

NEW ROOM TEMPERATURE LIQUIDS: SYNTHESIS AND CHARACTERIZATION

Macaev Fliur, Munteanu Viorica, Stingaci Eugenia, Barba Alic, Pogrebnoi Serghei
 Institute of Chemistry of the Academy of Sciences of Moldova, Academiei str. 3, MD-2028 Chişinău, Republic of Moldova
 E-mail : flmacaev@cc.acad.md, Phone (+373-22) 73-97-54, Fax (+373-22) 73-99-54

Abstract: New functionalized imidazolium salts that can be classified as ionic liquids were synthesized.

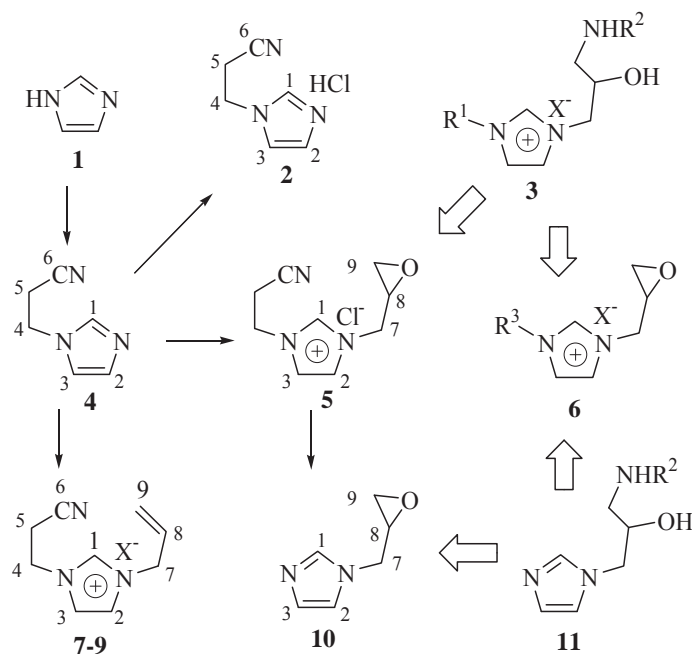
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1. INTRODUCTION

Room temperature ionic liquids (ILs) have been recognized as a new generation of solvents for “green chemistry” and represent remarkably promising classes of technologically useful and fundamentally interesting materials [1-6]. Most of them are quaternary imidazolium cations with inorganic counterions. Cation in these salts is appended to the organic group (usually saturated hydrocarbon fragments). However, some problems regarding the functionalization [2,7], coordination properties [4] of ILs still remain to be solved. It seems to us that functionalization of imidazoles by ethylcarbonitrile, allyl, 2,3-epoxypropyl fragments will lead to new properties of synthesized ILs. There are no literature data on use of 2-(1*H*-1-imidazolyl)ethylcarbonitrile **4** for synthesis of imidazolium salts with ILs properties.

2. RESULTS AND DISCUSSION

In continuation of our investigations [8,9] on the chemistry of intramolecular reaction of conjugate acceptors, we carried out the cyanoethylation of imidazole **1** into **4** via Michael addition of acrylonitrile. Taking into account the simplicity of the discussed reaction, no bis-product formation, it is possible to carry out the process technologically on large scale.



7: X= Br⁻, 8: X= BF₄⁻, 9: X= PF₆⁻

Most used ILs are based on 1,3-dialkylimidazolium cations and large anions (BF₄⁻, PF₆⁻, CF₃SO₃⁻, etc), but not halides, due to their relatively high melting point (MP). For example, 1-butyl-3-methylimidazolium chloride has MP 67°C. Although some imidazolium halide salts having long alkyl chains are known to form super-cooled liquids, but they show high viscosity [1-6]. There are also reports that some of allylimidazolium halide could be obtained as liquids [10].

We have synthesized new allylimidazolium compounds for the study of relation between structure and physical-chemical properties.

Table 1

Characteristic Data of Synthesized Compounds

Compound/ Molecular formula	Aggregation/ color	Metod ^a / Yield (%)	IR (Nujol) v, cm ⁻¹	Elemental analysis Calculated /Found		
				C	H	N
2 C ₆ H ₈ ClN ₃	Oil/White	C/66 D/95	3130, 1520, 1450, 1520 (CH=C); 2260 (CN); 670 (Cl)	45.72/ 45.66	5.11/ 4.98	26.66/ 26.51
4 C ₆ H ₇ N ₃	Oil/Yellow	99	3130, 1455, 1525 (CH=C); 2250 (CN)	59.49/ 59.33	5.82/ 5.99	34.69/ 34.98
5 C ₉ H ₁₂ ClN ₃ O	Oil/Yellow	B/75	3130, 1520, 1450 (CH=C); 2260 (CN); 670 (Cl)	50.59/ 50.46	5.66/ 5.64	19.67/ 19.87
7 C ₉ H ₁₂ BrN ₃	Oil/Yellow	A/98	3195 1560, 1420 (CH=C); 2260 (CN); 630 (Br)	44.65/ 44.43	5.00/ 4.88	17.36/ 17.39
8 C ₉ H ₁₂ BF ₄ N ₃	Oil/Yellow	A/87 B/94	3100 1560, 1420 (CH=C); 2250 (CN)	43.41/ 43.32	4.86/ 4.76	16.87/ 16.88
9 C ₉ H ₁₂ F ₆ PN ₃	Oil/ Pale-yellow	A/53 B/97	3185, 3120, 1570, 1450 (CH=C); 2260 (CN)	35.19/ 35.26	3.94/ 4.15	13.68/ 13.49
10^b C ₆ H ₈ N ₂ O	Oil/Colourless	A/70* A/75**	3130, 1550, 1450 (CH=C)	58.05/ 58.00	6.50/ 6.73	22.57/ 22.46

^aMethod: **A** – Reaction in Water; **B** - Reaction in Acetone; **C** - Reaction in MeCN; **D** - Reaction in MeOH.

^bMethod* - Use KPF₆ in Water; Method** - Use KBF₄ in Water.

Quaternization of **4** with allyl bromide yielded 1-allyl-3-(2-cyanoethyl)-1*H*-imidazolium bromide **7** as yellow liquid.

The next step was the metathesis of **7** with the appropriate inorganic salt (NaBF₄ or KPF₆) in water or acetone. Notable, caring out reaction in acetone leads to the highest yields of room temperature liquids **8**, **9** (See Tab. 1).

After developing successfully the synthesis of ionic liquids **7-9**, our interest was switched to evaluation of the usefulness of **4** for selective synthesis of salts, functionalized by 2,3-epoxypropyl chain. There are several advantages and reasons to synthesize the ionic liquids with a glycidyl group. The epoxides in the cation of glycidyl ionic liquids can react with different kind of nucleophiles, electrophiles and other reactants, resulting in the production of new ILs **3**, **6** with different groups [11]. We shall emphasize, that derivatives like **11**, could be applied in the cycloaddition of CO₂ as well as in medicinal chemistry studies by introduction imidazolium and other ammonium group to different aminosaccharides.

Table 2

NMR Spectroscopic Data of Synthesized Imidazolium Derivatives

№	Me- thod	The chemical shifts (δ, ppm, J/Hz)								
		1	2	3	4	5	6	7	8	9
2	¹ H	7.72 ^a s, 1H	9.41 s, 1H	7.94 s, 1H	4.57 ^c t, 2H, J=6.4	3.30 t, 2H J=6.4	-	-	-	-
	¹³ C	128.79	137.5	118.59	41.83	19.72	119.43	-	-	-
4	¹ H	6.95 s, 1H	7.43 s, 1H	6.95 s, 1H	4.13 t, 2H, J=6.94	2.69 t, 2H J=6.95	-	-	-	-
	¹³ C	128.57	137.29	118.35	69.56	19.49	119.18	46.26	68.67	41.26
5	¹ H	7.27 s, 1H	7.73 s, 1H	6.94 s, 1H	4.27 t, 2H, J=6.4	3.20 t, 2H, J=6.62	-	3.81-4.19 m, 2H	3.5-3.86 m, 1H	3.63-3.69 m, 2H
	¹³ C	128.57	137.29	118.35	69.56	19.49	119.18	46.26	68.67	41.26
7	¹ H	7.91 s, 1H	9.56 s, 1H	8.05 s, 1H	4.61 t, 2H, J=6.4	3.35 t, 2H, J=6.4	-	4.94 ^b d, 2H, J=5.71	5.8-6.21 ^d m, 1H	5.14-5.35 m, 2H
	¹³ C	122.67	136.5	120.3	44.46	18.89	117.53	50.85	131.37	122.68

8	¹ H	7.77 s, 1H	9.24 s, 1H	7.84 s, 1H	4.50 t, 2H, J=6.27	3.20 t, 2H, J=6.27	-	4.87 d, 2H, J=5.53	5.6-6.3 m, 1H	5.15-5.42 m, 2H
	¹³ C	122.77	136.59	120.41	44.53	18.89	117.62	50.95	131.43	122.61
9	¹ H	7.73 s, 1H	9.26 s, 1H	7.84 s, 1H	4.52 t, 2H, J=6.62	3.20 t, 2H, J=6.62	-	4.86 d, 2H, J=5.75	5.8-6.21 m, 1H	5.15-5.39 m, 2H
	¹³ C	122.86	137.0	120.38	44.56	18.65	117.67	51.02	131.45	122.65
10	¹ H	7.82 s, 1H	9.30 s, 1H	7.82 s, 1H		-			3.15-4.57 m, 5H	

^as-singlet, ^bd-doublet, ^ct-triplet, ^dm-multiplet

Chloride **5** was obtained by simple mixing of **4** and 2-chloromethyloxirane at room temperature. We tried to carry out anion exchange by similar manner as described above. However, compound **10** has isolated as main product.

It is known that dequaternization of 1-(2-cyanoethyl)-3-alkylazolium salts can be achieved by the addition of a strong base to the azolium salts [12]. During such reaction, formation of the cyanoethylated byproducts is possible, but we didn't observe any by-product.

It was worth to note that the mixture of **4** and epichlorohydrin refluxed in MeCN led to hydrochloride **2**. This result shows that other type of elimination takes place and is preferable. Additionally, **2** was prepared by treatment of **4** with a HCl solution in dry MeOH.

The structures of new salts were established based on their spectral data and elemental analysis. The chemical shifts of the imidazole ring protons strongly depend on anion nature (δ ppm = 9.41, 7.94 and 7.72 for **2**; 9.56, 8.05 and 7.91 for **7**; 9.24, 7.84, 7.77 for **8**; 9.26, 7.84 and 7.75 for **9**). Similar phenomenon was observed for ¹³C-chemical shifts for discussed fragment (δ ppm = 137.5, 128.79 and 118.59 for **2**; 136.5, 120.3 and 117.5 for **7**; 136.5, 131.43, 122.77 for **8**; 137.0, 131.45 and 122.88 for **9**) (See Table 2). Notable, chemical shifts of protons of cyanoethyl chain depend on anion nature, too (δ ppm = 3.30 and 4.57 for **2**; 2.69 and 4.13 for **4**; 3.20 4.27 for **5**; 3.35 and 4.61 for **7**; 3.20 and 4.50 for **8**; 3.20 and 4.52 for **9**). Small difference for ¹³C-chemical shifts (δ ppm = 119.43 for **2**; 119.18 for **4** and 117.53 for **7**; 117.62 for **8** and 117.67 for **9**, respectively) as well as IR absorption band of carbonitrile group were observed also (See Tab. 1 and 2).

The solvent's properties of the synthesized imidazolium salts are under investigation, and will be published soon.

It should be mentioned that during the preparation of current paper, the development of nitrile-functionalized ionic liquids for C-C coupling reaction was reported [13].

4. EXPERIMENTAL

All the solvents used were reagent quality, and all commercial reagents were used without additional purification. Removal of all solvents was carried out under reduced pressure. Melting points (uncorrected) were determined on a Boetius apparatus. Physical and analytical data of the synthesized compounds are given in Table 1. Analytical TLC plates were Silufol® UV-254 (Silpearl on aluminium foil, Czecho-Slovakia). IR spectra were recorded on a Specord 75 IR instrument. ¹H and ¹³C NMR spectra were recorded for d₆-DMSO 2-3% solution on a Bruker AC-80 (80 and 20 MHz) and on a Varian XL-400 spectrometer (399.95 MHz) apparatus and are given in Table 2.

Synthesis of 3-(1H-1-imidazolyl)propanenitrile hydrochloride **2**.

Method A): To a solution of **4** (2.18 g, 0.018 mol) in MeCN (10 ml) was added 2-chloromethyloxirane (1.63 g, 0.018 mol). The mixture was refluxed for 18 hours, concentrated under reduced pressure and dried under vacuum. Yield 1.87 g of **2**.

Method B): A mixture of **4** (1.45 g, 0.012 mol) and 18% solution of HCl in MeOH (5 ml) was stirred with for 2 days. The same workup as for method A was followed. Yield 1.85 g salt **2**.

Synthesis of 3-(1H-1-imidazolyl)propanenitrile **4**.

The mixture of imidazole **1** (40 g, 0.59 mol), acrylonitrile (33.85 g, 0.59 mol) and Et₃N (0.1 ml) in 80 ml toluene was refluxed for 30 hours. Solvent was removed under high vacuum to yield 71g (pure according spectral and TLC data) of compound **4**.

Synthesis of 1-(2-cyanoethyl)-3-(2-oxiranylmethyl)-1H-imidazolium chloride **5.** To a solution of **4** (2.13 g (0.018 mol) in 10 ml acetone 2-chloromethyloxirane (1.63 g, 0.018 mol) was added dropwise. The reaction mixture was stirred for a 25 hours. Solvent was removed in vacuum to give 2.84 g of viscously yellow oil **5**.

Synthesis of 1-allyl-3-(2-cyanoethyl)-1H-imidazolium bromide 7.

Product **7** (4.19 g) has prepared from **4** (2.13 g, 0.018 mol) and allyl bromide (2.13 g, 0.018 mol) by the same procedure as for preparation of **5**.

Synthesis of 3-allyl-1-(2-cyanoethyl)-1H-imidazolium tetrafluoroborate 8.

Method A): A solution of imidazolium bromide **7** (1.57 g, 0.0065 mol) in water (2 ml) containing (0.82 g, 0.0065 mol) KBF_4 was stirring at room temperature for 60 hours. The insoluble oily material was separated. It was then dissolved in CH_2Cl_2 , washed with H_2O and brine, dried over Na_2SO_4 , filtered, and concentrated to dryness. Salt **8** (1.4 g) was obtained as a pale yellow oil.

Method B): To a solution of bromide **7** (1.57 g, 0.0065 mol) in acetone (2 ml) was added KPF_6 (0.82 g, 0.0047 mol). The reaction mixture was stirred for a total 60 hours. Solids were filtered, and the solvent removed to give 1.51 g of oil **8**.

Synthesis of 3-allyl-1-(2-cyanoethyl)-1H-imidazolium hexafluorophosphate 9.

Method A): Bromide **7** (1.57 g, 0.0065 mol) has reacted with KPF_6 (1.19 g, 0.0065) according to the procedure described for the preparation of tetrafluoroborate **8** (See method A) to give salt **9** (1 g) as a pale yellow oil. Method B): Salt **9** (1.97 g) was prepared by use **7** (1.57 g, 0.0065 mol) and KPF_6 (1.19 g, 0.0065 mol) in acetone by the same procedure as for **8** (See method B).

Synthesis of 1H-imidazolyl(2-oxiranyl)methane 10

Method A): A solution of KPF_6 (0.86 g, 0.0047 mol) in 5 ml H_2O was added to **5** (1 g, 0.0047 mol). The reaction mixture was stirred for a total 35 hours. The insoluble oily material was separated. It was then dissolved in CH_2Cl_2 , washed with H_2O and brine, dried over Na_2SO_4 , filtered, and concentrated to dryness to give 0.40 g of viscously colorless oil **10**. Method B): Use of chloride **5** (1.2 g, 0.0056 mol) and solution of KBF_4 (0.7 g, 0.0056 mol) in water (5 ml) analogously Method A) afforded 0.46 g of oxirane **10**.

5. CONCLUSIONS

This work presents results of the synthesis and analyses of the effect of nature of C3 groups on imidazolium ring to aggregation of Br^- , Cl^- , BF_4^- and PF_6^- imidazolium salts.

6. ACKNOWLEDGMENTS

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