

N-oxidation of pyridine carboxylic acids using hydrogen peroxide catalyzed by a green heteropolyacid catalyst: Preyssler's anion, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$

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Abstract

The catalytic oxidation of pyridine carboxylic acids such as nicotinic acid, picolinic acid and quiniolinic acid to the corresponding N-oxides has been studied using hydrogen peroxide as an oxidant and Preyssler's catalyst as pure acid, $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ and mixed addenda, $\text{H}_{14}[\text{NaP}_5\text{W}_{29}\text{MoO}_{110}]$. The highly selective oxidations, gave good yields of the related N-oxides along with decarboxylation of the amines. In the production of pyridine N-oxides, the position of COOH group is found to play an important role in the product type and decarboxylation is only taken place at 2-position of nitrogen. The oxidation reactions were extended to other tertiary amines.

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1. Introduction

It was shown that some heteropolyanions exhibited interesting catalytic properties as green and eco-friendly catalysts for both redox and/or acid–base type reactions in industrial applications [1,2]. Examples of acid–base type catalysis are: cracking and alkylation of hydrocarbons, dehydration of alcohols, electrophilic addition of alcohols to olefines, etc. [3,4].

Heteropolyacids, both solid and in solution, are compared with the strongest mineral acids exhibiting even strength higher than mineral acids, and are comparable to that to the so-called superacids [5]. Until now, most of fundamental investigations and all practical applications used, Keggin heteropolyacids, with the general formula of anion $[\text{XM}_{12}\text{O}_{40}]^{\text{P}-}$ [6–8]. In recent years, interest in other heteropolyacids has grown.

Among a wide variety of studied heteropolyacids with different size and structures, there are only three anions, $[\text{NaSb}_9\text{W}_{21}\text{O}_{86}]^-$, $[\text{NaAs}_4\text{W}_{40}\text{O}_{140}]^{25-}$ and $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ that have been reported to encapsulate rare-earth ions [9–11]. The latter of these, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$, so-called

Preyssler's anion, has formed by five PW_6O_{22} units arranged in a crown (Fig. 1). However, it is very interesting that the Preyssler's anion, one of the largest known polyanions, has excellent potential application in catalysis. To the best of our knowledge, among the heteropolyacids, the catalytic behavior of Preyssler catalyst is has been largely overlooked and in many reports for that no catalytic capability has been mentioned [12,13]. This heteropolyacid is remarkable because of the following advantages: (1) strong Bronsted acidity with 14 acidic protons, (2) high thermal stability, (3) high hydrolytic stability (pH 0–12), (4) reusability, (5) safety, (6) quantity of waste, (7) separability, (8) corrosiveness, (9) high oxidation potential and (10) greenness. In addition, in our studies we have found this catalyst has unique stability in oxidation reactions with hydrogen peroxide.

Recently, we have developed a series of heteropolyacid catalyzed reactions such as oxidation of aldehydes and alcohols, esterification of aliphatic and aromatic carboxylic acids, direct dimerization of alcohols to the related esters and lactonization of diols, etc. [14]. We are interested on developing of applications of Preyssler in other areas because of its exclusive structure and properties.

Therefore, it is great interest to know, what occurs if the Preyssler's anion has been used in the oxidation of pyridines. Pyridine N-oxides in nanotechnology, industry and medicine, are important. Pyridine N-oxides are also versatile synthetic

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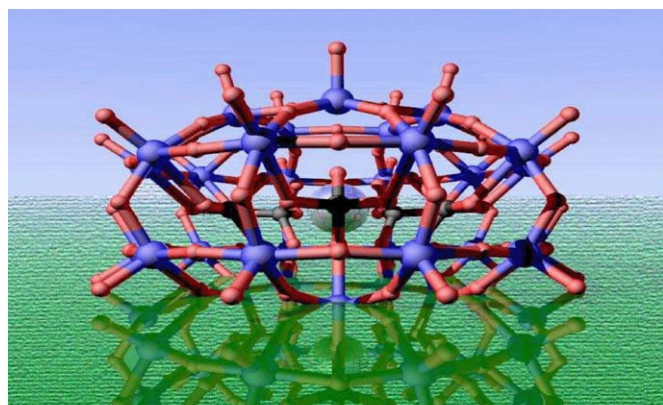


Fig. 1. Structure of Preyssler's anion.

intermediates and the chemistry and applications of N-oxides have recently received much attention due to their usefulness as synthetic intermediates and their biological importances [15]. Heterocyclic N-oxides are also useful as protecting groups, auxiliary agents, oxidants, ligands in metal complexes and catalysts [16].

Recently, pyridine N-oxide derivatives represented a new class of anti-HIV compounds, for which some members exclusively act through inhibition of HIV reverse transcriptase and thus characteristically behave as non-nucleoside reverse transcriptase inhibitors [17]. Interestingly, in the nanotechnology field, has been shown that nanoshampo including carboxylic acid pyridine N-oxide is a very powerful hair growth stimulator with a high level of safety [18].

Pyridine N-oxides usually are prepared by oxidation of pyridines using peracids such as meta-chloroperbenzoic acid and peracetic acid [19], from the esters of N-hydroxy-2-thiopyridone [20], by ring transformation of isoxazoles [21] and through cycloaddition reactions [22–25].

Catalytic methods for oxidation processes using aqueous hydrogen peroxide and molecular oxygen as oxidants and green catalysts in place of stoichiometric reagents are, however, now more desirable because of the need for the chemical industry to minimize waste production associated with stoichiometric reagents [26]. Over the years, many researchers have studied the N-oxidation of pyridines using hydrogen peroxide in the presence of metal complex catalysts [27]. However, such homogeneous catalysts are typically require special conditions to obtain good yields of N-oxides and some of them are toxic and expensive.

The environmental care is one of the world wide increasing worries. This fact encourages scientists to make efforts in finding processes working in this direction. Therefore, the replacement of environmental hazardous catalysts in various processes, as that related to the use of solid catalysts as alternative to different processes, is one of the innovative trends. For this reason, there is still a good scope for research towards finding green and eco-friendly catalysts.

In continuation of our works on catalytic applications of heteropolyacids [28,29] and extending the applications of Preyssler

catalyst, and because of importance of pyridine N-oxides in nanotechnology, medicine and industry, herein, we report that sodium-30 tungstoptentaphosphate, which so-called Preyssler's anion, with exclusive properties surpassing the other heteropolyacids as an effective catalyst for the selective oxidation of pyridine carboxylic acids such as: pyridine-2-carboxylic acid (picolinic acid), pyridine-3-carboxylic acid (nicotinic acid), pyridine-2,3-dicarboxylic acid (quinolinic acid) and other pyridines such as: 3-methyl pyridine (3-picoline) and 2-aminopyridine.

2. Results and discussion

The catalytic oxidation of tertiary amines to the corresponding N-oxides by Preyssler catalyst and hydrogen peroxide as oxidant was carried out in a biphasic mixture (non-polar solvent–15% aqueous hydrogen peroxide), over 6 h at reflux temperature. Tables 1 and 2 show the oxidation results using H_2O_2 in the presence of $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$, $\text{H}_{14}\text{-P}_5$, and $\text{H}_{14}[\text{NaP}_5\text{W}_{29}\text{MoO}_{110}]$, $\text{H}_{14}\text{-P}_5\text{Mo}$.

Toluene, benzene and carbon tetrachloride were examined as solvents. Among these solvents toluene was the solvent of choice. Water immiscible solvents like acetonitrile and ethanol were poor solvents at room and reflux temperature. The effects of COOH position, catalyst type and reaction time have been studied.

2.1. Effect of position of the COOH group

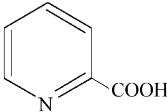
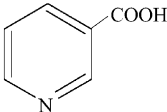
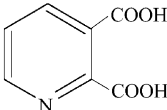
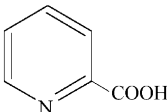
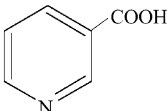
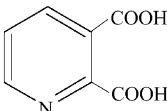
The effect of the COOH position in pyridine carboxylic acids has been examined in the presence of Preyssler catalyst. Our studies showed that for product type, the position of COOH group with respect to nitrogen is very important factor. In general, the observed selectivity was 100%.

Interestingly, the GC-Mass results, mass and melting points of pyridine N-oxides showed, pyridine-2-carboxylic acid, and pyridine-2,3-dicarboxylic acid can be oxidized along with decarboxylation to give decarboxylated pyridine N-oxides, while pyridine-3-carboxylic acid is oxidized to the related N-oxide without any decarboxylation.

The higher efficiency for decarboxylation in 2-position with respect to nitrogen for pyridine-2-carboxylic acid, and pyridine-2,3-dicarboxylic acid can, most probably, be explained in the following way: the carboxylate anion forming in the transition state is very close to the pyridine nitrogen, causing, to some extent, a repulsion between the identical negative charges, resulting in the planar carboxylate anion being in a perpendicular position with respect to the pyridine ring, which is therefore subjected to a better carboxylate anion elimination. Pyridine-2-carboxylic acid afforded the pyridine N-oxide exclusively, with excellent yield and 100% selectivity in toluene in the presence of $\text{H}_{14}\text{-P}_5\text{Mo}$. Also N-oxidation of pyridine-3-carboxylic acid and pyridine-2,3-dicarboxylic acid proceeded with good yields. An interesting observation in our system was high yield of 2-pyridine N-oxide in oxidation of pyridine-2-carboxylic acid.

Sharpless et al. have recently reported an efficient N-oxidation of pyridines using hydrogen peroxide catalyzed by methyl trioxorhenium [30]. However, their procedure is not

Table 1
N-oxidation of pyridine carboxylic acids using H₂O₂ and Preyssler catalyst with various solvents^a

Entry	Pyridine	Catalyst	Yield of N-oxide in toluene (%) ^b	Yield of N-oxide in benzene (%) ^b	Yield of N-oxide in carbon tetrachloride (%) ^b
1		H ₁₄ -P ₅ Mo	92.80	85.40	51.50
2		H ₁₄ -P ₅ Mo	67.28	58.89	42.90
3		H ₁₄ -P ₅ Mo	61.71	56.50	48.82
4		H ₁₄ -P ₅	79.50	70.50	42.32
5		H ₁₄ -P ₅	56.50	50.72	35.64
6		H ₁₄ -P ₅	48.50	44.74	39.64

^a Reaction conditions: pyridine (5×10^{-3} mmol), hydrogen peroxide (7.5 mL), catalyst (3×10^{-5} mol), solvent (10 mL), reflux, 6 h.

^b Determined by GC-Mass, based on decarboxylated products for pyridine-2-carboxylic acid and pyridine-2,3-dicarboxylic acid.

effective for the conversion of 2-substituted pyridines to N-oxide. As a matter of fact it requires a large amount of the expensive rhenium catalyst to attain high yields. We believe that our biphasic N-oxidation system using Preyssler catalyst, we describe here is more superior for oxidation pyridines which can be extended to pyridine-2-carboxylic acid.

To establish the generality of method, we selected three other pyridines with amino, methyl and bromo moieties. The catalytic oxidation of these pyridines have examined in solvents such as toluene, benzene and carbon tetrachloride in the presence of both Preyssler catalyst. The results are presented in Table 2. According to the results of pyridine carboxylic acids, again toluene was the best solvent and H₁₄-P₅Mo was better. The observed yields showed this N-oxidation was proceed efficiently for pyridines with methyl and amino groups. Trace yields were observed with bromo pyridine and the highest yield was observed with methyl pyridine. This behavior can be attributed to the electron-donating and electron-withdrawing properties of substituents.

2.2. Effect of the catalyst type

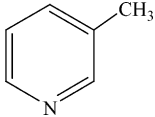
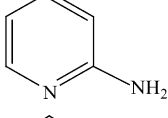
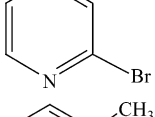
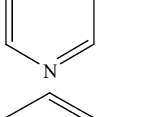
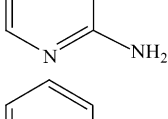
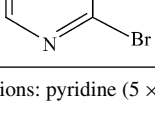
The results in Tables 1 and 2 show the presence of molybdenum ion in mixed addenda heteropolyacid, enhances the extent of N-oxidation. H₁₄-P₅ is less reactive, and yield using H₁₄-P₅ is lower when H₁₄-P₅Mo is used.

Mixed addenda heteropoly anions are formed by the substitution of one or more tungsten(VI) or molybdenum(VI) in heteropolyanions by another addenda atom like W(VI) and V(V). By variation of the addenda atoms, the electrochemical character of them can be widely changed. The addenda atoms can be ordered by decreasing oxidizing ability in the following way: V(V) > Mo(VI) > W(VI) [31–33].

Mixed addenda Preyssler catalyst is formed by the substitution of one tungsten(VI) ion by Mo(VI). Usually, tungsten heteropolyacids are the catalysts with stronger acidity, but lower oxidation potential compared to molybdenum analogue [34].

Because in this work, the studied reactions are oxidative-catalytic reactions, between two forms of Preyssler catalysts, H₁₄-P₅Mo showed higher catalytic activity than the H₁₄-P₅, which might be due to the high oxidizing potential. This result is in agreement with expectation and earlier works on oxidation of diols [14]. In order to compare the Preyssler with other Keggin heteropolyacids, this study in the oxidation of pyridine carboxylic acids was also extended to Keggin heteropolyacids such as: H₃[PW₁₂O₄₀] and H₃[PMo₁₂O₄₀]. All of the reactions with Keggin were carried out in optimum conditions: toluene as solvent, reflux temperature and 6 h. Our studies showed that under these conditions, the reaction yields were affected by changing the catalyst structure. The results of catalytic oxidation of

Table 2
N-oxidation of pyridines using H₂O₂ and Preyssler catalyst with various solvents^a

Entry	Pyridines	Catalyst	Yield of N-oxide in toluene (%)	Yield of N-oxide in benzene (%)	Yield of N-oxide in carbon tetrachloride
1		H ₁₄ -P ₅ Mo	95.00	74.00	62.00
2		H ₁₄ -P ₅ Mo	74.40	58.50	31.80
3		H ₁₄ -P ₅ Mo	Trace	Trace	Trace
4		H ₁₄ -P ₅	82.00	65.00	48.00
5		H ₁₄ -P ₅	62.50	47.20	18.60
6		H ₁₄ -P ₅	Trace	Trace	Trace

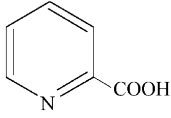
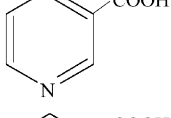
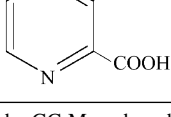
^a Reaction conditions: pyridine (5×10^{-3} mmol), hydrogen peroxide (7.5 mL), catalyst (3×10^{-5} mol), solvent (10 mL), reflux, 6 h.

pyridine carboxylic acids by hydrogen peroxide, with Preyssler catalyst and Keggin are compared in Table 3.

In general, the results indicate that the highest yield of pyridine N-oxides is obtained when the oxidation is carried out with Preyssler catalysts, and Keggin are less effective than Preyssler structure. Between two Keggin heteropolyacids, H₃[PMo₁₂O₄₀] shows a higher yield. Interestingly, even in Keggin heteropolyacids yields are higher in structure with Mo ion.

According to the literature the oxidation of organic substrates by hydrogen peroxide in the presence of H₃[PW₁₂O₄₀] and H₃[PMo₁₂O₄₀] proceeds via degradation of structure to a active peroxo polyoxometalate, {PO₄[MO(O₂)₂]₄}³⁻, M = W, Mo. Our studies in this work for separation of Preyssler catalyst after catalytic reaction showed that Preyssler catalyst catalyzes the reactions without any degradation of structure (Fig. 4).

Table 3
Comparison between Preyssler and Keggin catalysts in N-oxidation of pyridine carboxylic acids^a

Entry	Pyridine	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]	H ₁₄ [NaP ₅ W ₂₉ MoO ₁₁₀]	H ₃ [PW ₁₂ O ₄₀]	H ₃ [PMo ₁₂ O ₄₀]
1		79.50	92.80	54.20	68.42
2		56.50	67.28	37.50	52.16
3		48.50	61.71	20.30	36.28

Yields determined by GC-Mass, based on decarboxylated products for pyridine-2-carboxylic acid and pyridine-2,3-dicarboxylic acid.

^a Reaction conditions: pyridine (5×10^{-3} mmol), hydrogen peroxide (7.5 mL), catalyst (3×10^{-5} mol), toluene (10 mL), reflux, 6 h.

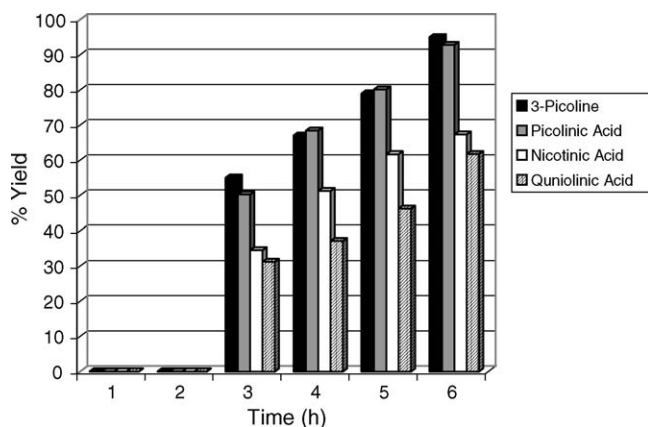


Fig. 2. Effect of the reaction time on products yield in oxidation of pyridines catalyzed by H_{14} - P_5 Mo in toluene.

The results point out that the catalytic effectiveness may be enhanced as the number of tungsten atoms (or the number of protons) is increased. Both possibilities stand to reason. The larger number of protons may lower the activation barrier to the oxidation reaction. In addition, the large anion also provides many “sites” on the oval-shaped molecule that are likely to render the catalyst effectiveness. What is of interest to us is the fact that Preyssler’s anion, with exclusive properties, is an effective catalyst surpassing the Keggin heteropolyacids in these reactions.

The mechanism of these reactions is likely complex and is not clear for us at this time. It is suggested that, Preyssler catalyst, catalyzes the oxidation of pyridines to related pyridine N-oxides by H_2O_2 at reflux temperature, with the H_2O_2 decomposition being the main reaction. A mechanism, including the oxidation of pyridines by HO and HO_2 radicals formed via the hydrogen peroxide decomposition, is suggested [37].

2.3. Effect of the reaction time

For all substrates in the presence of both catalysts and all solvents, the effect of reaction times on the percent yield of pyridine N-oxides was studied. The results in the toluene as the best solvent are shown in Figs. 2 and 3 for pyridine carboxylic acids.

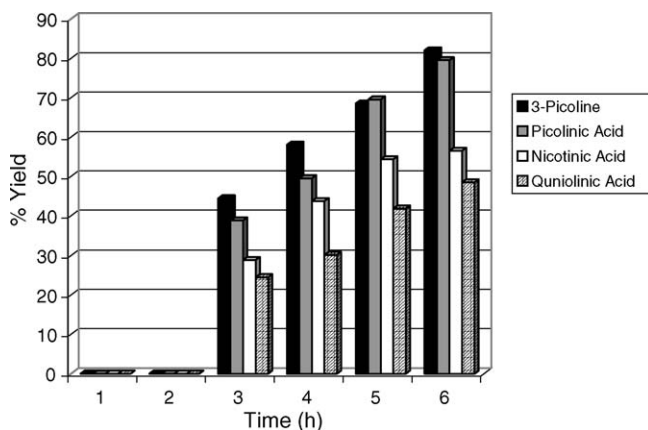


Fig. 3. Effect of the reaction time on products yield in oxidation of pyridines catalyzed by H_{14} - P_5 in toluene.

Among the other pyridines, the results only for 3-methyl pyridine (3-picoline) with the highest yield are shown. The results show that at the first and second hours of the reaction times, there is a trace amount of products and formation of significant pyridine N-oxides observes in the third hour. This behavior is quite general. There is an increase in the yields with increase in reaction times.

2.4. Reusability of the catalyst

The main problem, limiting the utility of homogeneously catalyzed processes, including difficulty in catalyst recovery and recycling and retention of their structures is well known.

It is well-known, Keggin heteropolyacids in biphasic systems or homogeneous conditions at 60–70 °C with the use of H_2O_2 have degraded to peroxo polyoxometalates and these compounds have been shown to be the active intermediates in these reactions [35,36]. An active peroxo polyoxometalate formed by interacting the Keggin heteropoly anion with H_2O_2 . The reaction takes place via the oxygen atom transfer from the peroxo polyoxometalate to the substrate.

In our studies has been found that Preyssler’s anion catalyzes oxidations of organic substances by H_2O_2 without any degradation of structure. This leads to the recovery and recyclability of catalyst, which is very important in catalytic processes, especially, in industry. Fig. 4 shows the IR spectrum of Preyssler’s anion before (a) and after (b) catalytic reaction. It seems clear

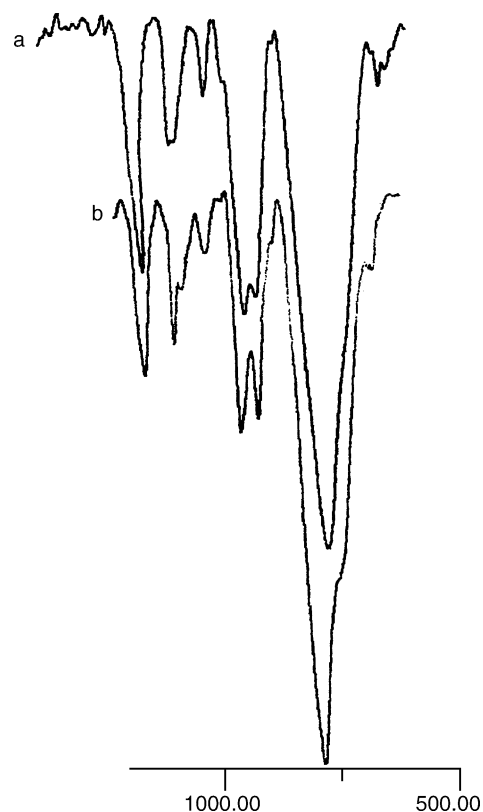


Fig. 4. IR spectrum of Preyssler’s anion before (a) and after (b) catalytic reaction.

that this catalyst catalyzes the N-oxidation of pyridines with retention of structure. Recovery has been decreased the catalytic activity only 2–4%.

3. Conclusion

In conclusion, a biphasic system consisting of hydrogen peroxide: non-polar solvent and Preyssler catalyst, efficiently oxidize pyridine-carboxylic acids to the corresponding pyridine N-oxides with decarboxylation in 2-position. The substrate type, solvent and reaction time as well as catalyst type are important factors.

At present, we are continuing to study selective oxidation of aromatic amines using Preyssler catalyst with the aim of developing environmentally benign chemical processes and extending Preyssler application [38].

4. Experimental

4.1. Chemicals and apparatus

Toluene, benzene, carbon tetrachloride, nicotinic acid, picolinic acid, quiniolic acid, 3-methyl pyridine, 2-amino pyridine and 2-bromo pyridine were obtained from commercial sources and used as received. Hydrogen peroxide was obtained from Merck Company and was standardized by well-known methods (Hydrogen Peroxide Product Information Manual, Analytical Procedure).

H₁₄-P₅ was prepared by passage of a solution of the potassium salt in water through a column (50 cm × 1 cm) of Dowex 50 W × 8 in the H⁺ form and evaporation of the elute to dryness under vacuum [29].

Molybdenum substituted Preyssler heteropolyanion, H₁₄-P₅Mo, was prepared as follows: 2.8 g (0.169 mol) Na₂WO₄·2H₂O and 2 g (0.008 mol) Na₂MoO₄·2H₂O were dissolved in 35 mL water and mixed at 60 °C for 30 min. Then this solution was cooled to room temperature, and 25 mL concentrated phosphoric acid was added. The resulted yellow solution was refluxed for 18 h. The solution was brought to room temperature, diluted with water and then during stirring, 10 g KCl was added. The mixture was stirred and then heated up to dryness. The product was dissolved in warm water and upon cooling to room temperature yellow crystals formed. Acidic form of molybdenum substituted heteropolyacid was obtained as described above for unsubstituted analogue.

4.2. Instruments

IR spectra were obtained with a Bruker 500 scientific spectrometer. GC-Mass analysis was performed on a GC-Mass model: 5973 network mass selective detector, GC 6890 Agilent. Mass spectra were obtained with a Massens POEKTROMETER CH-7A VARIN MAT BREMEN spectrometer. ¹H NMR spectra were recorded on a FT NMR Bruker 100MHZ Aspect 3000 spectrometer.

4.3. General procedure

Into a reaction vessel with a reflux condenser and thermometer were successively placed, solvent (10 mL), the catalyst (3×10^{-5} mol), pyridine (5×10^{-3} mmol) and 15% aqueous hydrogen peroxide (7.5 mL).

The reaction mixture was stirred at reflux temperature for 6 h, upon cooling the solid was filtered off, washed with water, diethyl ether and air dried. All pyridine N-oxides are known compounds and have been characterized by comparison of their GC-Mass, Mass, IR, ¹H NMR and melting points with those of authentic samples.

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