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A new approach to the synthesis of diacetals (diketals) pentaerythritol catalyzed by SO_3H-functionalized ionic liquids

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Abstract

In this article, an efficient, simple and environmentally friendly approach to the synthesis of diacetals (diketals) pentaerythritol using SO_3H-functionalized ionic liquids (ILs) as catalysts was reported. The ILs show high catalytic activity and reusability with good to excellent yields of the desired products. Hammett method has been used to determine the acidity order of these ionic liquids and the results are consistent with the catalytic activities observed in acetalization reaction. Maximum product yield of 93% was observed on using [PSPy][OTf] as catalyst and it can be reused at least 8 times without obvious activity loss.

Keywords: SO3H-functionalized ionic liquids; Diacetals (diketals) pentaerythritol; Catalyze; Hammett method; Reusability

Acetals are biologically important due to their role in the chemistry of carbohydrates [1,2]. Also, in the fragrance and pharmaceutical industries, acetals are used both as intermediates and as end products [3,4]. Several publications have described the preparation of diacetals pentaerythritol under acidic conditions [5–7]. However, many of these reported methods suffer from drawbacks such as harsh reaction conditions, unsatisfactory yields, cumbersome product isolation procedures, large excess of aldehyde (ketones), volatile and hazardous organic solvents, which have to be recovered, treated and disposed of. Therefore, the design and development of highly active catalysts aimed at overcoming these limitations have proven to be a significant challenging task.

During the past decade, ionic liquids (ILs) have received considerable attention as environmentally friendly and effective reaction media for a wide variety of organic reaction and other applications in chemistry [8–10]. The introduction of specific functionality has led to the identification of functionalized ionic liquids (FILs, or task-specific ionic liquids, TSILs) [11]. Among different kinds of FILs, SO_3H-functionalized ILs have been intensively studied over the past five years, because the existence of SO_3H-functional groups can obviously enhance their acidities and water solubilities [12,13]. And we also have reported that FILs with benzimidazolium cations could efficiently catalyze the acetalization of aromatic aldehydes with diols [14,15]. As an extension to our previous work on FILs catalysis, we envisaged that SO_3H-functionalized ILs (Fig. 1.) would be able to promote the synthesis of diacetals (diketals)

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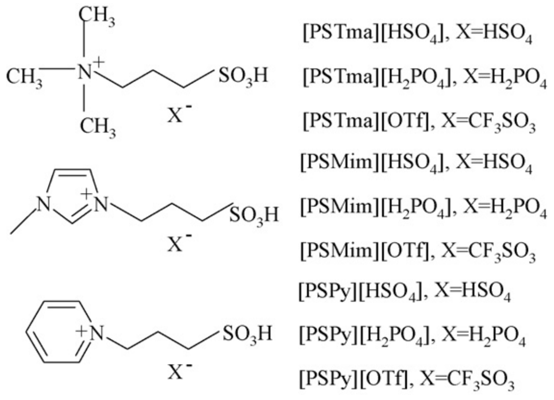

Fig. 1. Structures of SO_3H-functionalized ILs used in this paper.

pentaerythritol, and meanwhile maintain the biphasic properties of ionic liquid, thereby ensuring good recyclability and reusability. As far as we know, this is the first example of synthesis of diacetals (diketals) pentaerythritol in ILs.

1. Experimental

SO_3H-Functionalized ILs based on trimethylamine, 1-methylimidazole and pyridine were prepared according to the procedures reported by Cole *et al.* [16], Li *et al.* [17] and Xing *et al.* [18], respectively. The obtained ILs were identified by ^1H NMR and IR.

Typical procedure for the synthesis of diacetals (diketals) pentaerythritol: Weighted amounts of pentaerythritol, aldehyde (ketone) and ILs were added into a 25 mL round-bottom flask fitted with a reflux condenser. The acetalization was typically allowed to proceed for 1.5–4 h with vigorous stirring and maintained at the desired temperature. After the reaction, the mixture was placed for a while for the formation of two phases. The crude product was isolated by distillation and purified through recrystallization with ethanol as a solvent to give the title compound, which were characterized by FT-IR and ^1H NMR. The IL phase contained the produced water, could be easily recovered and reused in the next run after heat treatment under vacuum at 70 °C for 2 h.

2. Results and discussion

The measurement of the acidic scales of these SO_3H-functionalized ILs was conducted on an Agilent 8453 UV–vis spectrophotometer with a basic indicator according to the literature reported previously [15,16]. The maximal

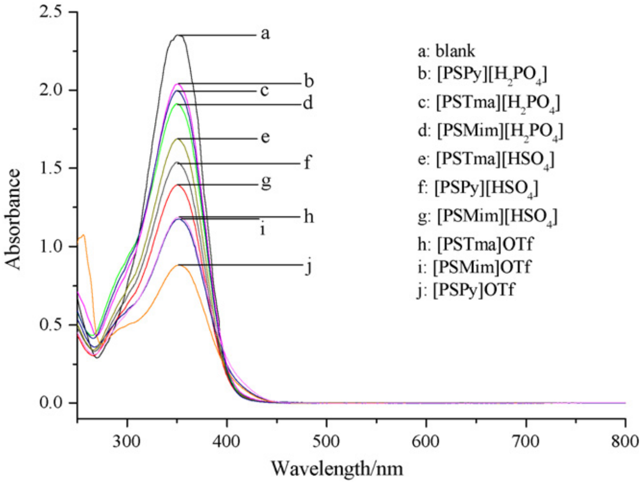

Fig. 2. Absorbance spectra of 4-nitroaniline for various SO_3H-functionalized ILs in CH_2Cl_2.

Table 1
Calculation and comparison of H_0 values of different SO_3H-functionalized ILs in CH_2Cl_2 (20 °C).

Entry	ILs	A_{max}	[I] (%)	$[IH^+]$ (%)	H_0
1	–	2.353	100.0	0	–
2	[PSTma][HSO_4]	1.689	71.8	28.2	1.40
3	[PSTma][H_2PO_4]	1.996	84.8	15.2	1.74
4	[PSTma][OTf]	1.184	50.3	49.7	1.00
5	[PSMim][HSO_4]	1.393	59.2	40.8	1.15
6	[PSMim][H_2PO_4]	1.912	81.3	18.7	1.63
7	[PSMim][OTf]	1.173	49.8	50.2	0.99
8	[PSPy][HSO_4]	1.537	65.3	34.7	1.26
9	[PSPy][H_2PO_4]	2.038	86.6	13.4	1.80
10	[PSPy][OTf]	0.882	37.5	62.5	0.77

Indicator: 4-nitroanline.

Table 2
Synthesis of dibenzalpentaerythritol catalyzed by various SO_3H-functionalized ILs.

Entry	ILs	Yield (%)[a]
1	[PSTma][HSO_4]	88
2	[PSTma][H_2PO_4]	86
3	[PSTma][OTf]	90
4	[PSMim][HSO_4]	88
5	[PSMim][H_2PO_4]	86
6	[PSMim][OTf]	90
7	[PSPy][HSO_4]	89
8	[PSPy][H_2PO_4]	86
9	[PSPy][OTf]	93

[a] Yield refers to isolated pure products: pentaerythritol (10 mmol), benzaldehyde (20 mmol), SO_3H-functionalized ILs (3 mmol), $T = 100$ °C, t = 1.5 h.

absorbance of the unprotonated form of the indicator was observed at 350 nm in CH_2Cl_2, Fig. 2. When an IL was added, the absorbance of the unprotonated form of the indicator decreased. Ultimately, we obtained the acidity order of the nine ILs with the following H_0 values (Table 1): [PSPy][OTf] (0.77) > [PSMim][OTf] (0.99) > [PSTma][OTf] (1.00) > [PSMim][HSO_4] (1.15) > [PSPy][HSO_4] (1.26) > [PSTma][HSO_4] (1.40) > [PSMim][H_2PO_4] (1.63) > [PSTma][H_2PO_4] (1.74) > [PSPy][H_2PO_4] (1.80), suggesting that the Brønsted acidity of [PSPy][OTf] was relatively stronger than the other eight ILs used in this work (Table 1, entries 2–10).

The reactants have good solubility in SO_3H-functionalized ILs while the diacetals and diketals are almost immiscible with ILs, which facilitate the shift of the equilibrium of acetalization reaction. The acetalization started as a homogeneous process and ended as biphasic. Table 2 shows the results of experiments carried out under the same

Table 3
Synthesis of pentaerythritol diacetals (diketals) catalyzed by IL [PSPy][OTf].

Entry	Aldehydes (Acetones)	Time (/h)	Yield (%)[a]	Mp (°C) Found	Mp (°C) Reported
1	Butyraldehyde	1.5	91	43–45	43–45
2	2-Furaldehyde	1.5	89	158–159	159–160
3	Benzaldehyde	1.5	93	155–156	155–156
4	2-Chloro benzaldehyde	1.5	94	141–142	141
5	4-Chloro benzaldehyde	1.5	94	201–202	200–201
6	4-Methoxy benzaldehyde	2.5	90	183–184	184–185
7	4-Methyl benzaldehyde	2.0	92	212–213	211–213
8	4-Nitro benzaldehyde	1.5	95	226–227	227–228
9	Acetophenone	3.0	86	147–148	147–148
10	Cyclohexanone	4.0	87	114–115	113–114

[a] Yield refers to isolated pure products: pentaerythritol (10 mmol), aldehyde (ketone) (20 mmol), [PSPy][OTf] (3 mmol), $T = 100$ °C.

Table 4
Recycling of the IL [PSPy][OTf] in the synthesis of dibenzalpentaerythritol.

Recycling time	1	2	3	4	5	6	7	8
Yield (%)[a]	93	93	92	93	92	91	91	90

[a] Yield refers to isolated pure products: pentaerythritol (10 mmol), aldehyde (ketone) (20 mmol), [PSPy][OTf] (3 mmol), $T = 100$ °C, t = 1.5 h.

reaction conditions for comparing the catalytic performances of these SO_3H-functionalized ILs. We found that [PSPy][Tf] might be best for the acetalization in all SO_3H-functionalized ILs, leading to 93% yield of dibenzalpentaerythritol. The sequence of catalytic activity observed in acetalization is in good agreement with the acidity order determined by the Hammett method. The increasing of the anion's Brønsted acidity of ILs improves the catalytic activity of the acidic ILs.

The acetalization of various aldehydes (ketones) with pentaerythritol has been investigated in IL [PSPy][OTf] (Table 3, entries 1–10). Ketones show less reactivity than aldehydes for this reaction, for example dibenzalpentaerythritol (Table 3, entry 3) was obtained in quantitative yield (93%) for 1.5 h whereas acetophenone (Table 3, entry 9) provided 86% yield of product for 3.0 h. As can be known from entries 3–8 in Table 3, a change in the substitutional group of the reactants impacts the yield of products. When 4-methoxybenzaldehyde (Table 3, entry 6) was treated with pentaerythritol in IL the reaction took longer (2.5 h) and the yield of di-4-methoxybenzal pentaerythritol was lower (90%), for the strong donor methoxy group reduced the reactivity. The reactivity order of aromatic aldehydes is 4-nitrobenzaldehyde > 4-chlorobenzaldehyde > benzaldehyde > 4-methylbenzaldehyde > 4-methoxybenzaldehyde, which is consistent with the report [19] that showed electron-withdrawing substituents enhanced the rate of acetal formation.

Compared with traditional acid catalysts, easy recycling is an attractive property of the acidic ILs. Consequently, we investigated the catalytic activity of recycled [PSPy][OTf] in the synthesis of dibenzalpentaerythritol. After acetalization the crude product could be conveniently isolated by distillation. The IL was assessed by ^{1}H NMR spectroscopy after treated under vacuum (0.01 T) at 70 °C for 2 h, and no traces of benzaldehyde and pentaerythritol were detected. As shown in Table 4, [PSPy][OTf] could be reused at least 8 times and the yield of dibenzalpentaerythritol was not less than 90%, which indicated that [PSPy][OTf] was highly efficient and recyclable catalyst for the synthesis of diacetals (diketals) pentaerythritol.

3. Conclusions

In conclusion, a new approach to the synthesis of diacetals (diketals) pentaerythritol was developed using SO_3H-functionalized ILs as catalysts. This catalytic system is stable, easily separable, and reusable. Furthermore, this series of SO_3H-functionalized ILs have higher catalytic activities under mild reaction condition without addition of any organic solvents or catalysts. Further investigations concerning the molecular geometries of these SO_3H-functionalized ILs and structure-catalytic activity relationship are currently underway.

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References

[1] D.M. Clode, Chem. Rev. 79 (1979) 491.
[2] J.J. Brown, R.H. Lenhard, S. Berstein, J. Am. Chem. Soc. 86 (1964) 2183.
[3] E. Saniger, J.M. Campos, A. Entrena, et al. Tetrahedron 59 (2003) 8017.
[4] K. Bruns, J. Conrad, A. Steigel, Tetrahedron 35 (1979) 2523.
[5] E. Bograchov, J. Am. Chem. Soc. 72 (1950) 2268.
[6] T.S. Jin, Y.S. Ma, Z.H. Zhang, Synth. Commun. 29 (1999) 1601.
[7] B. Rabindran Jermy, A. Pandurangan, Catal. Commun. 7 (2006) 921.
[8] T. Welton, Chem. Rev. 99 (1999) 2071.

[9] N. Gupta, G.L. Kad, J. Singh, Catal. Commun. 8 (2007) 1323.

[10] K. Hamza, H. Schumann, J. Blum, Eur. J. Org. Chem. 10 (2009) 1502.

[11] S.G. Lee, Chem. Commun. 10 (2006) 1049.

[12] X.M. Liu, M. Liu, X.W. Guo, et al. Catal. Commun. 9 (2008) 1.

[13] J.H. Olivier, F. Camerel, J. Selb, et al. Chem. Commun. 9 (2009) 1133.

[14] Y.Y. Wang, D. Jiang, L.Y. Dai, Catal. Commun. 9 (2008) 2475.

[15] Y.Y. Wang, W. Li, C.D. Xu, L.Y. Dai, Chin. J. Chem. 25 (2007) 68.

[16] A.C. Cole, J.L. Jensen, I. Ntai, et al. J. Am. Chem. Soc. 124 (2002) 5962.

[17] H.L. Li, S.T. Yu, F.S. Liu, et al. Catal. Commun. 8 (2007) 1759.

[18] H.B. Xing, T. Wang, Y.Y. Dai, et al. J. Mol. Catal. A: Chem. 264 (2007) 53.

[19] A. Clerici, N. Pastori, O. Porta, Tetrahedron 54 (1998) 15679.