Analysis on using a super acid catalyst, homoallylic alcohols are synthesised. Sodium zirconia

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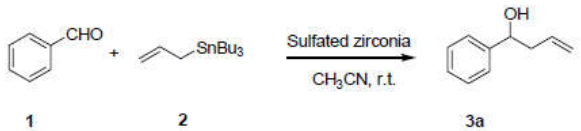
Abstract
In order to create homoallyllic alcohols in large quantities, the catalytic allylation of aldehydes was developed employing solid super acid, sulfated zirconia as a heterogenous catalyst. Sulfated zirconia in acetonitrile acts as a catalyst to effectively convert a wide variety of aromatic, aliphatic, and heterocyclic aldehydes into homoallyllic alcohols. Filtration makes it simple to recover the catalyst, which may then be utilized again for additional cycles with a slow loss of activity.
Keywords: Allylation, aldehydes, allyltin, sulfated zirconia, homoallylic alcohols.

INTRODUCTION

One of the most common ways to generate carbon-carbon bonds is by the allylation of carbonyl compounds. 1-5 Indeed, homoallylic alcohols play a crucial role in the production of a variety of physiologically active substances. 6–10 using Prins cyclization specifically for tetrahydropyran derivatives. As a result, a number of procedures have been devised for the allylation of aldehydes with different allylmetal complexes to produce homoallylic alcohols. 11-15 Allylstannanes are among the most desirable allylmetal reagents due to their strong reactivity and relative stability. 16 In general, it is known that acid catalysts encourage the nucleophilic addition of allyltin reagents to aldehydes. For the allylation of aldehydes using allylstanne, the most popular Lewis acids are BF3.OEt3, TiCl4, TMSOTf, and SnCl4. 17-24 The majority of these acids, however, are moisture sensitive and degrade while being worked up, thus they can't be recycled for further runs. Subsequently, water tolerant Lewis acids, in particular lanthanide triflates have been developed for the allylation of aldehydes.. However, most these catalysts are expensive therefore which limits their use in large scale synthesis. Therefore, the development of simple, convenient and recyclable reagents for the allylation of aldehydes would expend the scope this methodology.

Recently, the use of heterogeneous solid acid catalysts has received tremendous interest in different areas of organic synthesis.[25-27] The heterogenous solid acids are especially advantageous over conventional homogeneous acid catalysts as they can be easily recovered from the reaction mixture by simple filtration and can be reused after activation or without activation, thereby making the process economically more viable. Of several solid acids, sulfated zirconia shows excellent catalytic activity for various organic transformations.[28-36] The catalytic features of sulfated zirconia are different from the conventional acid catalysts. However, there are no reports on the use of sulfated zirconia for the synthesis of homoallylic alcohols.

Following our interest in developing new synthetic methodologies using solid acids, we herein reporta simple and efficient protocol for the allylation of aldehydes with allyltributylstannane using a catalytic amount of sulfated zirconia at room temperature.



Scheme 1: preparation of 1-phenyl-3-buten-1-ol 3a

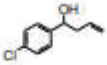
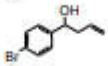
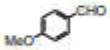
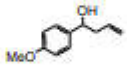
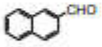
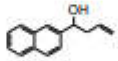
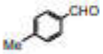
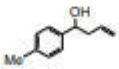
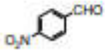
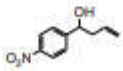
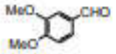
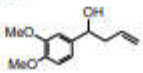
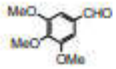
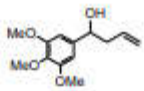
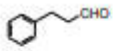
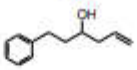
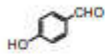
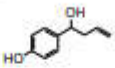
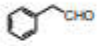
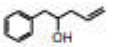
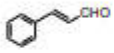
In a typical experiment, an equimolar amount of benzaldehyde (**1)** was treated allyltributylstannane (**2)** in the presence of 5 mol% of sulfated zirconia in acetonitrile at room temperature. The desired 1-phenyl-3-buten-1-ol **3a** was obtained in 95% yield (Scheme 1). The reaction was complete within 3h at room temperature. In order to optimize the reaction conditions, benzaldehyde was treated with allylstannane using different amounts of sulfated zirconia in various solvents. As shown in Table 1, high conversions were achieved in short reaction times in acetonitrile when compared to other solvents. The use of just 5 mol% of the catalyst is sufficient to promote the reaction. In the absence of sulfated zirconia, the reaction was sluggish and the conversion was less than 20% even after a prolonged reaction time (24 h). The result was obtained with 5 mol% of sulfated zirconia inacetonitrile at room temperature. Encouraged by this result, we turned our attention to perform the allylation with a variety of aldehydes under similar reaction conditions.

Entry	Solvent	Time (h)	Yield (%)
1	CH_3CN	3	95
2	CH_2Cl_2	24	80
3	Benzene	24	82
4	Acetone	24	65
5	Ethanol	24	70
6	--	24	<10

Table.1. Sulfated zirconia catalyzed synthesis of homoallylic alcohols

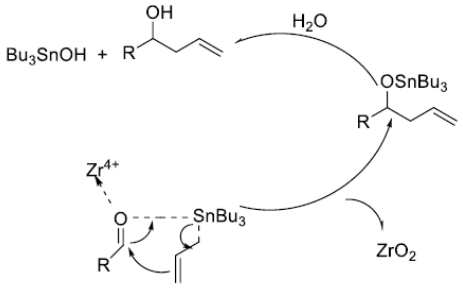
Interestingly, a wide range of substrates including aromatic, aliphatic and heterocyclic aldehydes reacted effectively with allylstannane in the presence of sulfated zirconia to give the corresponding homoallylic alcohols in excellent yields (Table 2). Both electron-rich and electron-poor substrates reacted well in good yields with a little influence of substituent on aromatic ring. This method is compatible with various functional groups such as nitro, hydroxyl and halide (entries b-d, h and l, Table 2). Notably, sterically hindered substrates such as 2-naphthaldehyde and 3,4,5-trimethoxybenzaldehyde participated well under similar conditions (entries f and j, Table 2). Acid sensitive substrates such as phenyl acetaldehyde and furfural also reacted well under the reaction conditions to give the homoallylic alcohols in good yields (entries m and p, Table 2). This method also works well with aliphatic substrates (entries k, o and r, Table 2). Furthermore, this method is clean and free from side reactions such as bis-allylation, which are normally observed in the allylation of methoxy substituted aryl aldehydes (entries e, i and j, Table 2). Also the insolubility of the catalyst in most of the organic solvents facilitates an ease separation of the catalyst. The catalyst was easily separated by a simple filtration and reused after activation with a gradual decrease in activity. The recovered sulfated zirconia was recycled in subsequent reactions. Thus, the method wasproved to be general and could be applied to a broad range of aldehydes (Table 2). All the reactions were carried out at room temperature in acetonitrile and the products were confirmed by their spectral data.

Table 2. Allylation of aldehydes with allyltributylstannane using sulfated zirconia

Entry	Aldehyde	Allyltributylstannane	Product (3)[a]	Time (h)	Yield (%)[b]
a				3.0	95
b				5.0	82
c				4.5	82
d				6.0	80
e				3.0	92
f				3.0	92
g				3.5	90
h				6.0	80
i				3.0	90
j				3.0	93
k				4.5	86
l				5.0	80
m				5.0	80
n				3.0	85
o				5.0	86
p				3.5	87
q				3.5	89
r				4.0	87

[a]All products were characterized by NMR, IR and mass spectrometry.
[b]Yield refers pure products after chromatograpy

A probable mechanistic pathway to explain the allylation process is depicted in Scheme 2. Mechanistically, the reaction was proposed to proceed by an initial coordination of Zr^{4+} with the carbonyl group which facilitates C-C bond formation. Subsequent hydrolysis of $–OSnBu_3$ results in the formation of homoallylic alcohol (Scheme 2). Furthermore, the acidity of the catalyst plays an important role not only in activation of the carbonyl carbon but also in weaking the carbon-stannane bond. This action makes the allylstannane more nucleophilic nature.



Scheme 2. A plausible reaction mechanism

General Procedure

To a mixture of aldehydes (2.0 mmol) and allyltributylstannane (2.0 mmol) in acetonitrile (10 ml) was added sulfated zirconia (5 mol%) at room temperature. The resulting mixture was stirred for a specified period (Table 2). After completion of the reaction, as indicated by TLC, the mixture was diluted with water and extracted with EtOAc (3 x 10 ml). The combined organic layers were concentrated in vacuo and purified by column chromatography on silica gel to afford pure homoallylic alcohols.

Spectral data for principal compounds :

3a: 1-Phenylbut-3-en-1-ol: Brown liquid, IR (neat): υ 3386, 3084, 2963, 2851,1643,1506,1455,1261,1108,973,758,734 cm^{-1} ; ^1H NMR ($CDCl_3$) : 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) ; ^{13}C NMR ($CDCl_3$) : δ 144.5, 134.8, 128.6, 127.9, 126.5, 118.4, 72.9, 42.6. ; EIMS *m/z* (%). 148 (M^+).

3e : 1-(4-Methoxyphenyl)-But-3-en-1-ol : Colourless oil ; IR (neat) : υ 3405, 3071, 2947, 2835, 1641, 1516, 1465, 1379, 1258, 1133, 1016, 945, 863, 749 cm^{-1}; ^1H NMR ($CDCl_3$) : 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).; ^{13}C NMR ($CDCl_3$) : δ 141.8, 137.2, 135.5, 129.6, 125.9, 118.5, 73.8, 44.6, 22.0.; EIMS *m/z* (%). 178 (M^+).

3p: 1-(2-Furyl) But-3-en-1-ol : Pale green liquid. IR (KBr) : υ 3408, 3076, 2989, 2843, 1645, 1568, 1504, 1435, 1261, 1138, 1055, 948, 867, 739 cm^{-1} ; ^1H NMR ($CDCl_3$) : 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* = 3.5 & 1.0 Hz).; ^{13}C NMR ($CDCl_3$) : δ 156.9, 142.1, 134.1, 119.6, 110.2, 106.1, 67.0, 40.6.; EIMS *m/z* (%). 138 (M^+).

CONCLUSION

In conclusion, utilizing sulfated zirconia, a cheap and non-corrosive catalyst, we have created a novel, operationally straightforward, and highly effective allylation method of aldehydes. The catalytic process takes place in acetonitrile at room temperature. High conversions, mild reaction conditions,

and ease of use are the key characteristics of this technology, which makes it an effective and appealing method for producing homoallylic alcohols.

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