NEW ROOM TEMPERATURE LIQUIDS: SYNTHESIS AND CHARACTERIZATION

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

Keyword: organic synthesis, ionic liquids, epoxides, nitriles, allylimidazoles.

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-(1H-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.

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.

### Characteristic Data of Synthesized Compounds

| Compound/Molecular formula | Aggregation/ color | Method\(^a\)/ Yield (%) | IR (Nujol) \(\nu\), cm\(^{-1}\) | Elemental analysis Calculated /Found
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<tbody>
<tr>
<td><strong>2</strong> C(<em>{6}H</em>{8}ClN_{3})</td>
<td>Oil/White</td>
<td>C/66 D/95</td>
<td>3130, 1520, 1450, 1520 (CH=C); 2260 (CN); 670 (Cl)</td>
<td>C 45.72/45.66 H 5.11/4.98 N 26.66/26.51</td>
</tr>
<tr>
<td><strong>4</strong> C(<em>{7}H</em>{7}N_{3})</td>
<td>Oil/Yellow</td>
<td>99</td>
<td>3130, 1455, 1525 (CH=C); 2260 (CN)</td>
<td>C 59.49/59.33 H 5.82/5.99 N 34.69/34.89</td>
</tr>
<tr>
<td><strong>5</strong> C(<em>{9}H</em>{12}ClN_{3}O)</td>
<td>Oil/Yellow</td>
<td>B/75</td>
<td>3130, 1520, 1450 (CH=C); 2260 (CN); 670 (Cl)</td>
<td>C 50.59/50.46 H 5.66/5.64 N 19.67/19.87</td>
</tr>
<tr>
<td><strong>7</strong> C(<em>{9}H</em>{12}BrN_{3})</td>
<td>Oil/Yellow</td>
<td>A/98</td>
<td>3195, 1560, 1420 (CH=C); 2260 (CN); 630 (Br)</td>
<td>C 35.19/35.26 H 3.94/4.15 N 13.68/13.49</td>
</tr>
<tr>
<td><strong>8</strong> C(<em>{6}H</em>{8}BF_{4}N_{3})</td>
<td>Oil/Yellow</td>
<td>A/87 B/94</td>
<td>3100, 1560, 1420 (CH=C); 2250 (CN)</td>
<td>C 44.65/44.43 H 4.86/4.76 N 17.36/17.39</td>
</tr>
<tr>
<td><strong>9</strong> C(<em>{9}H</em>{12}F_{6}PN_{3})</td>
<td>Oil/Pale-yellow</td>
<td>A/53 B/97</td>
<td>3185, 3120, 1570, 1450 (CH=C); 2260 (CN)</td>
<td>C 43.41/43.32 H 4.86/4.76 N 16.87/16.88</td>
</tr>
<tr>
<td><strong>10</strong> C(<em>{6}H</em>{8}N_{2}O)</td>
<td>Oil/Light yellow</td>
<td>A/70* B/75**</td>
<td>3130, 1550, 1450 (CH=C)</td>
<td>C 58.05/58.00 H 6.50/6.73 N 22.57/22.46</td>
</tr>
</tbody>
</table>

\(^a\)Method: A – Reaction in Water; B – Reaction in Acetone; C - Reaction in MeCN; D - Reaction in MeOH.

\(^b\)Method* - Use KPF\(_6\) in Water; Method** - Use KBF\(_4\) 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 (NaBF\(_4\) or KPF\(_6\)) 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 the glycidyl ionic liquids can react with different types 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 CO\(_2\) as well as in medicinal chemistry studies by introduction imidazolium and other ammonium group to different aminosacharides.

### NMR Spectroscopic Data of Synthesized Imidazolium Derivatives

<table>
<thead>
<tr>
<th>№</th>
<th>Method</th>
<th>The chemical shifts ((\delta), ppm, J/Hz)</th>
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<tbody>
<tr>
<td>2</td>
<td>(^1)H</td>
<td>7.72 s, 1H 9.41 s, 1H 7.94 s, 1H</td>
</tr>
<tr>
<td></td>
<td>(^13)C</td>
<td>128.79 137.5 118.59</td>
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<tr>
<td>4</td>
<td>(^1)H</td>
<td>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)</td>
</tr>
<tr>
<td></td>
<td>(^13)C</td>
<td>128.57 137.29 118.35 69.56 19.49 119.18</td>
</tr>
<tr>
<td>7</td>
<td>(^1)H</td>
<td>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)</td>
</tr>
<tr>
<td></td>
<td>(^13)C</td>
<td>122.67 136.5 120.3 44.46 18.89 117.53 58.05 6.50 7.32 22.46</td>
</tr>
<tr>
<td>8</td>
<td>(^1)H</td>
<td>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)</td>
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</tr>
<tr>
<td></td>
<td>(^13)C</td>
<td>122.67 136.5 120.3 44.46 18.89 117.53 50.85 131.37 122.68</td>
</tr>
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for anion nature, too (8 was re

... for 30 hours. Solvent was removed under high vacuum to yield 71 g (pure according spectral and TLC data)

... 3-(1H-1-imidazolyl)propanenitrile hydrochloride 2.

... 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 vaccum. 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 Et,N (0.1 ml) in 80 ml toluene was refluxed for 30 hours. Solvent was removed under high vacuum to yield 71 g (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 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) KBF4 was stirring at room temperature for 60 hours. The insoluble oily material was separated. It was then dissolved in CH2Cl2, washed with H2O and brine, dried over Na2SO4, 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 KPF6 (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 KPF6 (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 KPF6 (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.

Metod A): A solution of KPF6 (0.86 g, 0.0047 mol) in 5 ml H2O 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 CH2Cl2, washed with H2O and brine, dried over Na2SO4, 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 KBF4 (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-, BF4- and PF6- imidazolium salts.

6. ACKNOWLEDGMENTS

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7. REFERENCES