

# Hydrophobic *N,N*-Diarylammonium Pyrosulfates as Dehydrative Condensation Catalysts under Aqueous Conditions

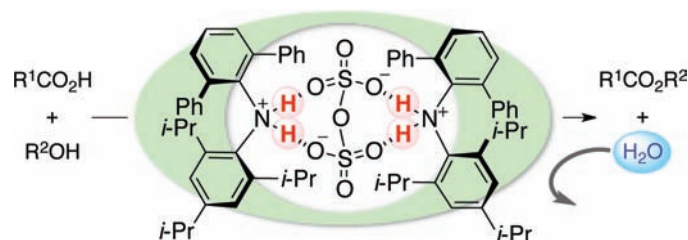
Akira Sakakura,<sup>†</sup> Yoshiki Koshikari,<sup>‡</sup> Matsujiro Akakura,<sup>§,||</sup> and Kazuaki Ishihara<sup>\*,‡,||</sup>

*EcoTopia Science Institute, Nagoya University, Japan, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan, Department of Chemistry, Aichi University of Education, Japan, and JST, CREST, Japan*

ishihara@cc.nagoya-u.ac.jp

Received October 12, 2011

## ABSTRACT



Oil-soluble *N,N*-diarylammonium pyrosulfates as nonsurfactant-type catalysts for the dehydrative ester condensation under aqueous conditions are described. Preheat treatment of dibasic sulfuric acid with bulky *N,N*-diarylamines generates water-tolerant salts of pyrosulfuric acid as active catalyst species. The present catalysts in water can also widely be applied to unusual selective esterifications and dehydrative glycosylation.

Water is a cheap, safe, and environmentally benign solvent when compared with organic solvents. Use of water will reduce the use of harmful organic solvents and is regarded as an important subject in green chemistry. In addition, water has unique physical and chemical properties, which allow us to realize reactivities that cannot be attained in organic solvents. Therefore, the use of water as a reaction solvent has received much attention in synthetic organic chemistry.<sup>1</sup> The dehydrative ester condensation reaction is one of the most fundamental organic transformation reactions.<sup>2</sup> Although several efficient catalysts have been exploited for the direct dehydrative ester condensation of an equimolar mixture of carboxylic acids and

alcohols, it is very difficult to conduct the dehydrative condensation in water, since a large amount of water also promotes hydrolysis of the condensation products. In 2001, Kobayashi and colleagues reported the dehydrative ester condensation between long-chain fatty acids and long-chain alcohols in water using *p*-dodecylbenzenesulfonic acid (DBSA) as a surfactant-type catalyst.<sup>3</sup> They claimed that DBSA and long-chain substrates would form emulsion droplets in water to accelerate the dehydration

<sup>†</sup> EcoTopia Science Institute, Nagoya University.

<sup>‡</sup> Graduate School of Engineering, Nagoya University.

<sup>§</sup> Department of Chemistry, Aichi University of Education.

<sup>||</sup> CREST.

(1) (a) Lindström, U. M., Ed. *Organic Reactions in Water*; Blackwell, Oxford, 2007. (b) Li, C.-J.; Chen, L. *Chem. Soc. Rev.* **2006**, *35*, 68. (c) Uozumi, Y.; Yamada, Y. M. A. *Chem. Rec.* **2009**, *9*, 51. (d) Raj, M.; Singh, V. K. *Chem. Commun.* **2009**, 6687. (e) Chanda, A.; Fokin, V. V. *Chem. Rev.* **2009**, *109*, 725.

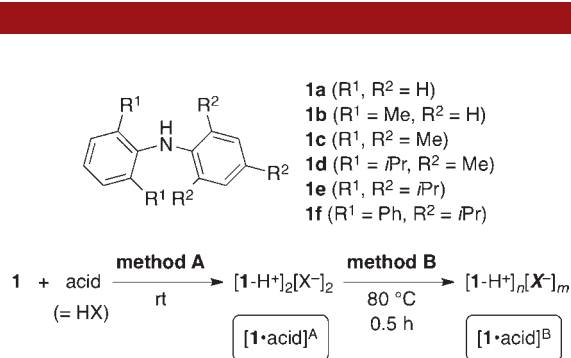
(2) (a) Ishihara, K. *Tetrahedron* **2009**, *65*, 1085. (b) Otera, J.; Nishikido, J. *Esterification*, 2nd ed.; WILEY-VCH: Weinheim, 2010.

(3) (a) Manabe, K.; Sun, X.-M.; Kobayashi, S. *J. Am. Chem. Soc.* **2001**, *123*, 10101. (b) Kobayashi, S.; Imura, S.; Manabe, K. *Chem. Lett.* **2002**, *31*, 10. (c) Manabe, K.; Imura, S.; Sun, X.-M.; Kobayashi, S. *J. Am. Chem. Soc.* **2002**, *124*, 11971. (d) Aoyama, N.; Kobayashi, S. *Chem. Lett.* **2006**, *35*, 238. (e) Shirakawa, S.; Kobayashi, S. *Org. Lett.* **2007**, *9*, 311.

(4) (a) Ishihara, K.; Nakagawa, S.; Sakakura, A. *J. Am. Chem. Soc.* **2005**, *127*, 4168. (b) Sakakura, A.; Nakagawa, S.; Ishihara, K. *Tetrahedron* **2006**, *62*, 422. (c) Sakakura, A.; Watanabe, H.; Nakagawa, S.; Ishihara, K. *Chem.—Asian J.* **2007**, *2*, 477. (d) Sakakura, A.; Nakagawa, S.; Ishihara, K. *Nat. Protoc.* **2007**, *2*, 1746.

(5) (a) Wakasugi, K.; Misaki, T.; Yamada, K.; Tanabe, Y. *Tetrahedron Lett.* **2000**, *41*, 5249. (b) Funatomi, T.; Wakasugi, K.; Misaki, T.; Tanabe, Y. *Green Chem.* **2006**, *8*, 1022. (c) Gacem, B.; Jenner, G. *Tetrahedron Lett.* **2003**, *44*, 1391. (d) Mercs, L.; Pozzi, G.; Quici, S. *Tetrahedron Lett.* **2007**, *48*, 3053.

reactions. Previously, we developed bulky *N,N*-diarylammonium pentafluorobenzenesulfonates as mild and highly active dehydrative ester condensation catalysts.<sup>4,5</sup> They successfully catalyze the reaction of an equimolar mixture of carboxylic acids and alcohols in less polar solvents such as heptane, even without the removal of the water produced. The high catalytic activity is attributed to the hydrophobic effect of bulky aryl groups of the catalysts.<sup>4c</sup> However, these bulky *N,N*-diarylammonium salt catalysts are almost inert under aqueous conditions, probably due to the transfer of pentafluorobenzenesulfonic acid to the aqueous layer. We report here the dehydrative ester condensation reactions catalyzed by *N,N*-diarylammonium pyrosulfates under aqueous conditions.



**Figure 1.** *N,N*-Diarylammonium salt catalysts [1•acid] for the dehydrative ester condensation in water.

We first examined the catalytic activities of various Brønsted acids and their ammonium salts with bulky *N,N*-diarylamine **1d**<sup>4</sup> (Figure 1) under aqueous conditions. The reaction of 4-phenylbutyric acid (1.1 equiv) with 1-dodecanol (4 mmol) was conducted in water (2 mL) at 60 °C for 6 h (Table 1). As a result, hydrophilic Brønsted acids such as trifluoromethanesulfonic acid (TfOH), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), *p*-toluenesulfonic acid (TsOH), 10-camphorsulfonic acid (CSA), and pentafluorobenzenesulfonic acid (C<sub>6</sub>F<sub>5</sub>SO<sub>3</sub>H) were almost inert under aqueous conditions,<sup>6</sup> although they can catalyze the same reaction in less polar solvents,<sup>4</sup> ionic liquids,<sup>7</sup> or under solvent-free conditions.<sup>8</sup> *N,N*-Diarylammonium salts, which were represented as [1•acid]<sup>A</sup>, were prepared by mixing an equimolar amount of **1d** and an acid in a homogeneous solution at ambient temperature and then evaporation of the solvent (method A). [1•acid]<sup>A</sup> would be dimeric complexes composed of two *N,N*-diarylammonium cations and two sulfonate anions: [ArNH<sub>2</sub><sup>+</sup>]<sub>2</sub>[X<sup>-</sup>]<sub>2</sub>, based on X-ray crystallographic analysis of [1a•H<sub>2</sub>SO<sub>4</sub>]<sup>A</sup>.<sup>4c,9</sup>

(6) Liu, Y.; Lotero, E.; Goodwin, J. G., Jr. *J. Mol. Catal. A: Chem.* **2006**, *245*, 132.

(7) (a) Wells, T. P.; Hallett, J. P.; Williams, C. K.; Welton, T. *J. Org. Chem.* **2008**, *73*, 5585. (b) Jiang, T.; Chang, Y.; Zhao, G.; Han, B.; Yang, G. *Synth. Commun.* **2004**, *34*, 225.

(8) Sakakura, A.; Koshikari, Y.; Ishihara, K. *Tetrahedron Lett.* **2008**, *49*, 5017.

(9) See Supporting Information for details.

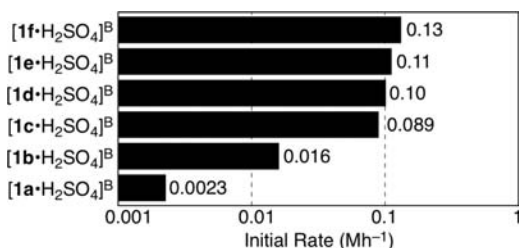
Disappointingly, [1•acid]<sup>A</sup> also gave similar results with the corresponding acids (data are not shown). Next, [1•acid]<sup>A</sup> were heated at 80 °C for 0.5 h (method B) before being used as catalysts for the dehydrative condensation reaction (Figure 1). *N,N*-Diarylammonium salts prepared by method B are represented as [1•acid]<sup>B</sup>. Very surprisingly, [1•H<sub>2</sub>SO<sub>4</sub>]<sup>B</sup>, which was a salt of extremely hydrophilic H<sub>2</sub>SO<sub>4</sub>, showed excellent catalytic activity under aqueous conditions and gave 1-dodecyl 4-phenylbutyrate in 85% yield. In contrast, *N,N*-diarylammonium salts of sulfonic acids [1•RSO<sub>3</sub>H]<sup>B</sup> were almost inert.

**Table 1.** Catalytic Activities of Brønsted Acids and Their Ammonium Salts with **1d** in Water<sup>a</sup>

acid [pK <sub>a</sub> ] <sup>b</sup>	yield of ester (%) <sup>c</sup>	[1•acid] <sup>B</sup>	yield of ester (%) <sup>c</sup>
TfOH [-0.74]	6	[1•TfOH] <sup>B</sup>	9
H <sub>2</sub> SO <sub>4</sub> [7.0]	15	[1•H <sub>2</sub> SO <sub>4</sub> ] <sup>B</sup>	<b>85</b>
TsOH [8.5]	23	[1•TsOH] <sup>B</sup>	11
CSA [9.0]	9	[1•CSA] <sup>B</sup>	7
C <sub>6</sub> F <sub>5</sub> SO <sub>3</sub> H [9.2]	11	[1•C <sub>6</sub> F <sub>5</sub> SO <sub>3</sub> H] <sup>B</sup>	13

<sup>a</sup> Conditions: 4-phenylbutyric acid (1.1 equiv), 1-dodecanol (4 mmol), and catalyst (5 mol %) in water (2 mL) at 60 °C for 6 h. <sup>b</sup> pK<sub>a</sub> values were measured in CD<sub>3</sub>CO<sub>2</sub>D. <sup>c</sup> Determined by <sup>1</sup>H NMR analysis.

The catalytic activities of [1•H<sub>2</sub>SO<sub>4</sub>]<sup>B</sup>, which were assessed by their initial rates (*v*<sub>i</sub>) of the dehydrative ester condensation under aqueous conditions, significantly depended on the steric bulkiness around ammonium protons (Figure 2).<sup>4b</sup> The use of *N,N*-diarylamines **1c–f** bearing substituents at each *ortho*-position successfully accelerated the reaction. The most sterically hindered [1f•H<sub>2</sub>SO<sub>4</sub>]<sup>B</sup> showed the highest catalytic activities. The catalytic activity of [1f•H<sub>2</sub>SO<sub>4</sub>]<sup>B</sup> (*v*<sub>i</sub> = 0.13 M h<sup>-1</sup>) was almost the same as that of DBSA (*v*<sub>i</sub> = 0.13 M h<sup>-1</sup>) and was ca. 60 times higher than that of [1a•H<sub>2</sub>SO<sub>4</sub>]<sup>B</sup> (*v*<sub>i</sub> = 0.0023 M h<sup>-1</sup>) under aqueous conditions.



**Figure 2.** Initial rates [M h<sup>-1</sup>] of ester condensation in water using [1•H<sub>2</sub>SO<sub>4</sub>]<sup>B</sup> (5 mol %). Conditions: 4-phenylbutyric acid (1.1 equiv) and 1-dodecanol (4 mmol) in water (2 mL) at 40 °C.

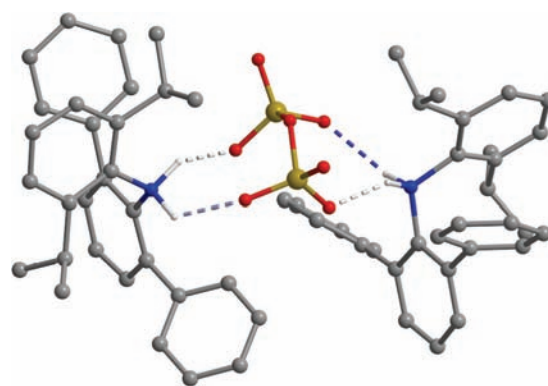
Next,  $[\mathbf{1}\bullet\text{H}_2\text{SO}_4]^{\text{A}}$  and  $[\mathbf{1}\bullet\text{H}_2\text{SO}_4]^{\text{B}}$  were compared by  $^1\text{H}$  NMR in  $\text{CD}_3\text{CN}$  (Table 2). Based on chemical shifts of the ammonium protons, the active catalyst  $[\mathbf{1}\bullet\text{H}_2\text{SO}_4]^{\text{B}}$  prepared by heat treatment (method B) was a species different from  $[\mathbf{1}\bullet\text{H}_2\text{SO}_4]^{\text{A}}$ , a simple salt of  $\mathbf{1}\mathbf{f}$  and  $\text{H}_2\text{SO}_4$ . In the case of  $[\mathbf{1}\mathbf{a}\bullet\text{H}_2\text{SO}_4]^{\text{A}}$  and  $[\mathbf{1}\mathbf{a}\bullet\text{H}_2\text{SO}_4]^{\text{B}}$ , both of which were almost inert under aqueous conditions, the chemical shift of the ammonium protons also shifted downfield by the heat treatment (7.19  $\rightarrow$  8.34 ppm). However,  $[\mathbf{1}\mathbf{a}\bullet\text{H}_2\text{SO}_4]^{\text{B}}$  was labile and gradually decomposed to  $[\mathbf{1}\mathbf{a}\bullet\text{H}_2\text{SO}_4]^{\text{A}}$  in  $\text{CD}_3\text{CN}$  at 60  $^\circ\text{C}$  for 6 h (8.34  $\rightarrow$  7.29 ppm), while  $[\mathbf{1}\mathbf{f}\bullet\text{H}_2\text{SO}_4]^{\text{B}}$  was stable under the same conditions.<sup>9</sup> In addition, the alkaline titration experiment showed that, in the case of  $[\mathbf{1}\mathbf{f}\bullet\text{H}_2\text{SO}_4]^{\text{B}}$ , only 29% of  $\text{H}_2\text{SO}_4$  was leaked to the aqueous layer, while large amounts of  $\text{H}_2\text{SO}_4$  were included in the aqueous layer in the cases of  $[\mathbf{1}\mathbf{f}\bullet\text{H}_2\text{SO}_4]^{\text{A}}$  and  $[\mathbf{1}\mathbf{a}\bullet\text{H}_2\text{SO}_4]^{\text{B}}$ .

**Table 2.** Comparison of *N,N*-Diarylammonium Salt Catalysts Prepared by Methods A and B

catalyst	yield of ester (%) <sup>a</sup>	chemical shift	content of $\text{H}_2\text{SO}_4$ in aq layer (%)
		of $\text{NH}_2$ in $\text{CD}_3\text{CN}$ (ppm)	
$[\mathbf{1}\mathbf{f}\bullet\text{H}_2\text{SO}_4]^{\text{A}}$	10	7.59	75
$[\mathbf{1}\mathbf{f}\bullet\text{H}_2\text{SO}_4]^{\text{B}}$	85	9.01	29
$[\mathbf{1}\mathbf{f}\bullet\text{H}_2\text{SO}_4(\text{SO}_3)_x]^{\text{A}}$	82	9.18	34
$[\mathbf{1}\mathbf{a}\bullet\text{H}_2\text{SO}_4]^{\text{A}}$	9	7.19	81
$[\mathbf{1}\mathbf{a}\bullet\text{H}_2\text{SO}_4]^{\text{B}}$	15	8.34 ( $\rightarrow$ 7.29) <sup>b</sup>	82
$[\mathbf{1}\mathbf{a}\bullet\text{H}_2\text{SO}_4(\text{SO}_3)_x]^{\text{A}}$	13	7.17	84

<sup>a</sup> The reaction of 4-phenylbutyric acid (1.1 equiv) with 1-dodecanol (4 mmol) in the presence of catalyst (5 mol %) was conducted in water (2 mL) at 60  $^\circ\text{C}$  for 6 h. Yields were determined by  $^1\text{H}$  NMR analysis.  
<sup>b</sup> Chemical shift of ammonium protons changed at 60  $^\circ\text{C}$  during 6 h.

These results showed that the heat treatment of  $[\mathbf{1}\mathbf{f}\bullet\text{H}_2\text{SO}_4]^{\text{A}}$  generated some water-tolerant salts as active catalyst species. According to Halstead's report that thermal decomposition of ammonium sulfate or ammonium hydrogen sulfate generates ammonium pyrosulfate,<sup>10</sup> we expected that the active species  $[\mathbf{1}\mathbf{f}\bullet\text{H}_2\text{SO}_4]^{\text{B}}$  might be ammonium salts of pyrosulfuric acid ( $\text{H}_2\text{S}_2\text{O}_7$ ). In fact,  $[\mathbf{1}\mathbf{f}\bullet\text{H}_2\text{SO}_4(\text{SO}_3)_x]^{\text{A}}$ , the ammonium salt of  $\mathbf{1}\mathbf{f}$  with oleum (containing ca. 30%  $\text{SO}_3$ ), also showed high catalytic activity (82% yield) even without heat treatment before use. In addition, the chemical shift of ammonium protons of  $[\mathbf{1}\mathbf{f}\bullet\text{H}_2\text{SO}_4(\text{SO}_3)_x]^{\text{A}}$  was almost identical to that of  $[\mathbf{1}\mathbf{f}\bullet\text{H}_2\text{SO}_4]^{\text{B}}$ . Theoretical calculation of the dissociation free energy showed that  $\text{H}_2\text{S}_2\text{O}_7$  is more acidic than  $\text{H}_2\text{SO}_4$ .<sup>9</sup> In the optimized geometry, the salt of  $\mathbf{1}\mathbf{f}$  and



**Figure 3.** B3LYP/6-31G(d) optimized geometry of  $[\mathbf{1}\mathbf{f}\text{-H}^+]_2\text{-}[\text{S}_2\text{O}_7^{2-}]$ . Hydrogen atoms, except for ammonium protons, are omitted for clarity. C = black, H = white, N = blue, O = red, S = yellow.

$\text{H}_2\text{S}_2\text{O}_7$  formed four hydrogen bondings in a bidentate fashion between two ammonium cations ( $\text{Ar}_2\text{NH}_2^+$ ) and a pyrosulfate anion ( $\text{S}_2\text{O}_7^{2-}$ ) (Figure 3). These results suggested that the ammonium salts of  $\text{H}_2\text{S}_2\text{O}_7$  should be more stable than those of  $\text{H}_2\text{SO}_4$ . This stability would increase the water tolerance of the active catalyst  $[\mathbf{1}\mathbf{f}\bullet\text{H}_2\text{SO}_4]^{\text{B}}$ . The fact that *N,N*-diarylammonium salts of dibasic sulfonic acids<sup>9</sup> were inert also implied that the formation of pyrosulfates was crucial for high catalytic activity.

The present hydrophobic *N,N*-diarylammonium pyrosulfate-catalyzed dehydrative ester condensation could be applied to the reactions of a variety of substrates (Table 3). Significantly,  $[\mathbf{1}\mathbf{f}\bullet\text{H}_2\text{SO}_4]^{\text{B}}$  showed higher catalytic activity than DBSA for the esterification of rather hydrophilic substrates (entries 1–6). For example, the reaction of hexanoic acid with 1-butanol was successfully catalyzed by  $[\mathbf{1}\mathbf{f}\bullet\text{H}_2\text{SO}_4]^{\text{B}}$  to give 1-butyl hexanoate in 80% yield (6 h), while the use of DBSA gave a 47% yield of the ester in

**Table 3.**  $[\mathbf{1}\mathbf{f}\bullet\text{H}_2\text{SO}_4]^{\text{B}}$ -Catalyzed Dehydrative Ester Condensation of Various Substrates under Aqueous Conditions<sup>a</sup>

entry	carboxylic acid	alcohol	temp (°C)	time (h)	yield (%) <sup>b</sup>
1	$\text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{H}$	$\text{HO}(\text{CH}_2)_3\text{CH}_3$	60	8	74 [60]
2	$\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}$	$\text{HO}(\text{CH}_2)_3\text{CH}_3$	60	6	80 [47]
3	$\text{CyCO}_2\text{H}$	$\text{HO}(\text{CH}_2)_2\text{CH}_3$	70	8	76 [48]
4	$\text{CyCO}_2\text{H}$	$\text{HO}(\text{CH}_2)_3\text{CH}_3$	70	6	85 [65]
5	$\text{CH}_3(\text{CH}_2)_6\text{CO}_2\text{H}$	$\text{HO}(\text{CH}_2)_3\text{OBn}$	60	8	75 [53]
6	$\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}$	$\text{HO}(\text{CH}_2)_6\text{SH}$	60	8	86 [66]
7		$\text{HO}(\text{CH}_2)_2\text{CH}_3$	80	19	81
8		$\text{HO}(\text{CH}_2)_3\text{CH}_3$	80	47	81

<sup>a</sup> Conditions: carboxylic acid (1.1 equiv), alcohol (4 mmol), and  $[\mathbf{1}\mathbf{f}\bullet\text{H}_2\text{SO}_4]^{\text{B}}$  (5 mol %) in the presence of water (2 mL) at 60–80  $^\circ\text{C}$ .  
<sup>b</sup> Determined by  $^1\text{H}$  NMR analysis. Data in brackets refer to NMR yield when DBSA (5 mol %) was used as a catalyst.

(10) (a) Halstead, W. D. *J. Appl. Chem.* **1970**, *20*, 129. (b) Jariwala, M.; Crawford, J.; LeCaptain, D. *J. Ind. Eng. Chem. Res.* **2007**, *46*, 4900.

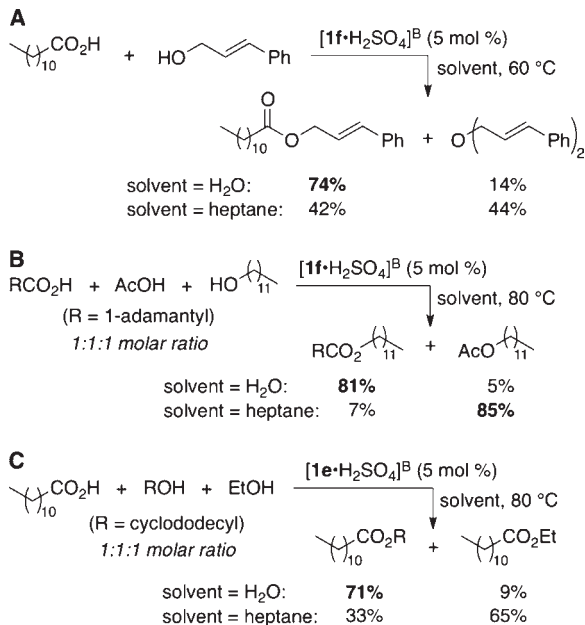
(11) (a) Grasa, G. A.; Singh, R.; Nolan, S. P. *Synthesis* **2004**, 971. (b) Hoydonckx, H. E.; De Vos, D. E.; Chavan, S. A.; Jacobs, P. A. *Top. Catal.* **2004**, *27*, 83. (c) Otera, J. *Chem. Rev.* **1993**, *93*, 1449. (d) Maegawa, Y.; Ohshima, T.; Hayashi, Y.; Agura, K.; Iwasaki, T.; Mashima, K. *ACS Catalysis* **2011**, *1*, 1178.

(12) Rode, B. M.; Engelbrecht, A.; Schantl, J. Z. *Phys. Chem. (Leipzig)* **1973**, *253*, 17.

the same reaction time. It is noteworthy that, for the ammonium salt catalyzed esterification of hexanoic acid with 1-butanol, the addition of NaOH (10 mol %) to the reaction mixture gave clear separation between the organic and aqueous layers, and the crude product could be easily obtained by simple decantation.<sup>9</sup> In contrast, the addition of NaOH (5 mol %) to the reaction mixture of the DBSA-catalyzed esterification did not give clear separation between the two layers, which was probably because DBSA acted as a surfactant. The esterification of  $\alpha,\beta$ -unsaturated carboxylic acids and sterically bulky carboxylic acids could also be catalyzed by  $[1\mathbf{f}\cdot\text{H}_2\text{SO}_4]^{\text{B}}$  to give the corresponding esters in good yields (entries 7 and 8).

The use of *N,N*-diarylammonium sulfate catalysts under aqueous conditions has an additional advantage in the ester condensations of acid-sensitive alcohols. For example, the esterification of cinnamyl alcohol with lauric acid (1.1 equiv) using  $[1\mathbf{f}\cdot\text{H}_2\text{SO}_4]^{\text{B}}$  (5 mol %) under aqueous conditions predominantly improved the yield of the ester (74%) (Scheme 1A). The use of water as a solvent also allowed us to achieve unusual selective ester condensations of two substrates based on the difference in hydrophobicity of the substrates. For example, when the reaction of a 1:1:1 molar mixture of 1-adamantanecarboxylic acid, acetic acid, and 1-dodecanol was conducted under aqueous conditions,

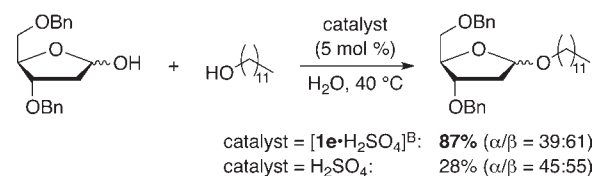
**Scheme 1.** Unusual Selective Ester Condensations under Aqueous Conditions



the ester of hydrophobic 1-adamantanecarboxylic acid was predominantly obtained in 81% yield along with the ester of hydrophilic acetic acid in 5% yield (Scheme 1B). On the other hand, the same reaction in heptane preferentially gave the acetate in 85% yield. The selective esterification of cyclododecanol (71%) over ethanol could also be achieved under aqueous conditions (Scheme 1C).

In addition, the  $[1\mathbf{e}\cdot\text{H}_2\text{SO}_4]^{\text{B}}$ -catalyzed dehydrative glycosylation of 3,5-*O*-dibenzyl-2-deoxy-D-ribose with 1-dodecanol under aqueous conditions gave the corresponding acetal in 87% yield, while the use of H<sub>2</sub>SO<sub>4</sub> as a catalyst decreased the yield (28%) (Scheme 2).

**Scheme 2.** Dehydrative Glycosylation



In conclusion, oil-soluble complexes of hydrophobic *N,N*-diarylamines with sulfuric acid successfully catalyzed dehydrative ester condensation reactions under aqueous conditions. The preheat treatment of dibasic sulfuric acid with bulky *N,N*-diarylamines was crucial for the generation of water-tolerant aggregated complexes of pyrosulfuric acid as active catalyst species. Further studies to elucidate the detailed aggregated structure of the *N,N*-diarylammonium pyrosulfate catalysts and their applications to other reactions under aqueous conditions are now underway. Water is still not commonly used as a solvent for organic synthesis despite the distinctive properties. The present nonsurfactant-type Brønsted acid catalysis will provide a new aspect of organic synthesis in water.

**Acknowledgment.** Financial support for this project was partially provided by JSPS.KAKENHI (20245022 and 23350039), NEDO, Yazaki Memorial Foundation for Science and Technology, and the Global COE Program of MEXT. The computations were performed using Research Center for Computational Science, Okazaki, Japan.

**Supporting Information Available.** Experimental details, characterization data of all new compounds, and crystal information file. This material is available free of charge via the Internet at <http://pubs.acs.org>.