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A Novel and Green Method for the Synthesis of Ionic Liquids Using the Corresponding Acidic Ionic Liquid Precursors and Dialkyl Carbonate

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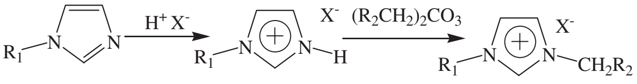
A novel and green method for the synthesis of dialkylimidazolium ionic liquids (ILs) has been developed. It was through a one-step alkylation of dialkyl carbonate with the corresponding acidic ionic liquid precursors (AILPs) prepared from the neutralization of imidazole derivatives with acids.

Ionic liquids (ILs) or room-temperature molten salts have recently attracted increasing attention due to their potential applications as green solvents, reusable catalysts, separation and extraction media, electrolytes, heat-transfer fluids, and others.[1] Generally, 1-alkyl-3-methylimidazolium halides, one type of common ILs, are synthesized by the reaction of 1-methylimidazole with alkyl halide.[2] However, for the volatile halogenoalkanes (bromomethane, chloromethane, chloroethane, 1-chloropropane, etc.), the low boiling points often lead to preparations requiring either a sealed tube or an elaborate apparatus as described in the synthesis of 1-ethyl-3-methylimidazolium chloride (EMImCl).[1,3] Therefore, imidazolium ILs with longer chain substituents (e.g., BMImCl, 1-butyl-3-methylimidazolium chloride) are more prefered because of the easier operation and more facile synthesis. However, in some special fields, such as biopolymers processing[4] and IL electrolytes,[5] the imidazolium ILs with shorter chain substituents are more desired for better results. Regarding the synthesis of non-halide anion imidazolium ILs, most reported procedures include at least one anion exchange step.[1,2,6] The anion exchange must employ Ag salts,[2] which would increase the cost. Another way is via the reaction of acids with 1-alkyl-3-methylimidazolium halides.[5,7] Unfortunately, the by-products, HX (X = Cl, Br, and I), are toxic and it is difficult to obtain pure non-halide anion imidazolium ILs by anion exchange.

Some progress has been made to synthesize imidazolium ILs with shorter chain substituents. For example, 1,3-dimethylimidazolium methyl sulfate (DMIm[CH_3SO_4]),[8] a low-cost reaction medium, was synthesized by 1-methylimidazole and dimethyl sulfate. But the methylating agent dimethyl sulfate is toxic. ILs with shorter-chain-substituent-C_2-symmetric-imidazolium cations were also successfully synthesized.[9] But the synthetic process is rigorous and anion exchange must be employed. Recently, dimethyl carbonate (DMC) has been applied in some organic syntheses as a green methylation agent.[10] For example, 1,3-dimethylimidazolium-2-carboxylate and 1-ethyl-3-methylimidazolium-2-carboxylate can be synthesized by the reaction of 1-methylimidazole/imidazole and DMC.[11]



X^- = acid group; R_1 = C_1~C_4 alkyl; R_2 = H, alkyl or aryl

Scheme 1. The procedure for the synthesis of dialkylimidazolium ionic liquids through the corresponding AILPs with dialkyl carbonate.

Table 1. AILPs synthesized with imidazole derivatives and acids[a]

Entry	Im	AC	AILPs	Y/%
1	MIm	HCl	HMImCl	>99.0
2	MIm	HBr	HMImBr	>99.0
3	MIm	HI	HMImI	>99.0
4	MIm	HNO_3	$HMImNO_3$	>99.0
5	MIm	HBF_4	$HMImBF_4$	99.0
6	MIm	CH_3CO_2H	$HMImCH_3CO_2$	99.0
7	MIm	$H_2C_2O_4$	$HMImC_2O_4$	99.0
8	MIm	HPF_6	$HMImPF_6$	99.0
9	EIm	HCl	HEImCl	>99.0
10	BIm	HCl	HBImCl	>99.0

[a]Im: imidazole derivatives, AC: acids, Y is the yield of product, MIm: 1-methylimidazole, HMIm: 1*H*-3-methylimidazolium, EIm: 1-ethylimidazole, HEIm: 1*H*-3-ethylimidazolium, BIm: 1-butylimidazole, HBIm: 1*H*-3-butylimidazolium.

The synthetic process is illustrated in Scheme 1. Various ILs reported in this paper were prepared by reaction of commercially available imidazole derivatives with inorganic acids to form acidic ionic liquid precursors (AILPs)[12] followed by their alkylation with dialkyl carbonate. The dialkylimidazolium IL yields were calculated by NMR.[13]

Table 1 shows the results of neutralization of three different imidazole derivatives with eight different acids providing ten different salts. These AILPs can be easily obtained by the reaction between imidazole derivatives and acids. This neutralization method is quite convenient and effective for synthesizing excellent ILs as well as designing suitable models for quaternized onium-type salts.

Table 2 shows the results of reactions between AILPs and dialkyl carbonate. No catalyst was used. The cations of these ILs can be designed by different dialkyl carbonate (Table 2) and different starting imidazole derivatives (Table 1); the anions can also be designed by different acids (Table 1). Simultaneously, no by-products, such as carbamates or 1,3-dimethylimidazolium-2-carboxylate were detected. This may be because we started with AILPs that can be considered as tertiary ammonium salts as

Table 2. Dialkylimidazolium ILs synthesized from AILPs and dialkyl carbonate[a]

Entry	AILPs	DAC	Product	Y/%
1	HMImCl	DMC	DMImCl	>99.0
2	HMImBr	DMC	DMImBr	>99.0
3	HMImI	DMC	DMImI	99.0
4	HMImNO$_3$	DMC	DMImNO$_3$	99.0
5	HMImBF$_4$	DMC	DMImBF$_4$	92.3
6	HMImCH$_3$CO$_2$	DMC	DMImCH$_3$CO$_2$	82.5
7	HMImC$_2$O$_4$	DMC	DMImC$_2$O$_4$	80.2
8	HMImPF$_6$	DMC	DMImPF$_6$	89.9
9	HMImCl	DBzC	BzMImCl	>99.0
10	HMImBr	DBzC	BzMImBr	>99.0
11	HMImNO$_3$	DBzC	BzMImNO$_3$	99.0
12	HMImCl	DEC	EMImCl	41.6
13	HMImBr	DEC	EMImBr	44.8
14	HMImCl	DPhC	MPhImCl	0
15	HEImCl	DMC	EMImCl	>99.0
16	HEImCl	DBzC	BzEImCl	99.0
17	HEImCl	DEC	DEImCl	40.2
18	HBImCl	DMC	BMImCl	>99.0
19	HBImCl	DBzC	BzBImCl	99.0
20	HBImCl	DEC	BEImCl	39.8

[a] DAC: dialkyl carbonate, Y is the yield of product, DMC: dimethyl carbonate, DMIm: dimethylimidazolium, DBzC: dibenzyl carbonate, BzMIm: 1-benzyl-3-methylimidazolium, DEC: diethyl carbonate, EMIm: 1-ethyl-3-methylimidazolium, DPhC: diphenyl carbonate, MPhIm: 1-methyl-3-phenylimidazolium, BzBIm: 1-benzyl-3-butylimidazolium, DEIm: diethylimidazolium, BzEIm: 1-benzyl-3-ethylimidazolium, BEIm: 1-butyl-3-ethylimidazolium.

explained in our recent study.[14] High yields (>80%) of dialkyl ILs were obtained except for the reaction of acidic ILs with diethyl carbonate (DEC) and diphenyl carbonate (DPhC).

The yield of dialkylimidazolium ILs depends on the anions of the AILPs and the alkyl groups attached to the dialkyl carbonate. The dialkyl ILs yields decreased in the order of $Cl^- \approx Br^- \approx I^- \approx NO_3^- > BF_4^- \approx PF_6^- > OAc^- \approx C_2O_4^{2-}$ (Table 2, Entries 1–8) when dimethyl carbonate reacted with different acidic ILs. The reactivity of the carbonates decreased in the order of: DMC ≈ dibenzyl carbonate (DBzC) > DEC > DPhC for the same acidic IL anions (Table 2, Entries 1, 9, 12, and 14; 2, 10 and 13; 4 and 11). These phenomena can be explained by the reactivity of the carbonates being affected by the stability of carbon cations (decreased order: benzyl > ethyl > methyl > phenyl) and the steric hindrance of the substituent groups in the carbonates (decreased order: benzyl > phenyl > ethyl > methyl). Our study also showed that the yields of ILs changed slightly when the AILPs differ from C$_1$ to C$_4$ (Table 2, Entries 1, 15, and 18; 9, 16, and 19; 12, 17, and 20).

In conclusion, we have explored a novel method for the synthesis of ILs. The reaction occurred through the electrophilic attack of the alkyl group from the dialkyl carbonate on the nitrogen atom in the reactant AILPs. Our study has revealed that AILPs that were synthesized by the reaction of strong acids with imidazole derivatives coupled with electron-withdrawing group(s), such as benzyl carbonate, on the methylene carbon of the dialkyl carbonate will favor the alkylation reaction, which is confirmed in Table 2. Certainly, more work is needed to clarify the mechanism in our synthetic method and to extend the synthesis to other anionic dialkyl ILs with different anions.

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13 See the Supporting Information for the details of the synthesis of AILPs, synthesis of dialkylimidazolium ILs with shorter chain substituents, and the calculation of dialkylimidazolium ILs yield. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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