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Solvent-Free Sonochemical Preparation of Ionic Liquids

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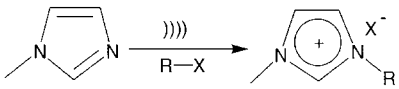
ABSTRACT



Where R = alkyl and X= Cl, Br or I

An ultrasound-assisted preparation of a series of ambient-temperature ionic liquids, 1-alkyl-3-methylimidazolium (AMIM) halides, which proceeds via efficient reaction of 1-methyl imidazole with alkyl halides/terminal dihalides under solvent-free conditions, is described.

The use of a large excess of conventional volatile solvents required to conduct a chemical reaction is of ecological and economic concern. Ambient-temperature ionic liquids encompassing 1,3-dialkylimidazolium salts (**I**) have shown great promise as an attractive alternative to conventional solvents.[1] Their potential for recyclability, ability to dissolve a variety of materials, and importantly their nonvolatile nature with barely measurable vapor pressure are some of their unique attributes responsible for newly found popularity. Although originally studied in electrochemistry,[2] ionic liquids are currently being explored as environmentally benign solvent substitutes for conventional volatile solvents in a variety of applications such as chemical synthesis,[1] liquid/liquid separations,[3] extractions,[4] dissolution,[5] catalysis,[6] biocatalysis,[7] and polymerization.[8]

The conventional preparation of ionic liquids using excess solvents leaves much to be desired, and improvements are sought. An efficient microwave-assisted preparation of 1,3-dialkylimidazolium halides has reduced the reaction time from several hours to a few minutes in a process that avoids the use of a large excess of alkyl halides/organic solvents as the reaction medium.[9] However, as a result of the exothermic nature of the reaction, continuous microwave heating may result in overheating that leads to the formation of colored products. In view of the emerging importance of the ionic liquids as reaction media and our general interest in the development of clean chemical processes,[10] we decided to address the main problem in dealing with these highly viscous materials wherein efficient mixing is a challenge. Ultrasound-accelerated chemical reactions are well-known and proceed via the formation and adiabatic collapse of the

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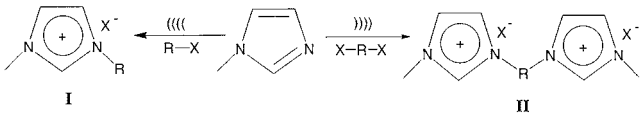
Table 1. Ultrasound-Promoted Preparation of 1-Alkyl-3-Methylimidazolium Halides



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entry	alkyl halide	RX, mmol	MIM, mmol	time, h	yield,[a] %	yield,[c] % (time, h)
1	1-bromopropane	11	10	2	95	0(2)
2	1-chlorobutane	11	10	6	24	0(6)
		220	200	2	86[b]	0(2)
3	1-bromobutane	11	10	2	94	0(6)
4	1-iodobutane	11	10	0.5	94	30(0.5)
5	2-bromobutane	11	10	4	93	0(6)
6	1-chlorohexane	11	10	6	31	0(6)
		220	200	0.5	89[b]	0(2)
7	1-bromohexane	11	10	2	91	0(6)
8	1-iodohexane	11	10	0.5	93	32(0.5)
9	1-iodoheptane	11	10	0.5	91	28(0.5
10	1-chlorooctane	11	10	6	42	0(6)
		220	200	0.25	93[b]	0(2)
11	1-bromooctane	11	10	2	93	0(6)
12	1-iodooctane	11	10	0.5	92	26(0.5)
13	1,4-dibromobutane	5	11	3	93	0(6)
14	1,4-diiodobutane	5	11	2	94	28(3)
15	1,6-dibromohexane	5	11	3	94	0(3)
16	1,6-diiodohexane	5	11	2	93	33(2)
17	1,8-dichlorooctane	100	220	0.25b	92	0(2)
18	1,8-dibromooctane	5	11	3	92	0(3)
19	1,8-diiodooctane	5	11	2	94	25(2)
20	ethylchloroacetate	11	10	0.5	98	34(3)

[a] Ultrasonic bath, Fisher Scientific (FS 220). [b] Probe system, Sonic & Materials Inc., model VCX 750, power 750 W, frequency 20 kHz, tip diameter 19 mm, amplitude 97%). [c] Reactions in oil bath at temperature reached under sonication conditions.

transient cavitation bubbles.[11] We now report an efficient method for the preparation of ionic liquids using ultrasound as the energy source by simple exposure of neat reactants in a closed container to irradiation using a sonication bath. The current solvent-free approach requires shorter reaction time and low reaction temperature in contrast to several hours needed under conventional heating conditions using an excess of reactants.

In the present study a laboratory ultrasonic cleaning bath was used for the preparation of 1,3-dialkylimidazolium halides. Initially, the effect of ultrasound on a series of reactions comprising alkyl halides and 1-methylimidazole (MIM) was examined (Table 1). During sonication, the formation of the ionic liquid could be visibly monitored as the reaction contents turned from a clear solution to opaque (emulsification) and finally a clear viscous phase or separation of solids occurred. Upon continuous irradiation for 2 h the temperature of the bath rose from 22 to 40 °C. At this stage, the workup only involved the removal of residual halide under vacuum or by washing with ethyl acetate/ether and drying.[10,12]

To establish the generality of the reaction a series of ionic liquids were prepared via this sonication protocol and then compared with the similar preparation using conventional heating in an oil bath (Table 1). Most of the halides used in this study were efficiently converted to the corresponding ionic liquids. The reactivity trend of halides was found to be in the order $I^- > Br^- > Cl^-$. The alkyl chlorides were relatively less reactive and required longer irradiation time and often some heating except for reactive entities such as ethyl chloroacetate (entry 20). The higher reactivity of bromides and iodides provided excellent yields with minimum sonication time, and the reactions were completed nearly at room temperature. To prepare chloride salts we explored the use of a probe system (Sonic & Materials Inc.) wherein an ultrasonic field is produced directly in the reaction vessel. A number of chloride salts could be easily prepared following this modified approach (entries 2, 6 and 10, Table 1). During sonication of 1-chlorobutane and MIM, the temperature of the reaction mixture rose from 22 to 80 °C and became constant at 80 °C. Upon formation of the ionic liquid due to exothermicity of the reaction, the temperature

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increased to 115 °C. Similarly, in the case of reaction between 1-chlorooctane and MIM the temperature reached 100 °C and upon formation of the ionic liquid it further increased to 125 °C.

Butyl, hexyl, and octyl dicationic salts (entries 13−19, Table 1) were also prepared efficiently by this methodology. From the NMR data the dicationic salts generated from chloroalkanes (entry 17, Table 1) were slightly contaminated with the corresponding monocationic intermediate (<5%). However, the diiodo and dibromoalkanes, being more reactive, afforded pure products. The purity of dicationic salts prepared via sonication was found to be superior to those prepared via conventional heating methods, presumably because of inefficient mixing and heat transfer in the latter, once the solid product (**II**) begins to form.

Interestingly, this ultrasound-accelerated method is adaptable for efficiently accomplishing a one-pot palladium acetate catalyzed Suzuki reaction of iodobenzene with 4-fluorophenylboronic acid at room temperature by subsequent addition of reactants to in situ generated ionic liquid. The ionic liquid and catalyst can be recycled four times without the loss of any reactivity (91%). The preparation of other ionic liquids bearing anions such as BF_4 is being explored via this method.

The ionic liquids prepared were characterized by spectral (^{1}H and ^{13}C NMR) and elemental analysis and were in good agreement with the literature reports.[12] Thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses showed that all ionic liquids were free of the starting materials and thermally stable up to 280 °C.

In conclusion, a solvent-free sonochemical protocol is developed for the clean synthesis of ambient-temperature ionic liquids at nearly room temperature. The in situ generation of ionic liquids and their subsequent utilization as reaction medium by sequential addition of reactants in the same pot renders this an ideal approach for chemical transformation.

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