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Lanthanum Trichloride: A Simple and Efficient Catalyst for Allylation of Aldehydes with Allyltributylstannane

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Abstract: Aldehydes undergo smooth nucleophilic addition with allyltributylstannane in the presence of lanthanum trichloride to afford the corresponding homoallylic alcohols in excellent yields. All the reaction conditions were carried out in acetonitrile solvent at room temperature. In all the cases, the catalyst was used in a catalytic amount (10% mol).

Keywords: Aldehydes, allytributylstannane, homoallylic alcohols, lanthanum trichloride

The allylation of aldehydes with allyltributylstannane is a powerful method for carbon–carbon bond formation. The homoallylic alcohols are important building blocks for the construction of various biologically active compounds.[1] Hence, the synthesis of homoallylic alcohols is important. Consequently, several methods have been developed for allylation of aldehydes with allylmetal complexes to produce homoallylic alcohols.[2,3] One of the most straightforward synthetic procedures involves the nucleophilic addition of allyltin reagents to aldehydes in the presence of catalysts. However, many of these catalysts are expensive, moisture sensitive, and difficult to handle and involve the use of strongly acidic conditions, which limit their use in the synthesis of

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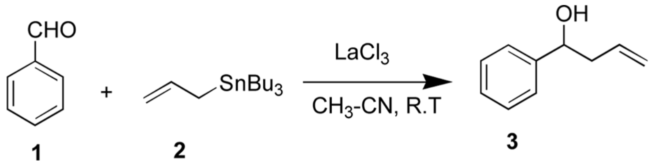


Scheme 1.

complex molecules containing acid-sensitive functionalities. Thus, there is scope for further improvements to create milder reaction conditions and better yields. Among Lewis acids, metals and transition-metal complexes have been extensively utilized to catalyze or promote the allylation in past years.[4–6] Water-tolerant Lewis acids have been developed as catalysts for the allylation of aldehydes, but they are rather expensive.[7,8] Therefore, there is interest in development of new catalysts for efficient allylation of aldehydes under mild reaction conditions. The catalyst lanthanum trichloride ($LaCl_3$) is known for various organic transformations in the literature as a mild, inexpensive, and moisture-stable Lewis acid.[9] However, there are no reports on allylation of aldehydes with lanthanum trichloride. In this article, we describe an efficient and high-yielding method for allylation of aldehydes with allyltributylstannane in the presence of lanthanum trichloride.

Accordingly, an equimolar amount of benzaldehyde **1** and allyltributylstannane **2** were treated in the presence of lanthanum trichloride (10% mol) to obtain the corresponding product of 1-phenyl-3-buten-1-ol in 93% yield (entry a) as shown in Scheme 1. The reaction proceeds smoothly at room temperature in acetonitrile solvent. Encouraged by the result obtained with benzaldehyde, we turned our attention to various aldehydes such as aliphatic, aromatic, α,β-unsaturated, heterocyclic, and alicyclic aldehydes. The acid-sensitive aldehydes such as furfural (entry c) and 2-phenylacetaldehyde (entry g) were efficiently converted into the corresponding homoallylic alcohols. In the case of α,β-unsaturated aldehyde (entry d), the allylation reaction takes place smoothly without forming 1,4-addition by-product. In a similar manner, 4-methoxybenzaldehyde (entry b) and 3,4,5-trimethoxybenzaldehydes (entry k) were reacted efficiently to give the corresponding homoallylic alcohols in excellent yields, and no bis-allylated products were observed. The aliphatic system of n-octnal (entry f), n-butanal (entry i), and cyclohexanal (entry l) were treated with allyltributylstannane in the presence of lanthanum trichloride to afford the corresponding homoalllylic alcohols in very good yields. The reactions were very clean, and no side products were observed. In general, all the reactions were carried out at room temperature in acetonitrile solvent. In all the cases, the catalyst was used in a catalytic amount (10% mol). The reactions were completed in 3.0 to 6.0 h, and the obtained yields ranged from 80% to 95%.The aliphatic aldehydes and electron-withdrawing group containing an aromatic system, such as 4-nitrobenzaldehyde (entry e), required a little more time for completion of the reaction.

The proposed mechanism shows that the catalyst lanthanum trichloride activates the carbonyl carbon rapidly, followed by the weakening of the carbon–stannane bond. This action makes the allyltributylstannane more nucleophilic and at the same time more susceptible to decomposition.

In conclusion, we have described here a simple, convenient, and efficient method for the preparation of homoallylic alcohols with various aldehydes and allyltributylstannane in the presence of lanthanum trichloride (10% mol). All the reactions were carried out at room temperature in acetonitrile. The salient features of this methodology are good conversions, mild reaction conditions, and simplicity in operation to isolate the products.

GENERAL EXPERIMENTAL PROCEDURE

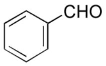
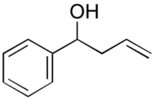
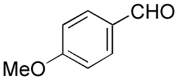
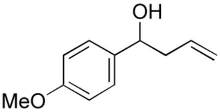
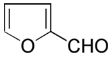
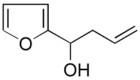
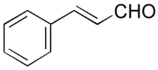
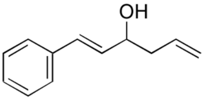
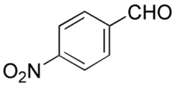
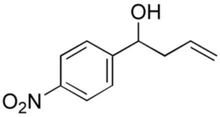
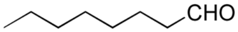
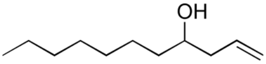
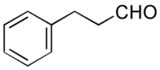
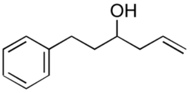
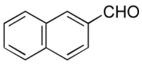
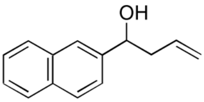
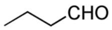
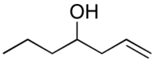
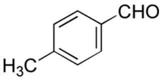
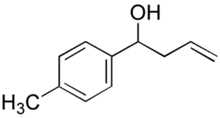
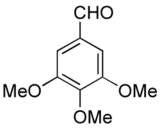
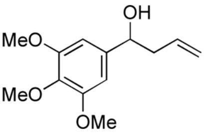
The catalyst lanthanum trichloride (0.2 mmol) was added to a stirred mixture of aldehyde (2 mmol) and allyltributylstannane (2 mmol) in acetonitrile (5 ml) at room temperature. The resulting reaction mixture was stirred for a specified period (Table 1). After completion of the reaction, as indicated by thin-layer chromatography (TLC), the solvent from the reaction mixture was removed under reduced pressure. Ethylacetate (10 ml) and water (10 ml) were added to the obtained residue, stirred well for some time, and extracted with ethylacetate. The organic layer was washed with water and brine and dried over Na_2SO_4. The ethylacetate was removed under reduced pressure, and the obtained crude homoallylic alcohol product was purified by column chromatography.

SPECTRAL DATA FOR SELECTED COMPOUNDS

1-Phenylbut-3-en-1-ol (3a)

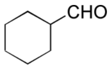
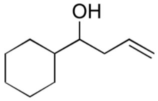
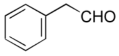
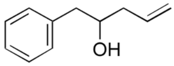
Colorless oil. IR (neat): ν 3416, 3081, 2965, 2853, 1647, 1508, 1459, 1263, 1104, 971, 759, 732 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.18 (brs, 1 H), 2.37–2.43 (m, 2 H), 4.63 (t, 1 H, $J = 6.0$ Hz), 5.05–5.20 (m, 2 H), 5.35–5.70 (m, 1 H), 7.27–7.40 (m, 5 H). EIMS: m/z (%). 148 (m$^+$ 12), 130 (10), 115 (15), 107 (100), 91 (20), 79 (54), 63 (25), 51 (33).

Table 1. Lanthanum trichloride–catalyzed allylation of aldehydes with allyltributylstannane

No.	Aldehyde	Homoallylicalcohol[a]	Reaction time (h)	Yield (%)[b]
a			4.0	93
b			3.5	93
c			3.0	94
d			4.0	83
e			6.0	86
f			5.5	85
g			6.0	87
h			4.5	90
i			5.0	80
j			3.5	92
k			3.0	95

(*Continued*)

Table 1. Continued

No.	Aldehyde	Homoallylicalcohol[a]	Reaction time (h)	Yield (%)[b]
l			5.5	86
m			4.5	90

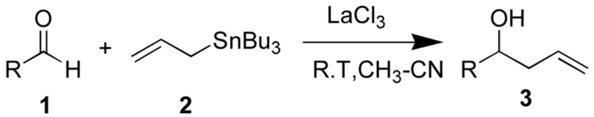
[a] All the products were characterized by spectroscopy data.
[b] Yields were isolated and not optimized.

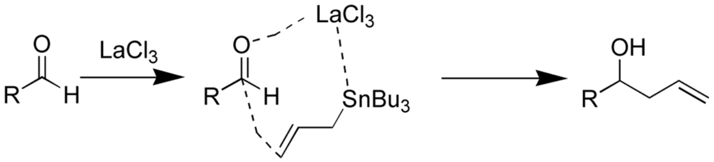
1-(2-Furyl)but-3-en-1-ol (3c)

Colorless oil. IR (neat): ν 3391, 3076, 2951, 2843, 1645, 1568, 1504, 1435, 1347, 1261, 1138, 1055, 948, 867, 739 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.10 (brs, 1 H), 2.50–2.60 (m, 2 H), 4.70 (t, 1 H, $J = 6.0$ Hz), 5.10–5.20 (m, 2 H), 5.70–5.80 (m, 1 H), 6.21 (dd, 1 H, $J = 0.8$ & 3.5 Hz), 6.29 (dd, 1 H, $J = 1.5$ & 3.5 Hz), 7.35 (dd, 1 H, $J = 2.5$ & 0.8 Hz). EIMS: m/z (%): 138 (m$^+$, 18), 119 (62), 96 (38), 91 (100), 89 (26), 77 (15), 63 (18), 49 (12), 29 (31).

1-Phenylhexa-1,5-dien-3-ol (3d)

Colorless oil. ^{1}H NMR (CDCl$_3$): δ 1.80 (brs, 1 H), 2.30–2.40 (m, 2 H), 4.30 (t, 1 H, $J = 6.5$ Hz), 5.10–5.20 (m, 2 H), 5.70–5.80 (m, 1 H), 6.20 (dd, 1 H, $J = 16.0$ & 6.0 Hz), 6.55 (d, 1 H, $J = 16.0$ Hz), 7.15–7.35 (m, 5 H).





Scheme 2. Proposed mechanism.

Phenylhex-1-en-4-ol (3g)

Colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.60–1.70 (m, 2 H), 1.80 (brs, 1 H), 2.05–2.20 (m, 2 H), 2.65–2.75 (m, 2 H), 3.50–3.60 (m, 1 H), 4.95–5.05 (m, 2 H), 5.65–5.75 (m, 1 H), 7.05–7.20 (m, 5 H).

1-(4-Methylphenyl)but-3-en-1-ol (3j)

Colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.96 (brs, 1 H), 2.30 (s, 3 H), 2.43–2.50 (m, 2 H), 4.65 (t, 1 H, $J = 6.0$ Hz), 5.05–5.15 (m, 2 H), 5.70–5.80 (m, 1 H), 7.06 (d, 2 H, $J = 7.5$ Hz), 7.19 (d, 2 H, $J = 7.5$ Hz).

1-Cyclohexylbut-3-en-1-ol (3l)

Colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.90–1.20 (m, 6 H), 1.60–1.70 (m, 5 H), 1.80 (brs, 1 H), 2.10–2.30 (m, 2 H), 3.30–3.40 (m, 1 H), 5.05–5.15 (m, 2 H), 5.75–5.85 (m, 1 H).

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