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NOVEL ACIDIC IONIC LIQUIDS AS EFFICIENT AND RECYCLABLE CATALYSTS FOR THE CYCLOTRIMERIZATION OF ALDEHYDES

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GRAPHICAL ABSTRACT



Abstract A mild, efficient, and ecofriendly procedure for cyclotrimerization of aldehydes was realized by using a series of novel Bronsted acidic ionic liquids (BAILs) consisting of double– SO_3H groups in cations as catalysts. Good conversion of aldehydes and selectivity of trialkyl-1,3,5-trioxanes were achieved by using 1 mol% of BAILs. In addition, the catalyst system could be recycled and reused at least eight times without apparent loss of activity.

Keywords Acidic ionic liquid; aldehydes; cyclotrimerization; trialkyl-1,3,5-trioxane

INTRODUCTION

Cyclotrimerization of aldehydes is an important reaction in organic synthesis to produce corresponding 1,3,5-trioxanes, which are widely used in various fields as constituents of stabilizers in color photography,^[1] flavoring materials, and carriers for scents, repellents, deodorants,^[2] and insecticide.^[3] Catalysts used for this reaction were generally proton acids such as H_2SO_4 and H_3PO_4 ;^[4,5] Lewis acid such as ZnC_1 ;^[4] solid acid such as ZrO_2 , $Zr(OH)_2$, TiO_2 , SnO_2 ,^[5,6] Al₂O₃, Y-zeolite,^[7,8] sulfonic cation resin,^[9] Me₃Si-Cl,^[10] and Cp₂Zr(Otf)₂;^[11] and Keggintype heteropolyacids such as $H_3PM_{12}O_{40}$, $H_3PW_{12}O_{40}$, and $H_4SiW_{12}O_{40}$.^[12] Although good results were obtained, the drawback of corrosion and environmental pollution caused by liquid acid catalysts and the rapid deactivation of solid acids because of the buildup of coke made them impossible to apply in industry. Therefore, to design and synthesize new catalysts possessing novel properties of high stability, environmentally friendliness, and reusability has long been pursued.

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Scheme 1. Structures of novel acidic ILs used in this study.

Ionic liquids (ILs) have attracted interest as environmentally benign media for catalytic processes because of their favorable properties. Brønsted acidic ILs, which possess the advantageous characteristics of solid acids and liquid acids, have been designed to replace traditional mineral liquid acids, such as sulfuric acid and hydrochloric acid.^[13] In recent years, ILs as media or catalysts in the cyclotrimerization of aldehydes have been reported,^[14,15] affording a new approach for catalytic cyclotrimerization. With the aim of developing a clean, highly efficient catalyst system for the cyclotrimerization of aldehydes, we synthesized a series of novel functional acidic ILs [Bis-BsPy][HSO₄]₂ (Bs = butyl-sulfonyl, Py = pyridine), [Bis-BsPy][CF₃SO₃]₂, and [Bis-BsPy][Ts-OH]₂ (Ts-OH = p-toluenesulfonic acid) (Scheme 1), consisting of pyridine-based dications and acid anions, which are highly active, easily recyclable, and air and moisture stable.

Because of their unique structures, they have quite strong acidity and very poor solubility in common organic solvents except for ethanol and methanol. These novel acidic ILs exhibited high activities in cyclotrimerization of aldehydes (Scheme 2) compared with the normal acidic ILs [Bis-Bpy][HSO₄]₂ (B = butyl) and [BsPy] [CF₃SO₃]. Moreover, the unique immiscibility of the novel acidic ILs with organic solvents makes the separation of them after reaction very facile.



Scheme 2. Cyclotrimerization of aldehydes catalyzed by ILs.

The *cis-trans* configuration of trialkyl-1,3,5-trioxanes was also determined with isolated triisopropyl-1,3,5-trioxane and triethyl-1,3,5-trioxane as examples by NMR spectroscopy. There is only one set of signals in the ¹H and ¹³CNMR spectra, which indicated that the products are all *cis, cis* isomers.

RESULTS AND DISCUSSION

Originally, a probe reaction of the cyclotrimerization of isobutylaldehyde to form triisopropyl-1,3,5-trioxane was carried out at 25 °C for 60 min under solventfree conditions catalyzed by these acidic ILs, and the results are shown in Table 1. The isobutylaldehyde conversion was affected by either cations or anions of the ILs employed, while this effect on the triisopropyl-1,3,5-trioxane selectivity was slight, giving 99.6–99.9% over all the ILs catalysts. Good conversion of 97.6% was obtained over -SO₃H functionalized IL [Bis-BsPy][HSO₄]₂ (entry 2, Table 1), while for $[Bis-BPy][HSO_4]_2$, without $-SO_3H$ groups in side chains, moderate conversion of 85.2% was achieved (Entry 1, Table 1), which indicated the Brønsted acidity of the ILs is the main factor for the reaction. Among the $-SO_3H$ functionalized ILs, when the acidic ILs have the same cation, the conversion over IL with $CF_3SO_3^-$ anion was the best (Table 1, entries 2–4). It might be that the acidities of IL with $CF_3SO_3^-$ were stronger than those with Ts-OH⁻ or HSO₄⁻. Although it has the same CF₃SO₃⁻ anion, the IL containing a single -SO₃H group in the cation moiety gave less conversion, 93.7% (Table 1, entry 5). Even so, to the best of our knowledge, the results obtained here with our novel acidic ILs are better than that reported in the literature.^[14,15]

Because of the excellent catalytic performance in cyclotrimerization of isobutylaldehyde, we chose $[Bis-BsPy][CF_3SO_3]_2$ as the catalyst to investigate further the effect of the amount of IL, reaction temperature, and reaction time on the reaction, and the results are listed in Table 2.

The conversion of isobutylaldehyde passed through a maximum and then decreased as the amount of IL was increased. The greatest conversion was obtained when the amount of IL was 1.0% (entry 4, Table 2), but the selectivity to triisopropyl-1,3,5-trioxane was almost unchanged (Table 2, entries 1–5). It revealed that the cyclotrimerization of isobutyraldehyde needed suitable acidity. When IL/ isobutyraldehyde = 0.1%, the weak acidity in the system was not favorable for the catalytic reaction. With the increasing of [Bis-BsPy][CF₃SO₃]₂ concentration, the acidity inside the system went up and the reaction rate increased. However, too much strong acidivity could decompose triisopropyl-1,3,5-trioxane,^[16] so 1.0% of [Bis-BsPy] [CF₃SO₃]₂ is the best dosage for the reaction.

Table 1. Cyclotrimerization of isobutylaldehyde catalyzed by different ILs^a

Entry	IL	Conversion (%)	Selectivity (%)	
1	[Bis-Bpy][HSO ₄] ₂	85.2	99.6	
2	[Bis-BsPy][HSO ₄] ₂	97.6	99.8	
3	[Bis-BsPy][CF ₃ SO ₃] ₂	98.3	99.9	
4	[Bis-BsPy] [Ts-OH] ₂	90.2	99.7	
5	[BsPy][CF ₃ SO ₃]	93.7	99.8	

^{*a*}IL/isobutylaldehyde = 0.5% (molar ratio).

Entry	Molar ratio of IL/isobutylaldehyde	Temperature (°C)	Time (min)	Conversion (%)	Selectivity (%)
1	0.1%	25	60	91.4	99.7
2	0.2%	25	60	94.6	99.7
3	0.5%	25	60	98.3	99.8
4	1.0%	25	60	98.8	99.8
5	2.0%	25	60	90.7	99.6
6	1.0%	0	60	93.2	99.7
7	1.0%	10	60	95.9	99.7
8	1.0%	40	60	81.1	99.1
9	1.0%	60	60	61.6	98.5
10	1.0%	25	10	91.4	99.9
11	1.0%	25	30	98.4	99.8
12	1.0%	25	120	97.7	99.8

Table 2. Effect of different reaction conditions using [Bis-BsPy][CF₃SO₃]₂ as catalyst

From the data in Table 2, we can see that temperature had a dramatic effect on the cyclotrimerization of isobutylaldehyde (entries 4 and 6–9). When the temperature increased from 0 to $25 \,^{\circ}$ C, the conversion of isobutylaldehyde increased from 93.2% to 98.8%; with further increase of the temperature, the conversion and selectivity decreased because of the reversible reactions of cyclotrimerization of aldehydes and decomposition of trialkyl-1,3,5-trioxane in the presence of acid with increasing temperature.^[17]

The degree of isobutylaldehyde conversion was also influenced by reaction time (Table 2, entries 4 and 10–12). When the reactant was stirred only 10 min, the isobutylaldehyde conversion of 91.4% and triisopropyl-1,3,5-trioxane selectivity of 99.9% could be reached, suggesting the high efficiency of the IL catalyst. After 60 min, the whole reaction tended to equilibrium with the conversion and the selectivity reached 98.8% and 99.8%.

The applicability of this catalytic system for other aliphatic aldehydes was also studied, and the results are summarized in Table 3. All of the aliphatic aldehydes examined were converted into the corresponding trialkyl-1,3,5-trioxane with high

Entry	Aldehyde	Conversion (%)	Selectivity (%)	
1	CH ₃ CH ₂ CHO	93.4	99.8	
2	CH ₃ (CH ₂) ₂ CHO	90.1	99.4	
3	(CH ₃) ₂ CHCHO	98.8	99.8	
4	(CH ₃) ₂ CHCH ₂ CHO	58.2	99.6	
5 ^b	CH ₃ (CH ₂) ₃ CHO	62.5	99.9	
6^b	CH ₃ (CH ₂) ₄ CHO	63.4	99.8	
7^b	CH ₃ (CH ₂) ₆ CHO	52.2	99.7	

Table 3. Cyclotrimerization of several aliphatic aldehydes catalyzed by [Bis-BsPy][CF₃SO₃]₂^a

^{*a*}Aldehyde (30 mmol), [Bis-BsPy][CF₃SO₃]₂/aldehyde = 1% (molar ratio), reaction temperature 25 °C, reaction time 60 min.

^b[Bis-BsPy][CF₃SO₃]₂/aldehyde = 2% (molar ratio).



Figure 1. Recycling of [Bis-BsPy][CF₃SO₃]₂ in the cyclotrimerization of isobutylaldehyde. Reaction conditions: isobutylaldehyde (30 mmol), [Bis-BsPy][CF₃SO₃]₂/isobutylaldehyde = 1% molar ratio, reaction temperature 25 °C, reaction time 60 min.

selectivity. Table 3 showed that the conversion of aliphatic aldehydes decreased with the growth of the carbon chain (Table 3, entries 1-2 and 5-7) and the cyclotrimerization of stright-chain aldehydes was more difficult compared with that of branched-chain aldehydes, which has the same number of carbons (Table 3, entries 2-5). We considered that the reason was the nucleophilic addition feature of the cyclotrimerization. Therefore, the reaction depends dramatically on the steric hindrance and the stabilization of the carbonium ion. The increasing length of the carbon chain enhanced the steric hindrance, which leads to the decrease of nucleophilic ability, and the branched chain may favor the formation of the stable carbonium ion and enhanced nucleophilic ability.

One of the greatest advantages of using ILs as catalysts is the convenient recovery because of unique solubility. The ILs with double $-SO_3H$ functional groups are hardly soluble in common organic solvents except for methanol and ethanol. The immiscibility of [Bis-BsPy][CF₃SO₃]₂ with *n*-hexane and the good solubility of triisopropyl-1,3,5-trioxane in *n*-hexane make the separation of the catalyst quite facile. After reaction, the IL was extracted by *n*-hexane (5 mL × 3) and vacuumized for 2 h at 80 °C for another cycle. The reusability of the recycled catalyst is shown in Fig. 1. It could be seen that [Bis-BsPy][CF₃SO₃]₂ was utilized repeatedly more than eight times without any apparent loss of conversion and selectivity.

CONCLUSION

In conclusion, a highly effective catalytic cyclotrimerization of aliphatic aldehydes using 1 mol% novel Brønsted acidic ILs as catalysts was successfully processed under mild reaction conditions, the conversion and selectivity could be up to 98.8% and 99.8%, respectively. The IL could be separated by extraction with *n*-hexane, and the activity did not change when it was recycled eight times. The present study shows that the novel double functional acidic ILs have potential application in the production of trialkyl-1,3,5-trioxane.

EXPERIMENTAL

Measurements

¹H NMR spectra and ¹³C NMR spectra in D_2O were recorded on an Inova 400-MHz instrument using tetramethylsilane (TMS) as internal standard. Elementary analysis were obtained with an Elementar Vario EL cube instrument. The products were identified and quantitatively analyzed by gas chromatography/mass spectrometry (GC/MS) (Agilent 7890/5975C) and GC (Agilent 6890 equipped with a SE-54 capillary column).

[Bis-BsPy][HSO₄]₂

4,4'-Di-(butyl-4-sulfonate) dipyridine was prepared according to a similar procedure.^[18] A mixture of 1,4-butanesultone and 4,4'-dipyridine in toluene was stirred at 80 °C for 12 h (molar ratio of 1,4-butanesultone to 4,4'-dipyridine is 2.1:1). After the reaction was completed, the obtained solid was filtered, washed with toluene and ether, and dried in vacuo. 4,4'-Di-(butyl-4-sulfonate) dipyridine was obtained as a white powdery solid in 89% yield. A stoichiometric amount of H₂SO₄ was added dropwise to 4,4'-di-(butyl-4-sulfonate) dipyridine. The mixture was stirred for 8 h at 60 °C to form the IL [Bis-BsPy][HSO₄]₂. The IL phase was then washed with toluene and dried in vacuo. The product was a yellow viscous liquid. Yield: 96%. ¹H NMR D₂O (δ ppm): 1.613 (h, *J*=7.7 Hz, 4 H), 2.005 (h, *J*=7.6 Hz, 4 H), 2.757 (t, *J*=7.6 Hz, 4 H), 4.538 (t, *J*=7.4 Hz, 4 H), 8.313 (d, *J*=6.4 Hz, 4 H), 9.880 (d, *J*=6.8 Hz, 4 H); ¹³C NMR D₂O (δ ppm): 20.735, 29.185, 49.781, 61.297, 126.940, 145.328, 149.989. Anal. calcd. for C₁₈H₂₈N₂O₁₄S₄: C, 34.61; H, 4.52; N, 4.49; S, 20.53. Found: C, 34.74; H, 4.56; N, 4.45; S, 20.43.

[Bis-BsPy][CF₃SO₃]₂, [Bis-Bspy] [Ts-OH]₂, and [BsPy][CF₃SO₃]

The procedure was the same as described for the preparation of [Bis-BsPy] [HSO₄]₂, and a yellow viscous liquid was obtained.

[Bis-BsPy][CF₃SO₃]₂. ¹H NMR D₂O (δ ppm): 1.747 (h, J=7.7Hz, 4 H), 2.147 (h, J=7.6Hz, 4 H), 2.895 (t, J=7.6Hz, 4 H), 4.679 (t, J=7.2Hz, 4 H), 8.446 (d, J=6.8Hz, 4 H), 9.027 (d, J=7.2Hz, 4 H); ¹³C NMR D₂O (δ ppm): 20.789, 29.260, 49.806, 61.380, 121.102 (J_{C-F} =315.3Hz CF₃), 126.226, 145.410, 150.095. Anal. calcd. for C₂₀H₂₆N₂O₁₂S₄F₆: C, 32.97; H, 3.60; N, 3.85; S, 17.60. Found: C, 32.80; H, 3.61; N, 3.51; S,17.58.

[Bis-BsPy] [Ts-OH]₂. ¹H NMR D₂O (δ ppm): 1.589 (h, J = 7.7 Hz, 4 H), 1.950 (h, J = 7.7 Hz, 4 H), 2.103 (s, 6 H), 2.738 (t, J = 7.6 Hz, 4 H), 4.464 (t, J = 7.2, 4 H), 7.052 (d, J = 8.0 Hz, 4 H), 7.380 (d, J = 8.0 Hz, 4 H), 8.190 (d, J = 6.4 Hz, 4 H), 8.796 (d, J = 6.8 Hz, 4 H); ¹³C NMR D₂O (δ ppm): δ 20.339, 20.792, 29.253, 49.795, 61.309, 125.184, 126.783, 129.556, 139.302, 142.253, 145.246, 149.528. Anal. calcd. for C₃₂H₄₀N₂O₁₂S₄: C, 49.73; H, 5.22; N, 3.62; S, 16.59. Found: C, 49.79; H, 5.16; N, 3.58; S, 17.01.

[BsPy][CF₃SO₃]. ¹H NMR D₂O (δ ppm): 1.635 (h, J = 7.8 Hz, 2 H), 2.027 (h, J = 7.6 Hz, 2 H), 2.816 (t, J = 7.6 Hz, 2 H), 4.512 (t, J = 7.6 Hz, 2 H), 7.923 (t, J = 7.2 Hz, 2 H), 8.416 (t, J = 4.6 Hz, 1 H), 8.725 (d, J = 5.6 Hz, 2 H); ¹³C NMR D₂O (δ ppm): 20.779, 29.236, 49.851, 61.108, 117.956 ($J_{C-F} = 315.4$ Hz CF₃), 128.214, 144.157, 145.590. Anal. calcd. for C₁₀H₁₄NO₆S₂F₃: C, 32.88; H, 3.86; N, 3.83; S, 17.55. Found: C, 32.71; H, 3.73; N, 3.87; S, 17.69.

[Bis-Bpy][HSO₄]₂

A stoichiometric amount of 1-bromobutane was added dropwise to a solution of 4,4'-dipyridine in toluene within an hour (molar ratio of 1-bromobutane to 4,4'-dipyridine is 2.1:1), and then the mixture was stirred at 80 °C for 12 h. The obtained white powdery solid was filtered, washed with toluene and ether, and dried in vacuo to afford pure 4,4'-dibutyl dipyridine bromide. Yield: 92%. The white powder and H₂SO₄ were mixed in a molar ratio of 1:2 in anhydrous toluene and heated at 60 °C for 8 h, followed by washing with toluene and drying in vacuo to obtain the final IL. The product was a yellow viscous liquid. Yield: 91%. ¹H NMR D₂O (δ ppm): 0.759 (t, *J*=7.2 Hz, 6 H), 1.195 (m, *J*=7.5 Hz, 4 H), 1.858 (h, *J*=7.5 Hz, 4 H), 4.520 (t, *J*=7.4 Hz, 4 H), 8.330 (d, *J*=6.4 Hz, 4 H), 8.890 (d, *J*=6.8 Hz, 4 H). ¹³C-NMR D₂O (δ ppm): 12.512, 18.606, 32.447, 61.834, 126.780, 145.272, 149.812; Anal. calcd. for C₁₈H₂₈N₂O₈S₂ : C, 46.54; H, 6.08; N, 6.03; S, 13.80. Found: C, 46.46; H, 5.93; N, 6.02; S, 13.78.

Typical Procedure

In a 50-mL three-necked flask equipped with a thermometer, a reflux condenser and a N₂-inlet valve, aldehyde (30 mmol) and IL (0.03-0.6 mmol) were added. The reaction mixture was stirred at 0–60 °C for 10–120 min. After reaction, *n*-hexane was added to the flask to dissolve the crystals, the products were identified and quantitatively analyzed by GC/MS (Agilent 7890/5975C) and GC (Agilent 6890 equipped with a SE-54 capillary column).

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