Rapid synthesis of homoallylic alcohol from aldehyde with allyltributylstannane under solvent-free conditions

Pranjal P. Bora, H. Atoholi Sema, Barisha Wahlang, and Ghanashyam Bez

Abstract: A catalytic amount (2 mol %) of phosphotungstic acid (PTA) is sufficient to synthesize homoallylic alcohol in excellent yields from aldehyde with allyltributylstannane upon grinding under solvent-free reaction conditions. Easy handling, very short reaction time, solvent-free reaction conditions, and aqueous workup free isolation protocol may make our method very useful for synthetic chemists.

Key words: aldehyde, allyltributylstannane, homoallylic alcohol, phosphotungstic acid, grinding.

Résumé : Une quantité catalytique (2 mol %) d'acide phosphotungstique (APT) est suffisante pour effectuer la synthèse d'alcools homoallyliques, avec d'excellents rendements, par broyage d'un aldéhyde avec de l'allyltributylstannane dans des conditions réactionnelles sans solvant. La facilité de la manipulation, son temps de réaction très court, les conditions réactionnelles sans solvant et le protocole d'extraction en milieu aqueux pourrait en faire une méthode très précieuse pour les chimistes de synthèse.

Mots-clés : aldéhyde, allyltributylstannane, alcool homoallylique, acide phosphotungstique, broyage.

[Traduit par la Rédaction]

Introduction

In recent years, organic synthesis under solvent-free conditions has been considered to be one of the most important features for designing environmentally benign reaction protocols.[1,2] The solvent-free reactions can eliminate a commonly encountered solubility problem associated with reactivity and make the work-up process very easy by eliminating tedious aqueous workup and subsequent removal of solvents. Ironically, solvent accounts for the high *E* factor[3] of a reaction, which is a measure of the total waste generated during a reaction process. In recent years, phosphotungstic acid ($H_3PW_{12}O_{40}$) has found a lot of attention for being an environmentally benign and commercially available solid compound. Being a pseudoliquid,[4] phosphotungstic acid (PTA) is considered to be a better catalyst for organic transformations[5–9] than conventional inorganic and organic acids.

Homoallylic alcohols are considered as one of the most ubiquitous building blocks in organic synthesis and their applications in the field of organic total synthesis and pharmaceutical research[10–12] are well documented. With the advent of the ring-closing metathesis (RCM) approach,[13] homoallylic alcohols and amines are finding new impetus in the synthesis of bioactive natural products.[14–16] Acid-catalyzed reaction of aldehydes with allyltributylsatannanes is one of the most frequently exercised protocols for generation of homoallylic alcohols at room temperature. Among the Lewis acids,[17–28] $BF_3{\cdot}Et_2O$, $SnCl_4$, $TiCl_4$, etc., are highly moisture sensitive and hence require strictly anhydrous conditions, whereas transition-metal complexes such as AgOTf, $ReBr(CO)_5$, and $Sc(OTf)_3$ are very expensive, although water-tolerant. Although palladium and platinum complexes were also used as catalysts,[29–31] they are highly expensive and require high temperatures and long reaction times. The use of solid-supported reagents, such as polymer-bound sulfonamide,[32] silica–$Bi(OTf)_2$,[33] Ln–resins,[34] pincer bis(oxazolinyl)phenyl ligands on solid support,[35] and titanium-exchanged ZSM-5 catalyst[36] have also been reported, but those methods require catalyst preparation before use. Therefore, introduction of a new catalyst system that can address these drawbacks, as well as being efficient, selective, high yielding, and environmentally friendly, cannot be overlooked. As most of these reactions have considerably long reaction times and use hazardous organic solvents, we were looking for a catalyst to reduce the reaction time for this conversion and that could work in the absence of any solvent. Here, we wish to report PTA as an effective catalyst for the synthesis of homoallylic alcohol from aldehyde with allyltributylstannane.

Experimental

General remarks

All reagents were commercially available and used without further purification. Most of the aldehydes were purchased from Sigma-Aldrich. The IR spectra were recorded on a PerkinElmer 983 spectrophotometer. For column chromatography, we employed Merck silica gel 60–120 mesh. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded

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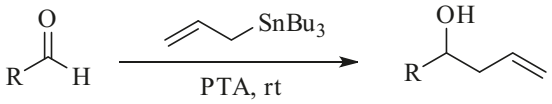
Table 1. Syntheis of homoallylic alcohols.



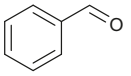
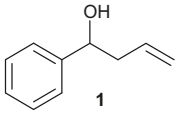
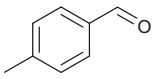
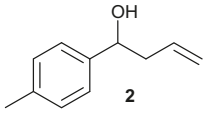
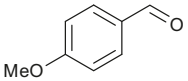
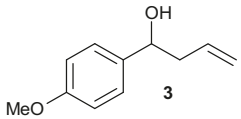
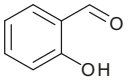
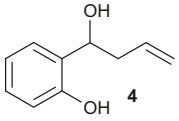
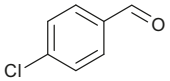
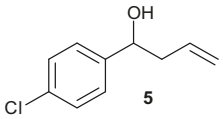
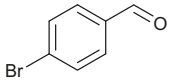
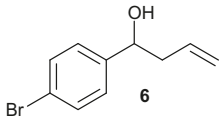
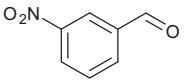
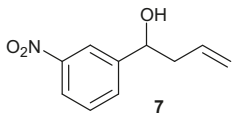
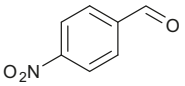
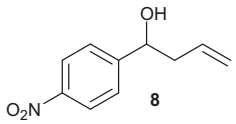
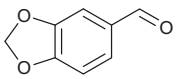
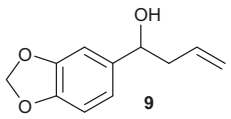
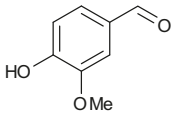
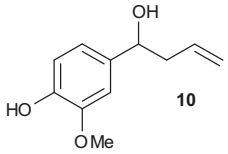
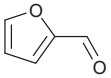
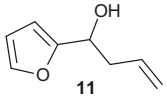
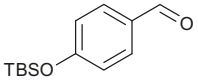
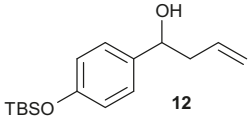
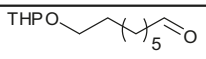
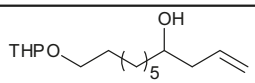
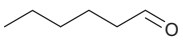
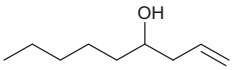
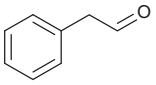
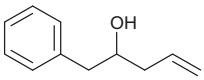
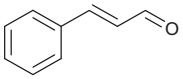
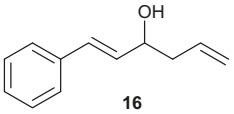
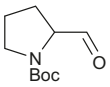
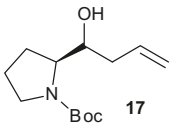
Entry	Substrate	Product	Time (min)	Yield (%)
1		 **1**	10	90
2		 **2**	10	91
3		 **3**	12	81
4		 **4**	10	83
5		 **5**	7	95
6		 **6**	7	96
7		 **7**	5	97
8		 **8**	5	99
9		 **9**	8	82
10		 **10**	20[a]	No reaction
11		 **11**	10	89
12		 **12**	10	88

Table 1. (*concluded*).

Entry	Substrate	Product	Time (min)	Yield (%)
13		 **13**	10	83
14		 **14**	10	93
15		 **15**	10	95
16		 **16**	10	92
17		 **17**	12	78

Note: Aldehyde–allyltributylstannane–PTA = 1:1.2:0.02, at room temperature. PTA, phosphotungstic acid.
[a]10 mol % of PTA.

on an AMX-400 MHz spectrometer using $CDCl_3$ as solvent and TMS as internal standard, unless otherwise stated. Mass spectra were obtained from a Waters ZQ 4000 mass spectrometer by the ESI method and the elemental analyses of the complexes were performed on a PerkinElmer-2400 CHN/S analyzer. Please see the Supplementary data for procedures and spectra.

Catalyst preparation

Phosphotungstic acid

Analytical grade $H_3PW_{12}O_{40}{\cdot}nH_2O$ was obtained commercially and used as a catalyst for the reaction.

Phosphotungstic acid/SiO_2

To a solution of $H_3PW_{12}O_{40}.nH_2O$ (0.5 g, 0.5 equiv by weight) in methanol (25 mL) was added silica gel (60–120 mesh, 4.5 g, 0.9 equiv by weight) and the mixture was stirred at room temperature for 6 h. Evaporation of methanol under reduced pressure gave a dry white powder. The catalyst was stored in a container for further use.

General procedure for phosphotungstic acid-catalyzed synthesis of homoallylic alcohol

A mixture of the aldehyde (1 mmol), allyltributylstannane (1.2 mmol), and phosphotungstic acid (0.02 mmol) was ground with a pestle in a mortar for the specified time (see Table 1). After complete conversion of the starting material, the crude mixture was dissolved in dichloromethane and directly loaded into a chromatography column charged with silica gel 60–120 mesh and eluted with a petroleum ether / ethyl acetate mixture as eluent in the appropriate ratio to obtain the pure product.

Spectral data for selected compounds

*1-(Benzo[*d*][1,3]dioxol-5-yl)but-3-en-1-ol (9)*

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 1.18 (s, 1H), 2.39 (t, J = 6.8 Hz, 2H), 4.57 (t, J = 6.4 Hz, 1H), 5.05–5.06 (d, J = 4.4 Hz, 1H), 5.07–5.10 (d, J = 11.2 Hz, 1H), 5.60 (m, 1H), 5.87 (s, 2H), 6.65–6.80 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 43.8, 73.1, 100.9, 106.3, 108.0, 118.4, 119.2, 134.4, 137.9, 146.9, 147.7. ESI MS (*m*/*z*): 215 (M^+ + 23). Elemental anal. calcd for $C_{11}H_{12}O_3$: C 68.74, H 6.29; found: C 68.61, H 6.12.

*1-(4-*tert*-Butyldimethylsilyloxyphenyl)but-3-en-1-ol (12)*

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 0.00 (s, 6H), 0.78 (s, 9H), 1.42 (s, 1H), 2.30 (t, J = 6.8 Hz, 2H), 4.48 (t, J = 6.8 Hz, 1H), 4.93 (d, J = 5.2 Hz, 1H), 4.93 (d, J = 5.2 Hz, 1H), 4.97 (d, J = 14.0 Hz, 1H), 5.60 (m, 1H), 6.62 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: –4.4, 18.2, 25.6, 43.7, 73.0, 118.2, 119.9, 126.9, 134.6, 136.5, 115.0. ESI MS (*m*/*z*): 215 (M^+ + 23). Elemental anal. calcd for $C_{16}H_{26}O_2Si$: C 69.01, H 9.41; found: C 69.02, H 9.37.

*12-(Tetrahydro-2*H*-pyran-2-yloxy)dodec-1-en-4-ol (13)*

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 1.25–1.30 (m, 10H), 1.45–1.84 (m, 10H), 2.09–2.33 (m, 2H), 3.34–3.4 (m, 2H), 3.47–3.52 (m, 1H), 3.63 (s, 1H), 3.69–3.75 (m, 2H), 3.84–3.89 (m, 1H), 4.57 (d, J = 4 Hz, 1H), 5.11–5.15 (m, 1H), 5.77–5.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 19.7, 25.5, 25.6, 26.2, 29.4, 29.5, 29.6, 29.7, 30.7, 36.8, 41.3, 62.3, 67.6, 70.6, 98.8, 118, 134.9. ESI MS (*m*/*z*): 307.1 (M^+ + 23). Elemental anal. calcd for $C_{17}H_{32}O_3$: C 71.79, H 11.34; found: C 70.43, H 11.62.

Non-1-en-4-ol (14)

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 0.62 (t, J = 6.8 Hz, 3H), 1.02–1.10 (m, 4H), 1.13–1.20 (m, 4H), 1.74 (s, 1H), 1.79–1.91 (m, 1H), 2.01–2.06 (m, 1H), 3.36 (m, 1H), 4.86 (m, 2H) 5.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 13.9, 22.5, 25.3, 31.8, 36.7, 41.8, 70.6, 117.8, 134.9. ESI MS (*m*/*z*): 151.1 (M^+ + 23). Elemental anal. calcd for $C_9H_{18}O$: C 76.00, H 12.76; found: C 75.29, H 12.53.

1-Phenylhexa-1,5-dien-3-ol (16)

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 1.86 (s, 1H), 2.26–2.39 (m, 2H), 4.27 (q, J = 6.4 Hz, 1H), 5.07 (d, J = 4.4 Hz, 1H), 5.10 (d, J = 10.8 Hz, 1H), 5.77 (m, 1H), 6.16 (dd, J = 16.0, 6.4 Hz, 1H), 6.52 (d, J = 16 Hz, 1H), 7.11–7.30 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 42.0, 71.7, 118.5, 126.5, 127.6, 128.5, 130.3, 131.5, 134.0, 136.6. ESI MS (*m*/*z*): 173 (M^+ – 1), 172 (100). Elemental anal. calcd for $C_{12}H_{14}O$: C 82.72, H 8.10; found: C 82.49, H 7.85.

tert-*Butyl 2-(1-hydroxybut-3-enyl)pyrrolidine-1-carboxylate (17)*

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 1.40 (s, 9H), 1.68 (m, 2H), 1.81 (m, 2H), 2.09 (m, 2H), 3.18 (m, 3H), 3.45 (m, 1H), 3.82 (s, 1H), 5.01 (d, J = 9.2 Hz, 1H), 5.04 (d, J = 15.6 Hz, 1H), 5.83 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 24.2, 27.4, 28.4, 37.1, 48.0, 62.6, 72.7, 79.9, 116.7, 135.6. ESI MS (*m*/*z*): 264 (M^+ + 23). Elemental anal. calcd for $C_{13}H_{23}NO_3$: C 64.70, H 9.61, N 5.80; found: C 64.41, H 9.85, N 6.19.

Results and discussion

Catalyst testing

In pursuance of our recent interests in PTA-catalyzed reactions,[37,38] we sought to use it for the allylation of aldehyde with allyltributylstannane. To achieve the stated objective, we stirred a mixture of *p*-nitrobenzaldehyde (1 mmol) with allyltributylstannane (1.2 equiv) in acetonitrile in the presence of 5 mol % of PTA. Upon constant monitoring by TLC, it was observed that the reaction was completed within 5 h to give 92% yield of the desired product.

As the surface area of PTA is smaller in comparison with its polyoxometalates, we wanted to know whether silica-supported PTA could reduce the reaction time. While using a PTA/SiO_2 reagent system, we initially opted to carry out the reaction in acetonitrile to mix the reacting species properly and found that the reaction was completed in 5 h to give 83% isolated yield of the desired product. Since the solvent is one of the most important contributors to the reaction rate, we wanted to use solvent-free conditions solely for carrying out the reaction.[39] When *p*-nitrobenzaldehyde (1 mmol) and allyltributylstannane (1.2 equiv) were stirred with the PTA/SiO_2 reagent system without using any solvent, complete conversion of the starting aldehyde took ~5 h. As these observations did not warrant any improvement over solution-phase stirring with PTA itself, we wanted to see the effect of grinding a mixture of aldehyde and allyltributylstannane with 5 mol % of the catalyst. To that effect, a mixture of *p*-nitrobenzaldehyde (1 mmol) and allyltributylstannane (1.2 equiv) was ground with a pestle in a mortar in the presence of 5 mol % of PTA. To our surprise, the reaction was completed within 5 min to give almost quantitative yield (Scheme 1).

Scheme 1. Synthesis of homoallylic alcohols.

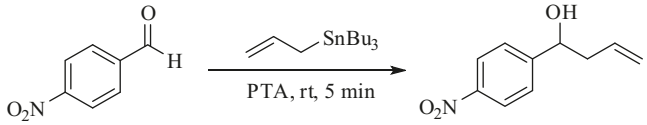


Table 2. Optimization of catalyst for the allylation of aldehyde.

Entry	Catalyst (mol %)	*p*-Nitrobenzaldehyde time (min)[a]	Hexanal time (min)[a]
1	1.0	120	300
2	1.5	15	25
3	2.0	5	10
4	4.0	5	9
5	5.0	5	9

Note: Aldehyde–allyltributylstannane, 1:1.2.
[a]The time for complete conversion.

Correlation of the catalyst ratio and reaction time

The fact that reaction proceeded slowly in the solution phase in the presence of PTA and silica-supported PTA suggests that the collision among the reactants upon grinding of the reaction mixture with PTA might have contributed to the shorter reaction time. It was observed that the reaction does not occur at room temperature, when a mixture of *p*-nitrobenzaldehyde and allyltributylstannane is ground in the absence of the catalyst. This established that there is no catalytic effect produced by the mortar and the pestle that might have contributed towards the shorter reaction time for completion. When complete conversion of the starting aldehyde was studied for the same reaction under catalytic conditions by varying the catalyst ratio, we found that 2 mol % of the catalyst is sufficient to complete the reaction within 5 min (Table 2). It was also observed that an amount of catalyst <2 mol % leads to increased reaction time for complete conversion, whereas an increased concentration of the catalyst up to 5 mol % could not reduce the reaction time significantly. We also tried to evaluate the reactivity pattern of aliphatic aldehyde by reacting a mixture of hexanal and allyltributylstannane in the presence of a catalytic amount of PTA (2 mol %) and found that the reaction takes a comparatively longer time.

Recovery of the catalyst

Since catalyst recovery is one of the most crucial components in catalytic reactions in general, we studied the reusability of the catalyst for successive batches for the reaction of *p*-nitrobenzaldehyde and allyltributylstannane using our reaction protocol. After completion of the reaction, diethyl ether was added to dissolve the product mixture and filtered to get the solid PTA residue. The PTA residue was washed thoroughly with diethyl ether and dried in an oven at 100 °C for 1 h and then cooled to room temperature. The recovered PTA catalyst obtained as mentioned was used for second, third, and fourth batches of the same reactants under similar reaction conditions without loss of appreciable activity in terms of reaction time and yield.

Generalization of the method

Having standardized the reaction parameters, such as the catalyst and the process, we set out to explore the general applicability of our method for both aromatic as well as aliphatic aldehydes[14] and its compatibility towards acid-sensitive functional groups (Table 1). It was observed that reaction worked exceedingly well for aromatic aldehydes having either +M or –M effect on the phenyl rings. The presence of phenolic an –OMe group in the para position of the aldehyde group did not have any noticable effect on the yield of the product, which is evident from the excellent yields of the products (Table 1, entry 3). Ironically, the vanillin (Table 1, entry 10) did not react despite the addition of 10 mol % of the catalyst under similar reaction conditions. It might be due to the poor electrophilicity of the aldehyde group resulting from the presence of the *p*-OH and *m*-OMe groups having +M effect on the phenyl ring. Several functional groups such as OTHP, methylenedioxy, etc., were hardly affected by the reaction conditions, as reflected by their excellent yields. From its excellent yield, we concluded that the OTBS (Table 1, entry 12) group is very stable under our reaction conditions. We did not observe any significant differences in reactivity for *m*- and *p*-nitrobenzaldehydes (Table 1, entries 7 and 8), as they took almost a similar reaction time for complete conversion. It is interesting to note that the aliphatic aldehydes (Table 1, entries 13–15) also gave excellent yields of their corresponding homoallylic alcohols upon grinding with allyltributylstannane in the presence of PTA. Excellent yield of homoallylic alcohol from cinnamaldehyde (Table 1, entry 16) shows that 1,2-addition is prefered in α,β-unsaturated aldehydes. *N*-Boc-pyrrolidine-2-carbaldehyde also generated its corresponding homoallylic alcohol (Table 1, entry 17) in good yield to verify the fact that the amide group, α to the aldehyde functionality, hardly has any negative impact on the efficiency of the reaction system.

Conclusion

This report introduces PTA as one of the most efficient catalysts for the allylation of aldehyde with allyltributylstannane. It has also established the fact that the catalytic activity increases manifold, resulting in a sharp reduction of reaction time, upon grinding the aldehyde and allyltributylstannane with PTA. Easy handling, very short reaction time, solvent-free reaction conditions, excellent yields, and a simple purification process devoid of aqueous workup may make our protocol very useful to synthetic chemists.

Supplementary data

Supplementary data are available with the article through the journal Web site (http://nrcresearchpress.com/doi/suppl/10.1139/v11-138).

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