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LETTERS

Ytterbium trichloride-catalyzed allylation of aldehydes with allyltrimethylsilane

Xinggao Fang, John G. Watkin and Benjamin P. Warner*

Mail Stop J514, Chemical Science & Technology (CST) Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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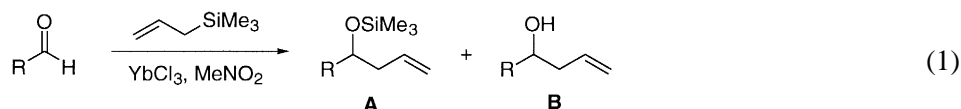
Abstract

Ytterbium chloride (YbCl_3) is found to be an effective catalyst for the allylation of both aromatic and aliphatic aldehydes using allyltrimethylsilane. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: aldehydes; allylation; dienes; lanthanides.

Lewis acid promoted allylation of aldehydes with allylsilanes or allylstannanes has been the subject of extensive investigation, since it affords synthetically useful allylic alcohols.¹ While most traditional Lewis acids such as TiCl_4 , BF_3 and SnCl_4 promote this reaction, recent work has demonstrated that several rare earth triflates, $\text{Ln}(\text{OTf})_3$ ($\text{OTf}=\text{O}_3\text{SCF}_3$), also catalyze the allylation of aldehydes.² For example, Aspinall and co-workers recently reported that ytterbium triflate ($\text{Yb}(\text{OTf})_3$) catalyzes the reaction of aldehydes with allyltributylstannane,³ while Aggarwal et al. have reported scandium triflate-catalyzed addition of the less reactive allyltrimethylsilane to aldehydes.⁴ Lanthanide-based Lewis acid catalysts also have the advantage of water stability^{2a,5} while most traditional Lewis acids are extremely moisture sensitive and require special care in handling and storage.

However, there does appear to be scope for improvement in this reaction—scandium triflate is extremely expensive while stannic compounds are known to be toxic. We previously found the more readily available and economical anhydrous YbCl_3 to be an efficient Lewis acid catalyst for the Diels–Alder reactions of unactivated dienes with unsaturated carbonyl compounds.⁶ Here we would like to report that commercial-grade anhydrous YbCl_3 is also an effective catalyst for allylation of both aromatic and aliphatic aldehydes with allyltrimethylsilane (Eq. (1)).



* Corresponding author. Tel: 505-665-6962; fax: 505-667-9905; e-mail: warner@lanl.gov (B. P. Warner)

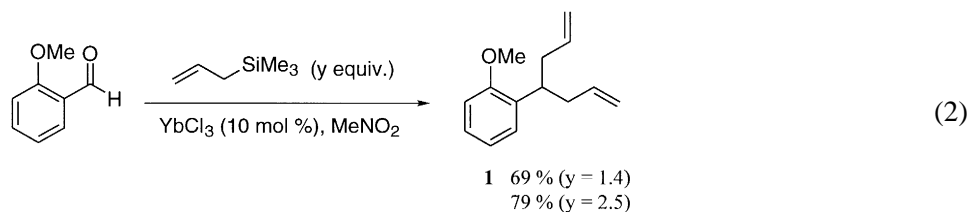
As shown in Table 1, allyltrimethylsilane reacts with a range of aromatic and aliphatic aldehydes, catalyzed by 10 mol% of YbCl_3 , in nitromethane at room temperature over about 16 h to give the respective allyl alcohols together with their trimethylsilyl ethers in high yields. It was found that the reaction may be run in air without loss of activity. However, attempts to run the reaction in water produced no allylated products, nor did attempted reactions employing acetonitrile or THF as solvent. The use of methylene chloride as solvent led to significantly lower yields of products.

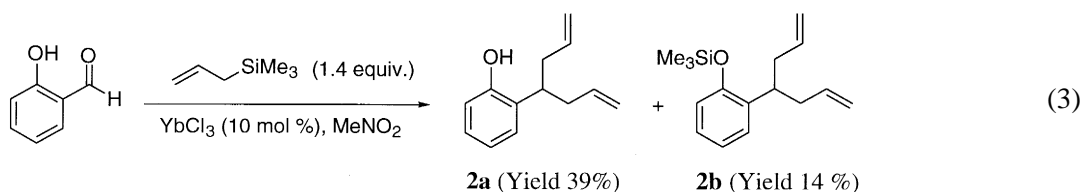
Table 1

Entry	R	Yield (%)	
		A	B
1	Ph	62	10
2	2-ClC ₆ H ₄	85	9
3	4-NO ₂ C ₆ H ₄	90	0
4	<i>c</i> -C ₆ H ₁₁	68	13
5	<i>n</i> -C ₇ H ₁₅	59	13
6	COOEt	36	41

Typical experimental procedure: To a stirred suspension of YbCl_3 (anhydrous, Strem Chemical Co., 50 mg) in nitromethane (3 mL) at room temperature was added the appropriate aldehyde (10 equivalents) followed by allyltrimethylsilane (14 equivalents). The resulting mixture was stirred overnight (ca. 16 h) at ambient temperature and quenched with aqueous NaHCO_3 . The mixture was then extracted with CH_2Cl_2 (3 \times) and the organic layer washed with saturated NaCl and dried over anhydrous Na_2SO_4 . Volatiles were removed and the residue purified by flash column chromatography on silica gel with hexane and ethyl acetate as eluents to give products as colorless oils. The products were analyzed by ^1H NMR and GC–MS spectroscopy.

Interestingly, the use of some benzaldehydes bearing electron-donating substituents on the benzene ring led to the isolation of ‘double allylation’ products in moderate yields (Eqs. (2) and (3)), with no mono-allylation product being detected even with the use of excess aldehyde.⁷ Analogous bis-allylation products were also observed when 2-furaldehyde was employed as substrate, although in lower yields. GC–MS analysis of the products of the bis-allylation reactions revealed the presence of bis(trimethylsilyl)ether, $\text{Me}_3\text{SiOSiMe}_3$, as by-product.





We have found very few literature reports of bis-allylation of carbonyl compounds.⁸ We note that previous reports of allylation of aldehydes in which lanthanide triflates were employed as catalyst make no mention of a bis-allylation reaction, even when >1 equivalent of allyltrimethylstannane was employed.

In summary, we have demonstrated that YbCl₃ is a practical Lewis acid catalyst for the allylation of various aldehydes with allyltrimethylsilane under very mild and convenient conditions, and that exclusive bis-allylation of certain electron-rich aldehydes is observed. Asymmetric versions of this catalyst are currently being explored in our laboratory.

Acknowledgements

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- Spectroscopic data for **1**: ¹H NMR (300 MHz, CDCl₃) δ 2.42 (t, *J*=7.8 Hz, 4H), 3.28 (quintet, *J*=7.1 Hz, 1H), 3.83 (s, 3H), 4.95 (m, 4H), 5.71 (m, 2H), 6.93 (m, 2H), 7.16 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 33.7, 39.0, 55.6, 110.8, 115.1, 120.6, 126.5, 127.0, 128.0, 133.0, 137.5, 161.0. MS (EI, *m/e*) 202 (M⁺), 161, 146, 91. Spectroscopic data for **2a**: ¹H NMR (300 MHz, CDCl₃) δ 2.40 (t, *J*=7.7 Hz, 4H), 3.13 (quintet, *J*=7.3 Hz, 1H), 4.66 (s, 1H, OH), 4.96 (m, 4H), 5.71 (m, 2H), 6.75 (d, *J*=7.8 Hz, 1H), 6.91 (t, *J*=7.5 Hz, 1H), 7.12 (m, 2H). MS (EI, *m/e*) 188 (M⁺), 147. Spectroscopic data for **2b**: ¹H NMR (300 MHz, CDCl₃) δ 0.32 (s, 9H), 2.39 (m, 4H), 3.20 (quintet, 1H, *J*=7.3 Hz), 4.97 (m, 4H), 5.71 (m, 2H), 6.79 (dd, *J*=8.1, 1.2 Hz, 1H), 6.94 (dt, *J*=7.6, 1.2 Hz, 1H), 7.07 (dd, *J*=7.3, 1.7 Hz, 1H), 7.12 (dt, *J*=7.6, 1.7 Hz, 1H). MS (EI, *m/e*) 260 (M⁺), 219, 203, 73. In addition, *p*-anisaldehyde (16% yield) and 2-furaldehyde (22% yield) gave exclusively double- rather than mono-allylation products.
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