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Synthesis of dioxanes via Prins reaction catalyzed by acyclic acidic ionic liquids

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ABSTRACT

Some recyclable acyclic SO_3H-functionalized ionic liquids have been used as environmentally benign catalysts for the synthesis of dioxanes by Prins reaction. The products could simply be separated from the catalysts by decantation. After separation from the reaction mixture the catalysts could be recycled and reused for several times without a noticeable decrease in the catalytic activity.

1. Introduction

The Prins reaction is an important carbon–carbon bond forming reaction in organic synthesis and usually used to the formation of dioxanes, unsaturated alcohols, etc. as the common products, which are widely used as solvents or intermediates [1]. Traditionally, dioxanes could be obtained via the Prins reaction carried out in the presence of strong protonic acid catalysts such as sulphuric acid and hydrochloric acid under the homogeneous conditions. However, the application of these mineral acids catalysts is limited due to their toxicity, corrosiveness, and the tedious work-up procedure [2]. Heterogeneous catalysts have also been used for the Prins reaction, including Lewis acids [3–5], Brønsted acids [6,7], solid acids [8–11], and other catalysts but with little success.

With the increasing public concern over environmental degradation and future resources, it is of great importance for chemists to come up with new approaches that are less hazardous to human health and environment [12,13]. Possessing the useful characteristics of solid acids and mineral acids, Brønsted acidic task-specific ionic liquids (TSILs) are designed to replace traditional mineral liquid acids, such as sulfuric acid and hydrochloric acid in chemical processes [14]. Such acidic TSILs have dual role (solvent and catalyst) in organic reactions [15–18]. Very recently, Wang et al. used TSILs containing imidazolium cation as catalysts for Prins reaction [19]. In fact, development and exploration of acidic TSILs are currently in the preliminary stage. However, TSILs with triphenylphosphinium or imidazolium as the cation are relatively expensive, which hinders their industrial applications. For economic and ecological reasons, there is a need to develop an environmentally benign method for the synthesis of 1,3-dioxanes.

We are especially interested in developing the potential use of efficient, environmentally benign TSILs catalysts. Hence, some novel SO_3H-functional halogen-free acidic ionic liquids that bear an alkane sulfonic acid group in an acyclic trialkylammonium cation have been synthesized and their catalytic activity for acid-catalyzed reactions has also been investigated in recent years [20–23]. In continuation of our work in studying acid-catalyzed reactions in ionic liquids, we wish to report here the synthesis of dioxanes via the Prins reaction catalyzed by acidic ionic liquids.

2. Experimental

2.1. Materials and methods

Melting points were determined on X-6 microscope melting apparatus. ^1H NMR spectra were recorded on Bruker DRX300 (300 or 500 MHz) and ^{13}C NMR spectra on Bruker DRX300 (75.5 MHz) spectrometer. Mass spectra were obtained with automated FININIGAN TSQ QUANTUM ULTRA AM (Thermal) LC/MS spectrometer. Qualitative and quantitative analysis of the product was obtained with automated FININIGAN Trace Ultra-Trace DSQ GC/MS spectrometer and Agilent 6870 GC spectrometer respectively. The conversions and the yields were determined by means of a GC chromatograph. The conversion and selectivity were calculated according to the concentration of reactant and product obtained. All chemicals (AR grade) were commercially available and used directly without further purification.

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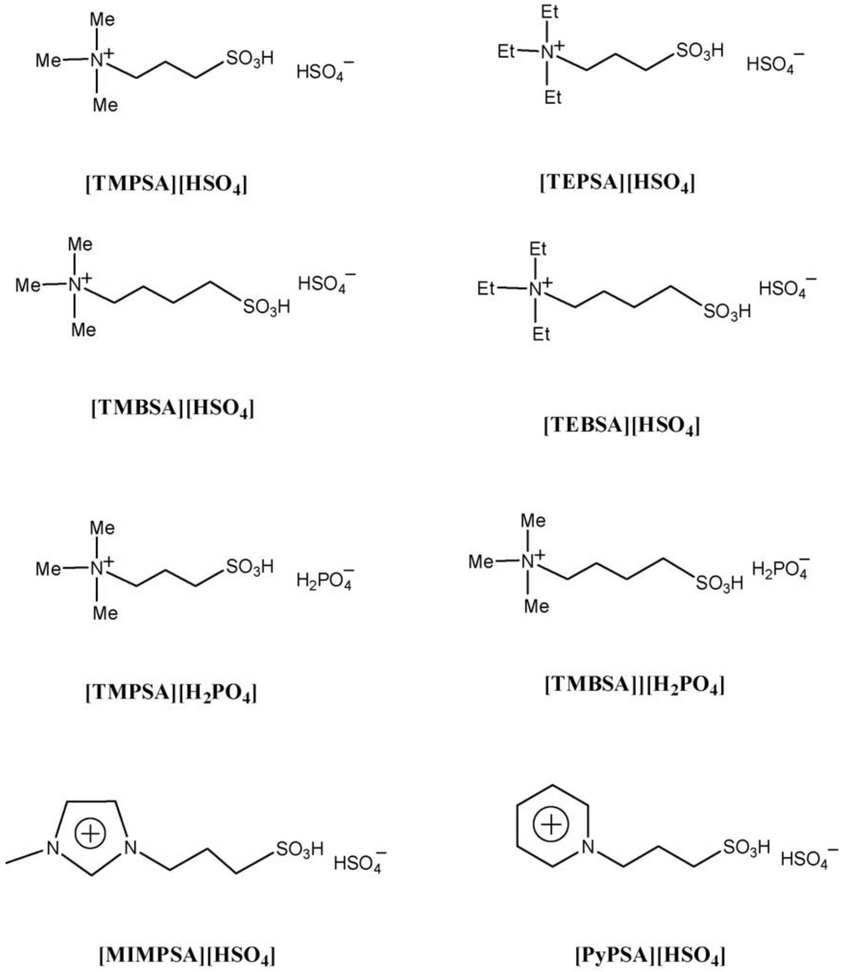

Scheme 1. Structures of the TSILs used in Prins reaction.

2.2. Synthesis of SO_3H-functional halogen-free acidic ionic liquid (TSILs)

For the present work, a series of TSILs were prepared and used as catalysts for synthesis of dioxanes. All acyclic SO_3H-functionalized halogen-free acids such as [TMPSA][HSO_4](N,N,N-trimethyl-N-propanesulfonic acid ammonium hydrogen sulfate), [TEPSA][HSO_4](N,N,N-triethyl-N-propanesulfonic acid ammonium hydrogen sulfate), [TMBSA][HSO_4](N,N,N-trimethyl-N-butanesulfonic acid ammonium hydrogen sulfate), [TEBSA][HSO_4](N,N,N-triethyl-N-butanesulfonic acid ammonium hydrogen sulfate), [TMPSA][H_2PO_4](N,N,N-trimethyl-N-propanesulfonic acid ammonium dihydrogen phosphate), and [TMBSA][H_2PO_4] (N,N,N-trimethyl-N-butanesulfonic acid ammonium dihydrogen phosphate) were synthesized according to our previous methods [20], the pyridine, imidazole-based SO_3H-functionalized ionic liquids for comparison were obtained according to reported methods [22]. The structures of TSILs (Scheme 1) were analyzed by ^1H NMR, ^{13}C NMR and MS spectral data.

The selected spectral data for SO_3H-functionalized halogen-free TSILs:

[TMPSA][HSO_4] ^1H NMR (300 MHz, D_2O): δ 3.22 (t, J = 7.2 Hz, 2H, N-CH_2-C-C-SO_3), 2.90 (s, 9H, N-CH_3), 2.73 (t, J = 7.8 Hz, 2H, N-C-C-CH_2-SO_3), 1.99 (m, 2H, N-C-CH_2-C-SO_3). ^{13}C NMR (75.5 MHz, D_2O): δ 65.00, 52.51, 47.89, 18.85. MS (m/z): 279.05 (M^+), 182.14 (100).

[TMPSA][H_2PO_4] ^1H NMR (300 MHz, D_2O): δ 3.20 (t, J = 7.2 Hz, 2H, N-CH_2-C-C-SO_3), 2.91 (s, 9H, N-CH_3), 2.71 (t, J = 7.8 Hz, 2H, N-C-C-CH_2-SO_3), 1.98 (m, 2H, N-C-CH_2-C-SO_3). ^{13}C NMR (75.5 MHz, D_2O): δ 64.20, 52.75, 47.90, 18.80. MS (m/z): 279.00 (M^+), 182.07 (100).

[TEPSA][HSO_4] ^1H NMR (300 MHz, D_2O): δ 3.22–3.05 (m, 8H, (6H + 2H), N-CH_2-CH_3, N-CH_2-C-C-SO_3), 2.85 (t, J = 7.2 Hz 2H, N-C-C-CH_2-SO_3), 1.97 (m, 2H, N-C-CH_2-C-SO_3), 1.12 (t, 9H, N-C-CH_3). ^{13}C NMR (75.5 MHz, D_2O): δ 56.00, 52.95, 48.34, 18.93, 8.04. MS (m/z): 321.05 (M^+), 322.05, 320.15, 194.05 (100).

[TMBSA][HSO_4] ^1H NMR (300 MHz, D_2O): δ 3.24 (t, J = 8.4 Hz, 2H, N-CH_2-C-C-C-SO_3), 2.99 (s, 9H, N-CH_3), 2.85 (t, J = 7.5 Hz, 2H, N-C-C-C-CH_2-SO_3), 1.82 (m, 2H, N-C-CH_2-C-C-SO_3), 1.70 (m, 2H, N-C-C-CH_2-C-SO_3). ^{13}C NMR (75.5 MHz, D_2O): δ 66.15, 53.16, 50.31, 21.46, 19.93. MS (m/z): 293.36 (M^+), 196.39 (100).

[TEBSA][HSO_4] ^1H NMR (300 MHz, D_2O): δ 3.15 (q, J = 7.2 Hz, 6H, N-CH_2-CH_3), 3.07 (t, J = 8.4 Hz, 2H, N-CH_2-C-C-C-SO_3), 2.82 (t, J = 7.2 Hz, 2H, N-C-C-C-CH_2-SO_3), 1.68 (m, 4H, N-C-C_2H_4-C-SO_3), 1.11 (t, J = 7.2 Hz, 9H, N-C-CH_3). ^{13}C NMR (75.5 MHz, D_2O): δ 56.21, 52.85, 50.32, 21.50, 20.20, 6.90. MS (m/z): 335.35 (M^+), 208.36 (100).

N-propanesulfonic acid pyridinium hydrogen sulfate [PyPSA][HSO_4] ^1H NMR (300 MHz, D_2O): δ 8.62 (d, J = 6.0 Hz, 2H, H-2, H-6), 8.30 (t, J = 7.8 Hz, 1H, H-4), 7.84 (t, J = 6.9 Hz, 2H, H-3, H-5), 4.51 (t, J = 7.5 Hz, 2H, N-CH_2-C-C-SO_3), 2.73 (t, J = 7.2 Hz, 2H, N-C-C-C-CH_2-SO_3), 2.18–2.23 (m, 2H, N-C-CH_2-C-SO_3). ^{13}C NMR (75.5 MHz, D_2O): δ 146.35, 144.70, 128.82, 60.28, 47.48, 26.47.