Synthesis of homoallylic alcohols by using a super acid catalyst Sulfated zirconia

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Abstract: The catalytic allylation of aldehydes were developed using solid super acid, sulfated zirconia as a heterogenous catalyst to produce homoallyllic alcohols in high yields. A high range of aromatic, aliphatic and heterocyclic aldehydes are efficiently converted into homoallyllic alcohols under the catalytic influence of sulfated zirconia in acetonitrile at room temperature. The catalyst can be easily recovered by filtration and reused for further cycles with a gradual decrease in activity.

Keywords: Allylation, aldehydes, allyltin, sulfated zirconia, homoallylic alcohols.

INTRODUCTION

The allylation of carbonyl compounds is one of the prime methods for carbon-carbon bond formation.¹⁻⁵ Indeed, homoallylic alcohols are important building blocks for the synthesis of various biologically active compounds ⁶⁻¹⁰ especially for tetrahydropyran derivatives by means of Prins cyclization. Consequently, several methods have been developed for the preparation of homoallylic alcohols by allylation of aldehydes with various allylmetal complexes.¹¹⁻¹⁵ Of various allylmetal reagents, allylstannanes are attractive because of their relative stability and high reactivity.¹⁶ Generally, acid catalysts are known to promote for the nucleophilic addition of allyltin reagents to aldehydes. The most widely used Lewis acids, for the allylation of aldehydes with allylstanne are BF₃.OEt₃, TiCl₄, TMSOTf and SnCl₄.¹⁷⁻²⁴ However, most of these acids are moisture sensitive and are decomposed during work-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

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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 report a 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

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prolonged reaction time (24 h). The result was obtained with 5 mol% of sulfated zirconia in acetonitrile at room temperature. Encouraged by this result, we turned our attention to perform the allylation with a variety of aldehydes under similar reaction conditions.

Table 1.Sulf	ated zirconia catalyzed syr	zirconia catalyzed synthesis of homoallylic alcohols				
Entry	Solvent	Time (h)	Yie l d (%)			
1	CH ₃ CN	3	95			
2	CH_2CI_2	24	80			
3	Benzene	24	82			
4	Acetone	24	65			
5	Ethanol	24	70			
6		24	<10			

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 3,4,5trimethoxybenzaldehyde 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 was proved 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.

Entry	Aldehyde	Allyltributylstannane	Product (3) ^a	Time (h)	Yield (%) ^b
а	СНО	SnBu ₃	OH	3.0	95
b	СІСНО	SnBu ₃	CI	5.0	82
с	Br	SnBu ₃	Br	4.5	82
d	Br CHO	SnBu ₃	Br OH	6.0	80
e N	1eO CHO	SnBu ₃	MeO	3.0	92
f	СССНО	SnBu ₃	OH	3.0	92
g N	Me CHO	SnBu ₃	Me	3.5	90
^h C	D ₂ N CHO	SnBu ₃	O ₂ N OH	6.0	80
i M	eO CHO	SnBu ₃	OH MeO MeO	3.0	90
j M	eO HeO OMe	SnBu ₃	MeO MeO OMe	3.0	93
k	ССНО	SnBu ₃	OH	4.5	86
I H	но СНО	SnBu ₃	ОН	5.0	80
m	Сто	SnBu ₃	ОН	5.0	80
n	СНО	SnBu ₃	OH	3.0	85
0	СНО	SnBu ₃	OH	5.0	86
р	Сно	SnBu ₃	O OH	3.5	87
q	СНО	SnBu ₃	Слудон он	3.5	89
r /	СНО	SnBu ₃	ОН	4.0	87

^aAll products were characterized by NMR, IR and mass spectrometry. ^bYield refers pure products after chromatograpy

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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 (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⁺).

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 (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⁺).

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 (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 = 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⁺).

CONCLUSION

In conclusion, we have developed a new, operationally simple, and highly efficient allylation process of aldehydes using inexpensive and non-corrosive sulfated zirconia as a catalyst. The reaction is catalytic and proceeds at room temperature in acetonitrile. The salient features of this methodology are high conversions, mild reaction conditions, and simplicity in operation which makes this protocol a useful and attractive strategy for the preparation of homoallylic alcohols.

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