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Short Communication

Functionalized ionic liquids based on imidazolium cation: Synthesis, characterization and catalytic activity for *N*-alkylation reaction

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ABSTRACT

The novel functionalized ionic liquids based on imidazolium cation are synthesized and characterized by studying its ^{1}H, ^{13}C, and ^{31}P NMR and elemental analysis. These ionic liquids have been reported as a highly efficient catalyst for *N*-alkylation reaction of aniline with butyl chloride. The reaction was efficiently performed in ionic liquid as an environmentally benign solvent with good yields without transition metal.

1. Introduction

Ionic liquids (ILs) are a class of organic salts that are liquid at or near room temperature. They are generally composed of a large asymmetric organic cation and either an organic or inorganic anion. Ever increasing interest in ionic liquids is ascribed to their distinguished advantages such as chemical and thermal stability, nondetectable vapor pressures, and structure and property tunabilities [1–3]. Exactly due to these appealing properties, ILs promise widespread application in industry. For example, ionic liquids are often considered as potential environmentally benign solvents to replace volatile organic compounds in chemical processes [4,5], owing to their extremely low vapor pressures. In addition, the application of ILs is also growing very rapidly in the following important fields: chemical reaction and catalysis [6–9], liquid–liquid extraction [10], electrochemistry [11,12], nanomaterial preparation [13,14], dissolution of biomass such as cellulose and chitosan [15–18] and so forth.

The wide range of possible cation–anion combinations allows ILs to be designed for particular purposes or to show a specific set of physicochemical properties [19]. Typical IL cations include alkylammonium, alkylphosphonium, *N*-alkylpyridinium, and *N*,*N*-dialkylimidazolium cations and anions for ILs are halide anions, tetrafluoroborate, hexafluorophosphate, tetrahalogenidoaluminate, trifluoromethylsulfonate (triflate) or bis(trifluoromethylsulfonyl)amide [3,20–25]. (Fig. 1). Of the wide range of possible ILs, those based on imidazolium cations have been the most widely studied to date [26].

Ionic liquids, especially imidazolium salts, are currently receiving a lot of attention in chemistry and have already proved to be useful solvents in organic synthesis. Some of the reactions already successfully carried out in imidazolium salts include Diels–Alder [27], Wittig [28], the Suzuki cross-coupling [29], Heck [30–32], oxidations [33–35], reductions [36], and hydrogenations [37,38].

N-Alkylated aromatic amines and their derivatives possess useful biological activities and exhibit extensive applications in the pharmaceutical, agrochemical, and optoelectronic fields [39]. Secondary aromatic amines play a key role as antioxidants in petrochemicals and as intermediates in the manufacturing of dyes, rubbers, and polymers [40–46]. The alkylation reaction of aniline with butyl chloride was studied in tetrabutyl ammonium salts by Monopoli and Nacci [47].

Our research is mainly devoted to the design and synthesis of functionalized ionic liquids and their role for the *N*-alkylation reaction. In this paper, a serious of imidazolium based protic ionic liquids was synthesized, characterized and employed as solvent for *N*-alkylation reaction of aniline and butyl chloride to form secondary amine without using transition metal additives and co-solvent.

2. Experiments

2.1. General remarks

All reactions for the preparation of ionic liquids were carried out under argon in flame-dried glassware using standard Schlenk techniques. Chemicals were obtained from Sigma Aldrich and Fluka. ^{1}H-NMR, ^{13}C-NMR, and ^{31}P-NMR spectra were recorded with a Varian AS 400 Merkur spectrometer operating at 400 MHz (^{1}H), 100 MHz (^{13}C) in $CDCl_3$, D_2O and DMSO-d_6 with tetramethylsilane as an internal

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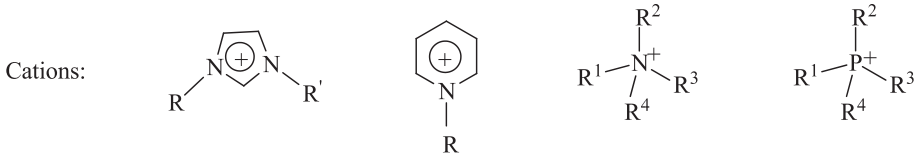


Fig. 1. Common cations and anions of room-temperature ionic liquids.

reference. Coupling constants (*J* values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, hept = heptet, and m = multiplet signal. All catalytic reactions were monitored on an Agilent 6890N GC system by GC-FID with a HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. GC–MS experiments were performed on an Agilent 6890N GC system with a 5973 N mass selective detector. Column chromatography was performed using silica gel 60 (70–230 mesh). Solvent ratios are given as v/v.

*2.2. Synthesis of 1,3-dialkylimidazole salts (**1–6**)*

*2.2.1. Synthesis of 1,3-dialkylimidazolium chloride (**1–2**)*

2.2.1.1. 1-methyl-3-ethylacetylimidazolium chloride, ***1a***. A mixture of 1-methylimidazole (0.10 mol) and ethylchloroacetate (0.12 mol) was stirred in DMF (5 mL) at 70 °C for 5 h. The product was washed with diethyl ether (3 × 30 mL) and dried under vacuum at 70 °C for 8 h. Yield: 1.69 g (83%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 10.31 (s, 1H, NC*H*N), 7.73, 7.62 (s, 2H, NC*HCH*N), 5.44 (s, 2H, NCH_2COOCH_2CH$_3$), 4.15 (q, 2H, *J* = 7.2 Hz, NCH$_2$COOCH_2CH$_3$), 4.02 (s, 3H, NCH_3), 1.22 (t, 3H, *J* = 7.2 Hz, NCH$_2$COOCH$_2$CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 166.2 (NCH$_2$COOCH$_2$CH$_3$), 138.6 (N*C*HN), 123.9, 123.2 (N*CH*CHN), 62.7 (NCH$_2$COO*C*H$_2$CH$_3$), 50.1(N*C*H$_2$COOCH$_2$CH$_3$), 36.7 (N*C*H$_3$), 14.0 (NCH$_2$COOCH$_2$*C*H$_3$). Anal. Calc. for $C_8H_{13}N_2O_2Cl$: C, 46.95; H, 6.40; N, 13.69. Found: C, 46.92; H, 6.43; N: 13.65%.

2.2.1.2. 1-Methyl-3-methoxyethoxymethylimidazolium chloride, 1b. A mixture of 1-methylimidazole (0.10 mol) and 2-methoxyethoxymethyl chloride (0.12 mol) was stirred in DMF (5 mL) at 70 °C for 5 h. The product was washed with diethyl ether (3 × 30 mL) and dried under vacuum at 70 °C for 8 h. Yield: 1.76 g (85%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 9.97 (s, 1H, NC*H*N), 7.46, 7.32 (s, 2H, NC*HCH*N), 5.34 (s, 2H, NCH_2OCH$_2$CH$_2$OCH$_3$), 3.62 (s, 3H, NCH_3), 3.27 (t, 2H, *J* = 1.8 Hz, NCH$_2$OCH_2CH$_2$OCH$_3$), 2.98 (t, 2H, *J* = 4.2 Hz, NCH$_2$OCH$_2$CH_2OCH$_3$), 2.78 (s, 3H, NCH$_2$OCH$_2$CH$_2$OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 137.1 (N*C*HN), 123.8, 121.4 (N*CH*CHN), 68.9 (NCH$_2$OCH$_2$CH$_2$OCH$_3$), 58.4 (NCH$_2$OCH$_2$CH$_2$OCH$_3$), 36.2, 36.1 (NCH$_2$OCH$_2$CH$_2$OCH$_3$), 30.9 (N*C*H$_3$). Anal. Calc. for $C_8H_{15}N_2O_2Cl$: C, 46.49; H, 7.32; N, 13.55. Found: C, 46.51; H, 7.35; N: 13.50%.

2.2.1.3. 1-n-Butyl-3-ethylacetylimidazolium chloride, ***2a***. A mixture of 1-butylimidazole (0.10 mol) and ethylchloroacetate (0.12 mol) was stirred in DMF (5 mL) at 70 °C for 5 h. The product was washed with diethyl ether (3 × 30 mL) and dried under vacuum at 70 °C for 8 h. Yield: 1.70 g (69%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 10.39 (s, 1H, NC*H*N), 7.72, 7.52 (s, 2H, NC*HCH*N), 5.44 (s, 2H, NCH_2COOCH$_2$CH$_3$), 4.23 (t, 2H *J* = 7.2 Hz, NCH_2CH$_2$CH$_2$CH$_3$), 4.14 (q, 2H, *J* = 7.2 Hz, NCH$_2$COOCH_2CH$_3$), 1.81 (pent, 2H, *J* = 7.5 Hz, NCH$_2$CH_2CH$_2$CH$_3$), 1.29 (hex, 2H, *J* = 7.5 Hz, NCH$_2$CH$_2$CH_2CH$_3$), 1.19 (t, 3H, *J* = 7.2 Hz, NCH$_2$COOCH$_2$CH_3), 0.85 (t, 3H, J = 7.2 Hz, NCH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 166.2 (NCH$_2$*C*OOCH$_2$CH$_3$), 138.2 (N*C*HN), 124.0, 121.6 (N*CH*CHN), 62.6 (NCH$_2$COO*C*H$_2$CH$_3$), 50.0 (NCH$_2$*C*OOCH$_2$CH$_3$), 49.8 (NCH$_2$CH$_2$CH$_2$CH$_3$), 31.9 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 19.3 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.9 (NCH$_2$COOCH$_2$CH$_3$), 13.3 (NCH$_2$CH$_2$CH$_2$*C*H$_3$). Anal. Calc. for $C_{11}H_{19}N_2O_2Cl$: C, 53.55; H, 7.76; N, 11.35. Found: C, 53.51; H, 7.73; N: 11.30%.

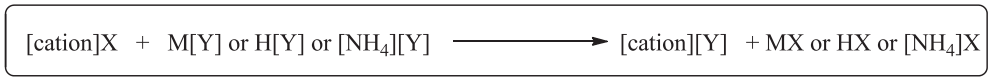
2.2.1.4. 1-n-Butyl-3-methoxyethoxymethylimidazolium chloride, 2b. A mixture of 1-butylimidazole (0.10 mol) and 2-methoxyethoxymethyl chloride (0.12 mol) was stirred in DMF (5 mL) at 70 °C for 5 h. The product was washed with diethyl ether (3 × 30 mL) and dried under vacuum at 70 °C for 8 h. Yield: 1.72 g (69%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 11.10 (s, 1H, NC*H*N), 7.55, 7.39 (s, 2H, NC*HCH*N), 5.92 (s, 2H, NCH_2OCH$_2$CH$_2$OCH$_3$), 4.34 (t, 2H *J* = 7.2 Hz, NCH_2CH$_2$CH$_2$CH$_3$), 3.88–3.85 (m, 2H, NCH$_2$OCH_2CH_2OCH$_3$), 3.56–3.53 (m, 2H, NCH$_2$OCH_2CH$_2$OCH$_3$), 3.33 (s, 3H, NCH$_2$OCH$_2$CH$_2$OCH_3), 1.93 (pent, 2H, *J* = 7.5 Hz, NCH$_2$CH_2CH$_2$CH$_3$), 1.40 (hex, 2H, *J* = 7.5 Hz, NCH$_2$CH$_2$CH_2CH$_3$), 0.98 (t, 3H, J = 7.2 Hz, NCH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 138.3 (N*C*HN), 121.9, 121.1 (N*CH*CHN), 79.1 (NCH$_2$OCH$_2$CH$_2$OCH$_3$), 71.2 (NCH$_2$OCH$_2$CH$_2$OCH$_3$), 69.8, 59.0 (NCH$_2$OCH$_2$CH$_2$OCH$_3$), 50.1 (NCH$_2$CH$_2$CH$_2$CH$_3$), 32.0 (NCH$_2$CH$_2$CH$_2$CH$_3$), 19.5 (NCH$_2$CH$_2$CH$_2$CH$_3$), 13.4 (NCH$_2$CH$_2$CH$_2$CH$_3$). Anal. Calc. for $C_{11}H_{21}N_2O_2Cl$: C, 53.11; H, 8.51; N, 11.26. Found: C, 53.15; H, 8.54; N: 11.27%.

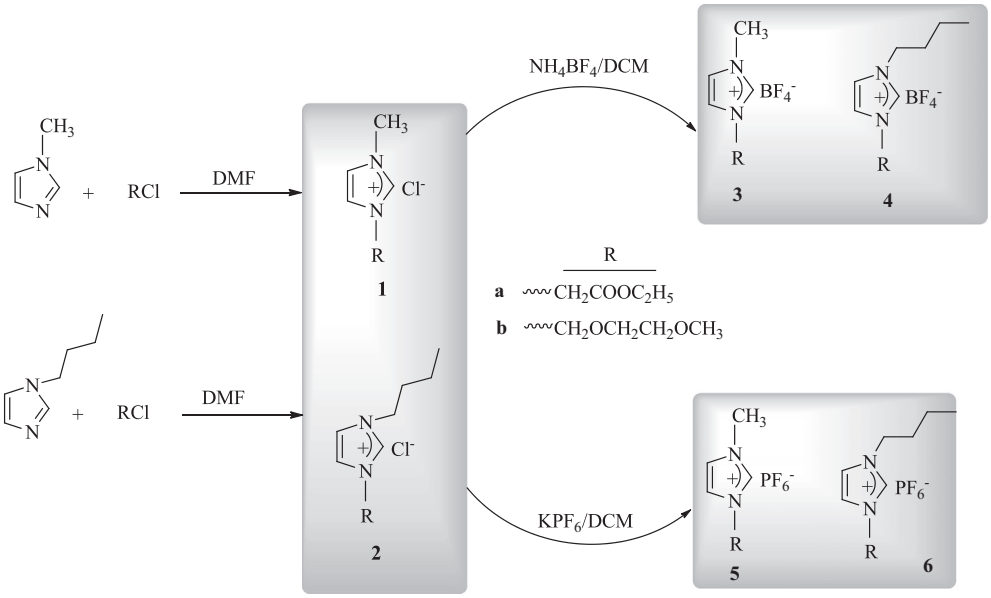
*2.2.2. Synthesis of 1,3-dialkylimidazolium tetrafluoroborate (**3–4**)*

2.2.2.1. 1-Methyl-3-ethylacetylimidazolium tetrafluoroborate, ***3a***. **3a** was prepared using ionic liquid **1a** with chloro anion at room temperature. A mixture of chloride salt (0.10 mol) and NH_4BF_4 (0.13 mol) in dichloromethane (50 mL) was stirred at room temperature for 24 h. After filtration, the solvent was removed by vacuum. The remaining viscous liquid was then dried under vacuum at 70 °C for 8 h to give the product. Yield: 1.87 g (73%).

^{1}H NMR (300 MHz, D_2O) δ (ppm) = 8.72 (s, 1H, NC*H*N), 7.43 (s, 2H, NC*HCH*N), 5.08 (s, 2H, NCH_2COOCH$_2$CH$_3$), 4.23 (q, 2H, *J* = 3.6 Hz, NCH$_2$COOCH_2CH$_3$), 3.87 (s, 3H, NCH_3), 1.23 (t, 3H, *J* = 3.6 Hz, NCH$_2$COOCH$_2$CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 168.2 (NCH$_2$COOCH$_2$CH$_3$), 137.4 (N*C*HN), 123.6, 123.5 (N*CH*CHN), 63.6 (NCH$_2$COO*C*H$_2$CH$_3$), 49.8(NCH$_2$*C*OOCH$_2$CH$_3$), 35.9 (N*C*H$_3$), 13.2 (NCH$_2$COOCH$_2$*C*H$_3$). Anal. Calc. for $C_8H_{13}F_4N_2O_2B$: C, 37.53; H, 5.12; N, 10.94. Found: C, 37.51; H, 5.16; N: 10.92%.



Scheme 1. Anion exchange reaction by metathesis of the halide salt with a metal or ammonium salt.



Scheme 2. Structure of the functionalized imidazolium based ILs.

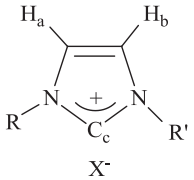
*2.2.2.2. 1-n-Butyl-3-ethylacetylimidazolium tetrafluoroborate, **4a**.* **4a** was prepared using ionic liquid **2a** with chloro anion at room temperature. A mixture of chloride salt (0.10 mol) and NH_4BF_4 (0.13 mol) in dichloromethane (50 mL) was stirred at room temperature for 24 h. After filtration, the solvent was removed by vacuum. The remaining viscous liquid was then dried under vacuum at 70 °C for 8 h to give the product. Yield: 1.73 g (58%).

^{1}H NMR (300 MHz, D_2O) δ (ppm) = 8.78 (s, 1H, NC*H*N), 7.50, 7.45 (s, 2H, NC*HCH*N), 5.08 (s, 2H, $NCH_2COOCH_2CH_3$), 4.24 (q, 2H, J = 7.2 Hz, $NCH_2COOCH_2CH_3$), 4.19 (t, 2H J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 1.81 (pent, 2H, J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 1.25 (hex, 2H, J = 7.8 Hz, $NCH_2CH_2CH_2CH_3$), 1.22 (t, 3H, J = 7.2 Hz, $NCH_2COOCH_2CH_3$), 0.86 (t, 3H, J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (75 MHz, D_2O) δ (ppm) = 168.2 ($NCH_2COOCH_2CH_3$), 136.7 (NCHN), 123.6, 122.3 (NCHCHN), 63.5 ($NCH_2COOCH_2CH_3$), 49.9 ($NCH_2COOCH_2CH_3$), 49.6 ($NCH_2CH_2CH_2CH_3$), 31.1 ($NCH_2CH_2CH_2CH_3$), 18.7 ($NCH_2CH_2CH_2CH_3$), 13.1 ($NCH_2COOCH_2CH_3$), 12.6 ($NCH_2CH_2CH_2CH_3$). Anal. Calc. for $C_{11}H_{19}F_4N_2O_2B$: C, 44.32; H, 6.42; N, 9.40. Found: C, 44.28; H, 6.45; N: 9.42%.

2.2.2.3. 1-n-Butyl-3-methoxyethoxymethylimidazolium tetrafluoroborate, 4b. **4b** was prepared using ionic liquid **2b** with chloro anion at room temperature. A mixture of chloride salt (0.10 mol) and NH_4BF_4 (0.13 mol) in dichloromethane (50 mL) was stirred at room temperature for 24 h. After filtration, the solvent was removed by vacuum. The remaining viscous liquid was then dried under vacuum at 70 °C for 8 h to give the product. Yield: 1.65 g (55%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.93 (s, 1H, NC*H*N), 7.58, 7.52 (s, 2H, NC*HCH*N), 5.56 (s, 2H, $NCH_2OCH_2CH_2OCH_3$), 4.19 (t, 2H J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 3.71–3.68 (m, 2H, $NCH_2OCH_2CH_2OCH_3$), 3.56–3.55 (m, 2H, $NCH_2OCH_2CH_2OCH_3$), 3.28 (s, 3H, $NCH_2OCH_2CH_2OCH_3$), 1.81 (pent, 2H, J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 1.27 (hex, 2H, J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 0.86 (t, 3H, J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) =

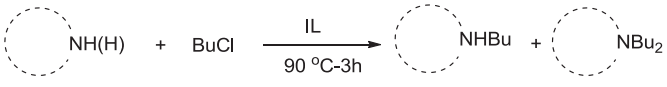
Table 1
Selected chemical shifts (δ values, ppm) for the new ILs.

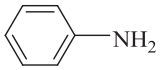
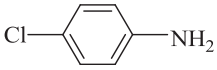
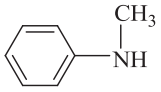
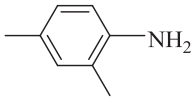


R	R′	X	IL	H_a	H_b	C_cH	C_cH
CH_3	CH_2CO_2Et	Cl	**1a**[a]	7.73	7.62	10.31	138.6
CH_3	$CH_2OCH_2CH_2OMe$	Cl	**1b**[a]	7.46	7.32	9.97	137.1
n-C_4H_9	CH_2CO_2Et	Cl	**2a**[a]	7.72	7.52	10.39	138.2
n-C_4H_9	$CH_2OCH_2CH_2OMe$	Cl	**2b**[a]	7.55	7.39	11.10	138.3
CH_3	CH_2CO_2Et	BF_4	**3a**[b]	7.73	7.43	8.72	137.4
n-C_4H_9	CH_2CO_2Et	BF_4	**4a**[b]	7.50	7.45	8.78	136.7
n-C_4H_9	$CH_2OCH_2CH_2OMe$	BF_4	**4b**[a]	7.58	7.52	8.93	135.7
CH_3	CH_2CO_2Et	PF_6	**5a**[c]	7.68	7.68	9.04	138.1
CH_3	$CH_2OCH_2CH_2OMe$	PF_6	**5b**[c]	7.54	7.45	8.85	136.4
n-C_4H_9	CH_2CO_2Et	PF_6	**6a**[c]	7.49	7.44	8.79	136.7
n-C_4H_9	$CH_2OCH_2CH_2OMe$	PF_6	**6b**[c]	7.57	7.51	8.93	135.7

[a] $CDCl_3$ was the solvent used.
[b] D_2O was the solvent used.
[c] DMSO-d_6 was the solvent used.

Table 2
N-alkylation of amines with butyl chloride in imidazolium based ionic liquids.



Entry	IL	Amine	Conv. (%)	Yield (%)[a]	
				A	B
1	**1a**		95	82	18
2	**1b**		44	100	–
3	**2a**		59	100	–
4	**2b**		75	100	–
5	**3a**		15	100	–
6	**4a**		10	100	–
7	**4b**		10	100	–
8	**5a**		5	100	–
9	**5b**		10	100	–
10	**6a**		32	100	–
11	**6b**		10	100	–
12	**1a**		30	90	10
13	**1b**		17	100	–
14	**2a**		42	100	–
15	**2b**		37	100	–
16	**3a**		10	100	–
17	**1a**		100	100	–
18	**1b**		98	100	–
19	**2a**		100	100	–
20	**2b**		85	100	–
21	**3a**		79	100	–
22	**4a**		75	100	–
23	**4b**		72	100	–
24	**5a**		74	100	–
25	**5b**		70	100	–
26	**6a**		75	100	–
27	**6b**		71	100	–
28	**1a**		54	100	–
29	**1b**		50	100	–
30	**2a**		53	100	–
31	**2b**		42	100	–
32	**3a**		38	100	–
33	**4a**		10	100	–
34	**4b**		12	100	–
35	**5a**		32	100	–
36	**5b**		30	100	–
37	**6a**		15	100	–
38	**6b**		13	100	–
39	**1a**		62	100	–
40	**2a**		50	100	–

[a] Reaction conditions: amine (0.55 mmol), butyl chloride (0.5 mmol), IL (0.10 g).

135.7 (N*C*HN), 122.9, 121.8 (NC*H*CHN), 70.5 ($NCH_2OCH_2CH_2OCH_3$), 68.6 ($NCH_2OCH_2CH_2OCH_3$), 58.0 ($NCH_2OCH_2CH_2OCH_3$), 49.6 ($NCH_2CH_2CH_2CH_3$), 31.1 ($NCH_2CH_2CH_2CH_3$), 18.7 ($NCH_2CH_2CH_2CH_3$), 12.6 ($NCH_2CH_2CH_2CH_3$). Anal. Calc. for $C_{11}H_{21}F_4N_2O_2B$: C, 44.02; H, 7.05; N, 9.33. Found: C, 44.08; H, 7.02; N: 9.32%.

2.2.3. Synthesis of 1,3-dialkylimidazolium hexafluorophosphate (**5–6**)

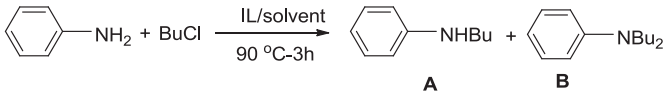
2.2.3.1. 1-Methyl-3-ethylacetylimidazolium hexafluorophosphate, ***5a.*** **5a** was prepared using ionic liquids **1a** with chloro anion at room temperature. A mixture of chloride salt (0.10 mol) and KPF_6 (0.13 mol) in dichloromethane (50 mL) was stirred at room temperature for 24 h. After filtration, the solvent was removed by vacuum. The remaining viscous liquid was then dried under vacuum at 70 °C for 8 h to give the product. Yield: 2.14 g (68%).

^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) = 9.04 (s, 1H, NC*H*N), 7.68 (s, 2H, NC*HCH*N), 5.21 (s, 2H, $NCH_2COOCH_2CH_3$), 4.20 (q, 2H, J = 3.6 Hz, $NCH_2COOCH_2CH_3$), 3.91 (s, 3H, N-CH_3), 1.24 (t, 3H, J = 3.6 Hz, $NCH_2COOCH_2CH_3$). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) = 167.3 ($NCH_2COOCH_2CH_3$), 138.1 (NCHN), 124.1 ve 123.8 (NCHCHN), 62.4 ($NCH_2COOCH_2CH_3$), 49.9($NCH_2COOCH_2CH_3$), 36.3 (NCH_3), 14.3 ($NCH_2COOCH_2CH_3$). ^{31}P NMR (600 MHz, DMSO-d_6) δ (ppm) = −144.20 (hept). Anal. Calc. for $C_8H_{13}F_6N_2O_2P$: C, 30.58; H, 4.17; N, 8.92. Found: C, 30.55; H, 4.13; N: 8.94%.

2.2.3.2. 1-Methyl-3-methoxyethoxymethylimidazolium hexafluorophosphate, 5b. **5b** was prepared using ionic liquids **1b** with chloro anion at room temperature. A mixture of chloride salt (0.10 mol) and KPF_6 (0.13 mol) in dichloromethane (50 mL) was stirred at room temperature for 24 h. After filtration, the solvent was removed by vacuum. The remaining viscous liquid was then dried under vacuum at 70 °C for 8 h to give the product. Yield: 2.27 g (72%).

^{1}H NMR (300 MHz, D_2O) δ (ppm) = 8.85 (s, 1H, NC*H*N), 7.54, 7.45 (d, 2H, J = 1.8 Hz, NC*HCH*N), 5.54 (s, 2H, $NCH_2OCH_2CH_2OCH_3$), 4.69 (s, 3H, $CH_2OCH_2CH_2OCH_3$), 3.68–3.67 and 3.56–3.55 (m, 4H, $NCH_2OCH_2CH_2OCH_3$), 3.28 (s, 3H, N-CH_3). ^{13}C NMR (75 MHz, D_2O) δ (ppm) = 136.4 (NCHN), 124.2, 121.6 (NCHCHN), 78.5 ($NCH_2OCH_2CH_2OCH_3$), 70.5, 68.6 ($NCH_2OCH_2CH_2OCH_3$),

Table 3
Solvent effect for the *N*-alkylation reaction of aniline with butyl chloride.



Entry	Solvent	Conv. (%)	Yield (%)	
			A	B
1	1a	95	82	18
2	2-Propanol	15	100	0
3 [47]	DMA	7	100	–
4	DMF	–	–	–
5	Toluene	–	–	–
6	Dioxane	–	–	–
7 [47]	DMSO	22	100	0

General conditions: IL (0.10 g), aniline (0.55 mmol), BuCl (0.5 mmol), stirred at 90 °C, 3 h, solvent 2 mL (entries 2–7).

58.1($NCH_2OCH_2CH_2OCH_3$), 35.8 (NCH_3). ^{31}P NMR (600 MHz, D_2O) δ (ppm) = −145.02 (hept). Anal. Calc. for $C_8H_{15}F_6N_2O_2P$: C, 30.39; H, 4.78; N, 8.86. Found: C, 30.35; H, 4.73; N: 8.84%.

2.2.3.3. 1-n-Butyl-3-ethylacetylimidazolium hexafluorophosphate, ***6a****.* **6a** was prepared using ionic liquids **2a** with chloro anion at room temperature. A mixture of chloride salt (0.10 mol) and KPF_6 (0.13 mol) in dichloromethane (50 mL) was stirred at room temperature for 24 h. After filtration, the solvent was removed by vacuum. The remaining viscous liquid was then dried under vacuum at 70 °C for 8 h to give the product. Yield: 2.20 g (62%).

^{1}H NMR (300 MHz, D_2O) δ (ppm) = 8.79 (s, 1H, NC*H*N), 7.49, 7.44 (s, 2H, NC*HCH*N), 5.07 (s, 2H, $NCH_2COOCH_2CH_3$), 4.22 (q, 2H, *J* = 7.2 Hz, $NCH_2COOCH_2CH_3$), 4.17 (t, 2H *J* = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 1.79 (pent, 2H, *J* = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 1.23 (hex, 2H, *J* = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 1.21 (t, 3H, *J* = 7.2 Hz, $NCH_2COOCH_2CH_3$), 0.85 (t, 3H, J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (75 MHz, D_2O) δ (ppm) = 168.2 ($NCH_2COOCH_2CH_3$), 136.7 (NCHN), 123.6, 122.3 (NCHCHN), 63.5 ($NCH_2COOCH_2CH_3$), 49.9 ($NCH_2COOCH_2CH_3$), 49.6 ($NCH_2CH_2CH_2CH_3$), 31.1 ($NCH_2CH_2CH_2CH_3$), 18.7 ($NCH_2CH_2CH_2CH_3$), 13.1 ($NCH_2COOCH_2CH_3$), 12.5 ($NCH_2CH_2CH_2CH_3$). ^{31}P NMR (600 MHz, D_2O) δ (ppm) = −145.07 (hept). Anal. Calc. for $C_{11}H_{19}F_6N_2O_2P$: C, 37.09; H, 5.38; N, 7.86. Found: C, 37.05; H, 5.35; N: 7.89%.

2.2.3.4. 1-n-Butyl-3-methoxyethoxymethylimidazolium hexafluorophosphate, 6b. **6b** was prepared using ionic liquids **2b** with chloro anion at room temperature. A mixture of chloride salt (0.10 mol) and KPF_6 (0.13 mol) in dichloromethane (50 mL) was stirred at room temperature for 24 h. After filtration, the solvent was removed by vacuum. The remaining viscous liquid was then dried under vacuum at 70 °C for 8 h to give the product. Yield: 2.33 g (65%).

^{1}H NMR (300 MHz, D_2O) δ (ppm) = 8.93 (s, 1H, NC*H*N), 7.57, 7.51 (s, 2H, NC*HCH*N), 5.54 (s, 2H, $NCH_2OCH_2CH_2OCH_3$), 4.17 (t, 2H *J* = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 3.68–3.67 (m, 2H, $NCH_2OCH_2CH_2OCH_3$), 3.56–3.54 (m, 2H, $NCH_2OCH_2CH_2OCH_3$), 3.27 (s, 3H, $NCH_2OCH_2CH_2OCH_3$), 1.79 (pent, 2H, *J* = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 1.25 (hex, 2H, *J* = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 0.85 (t, 3H, J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (75 MHz, D_2O) δ (ppm) = 135.7 (NCHN), 122.9, 121.8 (NCHCHN), 70.7 ($NCH_2OCH_2CH_2OCH_3$), 68.9 ($NCH_2OCH_2CH_2OCH_3$), 58.0 ($NCH_2OCH_2CH_2OCH_3$), 49.6 ($NCH_2CH_2CH_2CH_3$), 31.1 ($NCH_2CH_2CH_2CH_3$), 18.8 ($NCH_2CH_2CH_2CH_3$), 12.6 ($NCH_2CH_2CH_2CH_3$). ^{31}P NMR (600 MHz, D_2O) δ (ppm) = −145.05 (hept). Anal. Calc. for $C_{11}H_{21}F_6N_2O_2P$: C, 36.88; H, 5.91; N, 7.82. Found: C, 36.85; H, 5.95; N: 7.87%.

2.3. General procedure for the N-alkylation of aniline and butylchloride

Under an inert atmosphere, a mixture containing the ionic liquid (**1**–**6**) (0.1 g), amine (0.55 mmol), and butyl chloride (0.5 mmol) was heated at 90 °C for 3 h. The reaction mixture was then diluted with aqueous $NaHCO_3$ and extracted with Et_2O. The combined organic layers were dried with anhydrous $MgSO_4$, and the solvent was removed in vacuum. The crude mixture was analyzed by GC–MS and NMR spectroscopy.

3. Results and discussion

Ionic liquids can be prepared by direct quaternization of the alkylimidazole with alkyl halides. Different anions can subsequently be introduced by anion exchange (Scheme 1).

There are two basic methods for the preparation of ionic liquids: metathesis of a halide salt with, for instance, a silver, group 1 metal or ammonium salt of the desired anion and acid–base neutralization reactions.

The synthetic route used to prepare the new ionic liquids described herein is depicted in Scheme 2.

ILs were made in a two-stage procedure shown in Scheme 2. In the first step 1-methylimidazole and 1-butylimidazole were quaternized with ethylchloroacetate and 2-methoxyethoxymethyl chloride in dimethylformamide as solvent. During the second stage, the metathesis reaction was conducted in an solution. All of the tetrafluoroborates and hexafluorophosphates were prepared from chloride salts at room temperature. The synthesis and application of imidazolium based ionic liquids with an ester moiety have been shown in the literature [48–50].

The solubility experiment showed that these ILs are miscible relatively readily soluble in polar solvents such as methanol, ethanol, and acetone, and they are partially immiscible with nonpolar solvents such as diethyl ether and hexane. Additionally, all the new ionic liquids are highly viscous fluid. In addition, the treatment of these ILs under a vacuum at 200 °C for 24 h results in no loss of mass and thus verifies that the ILs are stable at relatively high temperature. All compounds were viscous liquids. Therefore we couldn't determined melting points. The imidazolium salts were characterized using ^{1}H, and ^{13}C NMR spectroscopies, and elemental analysis. The selected chemical shifts (δ values, ppm) for the new ILs were given in Table 1.

In the past two decades, ionic liquids have been widely used as "green solvents" replacing traditional organic solvents for organic synthesis and catalysis. The first example of the new ionic liquids, that currently are receiving so much attention as novel media for homogeneous catalysis, ethylmethylimidazolium tetrafluoroborate ($emimBF_4$) was reported by Wilkes and Zaworotko in 1992 [51]. Ionic liquids have recently gained great attention in a variety of chemical processes. They are being used as solvents for homogeneous catalysis for a variety of organic reactions [52–54]. We described *N*-alkylation reaction of aniline with butyl chloride without using transition metal. The reaction of aniline with butylchloride in the presence of ionic liquids was chosen as a model reaction. In order to study the influence of different anions, we used new ionic liquids bearing anions such as chloride (Cl^-), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-) (Table 2).

As shown in Table 2, aromatic amines bearing electron-donating substituents such as methyl (Table 2, entries 39 and 40) reacted slightly

more rapidly than those with electron-withdrawing groups such as chloride (Table 2, entries 12–16). When using morpholine as amine we observed that efficient substrate for the *N*-alkylation reaction to give the desired products in the yields of 71–100% (Table 2, entries 17–27). Between the ionic liquids, the nature of the anion appears to be the factor that has more effect on the yields of the reaction. Higher yields were achieved for chloride (Cl^-) ionic liquids, while those based on the tetrafluoroborate (BF_4^-) anion and hexafluorophosphate (PF_6^-) provided the lowest. As previously reported for related tetraalkylammonium based ionic liquids, the *N*-alkylation of aniline and butylchloride was retarded amount of 0.5 g ionic liquid at 3 h–90 °C [47]. In the present catalytic system used the amount of 0.1 g ionic liquid for the same reaction conditions. As shown in Table 3, cation part of ionic liquid did not cause remarkable difference on the catalytic performance.

To assess the impact of the polarity of the solvent on the *N*-alkylation of aniline with butyl chloride, we investigated this *N*-alkylation reaction in various solvents (Table 3). IL**1a** was chosen for further studies due to its high reactivity.

We investigated the solvents such as 2-propanol, DMA, DMF, toluene, dioxane, DMS and, ionic liquid (**1a**). The *N*-alkylation reaction led to very poor conversion when 2-propanol, DMA and DMSO are used as solvent. In the other solvents such as DMF, toluene and dioxane product formation was impossible under the same reaction conditions. Whereas, as indicated by the results in Table 3, ionic liquid (**1a**) proved to be excellent media for the *N*-alkylation reaction.

4. Conclusion

In this work, inexpensive and easily prepared ionic liquids have been shown to be an active, stable, versatile, and highly selective catalyst for the selective monoalkylation of amines. Desired products were obtained without any transition metal. In future *N*-alkylation reaction can be improved for amine and different alkyl and aryl halides. In addition to new ionic liquids, other catalytic systems such as esterification reaction can be used.

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