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LETTERS

Lanthanum triflate-catalysed allylation of aldehydes: crucial activation by benzoic acid

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Abstract—Lanthanum triflate in combination with benzoic acid catalyses the allylation of aldehydes at low catalyst loading, without the need to activate the catalyst in advance.

The use of lanthanide triflates as Lewis acid catalysts has been well documented.[1,2] Properties such as low toxicity, moisture and air tolerance and their recyclability make them attractive alternatives to Lewis acids such as $AlCl_3$.

We recently reported the use of benzoic acid to accelerate the reaction between aldehydes and allyltributyltin with ytterbium triflate as the catalyst.[3] That procedure used only 2 mol% of ytterbium triflate but required that the catalyst be activated by drying for 2 h at 160°C under vacuum immediately before use. The reaction also required an inert atmosphere. We now report that the use of benzoic acid eliminates the need to dry the catalyst and allows the use of a significantly cheaper and less active catalyst, lanthanum triflate.

During our study into the scope of the ytterbium triflate–benzoic acid allylation protocol, we found that lanthanum triflate was almost as effective a catalyst as ytterbium triflate for a variety of aldehydes. At this time, the catalyst was still being activated before use. The use of unactivated lanthanide triflate catalyst was reported by Umani-Ronchi et al. for the allylation of imines[4] and we decided to apply this to our lanthanum triflate allylation protocol. Table 1 shows the results of the allylation reaction between various aldehydes and allyltributyltin in which the lanthanum triflate catalyst and solvent were not dried.

The yields ranged from moderate to excellent with the lowest yields obtained for aliphatic aldehydes octaldehyde (55%) and the *gem*-dimethyl-substituted heptaldehyde (50%). In the case of the latter aldehyde, this could be due to the hindered nature of the carbonyl group.

Before the development of the unactivated catalyst protocol, the catalyst had been dried in the usual way and a comparison of the unactivated catalyst results with those obtained with the activated catalyst shows very little difference between them (Table 2).

We decided that an investigation into the mechanism was needed to obtain a clearer understanding of the role of the benzoic acid. A recent report commented that the formation of triflic acid (CF_3SO_3H) from the combination of the Lewis and Brønsted acids could be catalysing the reaction.[5] However, our own investigation showed that 6 mol% triflic acid did not catalyse the formation of the product. We believed what we were observing was a Brønsted assisted Lewis acid. A further study of the literature revealed other examples of this kind of Brønsted assisted Lewis acid acceleration. Kobayashi et al.[6] combined scandium triflate with HCl in a 1:1 ratio to produce a very active catalyst for the aldol reaction. A series of experiments confirmed that the Brønsted acid was **not** simply regenerating the catalyst and that the Brønsted and Lewis acids were acting together as a *combined catalyst* for the reaction. Individually they did not produce the same results. Ciufolini et al. reported an acceleration in a $Yb(fod)_3$ catalysed ene reaction.[7,8] This example closely relates to our situation. They speculated that carboxylic acid

Keywords: lanthanides; catalysis; tin; Brønsted acidity; Lewis acidity.

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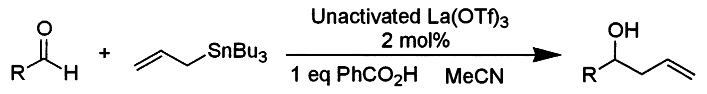
Table 1. Scope of allylation reaction with unactivated catalyst



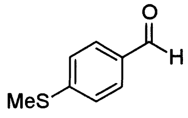
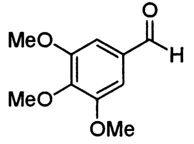
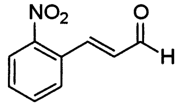
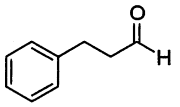
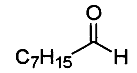
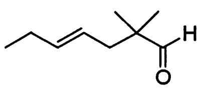
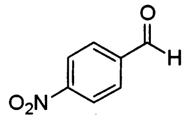
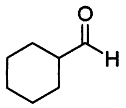
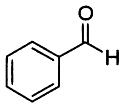
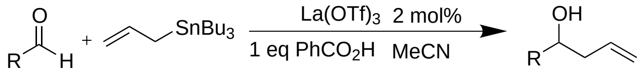
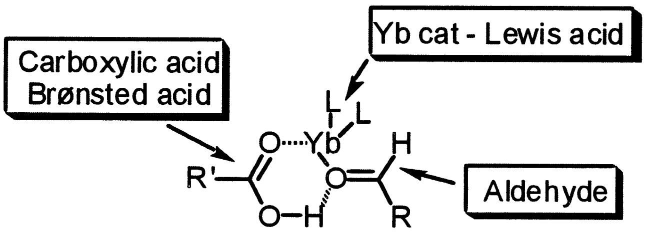
Aldehyde	Time/ mins	Yield/ %	Aldehyde	Time/ mins	Yield/ %
	90	69		110	88
	210	62		110	76
	170	55		75	50
	90	93		75	67
	130	79			

Table 2. Comparison of activated and unactivated catalyst



R	Activated catalyst		Unactivated catalyst	
	Time (min)	Yield (%)	Time (min)	Yield (%)
Ph	o/n	67	130	79
4-MeS-(C_6H_4)-	o/n	72	90	69
2-Nitrocinnamyl-	270	75	210	62
C_7H_{15}	225	70	170	55
4-NO_2-(C_6H_4)-	270	83	90	93
3,4,5-MeO-(C_6H_2)-	o/n	87	110	88
Hydrocinnamyl-	225	62	110	76

impurities combine with the Lewis acid to produce a 'double activation' of the aldehyde (Scheme 1). For our own investigation of the mechanism, we turned to GC reaction tracking to monitor the reactions with time and under various conditions.

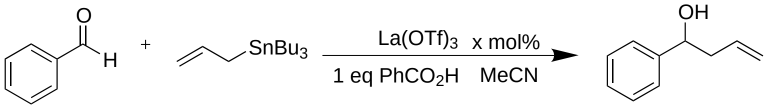


Scheme 1.

After carrying out various experiments both with 5 and 100 mol% lanthanide catalysts, we came to the following conclusions. The benzoic acid together with the Lewis acid form an *enhanced Brønsted acid* that catalyses the reaction. This was further confirmed by observing that 100 mol% catalyst without Brønsted acid did not catalyse the reaction in the same time, proving that the Brønsted acid does not simply regenerate the catalyst.

Various reports on the use of lanthanide catalysts have focused on their recyclability.[1,2] We decided to demonstrate that this was possible in our system. Our model reaction used benzaldehyde as the model aldehyde and 10 mol% lanthanum triflate catalyst, this was to facili-

Table 3. Catalyst recovery and re-use



Use	Mol% cat.	Time (min)	Yield (%)	Cat. recovered (%)
1st	10	120	83	88
2nd	2[a]	130	68	–

[a] Recovered catalyst.

tate its recovery. Using our procedure, we recovered 88% of the lanthanum triflate catalyst, which was then used in 2 mol% for its second use (Table 3). The recovered catalyst afforded the homoallylic alcohol in 68% yield, compare this with the fresh catalyst which affords the product in 79% yield in the same time.

In summary, we have reported the use of a less active catalyst in our benzoic acid–lanthanide triflate allylation protocol. We have eliminated the need to dry this catalyst before use, which is desirable in terms of both reaction times and convenience. We have also carried out an investigation into the mechanism and the role of the benzoic acid in order to obtain a better understanding of this simple allylation procedure.

Typical procedure: Lanthanum triflate (0.0141 g, 0.024 mmol, 2 mol%), benzoic acid (0.149 g, 1.22 mmol, 1 equiv.), freshly distilled (if liquid at rt) aldehyde (1.22 mmol, 1 equiv.) and allyltributylstannane (454 μl, 1.46 mmol, 1.2 equiv.) were dissolved in MeCN (2 mL). The reaction was monitored by thin layer chromatography and on completion was quenched with a 2 M NaOH solution (2 mL) and partitioned between water (10 mL) and DCM (10 mL). The aqueous layer was further extracted with DCM (3×10 mL). The combined organic extracts were dried with $MgSO_4$ and the solvent removed under reduced pressure to afford the crude product. Purification via flash column chromatography (typical eluant; 10–30% ether:petroleum ether) yielded the products.

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