 50–60°C. Upon completion of the reaction, the yellow mixture was cooled to room temperature and washed with ether several times to remove the excess iodoethane. After crystallization from acetonitrile/ether the compound was obtained as a light yellow solid: yield 17.2 g (65%); mp 97–99°C; IR: 3152, 3098, 2986, 1757, 1530, 1478, 1388, 961, 790 cm^{-1}; ^{1}H NMR: δ 10.00 (s, 1H), 8.26 (d, 1H, $J = 1.6$ Hz), 7.99 (d, 1H, $J = 1.6$ Hz), 4.30 (q, 2H, $J = 7$ Hz), 2.76 (s, 3H), 1.47 (t, 3H, $J = 7$ Hz); ESI-MS: m/z 139.11 (M^+, 60), 97.06 (85), 126.60 (100); UV-Vis (CH_3CN): λ_{max} 207 nm (ε 4.3 × 10^3), 247 nm (ε 2.9 × 10^3). Anal. Calcd for $C_7H_{11}N_2OI$: C, 31.60; H, 4.17; N, 10.53. Found: C, 31.50; H, 4.12; N, 10.69.

1-Acetyl-3-hexylimidazolium iodide (3b)

A mixture of 1-acetylimidazole (1.33 g, 0.01 mol) and 1-iodohexane (6.49 g, 0.03 mol) was heated to 50–60°C for 7 h. Upon completion of the reaction, the yellow mixture was cooled to room temperature and washed with ether and acetone to remove 1-iodohexane. This compound was obtained as a light yellow liquid: yield 1.76 g (55%); IR: 3092, 2931, 2858, 1718, 1668, 1544, 1409, 940, 762 cm^{-1}; ^{1}H NMR: δ 10.00 (s, 1H), 8.26 (d, 1H, $J = 2.3$ Hz), 8.01 (d, 1H, $J = 2.3$ Hz), 2.75 (s, 3H), 4.16 (t, 2H, $J = 7$ Hz), 1.72 (m, 8H), 1.24 (t, 3H, $J = 7$ Hz); ESI-MS: m/z 195.10 (M^+, 57), 153.00 (88), 126.60 (100); UV-Vis(CH_3CN): λ_{max} 208 nm (ε 4.8 × 10^3), 248 nm (ε 3.1 × 10^3). Anal. Calcd for $C_{11}H_{19}N_2OI$: C, 41.01; H, 5.94; N, 8.69. Found: C, 40.71; H, 5.65; N, 10.12.

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