

Ammonium nitrate as an efficient and green reagent for the oxidation of alcohols into their corresponding carbonyl compounds in the presence of heteropoly acids

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Abstract

In this study, a simple, cheap and green protocol for effective conversion of alcohols to corresponding carbonyl compounds in the presence of $H_{14}[NaP_5W_{30}O_{110}]$ and ammonium nitrate is reported. All known compounds were characterized by comparing their spectral data (FT-IR) and physical data with those reported. The progress of the reaction was monitored by thin layer chromatography (TLC) technique. The aliphatic products were detected by gas chromatography–flame ionization detector. Reactions were completed within 15-35 minutes at room temperature. In order to investigate the catalyst reusability, the oxidation of benzyl alcohol was carried out in the presence of $H_{14}[NaP_5W_{30}O_{110}]$. At the end of each reaction, the catalyst was separated and the recovered catalyst was reused for at least three runs without significant degradation in catalytic activity and performance.

Keywords: Alcohols; heteropoly acids; oxidation; heterogeneous catalyst; ammonium nitrate; energetic materials.

Introduction

Ammonium nitrate (AN) has been attracting attention over years as an oxidizer for

environmentally friendly, clean gas generating agents, because it does not give off harmful gases and solid burning residues

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and also because it is cheap [1-3]. Ammonium nitrate is used in many explosive applications, and it is relatively safe in comparison with other compounds of equal effect. It is one of the most commercially important ammonium compounds, and a principal component of most industrial explosives [4-6].

In recent years, various reagents have been reported for the oxidation reactions by using homogeneous catalysts supported metal ions and heterogeneous catalysts [7-13]. Among solid catalysts, heteropoly acids constitute a large class of compounds that are important for having physicochemical properties. They include; strong bronsted acidity, reversible transformations, activation of molecular oxygen and hydrogen peroxide, high proton mobility and solubility in polar solvents. These properties have made them more popular in many fields, such as catalysis, biology, medicine, magnetism, material science and photochemistry [14-18]. Heteropoly acids are classified according to their structures. The Keggin and the Wells-Dawson structures which are two kinds have been investigated more widely than others [19-26]. Using heteropoly acids in different areas of organic chemistry has reached to significant levels, not only for their possibility to perform synthesis

environmentally, but also for their usefulness [27,28]. Heteropoly acids have several advantages as catalysts which make them economically and environmentally practical. They are stronger acids than homogeneous acid catalysts such as sulfuric acid or ion exchange resins. Using heteropoly acids as a catalyst is important in the development of clean technologies, because it prevent the drawbacks of environmental pollution and avoids corrosion of the conventional technologies [27,28]. During Recent years, variety of oxidizing agents such as polyoxometalate anions has been investigated in many organic reactions.

The use of sandwich type polyoxometalates, $[WZnM_2 (H_2O)_2 (ZnW_9O_{34})_2]^{12-}$ (M=Mn(II), Zn(II)), for catalytic oxidation of alkenes, alcohols with aqueous hydrogen peroxide has been reported [29-31].

Solid heteropolyacids and their derivatives have been intensively studied because they can be used as excellent acidic and bifunctional catalysts in catalytic reactions [32-34]. In particular, the controlled oxidation of primary alcohols to aldehydes, without forming over-oxidized product is really a challenging task. On the other hand, different methods have traditionally been used for the oxidation of alcohols to their

corresponding carbonyl compounds. Representative oxidants for this purpose include KMnO_4 [35], MnO_2 [36], Cr(VI) [37], HNO_3 [38], hypervalent iodine [39], activated dimethyl sulfoxide (DMSO) [40], peroxides [41] and electrophilic halogens [42]. Although these methods have some synthetic advantages individually, but they still suffer from some drawbacks such as low yield, long reaction time, the use of toxic heavy metal reagents, harsh reaction conditions, inconvenient and tedious work-up, using excess amounts of oxidant and side reactions. Moreover, several reagents such as oxone / palygorskite [43], bismuth (III) oxide [44], and polymer bromide-DMSO [45], solid-supported Pd (0) [46], ion-supported methyl sulfoxide and oxalyl chloride [47], and catalytic methods using metals have been developed for these transformations [48]. Additionally, metal nitrates supported on inorganic supports have been used as oxidizing reagents. Iron (III) nitrate supported on silica gel (Silfen) [49], iron (III) nitrate or copper (II) nitrate supported on K10-clay (Clayfen or Clycop) [50], iron (III) nitrate mixed with HZSM-5 zeolite (Zeofen) [51] and ferric nitrate activated by heteropoly acids [52] are the reagents employed for the oxidation processes. Thus, the search for

environmentally friendly as well as economical oxidation processes continues.

On the other hand; recent rapidly growing environmental concerns need much greener oxidation protocols.

The oxidation of alcohols into corresponding carbonyl compound is widely recognized as one of the most fundamental transformations in both laboratory and industrial synthetic chemistry because the aldehydes and ketones serve as important intermediates for the synthesis of perfumery chemicals, pharmaceuticals, dyestuffs, agrochemicals, and polymers [53]. They were usually used for the synthesis of pharmaceuticals, flavors and fragrances. To accomplish such a conversion, several methods have been explored. These methods involve the use of expensive reagents, long reaction times, strongly acidic condition and tedious work-up procedure leading to the generation of a large amount of toxic waste. In the present article, we wish to report a new, efficient, simple and mild method for effective conversion of alcohols into their corresponding carbonyl compounds by heteropoly acids / ammonium nitrate system.

Experimental

Chemicals used in this work were purchased from Fluka (Switzerland) and were used without further purification.

$H_{14}[NaP_5W_{30}O_{110}]$, $H_4[PMo_{11}VO_{40}]$, $H_5[PMo_{10}V_2O_{40}]$ and $H_6[P_2W_{18}O_{62}]$ were prepared according to the literatures [54-62]. The products were characterized by FT-IR and comparison of their physical properties with those reported in the literatures. IR Spectra were recorded on a JASCO 6300 FT-IR spectrometer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The progress of the reaction was monitored by thin layer chromatography (TLC) technique. The aliphatic products were detected by gas chromatography–flame ionization detector (GC–FID; VARIAN C-P-3800 with FID detector, column CP-Sil 5 CB 30 m \times 0.32 mm). Preparative layer chromatography (PLC) plates were prepared from silica gel (Merck, HF₂₅₄) powder.

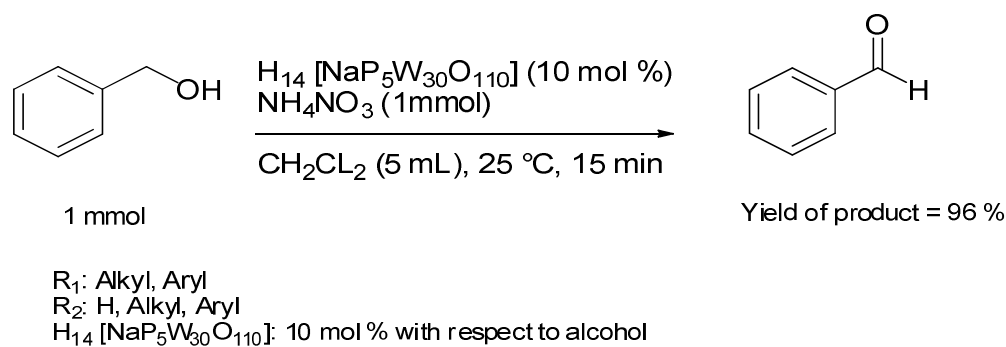
General Procedure for the oxidation of alcohol catalyzed by $H_{14}[NaP_5W_{30}O_{110}]$

Ammonium nitrate (0.08 g, 1 mmol) and $H_{14}[NaP_5W_{30}O_{110}]$ (10% mol with respect to alcohol) were mixed together in a mortar and were gently grounded by a pestle to obtain a homogeneous reagent. Then, the reagent added slowly to a vigorous stirring mixture of the corresponding alcohol (1 mmol) and dichloromethane (5 mL). The reaction mixture stirred at room temperature within

15–35 minutes. After the completion of the reaction (the progress of the reaction was monitored by TLC), the reaction mixture was filtered off and the residue washed with CH_2Cl_2 (3 \times 5 mL). The combined organic layer was washed with $NaHCO_3$ (5%) and dried over $MgSO_4$. The solvent was removed under reduced pressure to obtain almost pure carbonyl compound. Further purification performed by preparative layer chromatography (PLC) ((silica gel HF₂₅₄ powder), EtOAc-cyclohexane, 20:80). The aliphatic products in dichloromethane was dried with anhydrous $MgSO_4$ and detected by GC-FID.

Results and Discussion

Metal nitrates are known to oxidize alcohols [63]. Laura I. R. et al [64] used various metal nitrates and bromides for the selective sulfoxidation reaction and have shown that $Fe(NO_3)_3 \cdot 9H_2O$ - $FeBr_3$ was the most useful system. In the present work, we wish to report oxidation of various alcohols into their corresponding carbonyl compounds using NH_4NO_3 oxidant in the presence of a heteropoly acid as catalyst. The oxidation reaction system was optimized by using benzyl alcohol as a model reaction (Scheme 1).



Scheme 1. Oxidation of benzyl alcohol in the presence of H₁₄[NaP₅W₃₀O₁₁₀] and NH₄NO₃ as green system.

Optimization of alcohol oxidation conditions. In order to find an appropriate kind of HPA, we investigated several available HPAs such as H₁₄[NaP₅W₃₀O₁₁₀], H₄[PMo₁₁VO₄₀], H₅[PMo₁₀V₂O₄₀] and

H₆[P₂W₁₈O₆₂] (Table 1). According to the presented results in the Table 1, H₁₄[NaP₅W₃₀O₁₁₀] selected as the best catalyst among HPAs.

Table 1. Oxidation of benzyl alcohol to benzaldehyde using NH₄NO₃ in the presence of various heteropoly acids^a

Entry	Various acids	T (°C)	Time (min)	Yield ^b (%)
1	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]			96
2	H ₄ [PMo ₁₁ VO ₄₀]			78
3	H ₅ [PMo ₁₀ V ₂ O ₄₀]	25	15	83
4	H ₆ [P ₂ W ₁₈ O ₆₂]			87

^aReaction conditions: 1 mmol benzyl alcohol, heteropoly acid (10 mol % with respect to benzyl alcohol), NH₄NO₃ (1 mmol), 5 mL CH₂Cl₂.

^bIsolated yields.

After selecting an appropriate catalyst, we tried to find the optimum amount of the catalyst for the oxidation reaction (Table 2).

As it is shown in the Table 2, we found that the optimum amount of H₁₄ [NaP₅W₃₀O₁₁₀] is 10% mol with respect to alcohol.

Table 2. Effect of catalyst ratio on the oxidation of benzyl alcohol to benzaldehyde^a

Entry	Catalyst type	Heteropolyacid (HPA) Catalyst (mol %, mg)	oxidizing agent	Yield ^b (%)
1		0 (0)		28
2		1 (1.08 mg)		59
3	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]	5 (5 mg)	NH ₄ NO ₃	66
4		10 (10 mg)		96
5		15 (16.2 mg)		74

^aReaction conditions: 1 mmol benzyl alcohol, heteropoly acid (10 mol % with respect to benzyl alcohol), NH₄NO₃ (1 mmol), 5 mL CH₂Cl₂, 25 °C, 15 min.

^bIsolated yields.

According to the presented results in the Table 3, the optimum amount of the oxidizing agent for the reaction is equal to the amount of substrate in 1 mmol (Table 3).

Table 3. Optimization of oxidizing amount for the oxidation of benzyl alcohol to benzaldehyde in the presence of H₁₄[NaP₅W₃₀O₁₁₀]^a

Entry	Catalyst type and amount	Oxidizing agent type	Oxidizing agent amount (mmol)	Yield ^b (%)
1			0.1	25
2			0.5	59
3	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀], 10 mg	NH ₄ NO ₃	1	96
4			2	45
5			3	14

^aReaction conditions: 1 mmol benzyl alcohol, H₁₄[NaP₅W₃₀O₁₁₀] (% mol with respect to benzyl alcohol), NH₄NO₃, 5 mL CH₂Cl₂, 25 °C, 15 min.

^bIsolated yields.

In order to evaluate the effect of temperature on the oxidation of alcohols, the reactions were run at different range of temperature

from 15 to 35 °C (Table 4). According to the presented results in the Table 4, 25 °C was selected as optimum reaction temperature.

Table 4. Effect of reaction temperature on the oxidation of benzyl alcohol to benzaldehyde^a

Entry	Oxidation system (Catalyst / oxidizing agent)	Time (min)	T (°C)	Yield ^b (%)
1	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀](10 mg) / NH ₄ NO ₃ (1 mmol)	15 min	15	81
2			20	90
3			25	96
4			30	79
5			35	68

^a Reaction conditions: 1 mmol benzyl alcohol, H₁₄[NaP₅W₃₀O₁₁₀](% mol with respect to benzyl alcohol), NH₄NO₃ (1 mmol), 5 mL CH₂Cl₂.

^b Isolated yields.

In order to verify the effect of time, the reaction performed at different times (Table 5). Based on the presented results in the

Table 5, 15 min was selected as optimum reaction time (Table 5).

Table 5. Effect of the reaction time on the oxidation of benzyl alcohol to benzaldehyde^a

Entry	Oxidation system (Catalyst / oxidizing agent)	T (°C)	Time (min)	Yield ^b (%)
1	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀] / NH ₄ NO ₃	25 °C	5	47
2			10	68
3			15	96
4			20	61
5			25	55
6			30	47
7			35	23

^a Reaction conditions: 1 mmol benzyl alcohol, H₁₄[NaP₅W₃₀O₁₁₀](10 mg) (% mol with respect to benzyl alcohol), NH₄NO₃ (1 mmol), 5 mL CH₂Cl₂.

^b Isolated yields.

We performed the reaction in various solvents and the results were presented in the Table 6. As shown in the Table 6, dichloromethane is suitable solvent for the

oxidation reaction. Therefore, dichloromethane was selected as solvent for all of the oxidation reactions.

Table 6. Oxidation of benzyl alcohol to benzaldehyde using NH_4NO_3 in the presence of various solvents^a

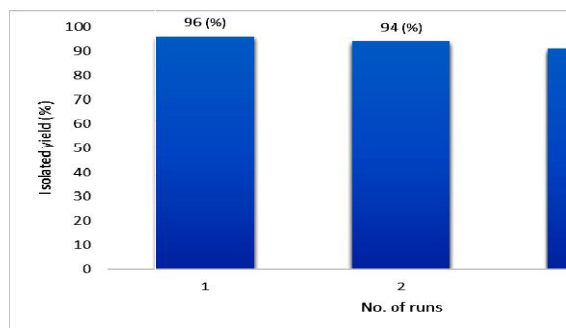
Entry	Solvent	T (°C)	Time (min)	Yield ^b (%)
1	EtOAc			85
2	Et ₂ O			84
3	Acetone			69
4	MeCN			84
5	CH ₂ Cl ₂	25	15	96
6	<i>n</i> -Hexane			86
7	Solvent free			61
8	H ₂ O			83

^a Reaction conditions; 1 mmol benzyl alcohol, $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ (10 % mol with respect to benzyl alcohol), NH_4NO_3 (1 mmol), 5 mL solvent.

^b Isolated yields.

Also, in order to investigate the catalyst reusability, the oxidation of benzyl alcohol was carried out in the presence of $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$. At the end of each

reaction, the catalyst was separated and the recovered catalyst was reused for at least three runs without significant degradation in catalytic activity and performance.

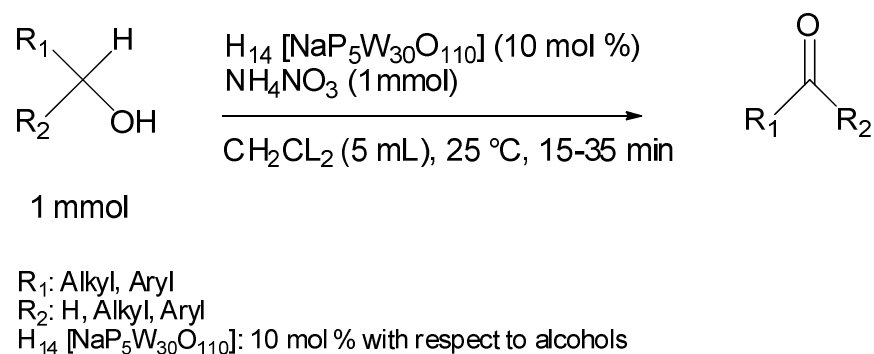
**Figure 1.** Reusability of $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ on the oxidation of benzyl alcohols

Finally, the optimized conditions (Scheme 2) were used for various alcohols to screen the generality of the work. The results for the oxidation of a variety of alcohols are summarized in Table 7. In this section, the system (with the identical reaction conditions

that optimized for benzyl alcohol) can be easily applied to various primary secondary and linear aliphatic alcohols as well as cyclic aliphatic alcohols. The oxidation of various benzyl alcohol derivatives gave the carbonyl compounds in high yields and short reaction

times. The oxidation time for aliphatic alcohols was fairly long. The donor substituted group in the benzene ring of benzylic alcohols accelerates the reaction rate (Table 7, entries 10, 11 and 15) and the withdrawing groups reduced the reaction rate

dramatically (Table 7, entries 2-9 and 12-14). Competing reaction such as over oxidation of aldehydes to the corresponding carboxylic acids was not observed in any of the cases under above conditions (Table 7).



Scheme 2. Oxidation of various alcohols in the presence of H₁₄[NaP₅W₃₀O₁₁₀] and NH₄NO₃ as green system

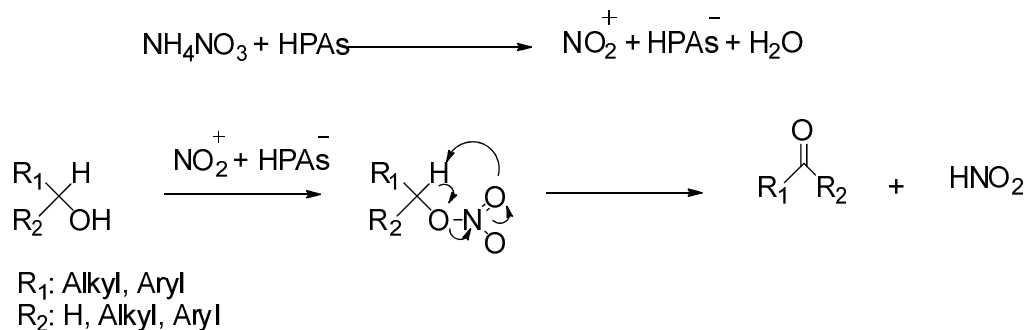
Table 7. Oxidation of various alcohols into their corresponding carbonyl compounds using NH₄NO₃ in the presence of H₁₄[NaP₅W₃₀O₁₁₀]^a

Entry	Alcohol	Carbonyl compound	Time (min)	Yield ^b (%)
1	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CHO	15	96
2	2-ClC ₆ H ₄ CH ₂ OH	2-ClC ₆ H ₄ CHO	20	93
3	3-ClC ₆ H ₄ CH ₂ OH	3-ClC ₆ H ₄ CHO	20	94
4	4-ClC ₆ H ₄ CH ₂ OH	4-ClC ₆ H ₄ CHO	20	92
5	2-BrC ₆ H ₄ CH ₂ OH	2-BrC ₆ H ₄ CHO	20	91
6	3-BrC ₆ H ₄ CH ₂ OH	3-BrC ₆ H ₄ CHO	20	94
7	4-BrC ₆ H ₄ CH ₂ OH	4-BrC ₆ H ₄ CHO	20	92
8	3-FC ₆ H ₄ CH ₂ OH	3-FC ₆ H ₄ CHO	20	91
9	4-FC ₆ H ₄ CH ₂ OH	4-FC ₆ H ₄ CHO	20	93
10	3-MeOC ₆ H ₄ CH ₂ OH	3-MeOC ₆ H ₄ CHO	15	97

11	4-MeOC ₆ H ₄ CH ₂ OH	4-MeOC ₆ H ₄ CHO	15	96
12	2-NO ₂ C ₆ H ₄ CH ₂ OH	2-NO ₂ C ₆ H ₄ CHO	20	93
13	3-NO ₂ C ₆ H ₄ CH ₂ OH	3-NO ₂ C ₆ H ₄ CHO	20	91
14	4-NO ₂ C ₆ H ₄ CH ₂ OH	4-NO ₂ C ₆ H ₄ CHO	20	89
15	4-MeC ₆ H ₄ CH ₂ OH	4-MeC ₆ H ₄ CHO	15	97
16	Benzhydrol	Benzophenone	25	89
17	Benzoin	Benzil	15	87
18	Isopropyl alcohol	Acetone	35	91
19	Cyclohexanol	Cyclohexanone	35	74

^aReaction conditions: 1 mmol alcohol, H₁₄[NaP₅W₃₀O₁₁₀] (10 mol% with respect to alcohol), NH₄NO₃ (1 mmol), 5 mL CH₂Cl₂, 25 °C.

^bIsolated yields (except entries nos. 18 and 19 that were resulted from GC).



Scheme 3. Proposed mechanism for the oxidation of alcohols in the presence of NO₂⁺

The mechanism proposed for the oxidation of alcohols using NH₄NO₃ in the presence of H₁₄[NaP₅W₃₀O₁₁₀] is depicted in Scheme 3.

Conclusion

In conclusion, we have developed a new, efficient, simple, green and mild method for the effective conversion of alcohols into their

corresponding carbonyl compounds with ammonium nitrate as an oxidant in the presence of H₁₄[NaP₅W₃₀O₁₁₀] heteropoly acid as catalyst at 25°C within 15-35 minutes.

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