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An efficient and green sonochemical synthesis of some new eco-friendly functionalized ionic liquids

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Abstract Considerable stress to replace a lot of volatile organic compounds which were used as solvents in synthetic organic chemistry has been done for many chemical industries. A suitable solution for these problems is found by using the ionic liquids as a clean medium of working and avoiding the solvent effect. The present work describes a facile and green ultrasound-assisted procedure as an environmentally friendly alternative to traditional methods for the preparation of a series of 26 new functionalized imidazolium-based ionic liquids. Their structures were characterized by FT-IR, ^1H , ^{13}C , ^{11}B , ^{19}F , ^{31}P NMR and mass spectra.

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1. Introduction

Over the past few decades the number of publications concerning room-temperature ionic liquids (RTILs) has increased substantially (Rogers and Seddon, 2002). (RTILs) provide a new class of solvents where molecules are composed of ions. At normal temperatures, ionic liquids have essentially zero-vapor pressure and are thermally stable over a wide range of temperature. Therefore, they are considered as environmentally friendly alternatives to the volatile organic compounds (VOCs).

RTILs have been also widely investigated for a variety of applications: the use as solvents or catalysts for chemical synthesis (Liu et al., 2003; Wang et al., 2007), media for electrodeposition of metals (Lin and Sun, 1999; Takahashi et al.,

1999; Endres, 2002; Ibrahim and Messali, 2011), electrolyte for electrochemical devices such as battery (Brennecke and Magin, 2001), supercapacitors (Ue et al., 2003; Balducci et al., 2004), as inhibitors of corrosion (Messali, 2011; Zarrouk et al., 2012a; Zarrouk et al., 2012b; Ibrahim et al., 2011), as fluids for thermal storage and exchange in solar concentrating power plants (Moens et al., 2003) and a wide electrochemical potential window (Ngo et al., 2000; Forsyth et al., 2004; Endres et al., 2006; Al-Ghamdi et al., 2011).

Recently, many chemists promoted to explore new methods for the clean and efficient synthesis of ILs since from the point of green chemistry, the conventional syntheses of the ILs themselves are not benign. In recent reports, several modifications have been attempted including solvent-free reactions, microwave irradiation (Anastas and Warner, 1998; Messali, 2011) ultrasound assisted procedures (Leveque et al., 2006; Messali, 2013). The use of the green technologies leads to large reductions in reaction times, enhancements in conversions, sometimes in selectivity, with several advantages of the eco-friendly approach (Deetlefs and Seddon, 2003; Loupy, 2004; Yi et al., 2005; Singh et al., 2005; Aupoix et al., 2010; Messali and Ahmed, 2011).

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In continuation of our previous work dealing with the development of novel functionalized ionic liquids and our general interests in green technologies such a MW-assisted or ultrasound-assisted chemical processes (Messali, 2013; Messali et al., 2013; Messali, 2011; Messali and Asiri, 2013) we present in the following an overview of our new study of the ultrasound-assisted synthesis of new functionalized imidazolium-based ionic liquids, showing the scope of this method.

2. Materials and methods

2.1. Experimental

All new compounds were synthesized and characterized by ^1H NMR, ^{13}C NMR, ^{19}F NMR, ^{11}B NMR, ^{31}P NMR, IR and LCMS. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz), ^{19}F NMR (376.5 MHz), ^{31}P NMR (162 MHz) and ^{11}B NMR (128 MHz) spectra were measured in DMSO, CDCl_3 or D_2O at room temperature. Chemical shifts (δ) were reported in ppm to a scale calibrated for tetramethylsilane (TMS), which is used as an internal standard (Taibah University, Madinah, Saudi Arabia). The LCMS spectra were measured with a Micromass, LCT mass spectrometer (Mohamed First University, Oujda, Morocco). FT-IR spectra were recorded in NaCl or KBr disk on a Shimadzu 8201 PC, FTIR spectrophotometer (ν_{max} in cm^{-1}) (Taibah University, Madinah, Saudi Arabia). The ultrasound-assisted reactions were performed using a controllable laboratory ultrasonic bath.

3. Synthesis

3.1. General procedure for the synthesis of imidazolium halides (4–7) using conventional method

To the solution of *N*-alkylimidazole (**1–3**) (1 eq) in toluene, was added the appropriate alkyl bromide (1.1 eq) at room temperature, followed by stirring at 80 °C for 18 h. The completion of the reaction was marked by the separation of oil or solid from the initially obtained clear and homogenous mixture of *N*-alkylimidazole and alkyl halide in toluene. The product was isolated by extraction or filtration to remove the unreacted starting materials and solvent. Subsequently, the imidazolium salt was washed with ethyl acetate. In each case, the IL/salt (**4–7**) was finally dried at a reduced pressure to get rid of all the volatile organic compounds.

3.2. General procedure for the synthesis of imidazolium halides (4–7) using under Ultrasonic irradiation

N-alkylimidazole (**1–3**) (1 eq) and the appropriate alkyl bromide (1 eq) were placed in a closed vessel and exposed to ultrasound irradiation for 5 h at 80 °C using a sonication bath. The product was then collected as described in the conventional procedure outlined earlier.

3.3. General procedure for the methathesis reaction of (4–7) leading to compounds (8–31) using conventional method

The quaternary salt (**4–7**) (1 eq) was dissolved in acetonitrile to obtain a clear solution. To this solution of quaternary halide

were added solution of sodium tetrafluoroborate, potassium hexafluorophosphate, trifluoroacetic acid sodium, sodium dicyanamide, sodium thiocyanate or sodium nitrate (1.2 eq), followed by stirring at 70 °C for 3 h. The cooled reaction mixture was filtered through Celite to remove solid metal halide. The evaporation of acetonitrile led quantitatively to the desired ionic liquids.

3.4. General procedure for the ultrasound-assisted methathesis reaction of (4–7) leading to compounds (8–31)

Imidazolium-halide salts (**4–7**) (1 eq) and NaBF_4 , KPF_6 , CF_3COONa , $\text{NaN}(\text{CN})_2$, NaNCS or NaNO_3 (1 eq) were placed in a closed vessel and exposed to ultrasound irradiation for 45 min at 70 °C using a sonication bath. The product was then collected as described in the conventional procedure outlined earlier.

3.5. Characterization

3.5.1. 1-Benzyl-3-(2-ethoxy-2-oxoethyl)-1*H*-imidazol-3-ium chloride **4**

White crystals, Mp 119–121 °C, ^1H NMR (400 MHz, CDCl_3) δ : 1.14 (t, $J = 7.6$, 3H), 4.07 (q, $J = 6.8$, 2H), 5.37 (s, 2H), 5.44 (s, 2H), 7.23–7.36 (m, 6H), 7.68 (d, 1H), 10.32 (s, 1H), ^{13}C NMR (100 MHz, CDCl_3) δ : 13.9 (CH_3), 50.1 (CH_2), 53.1 (CH_2), 62.6 (CH_2), 121.5 (CH), 124.1 (CH), 128.7 (CH), 129.2 (CH), 133.1 (C), 137.9 (CH), 166.2 (CO), IR (KBr): ν_{max} cm^{-1} 3132 (C–H, sp^2), 1726 (C=O), 1562–1448 (C=C), 1166 (C–N), 1030 (C–O), LCMS (M–Cl) 245 found for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_2^+$.

3.5.2. 1-Benzyl-3-(4-phenoxybutyl)-1*H*-imidazol-3-ium bromide **5**

White crystals, Mp 153–155 °C, ^1H NMR (400 MHz, CDCl_3) δ : 1.77 (quint, $J = 8$, 2H), 2.07 (quint, $J = 8$, 2H), 3.91 (t, $J = 8$, 2H), 4.35 (t, $J = 8$, 2H), 5.52 (s, 2H), 6.77–6.88 (m, 3H), 7.17–7.55 (m, 9H), 10.45 (s, 1H), ^{13}C NMR (100 MHz, CDCl_3) δ : 25.7 (CH_2), 26.9 (CH_2), 49.7 (CH_2), 53.2 (CH_2), 66.7 (CH_2), 114.4 (CH), 120.8 (CH), 122.2 (CH), 122.6 (CH), 128.9 (CH), 129.4 (CH), 129.5 (CH), 133.0 (C), 135.5 (CH), 158.6 (C), IR (KBr): ν_{max} cm^{-1} 3132 (C–H, sp^2), 1599–1471 (C=C), 1165 (C–N), 1082 (C–O), 815 (C–H, bending). LCMS (M–Br) 307 found for $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}^+$.

3.5.3. 3-(3-hydroxypropyl)-1-propyl-1*H*-imidazol-3-ium bromide **6**

^1H NMR (400 MHz, CDCl_3) δ : 0.82 (t, $J = 7.2$, Hz 3H), 1.79 (t, $J = 7.2$, Hz 2H), 2.01 (quint, $J = 7.6$ Hz, 2H), 2.18 (s, $J = 7.6$ Hz, 2H), 4.12 (t, $J = 7.6$ Hz, 2H), 4.37 (t, $J = 7.6$ Hz, 2H), 5.11 (s, 1H), 7.48–7.50 (m, 2H), 9.90 (s, 1H), ^{13}C NMR (100 MHz, CDCl_3) δ : 8.8 (CH_3), 21.6 (CH_2), 29.0 (CH_2), 45.1 (CH_2), 49.6 (CH_2), 55.2 (CH_2), 119.9 (CH), 120.8 (CH), 135.1 (CH), IR (NaCl): ν_{max} cm^{-1} 3213 (O–H), 3161 (C–H, sp^2), 1566 (C=C), 1161 (C–N), 1157 (C–O), LCMS (M–Br) 169 found for $\text{C}_9\text{H}_{17}\text{N}_2\text{O}^+$.

3.5.4. 3-(3-Hydroxypropyl)-1-pentyl-1*H*-imidazol-3-ium bromide **7**

^1H NMR (400 MHz, D_2O) δ : 0.67 (t, $J = 7.6$, 3H), 1.10–1.17 (m, 4H), 1.72 (quint, 2H), 1.94 (quint, $J = 7.6$, 2H), 3.41 (t,

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