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Thiazolium-ion based organic ionic liquids (OILs).[1,2] Novel OILs which promote the benzoin condensation.

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Abstract

4- and 5-methyl thiazole are readily alkylated with n-butyl bromide followed by anion exchange of Br^- for BF_4^- to give mobile, room-temperature ionic liquids. These liquids, when treated with small quantities of triethylamine, serve to promote the benzoin condensation of benzaldehyde. © 1999 Elsevier Science Ltd. All rights reserved.

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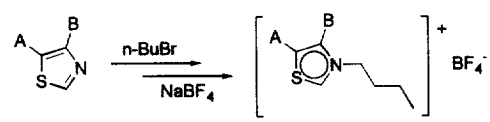
We have recently initiated research aimed at broadening the structural diversity of ions used for organic ionic liquid (OIL) formation, and to capitalize upon the potential for chemical reactivity by OIL-component ions. The first of these studies, in which we have reported the synthesis of OILs based upon the antifungal drug miconazole, has recently been published [1]. Here, we report the synthesis of two new ionic liquids, each of which acts to promote a classical organic reaction, the benzoin condensation [3,4].

Refluxing 4-methylthiazole (1) or 5-methylthiazole (2) in an excess of n-butyl bromide produces the respective 3-butyl-4/5-methylthiazolium bromides in quantitative yields [Scheme 1]. After ion exchange with $NaBF_4$ in methanol, the OILs 3 and 4 are isolated as stable, yellow-orange liquids.

Scheme 1



1 A = H, B = CH_3
2 A = CH_3, B = H

3 A = H, B = CH_3
4 A = CH_3, B = H

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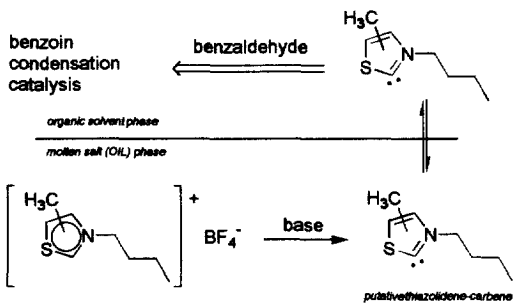
The ^{1}H-NMR spectra of the compounds are clean save for a small water peak and are consistent with the proposed cation structures, as are the ^{13}C-NMR spectra. FAB-MS data are also in accord with the proposed formulations [5].

After promotion with a small (~ 5 mol %) quantity of triethylamine, OILs 3 and 4 promote the coupling of benzaldehyde to benzoin. The reaction is accomplished when the promoted OIL is stirred under nitrogen as a clearly heterogeneous mixture with a toluene solution of benzaldehyde. Stirring together 1.5 g of either OIL with 200 mL of a 50% (v/v) solution of benzaldehyde in toluene gives in both cases approximately 80% conversion to benzoin after one week. Significantly, continued condensation of benzaldehyde is observed after decantation of the toluene layer from the OIL. We believe this observation to be consistent with a partitioning into the organic phase of the putative thiazolidene-carbene catalyst [Scheme 2].

Scheme 2



To our knowledge, OILs 3 and 4 are the first to be reported which incorporate a thiazolium cation, and as such represent a departure from common imidazolium- and pyridinium-ion based ionic liquids [2,8]. Additionally, our use of an OIL as a catalyst source compliments the demonstrated utility which ionic liquids exhibit as solvents for certain catalytic reactions and other processes [6-8]. Further studies by our group aimed at expanding the scope of OIL chemistry are currently underway.

References

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