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Effective Catalytic Conversion of Carbonyl groups to Oximes using

$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ in Green conditions

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Abstract: We reported catalytic conversion of carbonyl compounds to oximes using $H_{14}[NaP_5W_{30}O_{110}]/SiO_2(50\%)$ and hydroxylamine hydrochloride under free-solvent and room temperature.

Key words: Oxime, preyssler, heteropolyacid, catalyst, carbonyl

1. Introduction

Oximes are employed as ketone and aldehyde functional group equivalent in synthesis, both because they provide convenient protection for the carbonyl group and because they are important synthetic intermediates [1]. The addition of hydroxylamine hydrochloride to carbonyls to yield oximes is one of the best understood examples of a nonenzymatic addition-elimination reaction [2]. The process of this addition-elimination reaction usually was catalyzed by sulfuric acid that is highly corrosive and poses serious environmental hazards [3]. In 1988, a patent by Roffia et al. outlined the preparation of the cyclohexanone oxime, as key intermediate for preparation of nylon by liquid-phase ammoximation of cyclohexanone using ammonia hydrogen peroxide as the oxidizing agent and titanium silicate as the catalyst [4]. Usually, these reactions are carried out by use of various conventional mineral acids such as H_2SO_4 , HF, HCl, H_3PO_4 , etc. The replacement of these conventional hazardous and polluting corrosive liquid acid catalysts by solid acid catalysts is one of the demands and stringencies of the societies. Cleaner technology could be possible by making use of environmental friendly catalysts involving the use of solid acids. Recently, liquid acids have been replaced by solid acid catalysts such as p-toluenesulfonic acid, Nafion-H, resins, silica-alumina, zeolites, niobic acid, etc. [5,6]. The synthesis of some of these catalysts is difficult and there is always

the fear of unfavorable side reactions. Although many methods for the preparation of esters exist, there is still a good scope for research towards finding green and eco-friendly catalysts. Among solid catalysts, heteropolyacids constitute a large class of compounds that are remarkable owing to their 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 and more popular in many fields, such as catalysis, biology, medicine, magnetism, photochemistry and material science [7,8]. Heteropolyacids are classified in according to their structures. Two classes, the Keggin and the Wells–Dawson structures, have been investigated more extensively than others [9,10]. Heteropoly acids (HPAs) are well defined molecular clusters that are remarkable for their molecular and electronic structural diversity and their significance is quite diverse in many areas, e.g., catalysis, medicine, and materials science [11,12]. HPAs are complex proton acid that incorporate polyoxometalate anions (heteropolyanions) having metal-oxygen octahedra as the basic structural units and catalysis by them is a field of increasing importance [13]. Whereas a wide variety of these “magic” clusters have been reported to date [14], there are only three anions, $[\text{NaSb}_9\text{W}_{21}\text{O}_{86}]^-$ [15], $[\text{NaAs}_4\text{W}_{40}\text{O}_{140}]^{25-}$ [16], and $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ that have been reported to encapsulate rare-earth ions. In the latter of these, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$, the so-called Preyssler’s anion, Na^+ is encrypted inside a central cavity formed by five PW_6O_{22} units arranged in a crown [17], as shown schematically in Figure. 1.

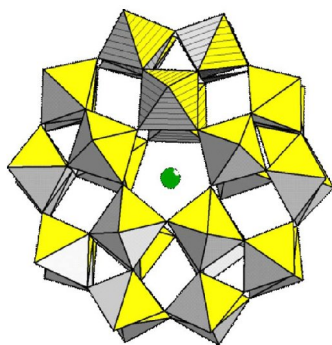
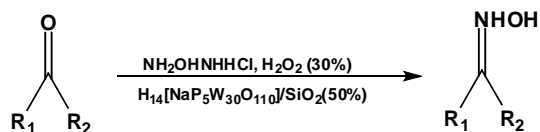


Fig 1. Structure of Preyssler Heteropolyanion

2. Results and Discussion

We reported conversion of the carbonyl compounds to oximes using $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ (50%) and hydroxylamine hydrochloride under free-solvent and room temperature, But the economic attractiveness of this process, however, may be limited by the use of H_2O_2 .



(Scheme 1)

But the reaction times were different for various carbonyl groups. As reported in the table 1, satisfactory results have been obtained in the condensation of a variety of aldehydes and ketones with hydroxylamine hydrochloride under solvent-free conditions in the presence of $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ (50%). In this research, was used from various carbonyl compounds in above conditions (Table 1).

Table 1. The yields of oximes in appropriate times, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ (50%) and at room temperature

Entry	Carbonyl compound	Oxime	Time (min)	^a Yield(%)
1			7	97
2			10	88
3			8	76
4	CH₃CH₂COCH₃		5	82
5			10	81
6			10	73
7			7	84.5
8			7	92
9			7	90
10			10	95
11			5	79

^aIsolated yields.

3. Conclusion

It can be emphasized that the reaction is clean, easy work-up, eco-friendly, environmentally friendly, high yields of products, high selectivity. Because, use of the solvent-free conditions is favorable, green. This catalyst is recyclable, easy recovery. The catalyst was reused in the next reaction without loss of the catalytic activities.

4. Experimental

4.1. Chemical materials

All chemical were commercially available and used without further purification.

4.2. Preparation of supported preyssler catalyst $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ (50%)

This catalyst provided in according to the literature [18]. All products were identified by their spectra and physical data with those of authentic samples. Melting points were measured by using capillary tubes on an electro thermal 9100 apparatus. 1H NMR spectra were recorded on a FT NMR Bruker 100 MHz. IR spectra were recorded as KBr disc on the FT-IR Bruker Tensor 27 spectrometer.

4.3. General procedure for the preparation of Oximes

A mixture of NH_2OHHCl (3 mmol), carbonyl compounds (1 mmol), peroxide hydrogen 30% (0.04 mol) and catalyst (0.04 mmol) were stirred at room temperature in appropriate times (Table 1).The progress of reaction was monitored by TLC using ether- CCl_4 . The mixture was filtrated to remove catalyst and then, mixed with water and extracted. The solvent was removed in vaccum to give pure product. Product was recrystallized from a suitable solvent to afford the TLC and 1H NMR pure products in 70-93% isolated yields.

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