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Zirconia Supported Phosphotungstic Acid Mediated Synthesis of Homoallylic Alcohols

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An alternative synthesis of homoallylic alcohols (3a-j) has been developed using zirconia supported tungstophosphoric acid (ZrO_2/PTA) as a heterogeneous catalyst with a variety of aromatic aldehydes (1a-j) and allyltributylstannane (2) at room temperature. The products were formed with in 2-5 h and good to high yields.

Key Words: Zirconia supported tungstophosphoric acid, allyltributylstannane, heterogeneous catalyst, temperature, homoallylic alcohols.

INTRODUCTION

Homoallylic alcohols[1] are important building blocks for the construction of various biologically active compounds and hence the synthesis of these compounds is highly useful. Nucleophilic addition of allyltin reagents to carbonyl compounds[2] in the presence of a catalyst is a straightforward method for the synthesis of homoallylic alcohols. A variety of Lewis acids (polymer-supported scandium[3], ligand accelerated cadmium[4], $NbCl_5$[5], $La(OTf)_3$[6], $CeCl_3$-$7H_2O$-NaI[7], $ReBr(CO)_5$[8], TCT[9], $HClO_4$-SiO_2[10] and potassium dodecatungstocobaltate trihydrate[11]) including $TiCl_4$, BF_3-Et_2O, $SnCl_4$, $InCl_3$, $AlCl_3$ and $MgBr_2$. The search for new reagents capable of mediating these reactions is still a matter of much concern.

In this paper we describes our results on the use of zirconia supported tungstophosphoric acid (ZrO_2/PTA) as a heterogeneous catalyst for the synthesis of homoallylic alcohols (**3a-j**) by the reaction of a variety of aromatic aldehydes and allyltributylstannane (**2**) at room temperature (Scheme 1).

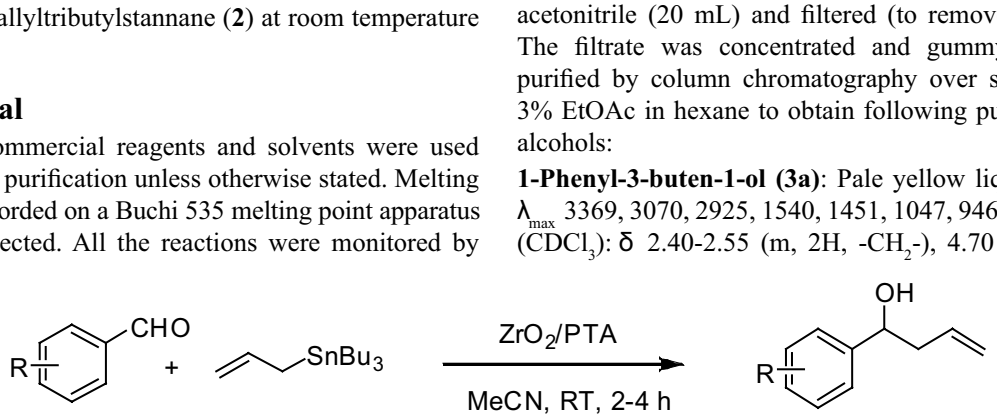
Experimental

All the commercial reagents and solvents were used without further purification unless otherwise stated. Melting points were recorded on a Buchi 535 melting point apparatus and are uncorrected. All the reactions were monitored by thin layer chromatography performed on precoated silica gel $60F_{254}$ plates (Merck). Compounds were visualized with UV light at 254 nm and 365 nm, I_2 and heating plates after dipping in 2% phosphomolybdic acid in 15% aq. H_2SO_4 soln. IR spectra were recorded on a Perkin-Elmer 683 or a 1310 FT-IR spectrometers with KBr pellets. NMR spectra were recorded on a Varian Unity-400 MHz and BRUKER AMX 300 spectrometers using TMS as an internal standard. Mass spectra were recorded on a VG Micromass 7070H and a Finnigan Mat 1020B mass spectrometers operating at 70eV.

General procedure for the preparation of homoallylic alcohols:

To a mixture of aldehyde (2.0 mmol) and allyltributylstannane (2.4 mmol) in acetonitrile (5 mL) ZrO_2/PTA (10 mol%) was added. The reaction mixture was stirred at room temperature and the reaction was monitored by TLC. After completion, the mixture was diluted with acetonitrile (20 mL) and filtered (to remove the catalyst). The filtrate was concentrated and gummy residue was purified by column chromatography over silica gel using 3% EtOAc in hexane to obtain following pure homoallylic alcohols:

1-Phenyl-3-buten-1-ol (3a): Pale yellow liquid, IR (neat): λ_{max} 3369, 3070, 2925, 1540, 1451, 1047, 946 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.40-2.55 (m, 2H, -CH_2-), 4.70 (t, 1H, -CH-),



1a-j **2** **3a-j**

Scheme 1: Synthesis of homoallylic alcohols

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5.10-5.20 (dd, 2H, =CH), 5.70-5.85 (m, 1H, -CH=), 7.20-7.35 (m, 5H, Ar-H).

1-(4-Methylphenyl)-3-buten-1-ol (3b): Pale yellow liquid, IR (neat): λ_{max} 3369, 3070, 2925, 1540, 1451, 1047, 946 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.35 (s, 3H, $-CH_3$), 2.40-2.55 (m, 2H, $-CH_2-$), 4.70 (t, 1H, -CH-), 5.10-5.20 (dd, 2H, =CH), 5.70-5.85 (m, 1H, -CH=), 7.20-7.35 (m, 5H, Ar-H).

1-(4-Bromophenyl)-3-buten-1-ol (3c): Pale yellow liquid, IR (neat): λ_{max} 3369, 3070, 2925, 1540, 1451, 1047, 946 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.40-2.55 (m, 2H, $-CH_2-$), 4.70 (t, 1H, -CH-), 5.10-5.20 (dd, 2H, =CH), 5.70-5.85 (m, 1H, -CH=), 7.20-7.35 (m, 5H, Ar-H).

1-(4-Chlorophenyl)-3-buten-1-ol (3d): Pale yellow liquid, IR (neat): λ_{max} 3369, 3070, 2925, 1540, 1451, 1047, 946 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.40-2.55 (m, 2H, $-CH_2-$), 4.70 (t, 1H, -CH-), 5.10-5.20 (dd, 2H, =CH), 5.70-5.85 (m, 1H, -CH=), 7.20-7.35 (m, 5H, Ar-H).

1-(2,4-Dichlorophenyl)-3-buten-1-ol (3e): Pale yellow liquid, IR (neat): λ_{max} 3369, 3070, 2925, 1540, 1451, 1047, 946 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.40-2.55 (m, 2H, $-CH_2-$), 4.70 (t, 1H, -CH-), 5.10-5.20 (dd, 2H, =CH), 5.70-5.85 (m, 1H, -CH=), 7.20-7.35 (m, 5H, Ar-H).

1-(4-Methoxyphenyl)-3-buten-1-ol (3f): Pale yellow liquid, IR (neat): λ_{max} 3369, 3070, 2925, 1540, 1451, 1047, 946 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.40-2.55 (m, 2H, $-CH_2-$), 4.70 (t, 1H, -CH-), 5.10-5.20 (dd, 2H, =CH), 5.70-5.85 (m, 1H, -CH=), 7.20-7.35 (m, 5H, Ar-H). **1-(3,4,5-Trimethoxyphenyl)-3-buten-1-ol (3g)**: Pale yellow liquid, IR (neat): λ_{max} 3369, 3070, 2925, 1540, 1451, 1047, 946 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.40-2.55 (m, 2H, $-CH_2-$), 4.70 (t, 1H, -CH-), 5.10-5.20 (dd, 2H, =CH), 5.70-5.85 (m, 1H, -CH=), 7.20-7.35 (m, 5H, Ar-H).

1-(4-Hydroxyphenyl)-3-buten-1-ol (3h): Pale yellow liquid, IR (neat): λ_{max} 3369, 3070, 2925, 1540, 1451, 1047, 946 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.40-2.55 (m, 2H, $-CH_2-$), 4.70 (t, 1H, -CH-), 5.10-5.20 (dd, 2H, =CH), 5.70-5.85 (m, 1H, -CH=), 7.20-7.35 (m, 5H, Ar-H).

1-(4-Nitrophenyl)-3-buten-1-ol (3i): Pale yellow liquid, IR (neat): λ_{max} 3369, 3070, 2925, 1540, 1451, 1047, 946 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.40-2.55 (m, 2H, $-CH_2-$), 4.70 (t, 1H, -CH-), 5.10-5.20 (dd, 2H, =CH), 5.70-5.85 (m, 1H, -CH=), 7.20-7.35 (m, 5H, Ar-H).

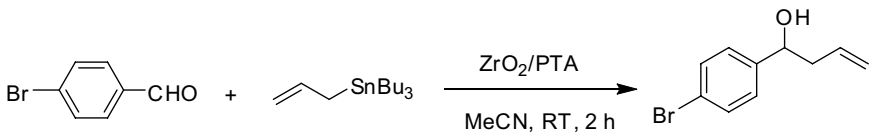
1-Naphthylphenyl-3-buten-1-ol (3j): Pale yellow liquid, IR (neat): λ_{max} 3369, 3070, 2925, 1540, 1451, 1047, 946 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.40-2.55 (m, 2H, $-CH_2-$), 4.70 (t, 1H, -CH-), 5.10-5.20 (dd, 2H, =CH), 5.70-5.85 (m, 1H, -CH=), 7.20-7.35 (m, 5H, Ar-H).

Results and Discussion

Upon screening with 4-bromobenzaldehyde, it was found that ZrO_2 supported PTA with low loading (10 mol%) is an efficient catalyst to bring about this transformation at room temperature. Blank experiments have shown that the PTA alone cannot bring about this transformation. In addition, only 10 mol% ZrO_2/PTA is sufficient for the synthesis of homoallylic alcohols from the reaction of various aldehydes with allyltributylstannane. In the absence of this catalyst only a trace of amount of homoallylic alcohol could be detected even after 10 h.

Encouraged by the results obtained from 4-bromobenzaldehyde with allyltributylstannane, we

Table 1: Optimizing the reaction conditions[a]



Entry	Catalyst (mol%)	Time (h)	Yield (%)[b]
1	ZrO_2/PTA (5)	2	76
2	ZrO_2/PTA (10)	2	88
3	ZrO_2/PTA (15)	2	90
4	ZrO_2/PTA (20)	2	91

[a]4-bromobenzaldehyde/allyltributylstannane/ZrO2/PTA - 2:2.4:10 (mol%)
[b]Isolated yields

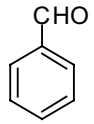
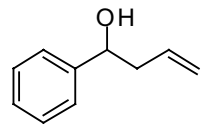
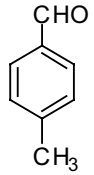
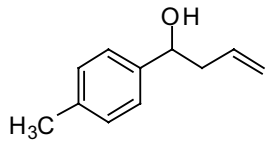
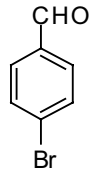
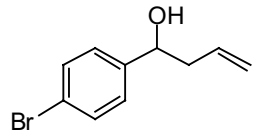
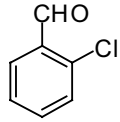
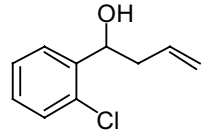
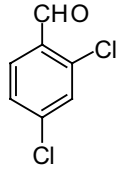
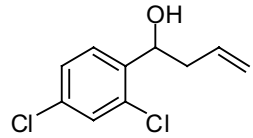
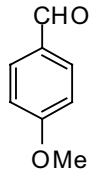
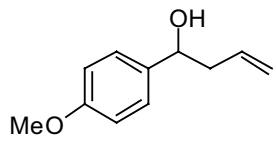
investigated a number of other aldehydes to probe their behavior under the current catalytic conditions. The aromatic aldehydes containing both electron-donating and electron-withdrawing groups in the aromatic ring proceeded smoothly.

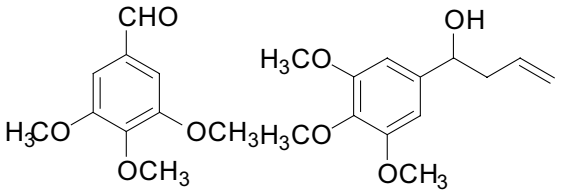
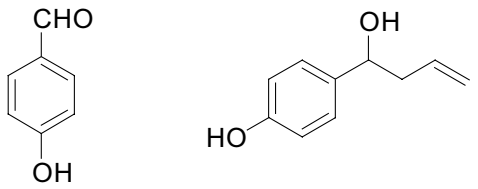
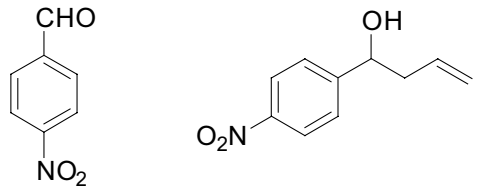
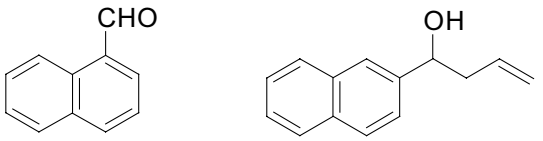
Next, we investigated the reusability and recycling of ZrO_2/PTA. At first, we put 4-bromobenzaldehyde (20 mmol), allyltributylstannane (21.6 mmol) and 100 mol% of ZrO_2/PTA in acetonitrile (50 mL) together, and then the mixture was stirred at room temperature. When the reaction was completed, the catalyst was separated by simple filtration by diluting with excess acetonitrile and recovered ZrO_2/PTA was activated and reused in subsequent reactions. Second and third reactions using recovered ZrO_2/PTA afforded similar yields to those obtained in the first run (88%). In the fourth and fifth runs, the yields were gradually decreased (80% and 75%).

Conclusions

In conclusion, we have successfully demonstrated a

Table 2: Synthesis of homoallylic alcohols using 10 mol% of ZrO_2/PTSA

Entry	Aldehyde (**1**)	Product (**3**)	Time (**h**)	Yield (**%**)
a			2	83
b			3	85
c			2	88
d			3	80
e			3	82
f			4	85

g		2	83
h		3	85
i		2	88
j		3	80

novel catalytic application of ZrO_2 supported phosphotungstic acid for the efficient synthesis of homoallylic alcohols. This simple procedure is efficient and can be applied to a variety of aromatic aldehydes to prepare homoallylic alcohols. The ambient reaction conditions, shorter reaction times, good to excellent product yields make this catalytic system an alternative method for the synthesis of homoallylic alcohols.

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