

AMBERLIST-15: AN EFFICIENT CATALYST FOR ALLYLATION OF ALDEHYDES WITH ALLYLTRIBUTYLSTANNANE

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ABSTRACT: A variety of aldehydes undergo smooth nucleophilic addition with allyltributyl stannane in the presence of solid acid catalyst amberlist-15 in acetonitrile solvent. The reaction conditions were very mild and the corresponding products of homoallylic alcohols were obtained in excellent yields.

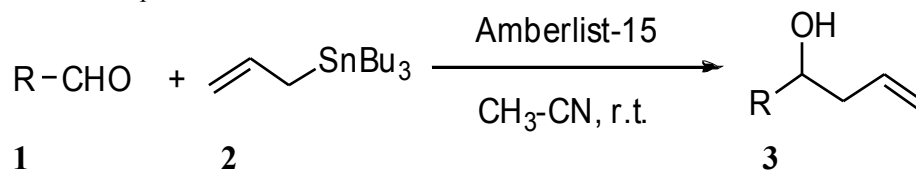
Keywords: Aldehydes, homoallylic alcohols, amberlist-15, allyltributylstannane.

INTRODUCTION

Homoallylic alcohols are important building blocks for the construction of various biologically active compounds.¹⁻⁵ Owing to their usefulness in organic synthesis homoallylic alcohols become more important. Consequently, several methods have been developed for allylation of aldehydes with allylmetal complexes to produce homoallylic alcohols.⁶⁻¹⁰ One of the most straight forward synthetic procedures involves the nucleophilic addition of allyltin reagents to aldehydes in the presence of Lewis acids. However, many of these catalysts are expensive, moisture sensitive and difficult to handle. Furthermore, most of the methods involve the use of strongly acidic conditions, which limit their use in the allylation of complex molecules containing acid sensitive functionalities. Thus there is a scope for further improvements towards milder reaction conditions and better yields. Among Lewis acids, especially metals or transition metal complexes have been extensively utilized to catalyze or promote the allylation in the past years.¹¹⁻¹⁸ However, the traditional methods using Lewis acids such as $\text{BF}_3 \cdot \text{OEt}_2$, TiCl_4 and SnCl_4 must be carried out under strictly anhydrous conditions. Water tolerant Lewis acids like Lanthanide triflates, have been developed as catalysts for the allylation of aldehydes, but they are rather expensive.¹⁹⁻²⁴ Therefore, there is an interest in development of a versatile catalyst for efficient allylation of aldehydes under mild reaction conditions. The obvious advantages of the solid acid catalysts in organic synthesis prompted us to explore the use of a macro reticular sulfonic acid based polystyrene cation exchange amberlist-15 resin. This catalyst is inexpensive, commercially available and catalyzes various organic transformations.²⁵⁻²⁸

RESULTS AND DISCUSSIONS:

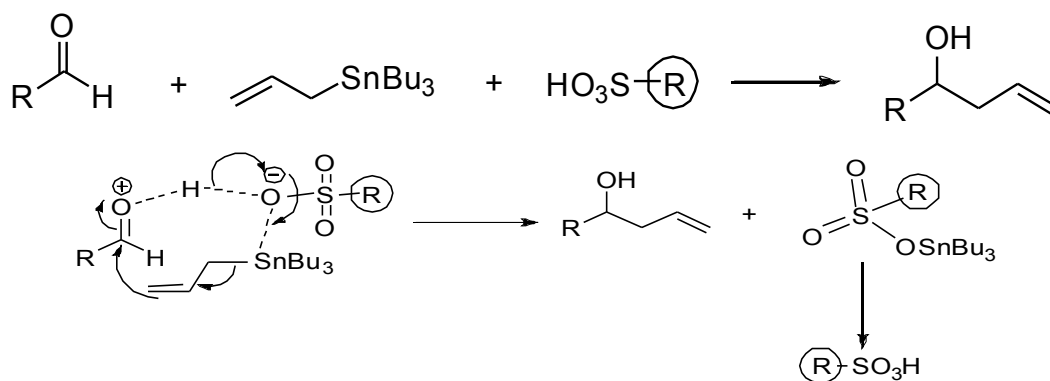
In recent years, heterogeneous catalysts are gaining much importance due to their interesting reactivity as well as economic and ecological point of view. In our previous report, we have explored this catalyst for regioselective ring opening of various oxiranes with amines. In continuation of our ongoing programme in developing new synthetic methodology,²⁹⁻³² herein, we report, an efficient protocol for allylation of aldehydes with allyltributylstannane using Amberlist-15 at room temperature.



Scheme 1

In a typical experiment, an equimolar amount of benzaldehyde and allyltributylstannane was treated in the presence of amberlist-15, to obtain the corresponding product of 1-phenyl-3-buten-1-ol in 90% yield (entry a). The reaction was completed within 3.0 hours in acetonitrile solvent at room temperature. Encouraged by this result, we turned our attention to carry out the reactions with a variety of aldehydes under similar reaction conditions. Interestingly, a wide range of substrates including aromatic, aliphatic, heterocyclic and α , β -unsaturated aldehydes reacted efficiently with allyltributylstannane in presence of the solid acid catalyst amberlist-15, to give the corresponding homoallylic alcohols in excellent yields. No bisallylated products were obtained with methoxy substituted arylaldehydes, which are normally observed in the allylation reactions^{2c} 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), no 1, 4-addition product, was observed. In a similar manner, 4-methoxybenzaldehyde was reacted smoothly to give the corresponding homoallylic alcohol in 93% yield (entry b) and the reaction time also very short. The aliphatic system of *n*-octanal (entry f) and cyclohexanal (entry l) were reacted very smoothly, while giving the required product in very good yield (entry c). The reaction proved to be general and could be applied to a broad range of aldehydes.

Mechanism.



Scheme 2. Plausible mechanism for the nucleophilic addition with allyltributylstannane using amberlist-15.

As shown in the proposed mechanism (Scheme 2), the acidic functionalized catalyst, amberlyst-15, activates the carbonyl carbon to take place the reaction. Furthermore, the acidity of the catalyst plays an important role not only in activation of carbonyl carbon but also in weakening the carbon-stannane bond. This action makes the allyltributyl stannane more nucleophilic.

CONCLUSIONS

In conclusion, we have demonstrated an efficient and simple method for the preparation of homoallylic alcohols with various aldehydes and allyltributylstannane in the presence of solid acid catalyst, amberlist-15. All the reactions were carried out at room temperature in acetonitrile solvent. The salient features of this methodology are high conversions, mild reaction conditions and simplicity in operation makes the catalyst a useful and attractive strategy over existing methods for the preparation of homoallylic alcohols.

Experimental section:

General Methods. IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer meter. ¹H NMR-spectra was recorded on Gemini-200 spectrometer in CDCl₃ using TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV.

General Procedure: To a mixture of aldehydes (2.0 mmol) and allyltributylstannane (2.0 mmol) in acetonitrile (10 mL) was added amberlist-15 (2.0 mmol) at room temperature. The resulting mixture was stirred for a specified period (Table 1). After completion of the reaction, as indicated by TLC, the reaction mixture was filtered and washed the solid with solvent (2x5 mL). The combined filtrates were concentrated under reduced pressure and the obtained crude product was dissolved in ethyl acetate and washed with water, brine and dried over Na₂SO₄. The ethyl acetate was removed under reduced pressure and the obtained crude homoallylic alcohol product was purified by column chromatography.

Spectral data for compounds:

1-Phenylbut-3-en-1-ol (3a): Light brownish liquid. IR (neat): ν 3386, 3084, 2963, 2851, 1643, 1506, 1455, 1261, 1108, 973, 758, 734 cm⁻¹; ¹H NMR (CDCl₃): δ 2.18 (brs, 1H), 2.37-2.43 (m, 2H), 4.63 (t, 1H, J = 6.0 Hz), 5.05-5.20 (m, 2H), 5.35-5.70 (m, 1H), 7.27-7.40 (m, 5H); ¹³C NMR (CDCl₃): δ 144.5, 134.8, 128.6, 127.9, 126.5, 118.4, 72.9, 42.6; EIMS m/z (%): 148 (m⁺, 12), 130 (10), 115 (15), 107 (100), 91 (20), 79 (54), 63 (25), 51 (33).

1-(4-Methoxyphenyl)but-3-en-1-ol (3b): Colorless oil. IR (neat): ν 3405, 3071, 2947, 2835, 1641, 1516, 1465, 1379, 1258, 1133, 1016, 945, 863, 749 cm⁻¹; ¹H NMR (CDCl₃): δ 2.25 (brs, 1H), 2.40 (t, 2H, J = 6.8 Hz), 3.80 (s, 3H), 4.62 (t, 1H, J = 6.8 Hz), 5.08-5.18 (m, 2H), 5.45-5.80 (m, 1H), 6.85 (d, 2H, J = 7.0 Hz), 7.24 (d, 2H, J = 7.0 Hz); ¹³C NMR (CDCl₃): δ 141.8, 137.2, 135.5, 129.6, 125.9, 118.5, 73.8, 44.6, 22.0; EIMS m/z (%): 178 (m⁺, 15), 163 (12), 147 (100), 120 (25), 106 (60), 76 (34), 63 (25), 51 (22).

1-(2-Furyl)but-3-en-1-ol (3c): Pale green liquid. IR (KBr): ν 3408, 3076, 2989, 2843, 1645, 1568, 1504, 1435, 1261, 1138, 1055, 948, 867, 739 cm⁻¹; ¹H NMR (CDCl₃): δ 2.10 (brs, 1H), 2.50-2.60 (m, 2H), 4.70 (t, 1H, J = 6.0 Hz), 5.10-5.20 (m, 2H), 5.70-5.80 (m, 1H), 6.21 (dd, 1H, J = 1.0 & 3.5 Hz), 6.29 (dd, 1H, J = 1.5 & 3.5 Hz), 7.35 (dd, 1H, J = 3.5 & 1.0 Hz); ¹³C NMR (CDCl₃): δ 156.9, 142.1, 134.1, 119.6, 110.2, 106.1, 67.0, 40.6; EIMS m/z (%): 138 (m⁺, 18), 119 (62), 103 (22), 96 (38), 91 (100), 89 (26), 73 (15), 69 (12), 63 (18), 49 (12), 39 (31).

(E)-1-Phenylhexa-1, 5-dien-3-ol (3d): Colorless oil: IR (neat): ν 3345, 3084, 2971, 2837, 1640, 1615, 1587, 1465, 1339, 1231, 1108, 1041, 1015, 986, 843, 746 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 1.80 (brs, 1H), 2.30-2.40 (m, 2H), 4.30 (t, 1H, $J = 6.5\text{Hz}$), 5.10-5.20 (m, 2H), 5.70-5.80 (m, 1H), 6.20 (dd, 1H, $J = 16.0$ & 6.0 Hz), 6.55 (d, 1H, $J = 16.0$ Hz), 7.15-7.35 (m, 5H); $^{13}\text{C NMR}$ (CDCl_3): δ 136.9, 134.1, 131.6, 130.2, 128.1, 127.6, 126.8, 118.9, 72.0, 42.6; EIMS m/z (%): 174 (m 25), 147 (18), 133 (45), 103 (100), 91 (10), 77 (58), 51 (35).

1-(4-Nitrophenyl)But-3-en-1-ol (3e): Brown oil. IR (neat): ν 3410, 3078, 2957, 2843, 1645, 1518, 1428, 1346, 1238, 1120, 1033, 967, 853, 751 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 2.30 (brs, 1H), 2.45-2.60 (m, 3H), 4.85 (dd, 1H, $J = 4.0$ & 8.0 Hz), 5.15 (d, 1H, $J = 17.0$ Hz), 5.25 (d, 1H, $J = 10.0$ Hz), 5.75-5.85 (m, 1H), 7.52 (d, 2H, $J = 8.5$ Hz), 8.20 (d, 2H, $J = 8.5$ Hz); $^{13}\text{C NMR}$ (CDCl_3): δ 151.6, 147.1, 133.6, 127.4, 124.5, 120.1, 72.3, 44.6; EIMS m/z (%): 193 (m 20), 166 (15), 147 (100), 135 (10), 120 (20), 76 (15), 51 (22).

Undec-1-en-4-ol ((3f)): Colorless liquid. IR (neat): ν 3330, 3055, 1642, 1589, 1512, 1497, 1416, 1365, 1278, 1208, 1173, 1120, 1094, 1010, 978, 865, 806, 769, 732 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 0.90 (t, 3H, $J = 6.5$ Hz), 1.15-1.30 (m, 10H), 1.35-1.45 (m, 2H), 1.80 (brs, 1H), 2.05-2.30 (m, 2H), 3.50-3.60 (m, 1H), 5.02-5.12 (m, 2H), 5.70-5.80 (m, 1H); $^{13}\text{C NMR}$ (CDCl_3): δ 135.8, 118.9, 71.5, 41.3, 37.6, 33.1, 30.2, 29.5, 26.2, 23.8, 14.1; EIMS m/z (%): 170 (m 100), 143 (15), 129 (10), 99 (20), 71 (15), 63 (12), 43 (25).

1-Phenylhex-5-en-3-ol (3g): Colorless oil: IR (neat): ν 3302, 3069, 2943, 2851, 1641, 1572, 1461, 1325, 1209, 1126, 1020, 953, 816, 739 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 1.60-1.70 (m, 2H), 1.80 (brs, 1H), 2.05-2.20 (m, 2H), 2.65-2.75 (m, 2H), 3.50-3.60 (m, 1H), 4.95-5.05 (m, 2H), 5.65-5.75 (m, 1H), 7.05-7.20 (m, 5H); $^{13}\text{C NMR}$ (CDCl_3): δ 141.6, 134.2, 128.5, 125.9, 118.5, 70.1, 42.3, 38.6, 32.1; EIMS m/z (%): 176 (m 18), 158 (12), 149 (20), 135 (80), 117 (15), 105 (100), 91 (10), 76 (35), 51 (28).

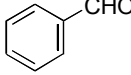
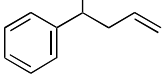
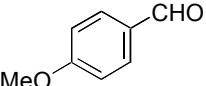
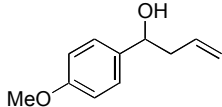
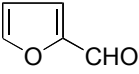
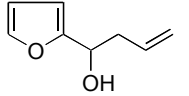
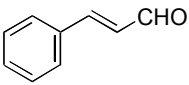
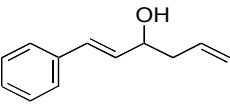
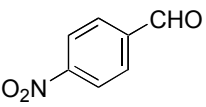
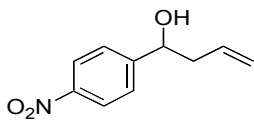
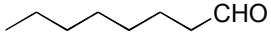
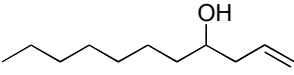
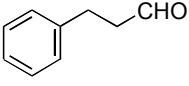
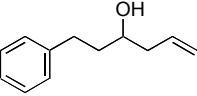
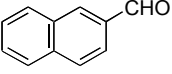
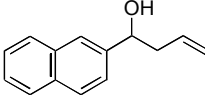
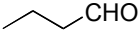
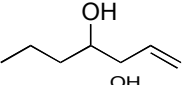
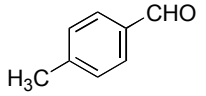
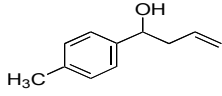
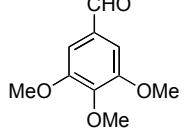
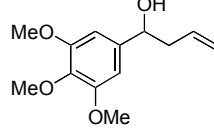
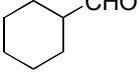
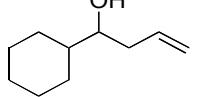
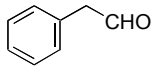
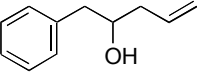
1-(2-Naphthyl)But-3-en-1-ol (3h): Colorless liquid. IR (neat): ν 3405, 3071, 2956, 2841, 1638, 1529, 1461, 1370, 1256, 1138, 1073, 948, 739 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 2.20 (brs, 1H), 2.45-2.55 (m, 2H), 4.85 (dd, 1H, $J = 4.5$ & 8.0 Hz), 5.10-5.20 (m, 2H), 5.70-5.80 (m, 1H), 7.35-7.45 (m, 3H), 7.70-7.80 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3): δ 141.4, 135.1, 133.9, 133.4, 128.9, 128.5, 127.9, 126.8, 126.0, 125.0, 124.6, 118.4, 72.9, 43.8; EIMS m/z (%): 198 (m 25), 171 (12), 157 (10), 127 (100), 102 (22), 76 (34), 51 (20).

1-(4-Methylphenyl)But-3-en-1-ol (3j): Thick Symp. IR (neat): ν 3390, 3053, 2967, 2839, 1645, 1432, 1328, 1215, 1108, 1035, 952, 871, 743 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 1.96 (brs, 1H, OH), 2.30 (s, 3H), 2.43-2.50 (m, 2H), 4.65 (t, 1H, $J = 6.0\text{Hz}$), 5.05-5.15 (m, 2H), 5.70-5.80 (m, 1H), 7.06 (d, 2H, $J = 7.5\text{Hz}$), 7.19 (d, 2H, $J = 7.5$ Hz); EIMS m/z (%): 178 (m 20), 163 (15), 147 (100), 120 (25), 106 (70), 89 (42), 76 (25), 64 (15), 51 (20).

1-(3, 4, 5-Trimethoxyphenyl)But-3-en-1-ol (3k): Colorless oil. IR (neat): ν 3396, 3084, 2951, 2839, 1640, 1518, 1435, 1342, 1253, 1130, 1026, 941, 873, 738 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 2.10 (d, 1H, $J = 3.0$ Hz), 2.48 (t, 2H, $J = 6.5$ Hz), 3.80 (s, 3H), 3.84 (s, 6H), 4.65 (t, 1H, $J = 6.5$ Hz), 5.10-5.20 (m, 2H), 5.75-5.90 (m, 1H), 6.80 (s, 2H); EIMS m/z (%): 238 (m 12), 223 (10), 207 (100), 192 (20), 176 (40), 169 (52), 154 (40), 139 (20), 106 (60), 76 (34), 63 (25), 51 (22).

1-Cyclohexylbut-3-en-1-ol (3l): Colorless liquid. IR (neat): ν 3332, 3065, 1642, 1586, 1510, 1493, 1426, 1345, 1265, 1122, 1057, 1015, 973, 895, 816, 741 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 0.90-1.20 (m, 6H), 1.60-1.70 (m, 5H), 1.80 (brs, 1H), 2.10-2.30 (m, 2H), 3.30-3.40 (m, 1H), 5.05-5.15 (m, 2H), 5.75-5.85 (m, 1H); $^{13}\text{C NMR}$ (CDCl_3): δ 136.1, 118.6, 75.5, 43.3, 39.1, 30.1, 28.6, 27.0, 26.8, 26.4. EIMS m/z (%): 154 (m 100), 127 (35), 113 (65), 83 (22), 56 (12), 42 (15).

Table 1: Amberlist-15 catalyzed allylation of aldehydes with allylstannane.

Entry	Aldehyde	Homoallylic alcohol	Reaction Time (h)	Yield ^b (%)
a			3.0	90
b			2.5	93
c			2.5	95
d			3.0	88
e			4.0	89
f			5.0	86
g			4.5	86
h			3.5	89
i			4.5	85
j			4.0	89
k			3.0	93
l			4.5	87
m			3.5	89

^aProducts were confirmed by their ¹H NMR, IR and mass spectroscopy.^bYields were isolated by column chromatography and unoptimized.

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