

Effective direct esterification of butanol by eco-friendly Preyssler catalyst, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$

Fatemeh F. Bamoharram^{a,**}, Majid M. Heravi^{b,*},
Mina Roshani^a, Manouchehr Jahangir^a, Ali Gharib^a

^a Department of Chemistry, Islamic Azad University, Mashhad Branch, Mashhad, Iran

^b Department of Chemistry, School of Sciences, Azzahra University, Vanak, Tehran, Iran

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Abstract

Direct esterification of butanol to butylbutanoate in the absence of butanoic acid has been investigated by a series of green solid acid catalysts, including $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$, $\text{H}_{14}\text{-P}_5$, $\text{H}_{14}[\text{NaP}_5\text{W}_{29}\text{MoO}_{110}]$, $\text{H}_{14}\text{-P}_5\text{Mo}$ and silica supported $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$, $\text{H}_{14}\text{-P}_5/\text{SiO}_2$, with H_2O_2 as oxidizing agent at reflux and at room temperatures. The performance of these eco-friendly catalysts were compared with H_2SO_4 . Maximum butylbutanoate yield and product selectivity (100%) was observed by using $\text{H}_{14}\text{-P}_5\text{Mo}$ as the catalyst. The effects of various parameters such as catalyst type, reaction times, reaction temperatures, and molar ratio of *n*-butanol to hydrogen peroxide have been studied. The green catalysts can be easily recovered and recycled with retention of their initial structure and activity.

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1. Introduction

The dimeric esterification of primary alcohols has been presented in many reports. Several methods for the dimeric esterification of primary alcohols, such as benzyltrimethylammonium tribromide in carbon tetrachloride, bromine–potassium bromate in water, sodium hypochlorite in acetic acid, sodium dichromate–sulfuric acid, calcium hypochlorite in acetonitrile–acetic acid, and sodium bromite in acetic acid have been employed for this propose [1–5].

Alternatively, dimeric esters can be obtained by bubbling oxygen into a solution of alcohol in acetic acid in the presence of cobalt acetate bromide [6]. Reduced copper and ruthenium catalyzed transformation of many primary alcohols to dimeric esters have also been reported [7,8]. The treatment of tributyl stannyl alkoxides by NBS in carbon tetrachloride afforded dimeric esters [9].

Many of these procedures suffer from lack of selectivity, unsatisfactory yields, being costly, toxicity of the reagents, or required special conditions. These limitations prompted us towards further investigation in search for a new catalyst, which will carry out the dimeric esterification under simpler experimental set up and eco-friendly conditions. Recently we have investigated direct transformation of diols to related cyclic esters, known as lactones, in the presence of Preyssler's anion as a green and eco-friendly catalyst, using hydrogen peroxide [10].

Green chemistry has been defined as a set of principles which reduce or eliminate the use of hazardous substances or catalysts [11]. Introducing clean processes and utilizing eco-friendly and green catalysts which can be simply recycled at the end of reactions have been under permanent attention and demands.

Recently, heteropolyacids (HPAs) which are low in toxicity and being recyclable have attracted special attention [12–14]. Many reactions catalyzed by Bronsted and Lewis acids now, in the presence of HPAs, proceed more effectively under milder conditions with greater selectivity, better yields, and shorter reaction times. Among HPAs, the application of Keggin and Wells–Dawson structures have been extensively studied [15–22].

* Corresponding author. Tel.: +98 9121329147; fax: +98 2188047861.

** Corresponding author.

E-mail addresses: fbamoharram@mshdiau.ac.ir (F.F. Bamoharram), mmh1331@yahoo.com (M.M. Heravi).

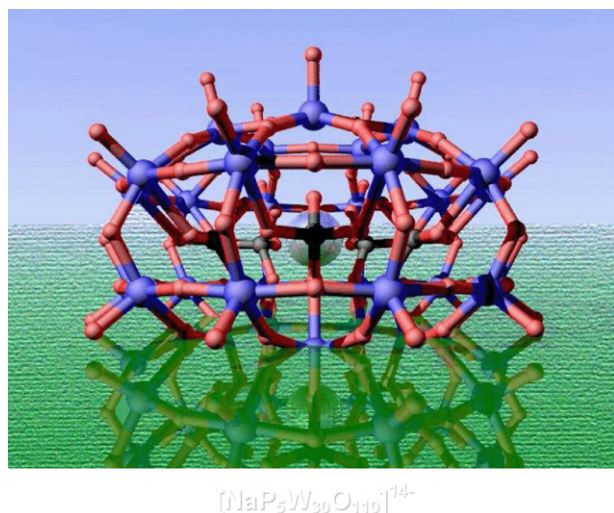


Fig. 1. Structure of Preyssler catalyst.

One of the intriguing heteropoly compounds is Preyssler's anion. The catalytic applicability of Preyssler's anion, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ with high thermal and hydrolytic stability throughout a wide pH range has been largely overlooked and only a few reports for catalytic performance of this catalyst have been cited [23]. This heteropolyacid is remarkable because of the following advantages (1) strong Bronsted acidity with fourteen titrable acidic protons, (2) high thermal stability, (3) high hydrolytic stability (pH 0–12), (4) reusability, (5) more safety, (6) lower waste quantity, (7) better separability, (8) less corrosiveness, (9) high oxidation potential and (10) greenness.

We are interested in catalytic reactions [24] and catalytic applicability of heteropoly compounds [25–28]. Recently, we have been exploring the application of the Preyssler catalyst for many reactions [26–28]. In our studies we have found this catalyst has unique stability in oxidation reactions with hydrogen peroxide and in contrast to Keggin, can catalyze oxidation reactions by using hydrogen peroxide as an oxidant without any degradation of structure [10,28].

This catalyst has a crown shape and has been formed by five units of PW_6O_{22} [29]. The structure of this anion is shown in Fig. 1. In continuation of our investigation on application of Preyssler's anion in organic synthesis, in this paper we wish to describe the direct esterification of butanol to butylbutanoate using the aforementioned anion. This ester is commercially important as a lacquer, artificial perfume, flavoring extract, etc. There are various references for, esterification of butanol in the presence of an acid, however there is only a few reports for direct esterification of 1-butanol to the butylbutanoate in the absence of an acid. In this research, we showed that without use of a carboxylic acid, and under milder conditions, by using inexpensive and available, Preyssler's anion, in dichloroethane, the dimeric ester can be easily synthesized in high yields.

In continuation of our recent works on Preyssler catalyst [26–28] we achieved our major goal which is the design and development of another application for the this catalyst in industry.

2. Experimental

2.1. Chemicals and apparatus

Butanol, sodium hydrogencarbonate, magnesium sulfate and hydrogen peroxide 30% were obtained from Merck and used as received. Solvents, sulfuric acid and Karl Fisher reagent were commercially available. The silica gel powder with mean particle size $15\ \mu\text{m}$ was purchased from Merck Company and was used as the catalyst support.

2.2. Catalyst preparation

$\text{H}_{14}\text{-P}_5$ was prepared by passage of a solution of the potassium salt [29] in water through a column ($50\ \text{cm} \times 1\ \text{cm}$) of Dowex 50w \times 8 in the H^+ form and evaporation of the elute to dryness under vacuum.

Molybdenum substituted Preyssler heteropolyanion, $\text{H}_{14}\text{-P}_5\text{Mo}$, was prepared as follows. 2.8 g (0.169 mol) $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and 2 g (0.008 mol) $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 35 mL water and mixed at 60°C for 30 min. The solution then 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 with stirring, 10 g KCl was added. The mixture was stirred and then heated up to dryness. The product was dissolved in warm water. Upon cooling to room temperature, a yellow crystals formed. Acidic form of molybdenum substituted heteropoly acid was obtained as described above for unsubstituted analogue.

Supported $\text{H}_{14}\text{-P}_5$ catalyst was prepared according to our previous reports [25,26], using impregnating a support in the form of powder (SiO_2) with an aqueous solution of the $\text{H}_{14}\text{-P}_5$. After stirring the mixture, the solvent was evaporated, dried at 120°C and was calcined at 250°C in a furnace prior to use.

2.3. Instruments

IR spectra were obtained on a Buck 500 scientific spectrometer. GLC analysis was performed on a Pu 4500 gas chromatograph with FID detector. ^1H NMR spectra were recorded on a FT NMR Bruker 100 MHz Aspect 3000 spectrometer.

2.4. Catalytic reaction

To a solution of 1-butanol (5 mmol) in dichloromethane (10 mL) different moles of H_2O_2 and catalyst (0.01 mmol) were added in a batch reactor. The reaction mixture was stirred for 4 h under reflux or 8 h at room temperature. The solution then treated with an aqueous solution of NaHCO_3 . The organic layer was separated and washed with water, dried over MgSO_4 , and evaporated under reduced pressure to give butylbutanoate as a colorless oil. The structure of product was confirmed by comparison of its boiling point, R_f values on TLC, retention times in GLC and spectroscopic data with those of authentic sample. The catalyst as acidic form recovered by centrifuging.

Table 1
Yields of butylbutanoate using various solvents^a

Entry	Solvent	Catalyst	% yield
1	Dichloroethane	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]	96.0
2	Dichloromethane	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]	59.2
3	Chloroform	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]	41.3
4	Carbon tetrachloride	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]	8.7
5	Benzene	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]	Trace
6	Dichloroethane	H ₁₄ [NaP ₅ W ₂₉ MoO ₁₁₀]	100.0
7	Dichloromethane	H ₁₄ [NaP ₅ W ₂₉ MoO ₁₁₀]	64.3
8	Chloroform	H ₁₄ [NaP ₅ W ₂₉ MoO ₁₁₀]	54.1
9	Carbon tetrachloride	H ₁₄ [NaP ₅ W ₂₉ MoO ₁₁₀]	14.6
10	Benzene	H ₁₄ [NaP ₅ W ₂₉ MoO ₁₁₀]	Trace

^a Reaction conditions: 1-butanol (5 mmol), solvent (10 ml), catalyst (0.01 mmol). Reflux temperature.

3. Results and discussions

The esterification reaction of butanol in dichloroethane in the presence of different forms of Preyssler catalyst under mild conditions gave butylbutanoate in good yields and selectivity.

This dimeric esterification of butanol was studied in different solvents including dichloromethane, dichloroethane, chloroform, carbon tetrachloride and benzene. Dichloroethane turned out to be the best solvent for this reaction. Data on the solvent effects for the best catalyst (H₁₄-P₅) are shown in Table 1. Coming to conclusion from these results, all reactions were performed in dichloroethane as a solvent of choice. The solvent effects are dominated by the interactions of the polarized polyanions with the solvent, to place the molecular orbitals at the appropriate level and or to lower the activation energy. This effect is higher for dichloroethane as solvent.

3.1. Effect of the mole numbers of hydrogen peroxide

The dimeric esterification of butanol must be performed with a calculated amount of hydrogen peroxide in dichloroethane as solvent and in the presence of H₁₄-P₅ as catalyst under reflux temperature. We have found out that the molar ratio of butanol to hydrogen peroxide is very important factor (Fig. 2). Fig. 2 shows

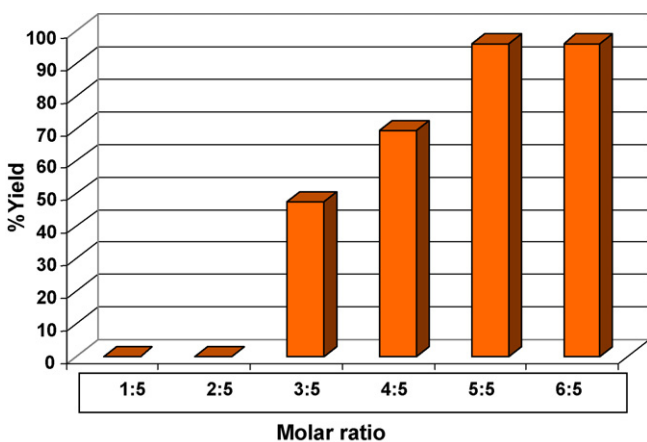


Fig. 2. The effect of butanol:hydrogen peroxide molar ratio (dichloroethane, reflux).

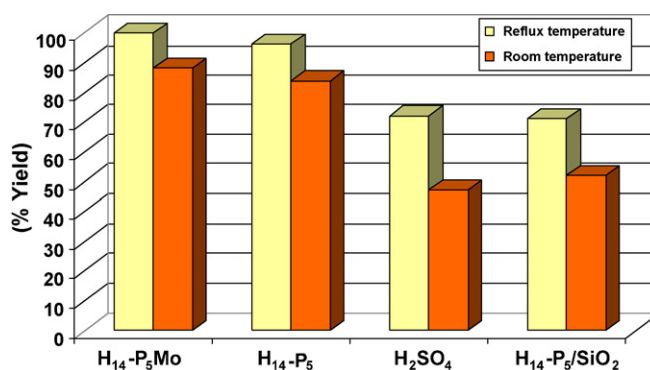


Fig. 3. Comparison of yields of butylbutanoate using Preyssler catalysts and sulfuric acid.

% yield of butylbutanoate versus the molar ratio of butanol:hydrogen peroxide. It is shown that the yield is maximum when the mmole numbers of hydrogen peroxide is 5. This finding is expected because we need formation of butanoic acid in the first stage. This behavior is accordance to our previous works in lactonization reactions [10]. All of the studies were performed with this molar ratio.

3.2. Effect of the catalyst type

Typical results obtained from various catalysts are given in Fig. 3. Good yields were obtained using all of these catalysts. In this figure, the yields of the preparation of butylbutanoate are compared, using the solid heteropolyacids of Preyssler and liquid acid (sulfuric acid) at reflux and room temperatures.

Among three forms of the Preyssler catalyst, H₁₄-P₅Mo shows higher activity. Interestingly, by replacing one of the tungsten atoms with molybdenum in the Preyssler heteropolyacid, the esterification yield reached to 100% in 4 h at reflux temperature. In general, a HPA with tungsten atom shows higher acidity, and also lower reduction potential than a molybdenum analogue [30]. This activity of H₁₄-P₅Mo is expected because, direct esterification of butanol to butylbutanoate is a catalytic-oxidative reaction. Because butylbutanoate is formed as the product and considering that hydrogen peroxide is needed, then there are two likely scenarios for the formation of butylbutanoate. (i) Oxidation of butanol to butanoic acid by hydrogen peroxide catalyzed by the Preyssler catalyst and then a catalytic esterification. (ii) The butanol is being oxidized to butanal which then forms a hemiacetal with the remaining butanol (here only weak acidity is needed); the hemiacetal is then oxidized to the ester. With respect to the high acidity of the Preyssler catalyst, the first pathway is more likely. The amount of hydrogen peroxide needed also appears to be consistent with first pathway.

Activity of supported and non-supported H₁₄-P₅, has been compared. The supported polyacid is less active than the non-supported form. One interpretation of this observation is that because of polyanion-support interactions, some protons of the polyacid and basic sites of the support can interact. This would lead to a diminished availability due to this extra ionic interaction [31].

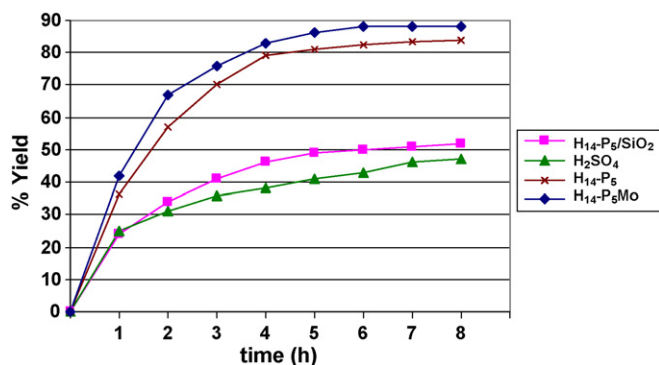


Fig. 4. The effect of reaction time on the yield of butylbutanoate in the presence of different catalysts (room temperature and optimum conditions).

In homogeneous conditions, this study was also extended to classical catalyst, like H₂SO₄. The comparisons at room and at reflux temperatures are shown in Fig. 3. The study of reaction progress at room and at reflux temperatures in the presence of H₁₄-P₅, H₁₄-P₅Mo, H₂SO₄ and H₁₄-P₅/SiO₂ are shown in Figs. 4 and 5, respectively. All of the reactions were carried out in optimum conditions (dichloroethane as solvent and mmole numbers of H₂O₂: 5)

The fact that H₂SO₄ is less active than the Preyssler catalyst is very interesting.

In green chemistry, there is a strong demand for new solid acids with favorable characteristics to replace conventional liquid and solid catalysts such as sulfuric acid, hydrochloric acid and ion-exchange resins [32]. Sulfuric acid poses serious environmental and operational problems.

For determination of difference acid strength between heteropolyacids and H₂SO₄, Drago et al. [33] calculated the dissociation constants of Keggin types with three protons. It was 10 and 14 times larger than those of paratoluenesulfonic acid and H₂SO₄. We titrated all of the protons of the Preyssler via potentiometric method. Since all of protons of Preyssler acid can be titrated, it is expected this constant be larger for Preyssler acid with 14 acidic protons. However, because our aim is not an analytical study we did not attempt to determine the dissociation constant. Our results in previous works [28] and this study have shown that this polyacid is very strong acid.

The radical products from the decomposition of hydrogen peroxide (HO• and HO₂•) act as the oxidants in the

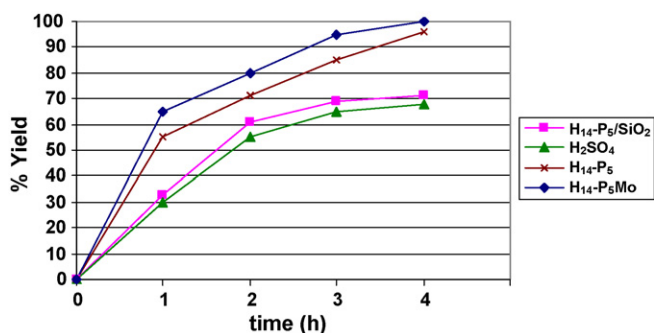


Fig. 5. The effect of reaction time on the yield of butylbutanoate in the presence of different catalysts (reflux temperature and optimum conditions).

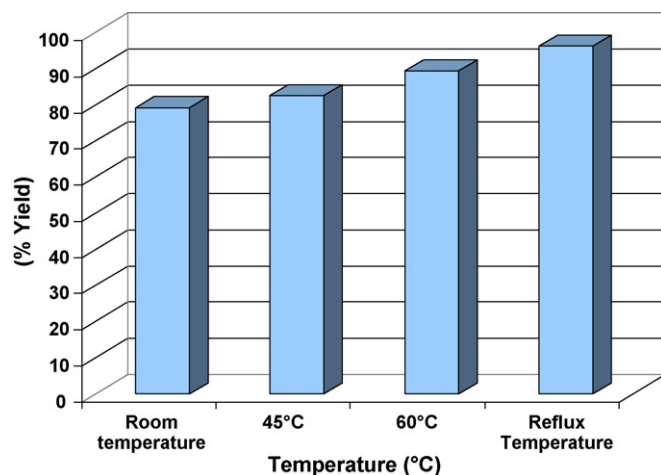


Fig. 6. Variation of yield of butylbutanoate with reaction temperature in optimum conditions.

Preyssler's anion catalyzed esterification at reflux temperature [34–36].

3.3. Effect of the reaction time

Typical time courses of the reactions with various forms of Preyssler catalyst and sulfuric acid are shown in Figs. 4 and 5 at room and reflux temperatures. The results show that in the initial stage of reaction, the reaction proceeded rapidly and became slow after about 2 h. The decreases in the reaction rate at the latter stages of the reaction are mainly due to the limitation of the equilibrium. The effect of reaction time on the % yield of butylbutanoate indicates that, yields strongly depend on reaction time. The best reaction time has been found to be 4 h at reflux temperature and 8 h in room temperature.

3.4. Effect of the temperature

Fig. 6 presents the yield of butylbutanoate versus reaction temperature in optimum conditions in the presence of H₁₄-P₅. *n*-Butylbutanoate is formed with 100% selectivity. This figure shows that the higher temperature results the greater conversion of *n*-butanol at a fixed contact time under otherwise identical conditions. Increasing the temperature is apparently favorable for the acceleration of the reaction.

3.5. Recovery and reusability of the Preyssler catalyst

Interestingly, we have found that the Preyssler catalyst can be simply recovered and reused several times without loss of activity and degradation of structure. The catalyst can be recycled and after three reactions, the yields decreases about 5–7%. This is a very important result. Whereas Keggin heteropolyacids convert to peroxopolyoxometalates in the presence of hydrogen peroxide and thus catalysis proceed via peroxo compound [37,38], the Preyssler catalyst can catalyze this reaction, without degradation of its structure. IR spectrum of this catalyst at the end of reaction showed that the structure of the Preyssler catalyst has been untouched.

4. Conclusions

In conclusion, we have provided an effective and green procedure for highly selective direct esterification of butanol. Simple experimental procedure as well as high yield and selectivity, makes this method a useful addition to the methodologies that require green superacid solid catalyst.

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