Catal Lett (2008) 121:77–80
DOI 10.1007/s10562-007-9295-2

[TMBSA][HSO_4] Ionic Liquid as Novel Catalyst for the Rapid Acetylation of Alcohols, Hydroxyesters and Phenols under Solvent-free Conditions

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Received: 29 May 2007 / Accepted: 4 October 2007 / Published online: 23 October 2007

Abstract Tri-methylammonium-butane sulfonate (TMBSA) ionic liquid (IL) catalyzed efficiently acetylation of acetic anhydride with various alcohols, hydroxyesters and phenols, under solvent-free conditions was described as a novel method. [TMBSA][HSO_4] ionic liquid (1.0 mol%) is able to promote quantitative acetylation at low temperature, in high conversion and selectivity (≥95%). The process is highly effective, environmentally benign, and very selective. Furthermore, [TMBSA][HSO_4] ionic liquid was conveniently separated with the products and easily recycled to catalyze acetylation reaction again with excellent yields.

Keywords Ionic liquid · TMBSA · Acetylation · Solvent-free

1 Introduction

With increasing environmental concerns and the regulatory constraints faced in the industry, the development of environmentally benign catalysts has become a crucial and demanding area in many modern organic reactions [1]. In recent years, ionic liquids (ILs) have attracted increasing interest and much attention has currently been focused on the organic reactions with ILs as catalysts or solvents and many organic reactions were performed in ILs with high performances [2–5]. Recently, the synthesis of "task-specific" ILs with special functions according to the requirement of a specific reaction has become an attractive field [6]. All these studies offered us the possibility of designing suitable catalysts for the appointed reaction.

The acetylation of alcohols and phenols is one of the most frequently used processes in organic synthesis. Numerous methods have been devised [7–9]. Recently, much attention has been focused on the acylation catalyzed with some novel catalysts. For instance, acylation could be proceeded using auminium triflate [7], 3-nitrobenzeneboronic acid [1], copper perchlorate [9], ferric perchlorate [10], Molecular iodine [11], Molecular iodine in isopropenyl acetate [7], $La(NO_3)_3{\cdot}6H_2O$ [12], *N*,*N*-dibromo-4-methylbenzenesulphonimide [13] and $NaHSO_4$ SiO_2 [14] using catalysts with high conversion and selectivity. However, most of these catalysts suffer from limitation such as long reaction time, expensive, harsh reaction conditions, moisture sensitive and toxicity etc. So, the suitable catalysts and new efficient methodologies are still in demand.

Herein, we report an efficient and environmentally friendly synthesis of acetylation by a number of alcohols, hydroxyesters and phenols with acetic anhydride, in excellent yield, in the presence of 1.0 mol% [TMBSA][HSO_4] ionic liquid at low temperature under solvent-free conditions in short times. To our knowledge, there is no literature report on acylation using functional acidic ionic liquids as catalyst. The product strctures were established through GC-MS.

2 Experimental

2.1 Preparation of Ionic Liquid [TMBSA][HSO_4]

The ionic liquid [TMBSA][HSO_4] used in the study, Scheme 1, was synthesized in accordance with the

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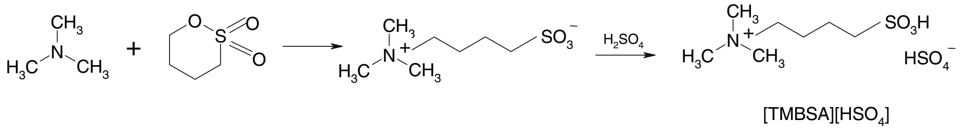
Scheme 1 Results of different runs in the experiment



procedures previously reported in the literature [15]. Therefore further purification was not necessary. As a novel functional Brønsted acidic IL, we find [TMBSA][HSO_4] is stable under an inert atmosphere.

2.2 Selected Spectral Data

NMR: ^{1}H NMR (DMSO, 500 MHz): δ_H 1.73 (2H, t, J = 8.0 Hz, –N–CH_2), 1.87 (2H, t, J = 8.0 Hz, –N–CH_2–CH_2–), 2.89 (2H, t, J = 7.0 Hz, –CH_2–), 3.03 (9H, m, –CH_3), 3.27 (2H, t, J = 4.0 Hz, –CH_2–S).

IR (ν/cm^{-1}): 3,394, 2,968, 1,481, 1,037 cm^{-1}.

2.3 General Procedure of Acetylation Reaction

In a typical reaction, reactants and the ionic liquid [TMBSA][HSO_4] as catalyst were added successively into a 100 mL round flask equipped with a thermometer, a magnetic stirrer, and a N_2-inlet valve. The reaction proceeded for a period of time ranging from 1 to 15 min with vigorous stirring. After the reaction, the mixture was placed for a while for the formation of two phases. The ionic liquid phase was simply separated and washed with ether, purified in vacuo and directly reused in subsequent runs. The upper organic phase was decanted and detected (Scheme 2).

$$\text{R-OH} \xrightarrow[\text{Ac}_2\text{O}]{[\text{TMBSA}][\text{HSO}_4]} \text{R-OAc}$$

Scheme 2

Qualitative and quantitative analysis was conducted with GC-MS (Agilent 6890 Series/5973 N) and GC (Agilent 6850), respectively. The concentration of reactant and product was directly given by the system of chemstation according to the area of chromatograph peak. Conversion and selectivity were calculated according to the concentration of reactant and product.

3 Results and Discussion

As shown in Table 1, rather pleasing results were obtained in the acetylation of acetic anhydride with various alcohols, hydroxyesters and phenols using [TMBSA][HSO_4] as catalyst.

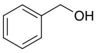
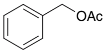
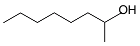
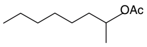
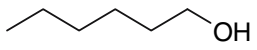
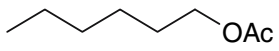
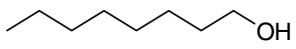
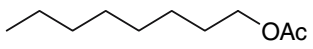
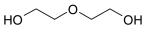
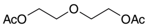
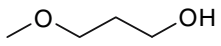
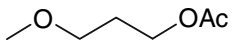
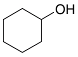
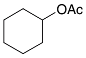
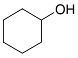
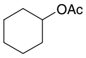
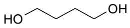
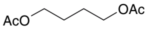
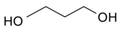
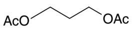
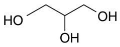
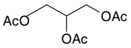
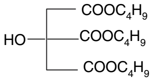
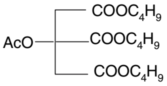
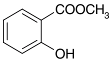
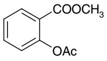
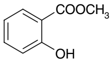
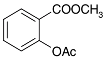
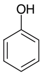
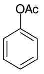
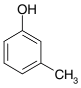
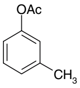
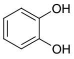
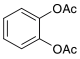
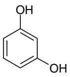
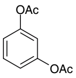
Through the experiment, we found that [TMBSA][HSO_4] exhibit the most excellent catalytic performance with high conversion and selectivity (≥95%) under mild reaction conditions (Table 1). Initially, a systematic study was carried out for catalytic evaluation of [TMBSA][HSO_4] for acetylation of benzyl alcohol with acetic acid without catalyst. No corresponding product was obtained. However, 1.0 mol % [TMBSA][HSO_4] as catalyst, a rapid acetylation occurred. Through the previor experiment, 1.0 mol% of catalyst was found to be effective for acetylation. Excess of acetic anhydride was necessary for the reaction to proceed at a reasonable rate and accelerate the solubility of solid substrates in the acetic anhydride. The structural properties of reactants in Table 1 were carefully examined and it was determined that the reaction time and temperature were affected by electronic and steric factors. High reaction temperature and long reaction time were needed when hydroxyl-esters were used as substrates due to steric hindrance and strong electron withdrawing effect (entries 12–14, Table 1). Reaction time of *o*-dihydroxybenzene is shorter than resorcin because high activity of *o*-dihydroxybenzene facilitates the shifting of the acetylation reaction equilibrium to the product side (entries 17,18, Table 1).

To investigate the reusability of [TMBSA][HSO_4] as a novel environmental friendly catalyst for acetylation reaction of acetic anhydride with various alcohols, hydroxyl-esters and phenols, we performed a series of recycle experiments. As ionic liquids have no detectable vapor pressure and are immiscibility with organic compounds or solvents, hence many environmental and safety problems associated with organic solvents are avoided [16]. Results from different runs were plotted in Fig. 1. Conversions from different runs remained nearly the same up to five cycles with the complete selectivity.

4 Conclusion

In summary, [TMBSA][HSO_4] was successfully prepared and utilized as an effective catalyst for acetylation reaction under solvent-free conditions. The use of [TMBSA][HSO_4] in acetylation reaction can be considered as an interesting new alternation. The product was easily separated with high conversion and selectivity. Furthermore, [TMBSA]

Table 1 Acetylation of alcohols, phenols, hydroxyester with acetic anhydride catalyzed by [TMBSA][HSO$_4$]

Entry	Substrate	Product	Mole ratio of substrate/ acetic anhydride	Temperature (°C)	Time (min)	Conversion (%)	Selectivity (%)
1			1:1.1	25	2	99	100
2			1:1.1	25	5	99	100
3			1:1.1	25	3	98	100
4			1:1.1	25	5	96	100
5			1:2.2	25	3	96	100
6			1:1.1	25	4	97	100
7			1:1.1	25	5	96	100
8			1:1.1	50	2	98	100
9			1:2.2	25	12	98	100
10			1:2.2	25	2	99	100
11			1:3.3	50	1	95	100
12			1:1.1	50	15	89	95
13			1:1.1	25	15	85.4	100
14			1:1.1	50	10	96	100
15			1:1.1	25	1	96	100
16			1:1.1	25	1	98	100
17			1:4.0	25	3	98	100
18			1:4.0	25	5	97	100

[a] Mole ratio of [TMBSA][HSO$_4$]/substrate all were 1.0 mol%

[b] Conversion and selectivity of product are based on GC-MS

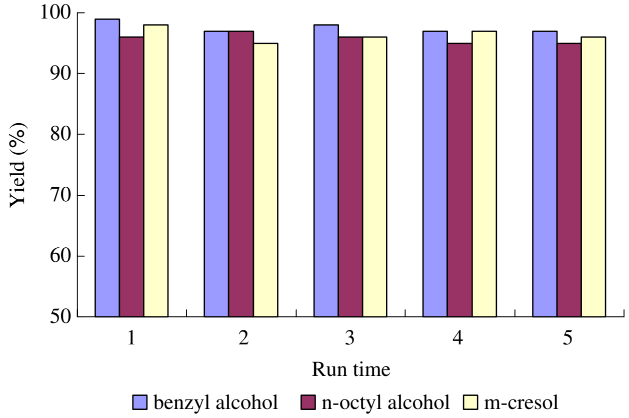


Fig. 1 Results of different runs in the experiment

[HSO$_4$] was conveniently separated from the products, easily recycled for another round of reaction and reused to produce almost identical results. No organic solvent was used. These will significantly reduce the effect of the reaction on environment and thus pave a way for the large scale applications. Further applications for other reaction systems are currently under investigation.

Acknowledgment We gratefully appreciate the financial support from the National Key Technology R&D Program (No. 2006BAE03B06).

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