

Short communication

A catalytic method for synthesis of γ -butyrolactone, ϵ -caprolactone and 2-cumaranone in the presence of Preyssler's anion, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$, as a green and reusable catalyst

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Abstract

γ -Butyrolactone, ϵ -caprolactone and 2-cumaranone are synthesized from related diols, using Preyssler heteropolyacids, $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ and $\text{H}_{14}[\text{NaP}_5\text{W}_{29}\text{MoO}_{110}]$ as catalyst, and hydrogen peroxide as oxidizing agent. The performance of eco-friendly Preyssler catalysts was compared with H_2SO_4 and the catalytic activity of H_2SO_4 is found to be lower than Preyssler catalysts. The effects of various parameters such as amount of diol, temperature, solvent and time were studied. In all cases, the Preyssler catalyst was easily recovered and recycled with retention of their initial structure and activity.

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1. Introduction

Lactones of five, and larger rings, are of interest because of their applications in building up biologically active compounds which exhibit various pharmacological activities [1–5]. They can be also used for the synthesis of polyesters [6,7].

There are a number of methods concerning the lactonization of diols. Many catalytic methods including heterogeneous liquid phase lactonization of diols using vanadomolybdophosphoric acid immobilized on polyaniline [8], lactonization of α -, ω -diols by use of the sodium bromate–hydrobromic acid system [9], cyclo carbonylation of allylic alcohols [10,11], and direct insertion of carbon monoxide into cyclic ethers [12], with palladium-based catalysts have been reported. Most of these catalysts are expensive and the applications of them cause some drawbacks such as environmental problems, long reaction times and tedious work up procedure.

Green/sustainable chemistry (GSC) is, in a word, chemistry and chemical technology for environmentally friendly products and processes. Green chemistry has been defined as a set of principles that reduces or eliminates the use or generation of hazardous substances throughout the entire life of chemical materials [13,14]. If one compares the technology with medical care, GSC focuses on precaution (or prevention) rather than diagnosis and cure. Here, the idea of placing more stress on the stage of design, as stated in the definition [13,14], is important and useful. Heteropolyacids as solid acid catalysts are green with respect to corrosiveness, safety, quantity of waste, and separability and it is well known that the use of heteropolyacid catalysts for organic synthesis reactions can give a lot of benefits. Heteropolyacids are widely used in variety of acid catalyzed reactions [15–20].

It is known that heteropolyacid catalysts are active in the lactonization of 1,4-butanediol into γ -butyrolactone, which is an important chemical as a solvent and as a precursor for the synthesis of *N*-methyl-2-pyrrolidone and 2-pyrrolidone [21–23].

One of the unique features that make solid heteropolyacids economically and environmentally attractive is their stability and Bronsted acidity.

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Although a wide variety of heteropolyacids have been reported as green and effective catalysts [24–28], there are only a few reports for application of Preyssler catalyst. This heteropolyacid with fourteen acidic protons is an efficient “supper acid” solid catalyst with unique hydrolytic stability (pH 0–12) [29].

Recently, we have been exploring the application of this catalyst and have found that this catalyst in different forms are very effective in catalytic processes [30–33].

Because of interesting importance of lactones and in continuation of our interest in application of heteropolyacids in organic synthesis [34,35], specially, in this article we wish to report our results for the synthesis of lactones using Preyssler catalyst in various conditions.

Our findings indicate that Preyssler catalyst render effective lactonization of 1,4-butanediol, 1,6-hexanediol and 1,2-benzene dimethanol to γ -butyrolactone, ϵ -caprolactone and 2-cumaranone respectively with high yields and excellent selectivity by using hydrogen peroxide. Also we have found that, in spite of degradation of the Keggin heteropolyacids in the presence of hydrogen peroxide [36], Preyssler catalyst catalyzes the lactonization reactions with complete retention of structure. The effects of various parameters such as amount of diol, temperature, solvent and time were studied. For expanding of our work we studied, using urea-hydrogen peroxide (UHP- H_2O_2) and DABCO- H_2O_2 . In the last few years, several reports appeared on the use of UHP and DABCO- H_2O_2 for the conversion of amines to nitroalkanes, Bayer–Villiger oxidations of ketons to lactones, oxidations of sulfides to sulfones, conversion of pyridines to pyridine *N*-oxides, epoxidation of styrene and alkenes, epoxidation of allylic alcohols and alkenes, oxidation of diols with methyltrioxo rhenium, oxidation of thiols to disulfides, oxidation of aromatic aldehydes, oxidation of imines to oxaziridines and nitrores, and asymmetric epoxidation catalyzed by oligopeptides [37–50].

Hence, it was thought that instead of aqueous hydrogen peroxide, anhydrous UHP- H_2O_2 or DABCO- H_2O_2 can be used as the oxidizing agent. A major advantage of UHP lies in its potential for releasing anhydrous H_2O_2 into solution in a controlled manner [51]. Literature survey, revealed that UHP and DABCO- H_2O_2 are insoluble in common organic solvents such as chloroform as solvent of choice in our reactions [52,53].

The major aim described in this work is the design and development of applications for Preyssler catalyst with exclusive properties including high thermal and hydrolytic stability and strong acidity.

2. Experimental section

2.1. Chemicals and apparatus

All solvents and diols were purchased from commercial sources. $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ was prepared by passage of a solution of the potassium salt in water through a column (50 cm \times 1 cm) of Dowex 50w \times 8 in the H^+ form and evaporation of the elute to dryness under vacuum [30].

Molybdenum substituted Preyssler heteropolyanion, $\text{H}_{14}[\text{NaP}_5\text{W}_{29}\text{MoO}_{110}]$, was prepared as follow: 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 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 during stirring 10 g KCl was added. The mixture was stirred and then evaporated 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.

Supported heteropolyacid catalyst was synthesised according to our previous report [30] using impregnating a support in the form of powder (SiO_2) with an aqueous solution of the $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$. After stirring of the mixture, the solvent was evaporated, dried at 120 °C and was calcined at 250 °C in a furnace prior to use. Hydrogen peroxide was obtained from Merck Company and was standardized by online internet methods (Hydrogen Peroxide Product Information Manual, Analytical Procedure).

2.2. Instruments

IR spectra were obtained with 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.

2.3. General procedure for lactonization reaction

In a round-bottom flask equipped with a thermometer and reflux condenser, diol (1.15×10^{-2} mol), catalyst (0.15×10^{-4} mol) and solvent (10 ml) were placed and the hydrogen peroxide 30% (0.046 mol) was added. The reaction mixture was heated with stirring for 6 h at reflux temperature (boiling point of solvents). The progress of reaction was followed by measuring the amount of produced water by Karl–Fisher titration. After 6 h, the reaction mixture was cooled to room temperature. To this mixture saturated sodium carbonate and sodium sulfite 20% were added respectively, and the solution was extracted with dichloromethane (3×10 ml). The organic phase was dried on magnesium sulfate and evaporated under reduced pressure. The lactones were purified by column chromatography using petroleum ether and diethyl ether as eluant.

3. Results and discussion

As mentioned earlier, we have previously explored the esterification reaction of salicylic acid with aliphatic and aromatic alcohols in the presence of Preyssler catalyst in homogeneous and heterogeneous conditions to produce esters [31].

In continuation of our interest in this area, we have explored the dimeric esterification of butanol to butylbutanoate and we have found a good selectivity and yield for the preparation of butylbutanoate [32].

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