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Lanthanide Bis[bis(1,1,1,3,3,3-hexafluoro-2-propoxy)sulfonyl]amide as a Novel Effective Acylation Catalyst†

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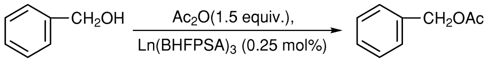
Lanthanide complexes $Ln(BHFPSA)_3$ $\{BHFPSA = N[SO_2OCH(CF_3)_2]_2\}$ catalyse the acylation of alcohols or phenols under very mild conditions to afford esters in high yields.

Although 4-(dimethylamino)pyridine, 4-pyrrolidinopyridine and tributylphosphine (Bu_3P) *etc.* are known to be effective basic catalysts in the acylation of alcohols with acid anhydrides, there is great demand for acid catalysts to generate esters under mild conditions.[1–4] Since metal triflates have been employed as versatile Lewis acid catalysts,[5] we are interested in preparing some metal bis[bis(perfluoroalkyl)sulfonyl]amides or bis[bis(polyfluoroalkoxy)sulfonyl]amides to investigate their utility as Lewis acid catalysts.[6–8] We report here on the acylation of alcohols or phenols with acid anhydrides by using a catalytic amount of the lanthanide bis[bis(1,1,1,3,3,3-hexafluoro-2-propoxy)sulfonyl]amide [$Ln\{N[SO_2OCH(CF_3)_2]_2\}_3$ or $Ln(BHFPSA)_3$].

Results and discussion

Initially, the model reaction of benzyl alcohol (1 equiv.) with acetic anhydride (1.5 equiv.) in dichloromethane at 30 °C was carried out to screen the catalytic activities of lanthanide bis[bis(1,1,1,3,3,3-hexafluoro-2-propoxy)sulfonyl]amides as the Lewis acids (Table 1). Compared with the samarium triflate [$Sm(OTf)_3$], the catalytic amount of $Ln(BHFPSA)_3$ (0.25 mol%) showed very strong Lewis acid catalytic activities in the model reaction and $Yb(BHFPSA)_3$ was found to be the most effective. Ishihara *et al.*'s results[4] indicated that the lanthanide triflates, $Ln(OTf)_3$, were not good catalysts for the acylation of alcohols. Thus, the enhanced Lewis acidity of the lanthanide metal ions might be attributed to the bulky and weakly coordinating properties of their counter anion, $[N\{SO_2OCH(CF_3)_2\}_2]^-$.[9,10] As $Sm(BHFPSA)_3$ was more easily prepared and its catalytic activity was similar to that of $Yb(BHFPSA)_3$ we used it as the catalyst in most cases.

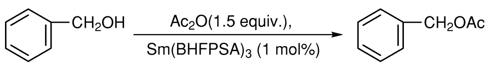
Table 1 $Ln(BHFPSA)_3$ catalysed acetylation of benzyl alcohol in CH_2Cl_2 at 30 °C[a]



Entry	Catalyst	*t*/min	Conversion (%)[b]
1	No cat.	1440	<10
2	$Sm(OTf)_3$[c]	640	<40
3	$La(BHFPSA)_3$	60	99
4	$Sm(BHFPSA)_3$	17	99
5	$Ga(BHFPSA)_3$	13	99
6	$Yb(BHFPSA)_3$	9	99

[a] A solution of benzyl alcohol (0.25 M) was used. [b] The conversion was determined by gas chromatographic analysis of the crude product. [c] 1 mol% catalyst was used.

Table 2 Effect of solvents on acetylation catalysed by $Sm(BHFPSA)_3$[a]



Entry	Solvent	*t*/min	Conversion (%)[b]
1	CH_3NO_2	1 (35[c])	99
2	CH_2Cl_2	4	99
3	$PhCH_3$	6	99
4	THF	6	99
5	Et_2O	10	99
6	$CHCl_3$	56	99
7	DMF	611	99
8	CH_3CN	620	99

[a] A solution of benzyl alcohol (0.25 M) was used. [b] The conversion was determined by gas chromatographic analysis of the crude product. [c] 0.1 mol% catalyst was used at 0 °C.

The effect of solvents on the model reaction under the influence of 1 mol% of $Sm(BHFPSA)_3$ is shown in Table 2. Under these conditions, the solvent effect on the catalytic reaction might depend on the polarity and coordinating property of these solvents. The reaction proceeded faster in nitromethane than in other organc solvents and it was much slower in dimethylformamide and acetonitrile.

Several examples of the acylation of different alcohols with acid anhydrides catalysed by $Sm(BHFPSA)_3$ are shown in Table 3. In most cases the reactions took place smoothly in the presence of 0.1–0.25 mol% of catalyst to afford the esters in good yields under very mild conditions. The acylation of *sec*-phenethyl alcohol with acetic anhydride in nitromethane proceeded more than ten times faster than that in dichloromethane (entries 2 and 3 in Table 3) and the acylation of *sec*-phenethyl alcohol (1 equiv.) with benzoic anhydride (1 equiv.) also gave a satisfactory result after the reaction had proceeded for only two hours (entry 5 in Table 3). In the case of acylation of phenols with acetic anhydride, that of 2,6-di-*tert*-butyl-4-methylphenol was relatively slow even in nitromethane in comparison with the acylation of other phenols (entries 6–12 in Table 3). For acid-sensitive substrates such as tertiary alcohols, the reaction successfully proceeded using acid anhydride as a solvent under very mild conditions and the amount of esters increased when the reactions were carried out at as low a temperature as possible (entries 13–17 in Table 3). In most cases of DMAP or PPY-catalysed acetylation of tertiary alcohols, it is necessary to use more than 10 mol% of DMAP or PPY and an excess of amine at conditions of high concentration.[1,2] It is noted that when 1 mol% of $Sm(BHFPSA)_3$ was used to catalyse the acylation of 1-ethylcyclohexanol with acetic anhydride at 0 °C, a yield of more than 95% for the olefin was detected after just 3 min. This indicated that the acylation would proceed more smoothly when less catalyst is used.

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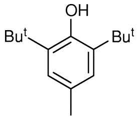
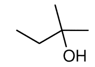
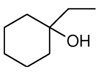
Table 3 Sm(BHFPSA)$_3$ catalysed acylation with acid anhydrides

Entry	Alcohol or phenol	(RCO)$_2$O (equiv.)	Sm(BHFPSA)$_3$ (mol%)	Conditions[a]	Yield (%)[b]
1	PhCH$_2$CH$_2$OH	Ac$_2$O (1.5)	0.25	30, 50	90
2	PhMeCHOH	Ac$_2$O (1.5)	0.25	30, 101	93
3			0.1	30, 13[c]	91
4			[Yb(BHFPSA)$_3$ (0.1)]	30, 8[d]	91
5		(PhCO)$_2$O (1.0)	1.0	30, 120[c]	75
6	PhOH	Ac$_2$O (1.5)	0.25	30, 46	92
7	*o*-ClC$_6$H$_4$OH	Ac$_2$O (1.5)	0.25	30, 138	93
8	*p*-ClC$_6$H$_4$OH	Ac$_2$O (1.5)	0.25	30, 90	90
9	*p*-MeC$_6$H$_4$OH	Ac$_2$O (1.5)	0.25	30, 48	92
10	*p*-O$_2$NC$_6$H$_4$OH	Ac$_2$O (1.5)	0.25	30, 297	94
11			0.25	30, 90[c]	95
12		Ac$_2$O (1.5)	1.0	30, 90[c]	95
13		Ac$_2$O[e]	0.1	30, 25	65[f]
14			0.1	0, 360	85[f]
15			0.1	−18, 840	90[f]
16		Ac$_2$O[e]	0.1	30, 50	83[f]
17			0.1	0, 960	96[f]
18			1.0	0, 3	0 (95[g])

[a] Unless otherwise noted, a dichloromethane solution of the substrate (0.25 M) was used. [b] Unless otherwise noted, the isolated yield by column chromatography on silica gel is indicated. [c] Nitromethane as a solvent was used in place of dichloromethane. [d] Yb(BHFPSA)$_3$ 0.1 mol% was used in place of Sm(BHFPSA)$_3$ in CH$_3$NO$_2$. [e] Acetic anhydride as a solvent was used in place of dichloromethane. [f] The yield was determined by gas chromatographic analysis of the crude product. [g] The yield of olefins was determined by gas chromatographic analysis of the crude product.

In summary, a novel and effective Lewis acid catalyst for the acylation of alcohols with acid anhydride under very mild conditions has been demonstrated. The results show that Ln(BHFPSA)$_3$ is a stable acylation catalyst that is insensitive to protic substances such as alcohols and carboxylic acids.

Experimental

A typical experimental procedure is described for the acylation of *sec*-phenethyl alcohol with acetic anhydride using samarium tris{bis[bis(1,1,1,3,3,3-hexafluoro-2-propoxy)sulfonyl]amide} [Sm(BHFPSA)$_3$] as catalyst. Samarium sesquioxide (Sm$_2$O$_3$, 0.4491 g, 1.29 mmol) was added to an aqueous solution (50 v/v%) of bis[bis(1,1,1,3,3,3-hexafluoro-2-propoxy)sulfonyl]amine,[8] H[NSO$_2$OCH(CF$_3$)$_2$]$_2$, (3.6870 g, 7.73 mmol) and the mixture was stirred at 30 °C for 1 h. The remaining solid was filtered off and evaporation *in vacuo* gave a solid residue of samarium amide. Overnight dehydration under 1 mmHg at 80 °C gave anhydrous Sm(BHFPSA)$_3$ (1.27 mmol, 98% yield).

Sm(BHFPSA)$_3$ (7.6 mg, 4.8 μmol), *sec*-phenethyl alcohol (0.5880 g, 4.8 mmol), and nitromethane (19 ml) were placed in a two-necked reaction flask and then acetic anhydride (0.68 ml, 7.22 mmol) was rapidly added to the flask under electromagnetic stirring at 30 °C. The reaction was monitored by the TLC. After 13 min the reaction was finished. The nitromethane was evaporated and the residue was extracted with diethyl ether. The ether solution was then successively washed with aqueous sodium hydrogencarbonate and water. The organic layer was dried over magnesium sulfate, filtered, and concentrated *in vacuo* to afford the crude product. Further purification was performed by column chromatography on silica gel (0.71 g, 91% isolated yield).

Selected data for Sm(BHFPSA)$_3$: IR (Nujol, cm^{-1}) 1638(w), 1290(m), 1240(m), 1200(s), 1155(m), 1040(m), 900(w), 688(m); δ_H (80 MHz, CD$_3$CN/TMS) 5.56 (spt, CH); δ_F (CD$_3$CN/C$_6$F$_6$) 90.8 (d, CF$_3$) (Found: C, 13.4; H, 0.7; N, 2.6. C$_{18}$H$_6$F$_{36}$N$_3$O$_{18}$S$_6$Sm requires C, 13.7; H, 0,4; N, 2.7%).

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