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Catalytic propargylation of aldehydes with allenyltributylstannane by ytterbium triflate

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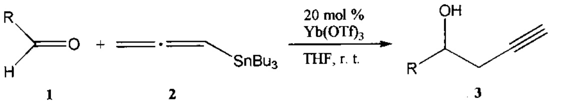
Abstract

The first ytterbium triflate [$Yb(OTf)_3$]-catalyzed propargylation of various aldehydes with allenyltributylstannane to afford homopropargyl alcohols in good yields is described. The present result provides a versatile tool for preparation of an array of homopropargyl alcohols from the reaction of aldehydes with allenyltributylstannane; which are known to possess low reactivity.

Keywords: Allenyltributylstannane; Catalytic propargylation; Ytterbium triflate

The carbon–carbon bond-forming reaction has been considered one of the most challenging subjects in organic synthesis. A variety of organometals have been utilized for the above-mentioned purpose. Amongst these organometals, organotin compounds have been one of the most frequently used by virtue of their high reactivity and selectivity. In general, the majority of examples using organotin compounds reported to date are based on Lewis acid-promoted reactions of allylstannanes with aldehydes (or their corresponding imines) affording homoallyl alcohols (or their corresponding homoallyl amines) [1]. However, there are few examples using allenyltributylstannane compared with those using allylstannane, presumably due to its low reactivity. Even the reactions of allenyltributylstannanes with aldehydes employed so far giving homopropargyl alcohols required more than stoichiometric amounts of Lewis acid to accomplish the desired reaction [2,3]. In this paper, the first $Yb(OTf)_3$-catalyzed reaction of aldehydes with allenyltributylstannane [4] to afford homopropargyl alcohols in good yields is described Eq. (1) [5][1].



1 **2** **3** (1)

Initial studies focused on the development of optimal conditions for the present reaction. At the outset, the reaction of benzaldehyde **1a** with allenyltributylstannane **2** in THF using 20 mol% $Yb(OTf)_3$ at room temperature was undertaken. As expected, ^{1}H-NMR analysis of the reaction mixture revealed that the corresponding homopropargyl alcohol **3a** was produced in 82% yield. However, several other solvents such as CH_2Cl_2, CH_3CN and *n*-hexane gave the desired product in lower yield.

Table 1
$Yb(OTf)_3$-catalyzed propargylation of aldehydes [a]

Entry	Aldehyde	Yield (%)[b]
1	Benzaldehyde (**1a**)	82(73) [d]
2 [c]	*p*-Nitrobenzaldehyde (**1b**)	91(87) [d]
3	2-Furfural (**1c**)	71
4	*n*-Octanal (**1d**)	66
5	*n*-Hexanal (**1e**)	60
6	*m*-Methoxybenzaldehyde (**1f**)	60
7	*p*-Methoxybenzaldehyde (**1g**)	41

[a] Unless otherwise noted, all reactions were carried out in the presence of $Yb(OTf)_3$ (20 mol%) in THF at room temperature for 4 days.

[b] ^{1}H-NMR yields.

[c] The reaction was carried out for 2 days.

[d] Isolated yields.

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[1] O–Sn bond which was generated from the reaction of aldehyde with the tin compound would be hydrolyzed in the work-up stage.

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The results obtained for various substrates are summarized in Table 1. The aldehydes **1a**,**b** possessing a phenyl or an electron-deficient aryl substituent reacted effectively with allenyltributylstannane **2** to afford homopropargyl alcohols **3a**,**b**, respectively, in high yields (entries 1 and 2). In addition, 2-furfural (**1c**) converted smoothly to the desired alcohol **3c** in good yield (entry 3). Even the aldehydes **1d**,**e**, having an aliphatic substituted R group, also gave good results (entries 4 and 5). When the benzophenone was used as a carbonyl compound, the desired propargylated product was produced in lower yield (less than 40%) even with prolonged reaction time. It is worth noting that the present reaction of aldehyde with allenyltributylstannane could be used as a useful way affording propargyl alcohols without transposition giving allenyl or scrambling products [6,7].

The ytterbium triflate-catalyzed reaction of benzaldehyde (**1a**) with allenyltributylstannane (**2**) is representative. Benzaldehyde (**1a**) (0.05 ml, 0.5 mmol) was added to a solution of $Yb(OTf)_3$ (0.061 g, 98 mmol) and allenyltributylstannane 2 (0.198 g, 0.6 mmol) in THF (2 ml) under an Ar atmosphere. The reaction mixture was then stirred at room temperature. When the starting aldehyde was completely consumed, the reaction mixture was quenched with water and then extracted with diethyl ether. After the evaporation of diethyl ether, the resulting crude oil was treated with ethyl acetate (2 ml) and a saturated KF solution (3 ml). The mixture was stirred for 5 h and then extracted with diethyl ether. After the usual work-up, the product **3a** was isolated by column chromatography on silica gel using *n*-hexane:ethyl acetate (10:1) as eluent in 73% yield (0.054 g)[2,3].

In summary, the first $Yb(OTf)_3$-catalyzed efficient propargylation of aldehydes with allenyltributylstannane has been developed. $Yb(OTf)_3$ is a relatively nontoxic and easily handled catalyst in comparison with classical Lewis acid. Therefore, the present reaction provides a versatile tool for the preparation of an array of homopropargyl alcohols.

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[2] When the $Sc(OTf)_3$ was used as a catalyst, the desired product **3a** was produced in 72% ^{1}H-NMR yield. However, in the case of $La(OTf)_3$, only trace amounts of product was obtained.

[3] Selected spectral data for compound **3a**: ^{1}H-NMR (270 MHz) ($CDCl_3$) δ 7.41–7.23 (m, 5H), 4.87 (t, 1H, $J = 6.1$ Hz), 2.62 (d, 2H, $J = 6.1$ Hz), 2.16 (s, 1H), 2.03 (s, 1H). MS (m/z) 146. Anal. Calc. C,82.160; H, 6.985. Found C, 82.201; H, 6.888.