Cationic Organotin Clusters for Highly Efficient Alcohol Acetylation Catalysts

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The effectiveness of cationic species for increasing the catalytic activity of organotin Lewis acids has been assessed by comparing two types of cationic organotin clusters, $[Bu_2Sn(OH)(H_2O)]_2{}^{2+}2OTf^-$ and $[(BuSn)_{12}O_{14}(OH)_6]^{2+}Cl^-{}_2{\cdot}2H_2O$, with neutral clusters in alcohol acetylation. The Sn_2 dication is extremely active, with a catalyst concentration of 0.001 mol %, sufficient to give a quantitative yield. The Sn_{12} dication is slightly less active but gives high levels of chemoselectivity and primary/secondary alcohols selection. The neutral clusters are less effective catalysts. A variety of synthetic applications are feasible by changing the Lewis acidity of the catalysts.

Introduction

Although organotin compounds possess some degree of Lewis acidity, it is usually not sufficient to induce synthetically useful reactions. If the reactivity of organotin compounds is increased, then they could become versatile and unique Lewis acid catalysts because most of them are thermally and hydrolytically stable. We have advanced two strategies along this line. One is to make use of entropy gain induced by distannoxane template effects,[1] and the other is to increase the acidity by attaching electron-withdrawing groups on tin.[2] The ultimate forms of the latter case should give rise to organotin cations which are expected to further enhance the catalytic potential.

Despite their long history,[3] however, only a limited number of the cationic compounds have been isolated. The trimethyltin cation hydrates[4] and ammoniates[5] have been known since the 1960s, whereas diorganotin dications stabilized by internal coordination with alkynylborates[6a,b] or bidentate phosphine oxides[6c] were reported recently. The Sn_{12} dications, $[(RSn)_{12}O_{14}(OH)_6]^{2+}$, were also produced and fully characterized.[7] More recently, we prepared novel Sn_2 dications, $[R_2SnOH(H_2O)]^+{}_2 2OTf^-$ ($Tf = CF_3SO_2$).[8]

In general, the use of organotin cations in organic reactions is not straightforward since most of them are neither necessarily stable in air nor soluble in organic solvents. Nevertheless, the two types of organotin cluster dications described above are unique in that both are easy to prepare, stable in air, and soluble in organic solvents. In this paper, we disclose that these compounds are effective catalysts for alcohol acetylation and elucidate the importance of the cationic character for attaining high catalytic activity by comparison with nonionic organotin catalysts.[9]

Results and Discussion

The organotin compounds screened in this study are shown in Chart 1. They are basically classified into four categories. Organotin hydroxides, **1**, **2**, **4**, and **5** have in common tin−hydroxyl bridges, yet their structural

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Chart 1

$[R_2Sn(OH)(OTf)(H_2O)]_2$

1: R = *n*-Bu
2: R = *t*-Bu

$[(BuSn)_{12}O_{14}(OH)_6]Cl_2\ 2H_2O$

3

$[t\text{-}Bu_2Sn(OH)(X)]_2$

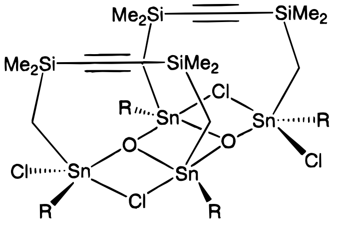
4: X = Cl
5: X = NO_3

$[ClBu_2SnOSnBu_2Cl]_2$

6

$\{[R(Cl)Sn(CH_2)_4Sn(Cl)R]O\}_4$

7: R = $(CH_3)_3CCH_2$
8: R = $(CH_3)_2CHCH_2$
9: R = $(CH_3)_3SiCH_2$



10: R = $(CH_3)_3SiCH_2$

Scheme 1

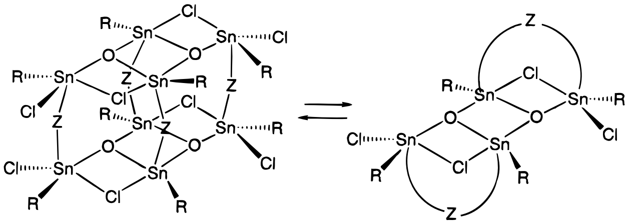


Table 1. Comparison of Catalytic Activity of Various Organotin Lewis Acids in Acetylation of 2-Phenylethanol[a]

$$Ph(CH_2)_2OH \xrightarrow[30\ °C]{Ac_2O/cat} Ph(CH_2)_2OAc$$

entry	cat (conc/mol %)	reactn time	yield (%)[b]
1	**1** (0.125)[c]	10 min	>99
2	**1** (0.01)	10 min	93
3	**1** (0.005)[d]	0.5 h	93
4	**2** (0.125)[c]	10 min	>99
5	**2** (0.01)	10 min	95
6	**2** (0.005)[d]	0.5 h	90
7	**2** (0.001)[e]	4.5 h	89
8	**3** (0.02)[c]	5 h	95
9	**3** (0.01)	5 h	85
10	**3** (0.02)[e]	16 h	>99
11	**3** (0.002)[d]	6 h[f]	98
12	**4** (0.1)	24 h	82
13	**5** (0.1)	24 h	92
14	**6** (0.06)[c]	5 h	52
15	**7** (0.03)[c]	5 h	56
16	**8** (0.03)[c]	5 h	60
17	**9** (0.03)[c]	5 h	69
18	**10** (0.06)[c]	5 h	43

[a] Reaction conditions: ROH (5 mmol); Ac_2O (1 mL). [b] Determined by GLC. [c] The catalyst concentration with 0.0025 g atom Sn/mol. [d] The catalyst in 1 mL of toluene (see text). [e] CH_2Cl_2 (2 mL) was used as a solvent. [f] At 50 °C.

features are considerably different. *n*-Butyltin triflate **1** has a nonionic structure with six-coordinate tins in the solid state but dissociates into a dicationic species with five-coordinate tins and triflate anions in solution.[8] *tert*-Butyl derivative **2** is ionic both in the solid state and in solution.[8] By contrast, both **4**[10] and **5**[8] are neutral with covalently bonded Cl or NO_3 ligands. The second group involves a simple ladder structure (**6**[1] and **10**[11]). However, the latter differs from the former in having silylacetylene bridges between tin atoms. Third, compounds **7**–**9** have a double ladder structure but partially dissociate into a single ladder in solution, as shown in Scheme 1.[12] The fourth category is a soccerball-like cluster for **3**.[7b]

The catalytic activities of these compounds were compared for acetylation of 2-phenylethanol by acetic anhydride (Table 1). Since these catalysts involve different numbers of tin atoms in the respective molecules, the direct comparison was made by adjusting the catalyst concentration so as to give the same level in regard to a single tin atom (0.0025 g atom/mol) (entries, 1, 4, 8, 14–18).[13] Under these conditions, quantitative yields were obtained after 10 min with **1** and **2** (entries 1 and 4) and after 5 h with **3** (entry 8), while nonionic cluster catalysts, **6**–**10**, resulted in only modest yields (entries 14–18). Apparently, the cationic cluster exhibited activities superior to the neutral ones. The importance of the cationic character of the organotin species is further obvious from the decreased catalytic activities of **4** and **5** (entries 12 and 13). Despite the close structural similarity between these compounds and the triflates, **1** and **2**, the higher catalytic activities of the latter are ascribed to their ionic dissociation in solution, as was proved by electrical conductivity measurements.[8]

We reduced the catalyst concentration to reveal the lowest limit (entries 2, 3, 5–7) and found that a 0.005 mol % concentration of **1** and **2** was sufficient to give quantitative yields after 30 min. The concentration could be reduced to 0.001 mol % with **2** if the reaction was run for a longer time.[14] In experiments with extremely low catalyst loading (below 0.005 mol %), the catalysts were added as solution in toluene (1 mL). It should be emphasized, however, that even such a small amount of catalysts played a crucial role because only a 2% yield of 2-phenylethyl acetate was obtained without catalyst under the same conditions. On the other hand, **3** proved to be somewhat less active than **1** and **2**. Under the standard conditions (at 30 °C), a quantitative yield was obtained after 5 h (entry 8). The use of a half amount of the catalyst resulted in a slight decrease of yield (entry 9), and further reduction of the catalyst concentration did not afford sufficient yields. However, a quantitative yield was obtained even with a 0.002 mol % catalyst concentration if the reaction was conducted at 50 °C (entry 11). In this run, the catalyst in toluene solution was used as described above. The use of CH_2Cl_2 as solvent (2 mL) also exerted no serious influence (entry 10) and broadens the scope of this protocol because substrates not soluble in Ac_2O are employable as well. The lower catalytic activity of Sn_{12}

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[13] It may be said that this treatment is valid simply from the statistical point of view. Actually, it is not plausible that more than two reactions sites, if available, in a single catalyst molecule work simultaneously. Thus, a single reaction site in a single molecule assumes that the activity of catalysts may be better assessed in terms of the catalyst concentration itself. In any event, the difference in these criteria does not influence the conclusion given in this paper in a qualitative sense.

[14] The slightly higher activity of **2** as compared to **1** may be correlated with the larger electrical conductivity.[8]

Table 2. Acetylation of Various Alcohols and Phenol under Catalysis of 3[a]

$$\mathrm{ROH} \xrightarrow[30\ °\mathrm{C}]{\mathrm{Ac_2O}/\mathbf{3}} \mathrm{ROAc}$$

entry	alcohol	cat conc (mol %)	reactn temp (°C)/time (h)	yield (%)
1	$C_8H_{17}OH$	0.002	60/5	>99[b]
2	$PhCH(OH)CH_3$	0.2	30/7	23[b]
3	$PhCH(OH)CH_3$	0.2	40/7	83[b]
4	$C_6H_{13}CH(OH)CH_3$	0.2	40/7	75[b]
5	*cyclo*-$C_6H_{11}OH$	0.1	30/16	3[b]
6	$PhCH_2C(OH)(CH_3)_2$	0.02	30/5	1[b]
7	$PhCH_2C(OH)(CH_3)_2$	0.2	50/48	91[b]
8	$THPO(CH_2)_4OH$	0.02	30/5	83[c]
9	$TBSO(CH_2)_4OH$	0.05	30/5	>99[c]
10	geraniol	0.02	40/5	>99[c]
11	PhOH	0.1	30/5	38[b]
12	PhOH	0.03	50/14	94[b]

[a] Reaction conditions: ROH (5 mmol); Ac_2O (1 mL). [b] Determined by GLC. [c] Isolated yield after column chromatography.

Table 3. Selective Acetylation of Primary Alcohol Over Secondary Alcohol Under Catalysis of 3[a]

$$\begin{matrix}\mathrm{ROH\ (primary)} \\ \mathrm{R'OH\ (secondary)}\end{matrix} \xrightarrow[30\ °\mathrm{C}]{\mathrm{Ac_2O/cat}} \begin{matrix}\mathrm{ROAc} \\ \mathrm{R'OAc}\end{matrix}$$

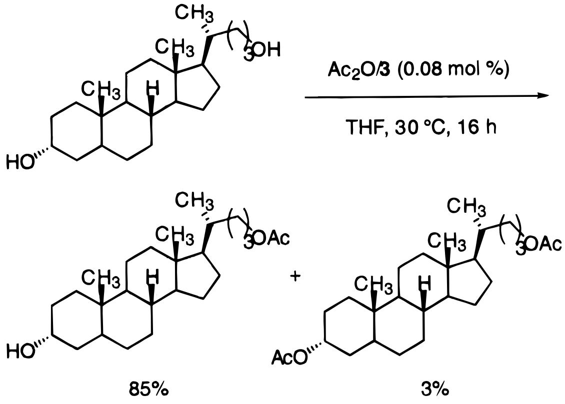
entry	ROH R′OH	cat conc (mol %)	reactn temp (°C)/time (h)	yield (%)[b]	
1	$Ph(CH_2)_2OH$ $PhCH(OH)CH_3$	0.02	30/16	95 11	(90:10)
2	$Ph(CH_2)_2OH$ $PhCH(OH)CH_3$	0.08	30/5	95 6	(94:6)
3	$Ph(CH_2)_2OH$ $PhCH(OH)CH_3$	0.08	40/1	99 5	(95:5)
4	$C_8H_{17}OH$ $C_6H_{13}CH(OH)CH_3$	0.05	30/5	65 2	(97:3)
5	$C_8H_{17}OH$ $C_6H_{13}CH(OH)CH_3$	0.05[c]	40/9	100 9	(92:8)
6	$C_8H_{17}OH$ *cyclo*-$C_6H_{11}OH$	0.03	30/4	85 3	(97:3)

[a] Reaction conditions: ROH (2.5 mmol); R′OH (2.5 mmol); Ac_2O (1 mL). [b] Determined by GLC. [c] THF (1 mL) was added.

dication **3** compared with those of Sn_2 dications, **1** and **2**, can be interpreted in terms of effective positive charge. In **1** and **2**, the charge is condensed on the relatively small Sn_2O_2 moiety, while in **3**, the charge can be dispersed over the larger $Sn_{12}O_{20}$ cluster surface. It was specifically suggested that the charges are shared by the six tin atoms located on the both polar sites of the spherical molecules.[7c] The overall result is that the acidity of the respective tin atoms in the Sn_{12} dication is lower than that in the Sn_2 dication.

Quite naturally, the increase in acidity is favorable for the high catalytic activity on one hand, but unfavorable for selectivities on the other. In fact, acid-sensitive tetrahydropyranyl (THP) and *tert*-butyldimethylsilyl (TBS) groups were not tolerated in the reaction catalyzed by **1** and **2**. By contrast, these groups survived in the reaction catalyzed by **3** (vide infra). In this sense, this catalyst may find broader applications. Thus, we carried out acetylation of various alcohols under catalysis of **3** (Table 2). The low catalyst loading (0.002 mol %) was feasible for 1-octanol at 60 °C (entry 1). Secondary alcohols sluggishly reacted at 30 °C (entries 2 and 5) but underwent smooth acetylation at 40 °C (entries 3 and 4). Even a tertiary alcohol was acetylated at 50 °C (entry 7). Acid-sensitive substrates were successfully employed without any decomposition or side reactions (entries 8−10). Phenol also underwent facile acetylation at 50 °C, although the yield was not satisfactory at 30 °C (entries 11 and 12). The high chemoselectivity obtained with **3** is rather unexpected because this compound is more acidic than the nonionic compounds on the basis of the catalytic activity. Probably, the acidity is increased substantially but not beyond the degree where acid-sensitive groups cannot survive. It follows from these results that various kinds of synthetic applications are feasible by controlling the catalyst acidity.

The selective acetylation of primary alcohol in the presence of secondary alcohol is of great synthetic value. Previously, we realized nearly perfect selection by use of alkenyl acetate under distannoxane catalysis.[1b,c] The use of acetic anhydride, however, resulted in lower selectivities: 94:6 for 2- and 1-phenylethanols and 92:8 for 1- and 2-octanols.[1c] Encouraged by the results obtained in Table 2, we were intrigued to investigate the competition between primary and secondary alcohols. As shown in Table 3, the preference for primary alcohols was similar to or better than that in the distannoxane-catalyzed reactions. Particularly notable are the high selectivities with high conversions. In general, as the reaction proceeds, the proportion of the secondary acetate in the product increases and, thus, it is difficult to keep a high primary/secondary acetate ratio over 90% conversions. Nevertheless, the present protocol gave rise to high selectivities with more than 90% yields. Competition between octanols are less selective than the other alcohols, and high selectivity was achievable only at relatively low conversion (entry 4). However, addition of THF dramatically improved the selectivity even at 40 °C (entry 5). This is explained by coordination of THF on tin, which reduced the acidity of the catalyst. Besides the acyclic secondary alcohols, cyclohexanol was also discriminated successfully (entry 6). The intramolecular competition also gave rise to an analogous outcome (eq 1).



(1)

One may suppose that **3** is not a really catalytically active species in the present reaction since this compound is reported to react with acetic acid to give $[BuSn(O)OAc]_6$.[7b] This is not the case, however, on the basis of the following facts. This compound is not soluble in Ac_2O, while the reaction with **3** is totally homogeneous. Moreover, the hexamer is much less active as a catalyst than **3**: the reaction with this species (0.08 mol %) under the otherwise same conditions afforded only a

58% yield of 2-phenylethyl acetate after 6 h. The monobutyltin hexamer was recovered from the **3**-catalyzed reaction after the standard aqueous workup. However, it was unambiguously proved that the hexamer was formed during workup. When the reaction mixture was washed with $NaHCO_3$ repeatedly until Ac_2O and acetic acid had completely disappeared, **3** was recovered in 61% yield. The relatively low yield is due to the emulsion formation between the organic and aqueous phases. As a result, the two phases could not be separated cleanly and some portion of **3** was lost in the aqueous phase. If the hexamer is formed, it should be recovered from the organic phase because we confirmed that this compound is very soluble in EtOAc and could be recovered quantitatively. Apparently, the hexamer was formed by reaction of **3** with the remaining Ac_2O or acetic acid during evaporation in the standard operation. There is another possibility that smaller BuSn(O)OAc aggregates that might have transiently appeared by reaction of **3** with Ac_2O or acetic acid may work as real active species. However, the hexamer is a highly thermodynamically stable form which emerges immediately from the reaction between **3** and Ac_2O or acetic acid, and no such transient species have been detected. This was unambiguously confirmed by Ribot et al.[15] They investigated the reaction of **3** with varying amounts of acetic acid. With low acid/**3** ratio (≤ 2), the hydroxyls of **3** is simply acetylated without destruction of the Sn_{12} framework. For the ratio equal to 12, this framework is totally converted to the hexamer. Very importantly, for intermediate ratios, both clusters coexist on the basis of ^{119}Sn NMR and FTIR. No other species were detected at all. Thus, it is not plausible that the smaller aggregates are responsible for the catalysis.

The precise mechanism of the Sn_{12}-catalyzed acetylation is not yet clear. However, it was disclosed that two of the hydroxy groups at six-coordinate tin centers are readily converted to methoxyls upon dissolving **3** in methanol.[7b] Accordingly, it is reasonably postulated by analogy with the mechanism of distannoxane catalysis[1a] that the present reaction is initiated by alkoxy formation followed by coordination of acetic anhydride on an adjacent tin atom. Apparently, upon a slight decrease of acidity, the steric bulk of the Sn_{12} dication could be reflected by discrimination between primary and secondary alcohols.

In conclusion, it has been proved that the use of cationic species increases the catalytic activity of organotin Lewis acids. The Sn_2 cations, **1** and **2**, exercised extremely high catalytic activities for acetylation of alcohols. Although the activity of Sn_{12} dication **3** was lower than those of **1** and **2**, such mildness gave rise to both chemoselectivity and primary/secondary alcohol selectivity. Consequently, versatile synthetic applications are accessible by switching the organotin catalysts depending on the purposes. If the reduction of the catalytic amount is of prime importance, the Sn_2 dications are the catalysts of choice. Alternatively, if both considerable catalytic activity and selectivities are required, then the Sn_{12} dication serves best to this end. Finally, if the selectivities are the crucial requirements, the neutral distannoxanes should be used.

Experimental Section

Acetic anyhydride was used without purification. GLC analysis was performed on a Shimdzu GC-17A gas chromatograph with a capillary column, CBP1-M25. The organotin catalysts **1**,[8] **2**,[8] **3**,[7] **4**,[10a] **5**,[8] **6**,[1c] **7**−**9**,[12] and **10**[11] were prepared according to the literature methods. 2-Octyl acetate,[16] 1,1-dimethyl-2-phenylethyl acetate,[17] 4-perhydro-2*H*-pyran-2-yloxybutyl acetate,[1c] 4-(*tert*-butyldimethylsilyloxy)butyl acetate,[1c] and steroid diol acetate[18] have been described in the literature, and the other acetates are commercially available.

Acetylation of 2-Phenylethanol Catalyzed by 1 (Representative, Entry 2 in Table 1). A stock solution of the catalyst was freshly prepared from **1** (4.2 mg, 5.0×10^{-3} mmol) and Ac_2O (10 mL), and 1 mL of the solution was transferred with a syringe into a reaction vessel containing 2-phenylethanol (611 mg, 5.0 mmol). The solution was stirred for 10 min at 30 °C. After usual workup with aqueous $NaHCO_3$ solution and EtOAc, the organic layer was dried over $MgSO_4$ and evaporated. GLC analysis of the crude mixture showed a 93% yield of 2-phenylethyl acetate.

Recovery of 3 from the Acetylation Reaction. A mixture of **3** (508 mg, 0.2 mmol), Ac_2O (20 mL), and BuOH (100 mmol) was stirred at 30 °C. The reaction mixture was poured into an ice-cooled $NaHCO_3$ solution, and the mixture was stirred vigorously at 0 °C for 1 h. The mixture was combined with 500 mL of EtOAc. The organic layer was separated and washed with saturated $NaHCO_3$ (200 mL × 3) until Ac_2O and acetic acid disappeared completely (checked by GLC). Then, the organic layer was washed with water followed by brine and dried ($MgSO_4$). The yield of BuOAc was determined to be 100% by GLC analysis of the organic layer with tetradecane as an internal standard. Evaporation of the organic layer left **3** (308 mg, 61%).

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