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Solvent-free synthesis of ionic liquids under microwave irradiation. Method, development and scale-up

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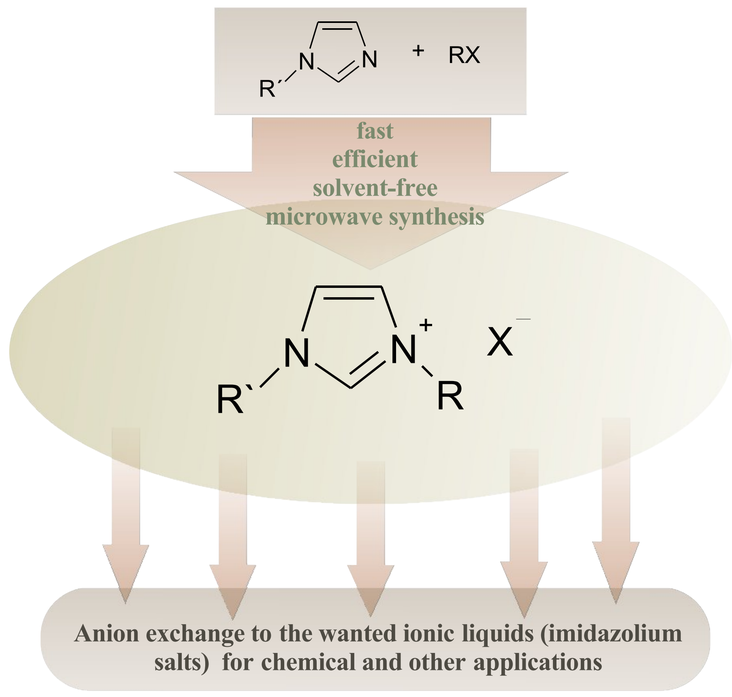
Introduction

Applications of Ionic Liquids (ILs) as alternative reaction media has been described frequently during the last years. The various areas of applications show an increasing requirement of larger amounts of ILs.

The most frequently described ILs are quarternary nitrogen compounds, mainly 1,3-dialkylimidazolium salts. The most commonly used ILs received preferentially by exchanging the anion of an imidazolium halide by an anion which caused the favored properties.

So it is necessary to concentrate on synthesis of imidazolium halides, because they are precursors to required Ils. The syntheses of 1,3-dialkylimidazolium halides predominantly occur by the quarternization of N-alkylimidazoles by alkyl halides.



Compared to classical quarternization by conventional heating microwave synthesis route accompanies with short reaction times[1,2].

We show on the one hand that it is possible to synthezise 1,3-dialkylimidazolium halides in laboratory scale (up to 2 mol) with high cleaness and good yields in short reaction times by microwave irradiation (table 1, scheme 1).

On the other hand we find the option to continue the scale-up this reaction by using continous microwave devices (pict. 3). E.g. experiments to synthesize 1-butyl-3-methylimidazolium chloride show an scale between 2 and 3 mol/h. Further investigations to enlarge this scale are executed.

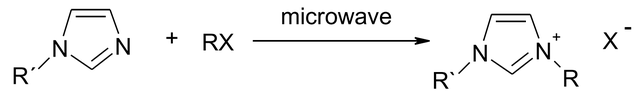
Experimental

Table 1: Microwave assisted synthesis of 1,3-dialkylimidazolium halides

educts	product	time [min]	yield [%]
N-methylimidazole ethyl bromide	1-butyl-3-methylimidazolium bromide	40	82
N-methylimidazole butyl chloride	1-butyl-3-methylimidazolium chloride	70	95
N-methylimidazole butyl bromide	1-butyl-3-methylimidazolium bromide	45	92
N-ethylimidazole butyl bromide	1-butyl-3-ethylimidazolium bromide	45	86
N-methylimidazole hexyl chloride	1-hexyl-3-methylimidazolium chloride	60	94

Reaction conditions:
Reaction mixture, N-alkylimidazole and alkyl halide (molar ratio 1:1,1) were placed in the microwave reactions vessel (reactor pict. 1-2) and a predefined microwave program (scheme 2) was started until the reaction was complete (single ionic phase). The product washed several times with ethyl acetate or ether and dried under vacuum to give white solids or colourless to light yellow liquids.

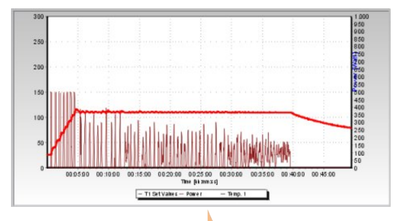
Scheme 1: Microwave assisted synthesis of 1-R-3-R´-imidazolium salts



a) R´: methyl; R: propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, phenethyl, benzyl, 4-methylbenzyl; X: Cl^-
b) R´: ethyl; R: propyl, butyl, hexyl, decyl; X: Cl^-
c) R´: methyl, ethyl; R: ethyl, propyl, butyl, hexyl; X: Br^-
d) R´: methyl, ethyl; R: methyl, ethyl; X: toluene-4-sulfonate

Scheme 2: Microwave program for batch synthesis

step	time [Min]	power [W]	temperature [°C]
1	5	400-500	rt-110
2	40-90	200-400	110
3	15	0	cooling



Laboratory microwave equipment

0,15 mol

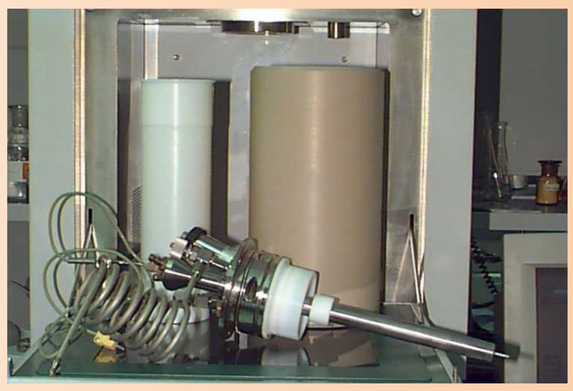
Picture 1: Microwave parallel reactor

6-fold (10-fold) rotor system HPR 1000/6 (10), Fa. MLS GmbH Leutkirch/Allgäu, Germany

- → 6 (10) identical teflon pressure vessels
- → reaction volume up to 60 ml per vessel
- → fibre-optic temperature control
- → magnetical agitation

2 mol

Picture 2: Microwave autoclave



"µClave", Fa. MLS GmbH Leutkirch/Allgäu, Germany

- → autoclave reactor
- → reaction volume up to 500 ml
- → up to 260°C and 60 bar
- → temperature and pressure sensor
- → mechanical or magnetical agitation

>3 mol/h

Picture 3: Continuous microwave system

"contFlow", Fa. MLS GmbH Leutkirch/Allgäu, Germany

- → flow reactor
- → variable reactors
- → up to 10 L/ hour
- → up to 180°C and 60 bar
- → temperature sensor and pressure sensor

In the difference to household microwave devices the used microwave laboratory devices (microwave system ETHOS®, Fa. MLS GmbH Leutkirch/Allgäu, Germany) work with an unpulsated power supply. Thus the microwave energy is entered continuously with the selected microwave power, not with the full system power in time interval.

A further difference of these microwave devices exists in good temperature dependent (fiber-optic temperature measurement) and/or pressure dependent (pressure sensor) reaction control. That means a chosen program control the reaction parameters (time, temperature, pressure, agitation and flow). So it is possible to control the reaction by predetermined parameters. The system manages the irradiated microwave energy by the chosen parameters (max. temperature and/or pressure).

The mixing of the reaction media can take place mechanically (magnetic or mechanical stirrer/ agitator).

In conclusion, the used microwave system is the best suitable equipment for synthesis of 1,3-methylimidazolium halides up to large scale.

References:
[1] R.S. Varma, V.V. Namboodiri, *Chem Commun.*, 2001, 643
[2] M.C. Law, K.-Y. Wong, T.H. Chan, *Green Chem.*, 2002, **4**, 328-330

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