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## Tin(IV) bis(perfluoroalkanesulfonyl)amide complex as a highly selective Lewis acid catalyst for Baeyer–Villiger oxidation using hydrogen peroxide in a fluorous recyclable phase

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Abstract— $Sn[N(SO_2C_8F_{17})_2]_4$  catalyst was shown to give an excellent yield and selectivity in a fluorous biphasic catalytic system for Baeyer–Villiger oxidation of cyclic ketones by 35% aqueous hydrogen peroxide, a green, safe and cheap oxidant. Furthermore, the catalyst was completely recovered and reused in the fluorous immobilized phase without loss of activity. © 2003 Elsevier Science Ltd. All rights reserved.

Since the technique of Fluorous Biphasic System (FBS), as a phase-separation and catalyst immobilization technique, was first introduced by Horváth and Rábai in 1994,<sup>1</sup> it has been used for some organic syntheses.<sup>2</sup> On the other hand, the Baeyer-Villiger (BV) oxidation was reported as early as 1899, and it still plays an important role in practical processes.<sup>3</sup> With the increase in environmental concern, much research has focused on the development of a catalytic BV oxidation process using the green and cheap hydrogen peroxide,<sup>4</sup> such as with metal complexes (based on Re, Pt) and acid zeolitic catalysts (like HZSM-5, USY) to facilitate the nucleophilic attack of hydrogen peroxide on the electrophilic carbonyl carbon. However, most of them showed either a poor selectivity or a low turnover number (TON) for the desired esters and lactones. Accordingly, some researchers have begun to consider an alternative reaction route consisting of an initial activation of carbonyl groups to increase the electrophilicity of the carbonyl carbon and a subsequent interaction with hydrogen peroxide.<sup>5</sup> Since Lewis acid catalysts can activate carbonyl groups, our interest was concentrated on metal complexes with perfluorinated ligands, whose Lewis acidity can be adjusted by the choice of different metals (e.g. Sn, Yb) and nucleophilicity by the variation of the

fluorine load in different perfluorinated ligands (e.g.  $-C_8F_{17}$ ,  $-CF_3$ ). Here, we will report our newest results on a successful approach to FBS, i.e. perfluoro(methylcyclohexane)/1,2-dichloroethane and perfluoro(methylcyclohexane)/1,4-dioxane systems for BV oxidation using 35% H<sub>2</sub>O<sub>2</sub> catalyzed by tin(IV) bis(perfluorooctanesulfonyl)amide complex<sup>6</sup> (Fig. 1).



 $Sn[N(SO_2CF_3)_2]_4$  core part is optimized by MNDO/AM1 method and  $C_8F_{17}\text{-}chains$  by Universal Force Field with the fixed core geometry.

Figure 1. MNDO/FF optimized structure of  $Sn[N(SO_2C_8F_{17})_2]_4$ .

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BV oxidation of adamantanone in FBS was firstly examined with various Lewis acid catalysts (Scheme 1),<sup>†</sup> whose representative results were summarized in Table 1. In the absence of the catalyst (entry 11), both conversion and selectivity were poorest. All of the metal complexes (Sn<sup>II</sup>, Hf<sup>IV</sup>, Sc<sup>III</sup>, Yb<sup>III</sup>) with  $-N(SO_2C_8F_{17})_2$ ligand (entries 2, 5, 7 and 9) gave better yield and TON than those with -OSO<sub>2</sub>CF<sub>3</sub> ligand (entries 3, 6, 8 and 10), but no significant difference in selectivity. These results can be attributed to the presence of the powerfully electron-withdrawing  $-N(SO_2C_8F_{17})_2$  ligand bearing the higher fluorine load on the metal center: the electrophilicity of the carbonyl carbon would have been increased making it be more easily attacked by the poor nucleophile H<sub>2</sub>O<sub>2</sub>.<sup>7,8</sup> This ligand effect was further clearly proven by the Sn-based catalysts: yield and TON followed the order of  $Sn[N(SO_2C_8F_{17})_2]_4>$  $Sn[N(SO_2C_8F_{17})_2]_2 > Sn(OSO_2CF_3)_2$  (entries 1-3). As for



Scheme 1. Baeyer-Villiger oxidation of 2-adamantanone.

 Table 1. Baeyer–Villiger oxidation of 2-adamantanone in fluorous biphasic system under the conditions in Scheme 1

Entry	Catalyst	Yield (%) <sup>a</sup>	Selectivity (%) <sup>b</sup>	TON <sup>c</sup>
1	$Sn[N(SO_2C_8F_{17})_2]_4$	93 (91) <sup>d</sup>	99	94
2	$Sn[N(SO_2C_8F_{17})_2]_2$	48	83	58
3	$Sn(OSO_2CF_3)_2$	37	87	42
4	SnCl <sub>4</sub>	41	79	52
5	$Hf[N(SO_2C_8F_{17})_2]_4$	82	92	88
6	$Hf(OSO_2CF_3)_4$	41	91	43
7	$Sc[N(SO_2C_8F_{17})_2]_3$	53	69	77
8	$Sc(OSO_2CF_3)_3$	31	66	47
9	$Yb[N(SO_2C_8F_{17})_2]_3$	31	73	41
10	$Yb(OSO_2CF_3)_3$	19	83	23
11	None	2	26	_

<sup>a</sup> GC yields (internal standard: *n*-nonane).

<sup>b</sup> Selectivity: mmol of produced lactone/mmol of reacted ketone.

<sup>d</sup> Value in parenthesis refers to the isolated yield.

M[N(SO<sub>2</sub>C<sub>8</sub>F<sub>17</sub>)<sub>2]<sub>n</sub></sub> (n=3, 4) complexes, yield, selectivity and TON were in order of Sn<sup>IV</sup>>Hf<sup>IV</sup>>Sc<sup>III</sup>>Yb<sup>III</sup> (entries 1, 5, 7 and 9), except that the selectivity of Yb<sup>III</sup> was slightly higher than that of Sc<sup>III</sup>. With respect to Sn[N(SO<sub>2</sub>C<sub>8</sub>F<sub>17</sub>)<sub>2</sub>]<sub>4</sub> (entry 1), a conversion of 94% was obtained which corresponded to a TON of 94 (for 2 h at 25°C), while the selectivity towards the lactone was 99%. Such a result showed a great improvement in the reaction conditions compared with the best reported Sn-zeolite catalytic system<sup>5</sup> (TON of about 116 for 6 h at 56°C).

As our previously reported lanthanide complex catalysts,<sup>9</sup> Sn[N(SO<sub>2</sub>C<sub>8</sub>F<sub>17</sub>)<sub>2</sub>]<sub>4</sub> was also found to be completely immobilized and could be reused in the fluorous phase,<sup>10</sup> i.e. completely remained in the fluorous phase and recycled without depression of its catalytic activity as shown in Figure 2. These results manifested that even after the catalyst was recycled four times, the GC yield still kept higher than 90%.

The possibility of recycling  $Sn[N(SO_2C_8F_{17})_2]_4$  catalyst in the BV oxidation of cyclobutanone was also investigated (Scheme 2). It was found that there was almost no reduction of the catalytic activity (yield: 93–95%) and no other by-products detected except for the desired lactone formation (selectivity: 96–100%).

In order to analyze and quantify the catalyst recovery, the reaction rates (=activity) at different cycle times were compared. In Figure 3, the representative results obtained from cyclobutanone oxidation were shown. It can be found that there was almost no difference for



Figure 2. Recycles of  $Sn[N(SO_2C_8F_{17})_2]_4$  catalyst in Baeyer–Villiger oxidation of 2-adamantanone.



Scheme 2. Baeyer-Villiger oxidation of cyclobutanone.

<sup>&</sup>lt;sup>c</sup> Turnover number: mmol converted adamantanone/mmol catalyst.

<sup>\*</sup> Typical procedure: To a mixture of perfluoro(methylcyclohexane) (3 mL) and 1,2-dichloroethane (3 mL) were added Sn[N(SO<sub>2</sub>C<sub>8</sub>F<sub>17</sub>)<sub>2</sub>]<sub>4</sub> (81 mg, 0.02 mmol), 2-adamantanone (300 mg, 2.00 mmol) and 35% H<sub>2</sub>O<sub>2</sub> (194 mg, 2.00 mmol). The reaction mixture was stirred continuously at 25°C for 2 h. Once the stirring was stopped, the reaction mixture separated into two liquid phases within 10 s. An upper 1,2-dichloroethane phase afforded pure lactone (302 mg, 91%) yield) by silica gel chromatography, while the lower fluorous phase was reused in subsequent reactions. The amounts of H<sub>2</sub>O<sub>2</sub> both in the upper organic phase and lower fluorous phase were titrated with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> after their respective sampling. With respect to the system of 1,4-dioxane/perfluoro(methylcyclohexane), H<sub>2</sub>O<sub>2</sub> can be dissolved in the upper 1,4-dioxane phase completely. In the system of 1,2-dichloroethane/perfluoro(methylcyclohexane), H2O2 was partially (<10%) dissolved in the upper 1,2-dichloroethane phase and the other stayed above this phase.

the formation rate of  $\gamma$ -butyrolactone at cycles 1 and 4 within 1 h reaction time, which confirmed that there was not only no loss of the catalyst but also no depression of catalytic activity during the repetition. Accordingly, it can be deduced 99% of the catalyst should still remain in the fluorous phase even after the fourth cycle.<sup>11</sup> In fact, the product yield kept a constant level in a specific period (e.g. about 1 h for cycle 1 in Fig. 3), which is a criteria for us to determine the reaction time.

In Table 2, a series of BV oxidation of ketone substrates were examined to evaluate the above catalytic system. It was found that  $Sn[N(SO_2C_8F_{17})_2]_4$  can give a



**Figure 3.** Lactonization of cyclobutanone catalyzed by  $Sn[N(SO_2C_8F_{17})_2]_4$  at different cycles under the conditions in Scheme 2.

relatively high selectivity to the desired lactone (>91%) for all of these BV reactions (the upper one in case of entries 2, 3, 5 and 6), which can be viewed as superior to most of the reported catalytic systems with 35% H<sub>2</sub>O<sub>2</sub> where a mixture of lactone, epoxide and epoxylactone was produced.<sup>4</sup> Furthermore, in our catalytic system, no significant  $H_2O_2$  decomposition was detected. It may be noticed the conversions for cyclopentanone, cyclohexanone, menthone and camphor only reached a moderate level (entries 2, 3, 5 and 6), a little lower than the reported ones.<sup>12</sup> This can be contributed to the differences of aqueous hydrogen peroxide concentration and the ratio of substrate/H<sub>2</sub>O<sub>2</sub>, i.e. 50% higher and excess H<sub>2</sub>O<sub>2</sub> were used in their works, whereas 35% and equimolar  $H_2O_2$  in ours. As an ideal catalytic synthesis, it not only takes account of the high catalytic activity, but also accounts for the atom economy, safety and easy handing.<sup>11</sup> Since combination of higher concentration  $H_2O_2$  (>50%) with ketones was potentially explosive, it is very significant to develop a practical system with 35% H<sub>2</sub>O<sub>2</sub> for the industrial operation. On the other hand, the present turnover frequency (TOF) of the system Sn[N- $(SO_2C_8F_{17})_2]_4/H_2O_2/cyclohexanone$  (upper one of entry 3 in Table 2) amounted to 36  $h^{-1}$ , which was comparable to the reported TOF of 23  $h^{-1}$  with the catalyst (Sn-MCM-41) for the same reaction.<sup>13</sup> In order to increase the conversion of cyclopentanone, cyclohexanone, menthone and camphor, we have conducted these reactions with an excess amount of catalyst and/ or a prolonged reaction time. As shown in Table 2 (the lower one in case of entries 2, 3, 5 and 6), the conversion was improved, but the selectivity was not signifi-

Entry	Substrate	Product	$Sn[N(SO_2C_8F_{17})_2]_4 \pmod{\%}^{e}$	Conditions	Conversion (%)	Selectivity (%) <sup>f</sup>
1ª	Ľ	Ċ	1	50 °C, 1 h	96	99
2ª	$\overset{\texttt{l}}{\bigcirc}$	Ů	1 3	50 °C, 2 h 50 °C, 5 h	59 70	91 82
3 <sup>ª, c</sup>		Ċ	1 1	25 °C, 1 h 25 °C, 4 h	36 73	98 66
4 <sup>6</sup>	₽°	$\int c c$	1	25 °C, 2 h	94	99
5⁵	ALO	d d d d	3 5	50 °C, 5 h 50 °C, 5 h	67 84	99 75
6 <sup>6</sup>	Ko	K	3 3	70 °C, 2 h 70 °C, 10 h	43 70	99 77

Table 2. Baeyer-Villiger oxidation of ketones

<sup>a</sup>Other reaction conditions were same as in Scheme 2. <sup>b</sup>Other reaction conditions were same as in Scheme 1. <sup>c</sup>Molar ratio of ketone:H<sub>2</sub>O<sub>2</sub> is 1:0.8. <sup>d</sup>Regioselectivity: >99% determined by GC and <sup>1</sup>H NMR analysis. <sup>e</sup>mol% of Sn[N(SO<sub>2</sub>C<sub>8</sub>F<sub>17</sub>)<sub>2</sub>]<sub>4</sub> catalyst with respect to the ketones. <sup>f</sup>mmol of produced lactone/mmol of reacted ketone. cantly satisfactory. In addition, the possibility of the present catalytic system for BV oxidation of aromatic ketone (e.g. acetophenone) was also investigated, but obtained 20% yield. How to achieve a higher yield for BV oxidations of aromatic ketone left us further work.

Additionally, it was also confirmed that such a high selectivity could not be achieved when the catalyst was used in an organic monophase, i.e. either 1,2dichloroethane as a solvent for adamantanone BV oxidation (selectivity: 81%) or 1,4-dioxane for cyclobutanone BV oxidation (selectivity: 65%), which were considerably lower than those of FBS (selectivity: 99% of entry 1 in Table 1; 99% of cycle 1 in Scheme 2). Another exceptional advantage in FBS is that the catalyst can be recovered and reused as described above, which is an impossible task in the organic monophase system. Moreover, it is worth pointing out that such results benefit greatly from both the efficient Lewis acidity<sup>14</sup> of  $Sn[N(SO_2C_8F_{17})_2]_4$  and the unique solution property of FBS.

In conclusion,  $Sn[N(SO_2C_8F_{17})_2]_4$  has proved to be a favorable catalyst for the BV oxidation of cyclic ketones in FBS not only due to the improved selectivity but also due to the environmental benignity. We believe that the following results endow the catalytic approach with great potential for synthetic application: (1) 35% aqueous hydrogen peroxide, a safe and economic oxidant for practical processes, was shown to provide satisfactory oxidizing ability; (2) the catalyst, completely immobilized in the fluorous phase, can be recovered and reused; (3) high yields and purities of lactone can be obtained under very mild conditions.

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