

Lactonization of various diols, using transition metal-substituted keggin catalysts [PW11MO40]⁷⁻, (M= Co(II), Ni(II), Cu(II), Zn(II))

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Abstract: Potassium salts of the monosubstituted Keggin polyoxometalates, [PW11MO40]⁷⁻, (M= Co(II), Ni (II), Cu(II), Zn(II)), were used as catalysts for lactonization of 1,4-butane diol, 1,6-hexane diol and 1,2-benzene dimethanol, in the presence of hydrogen peroxide as an oxidant. The effects of various parameters such as amount of the oxidant and diol, solvent type, temperature and reaction time have been studied. The results show that [PW11CoO40]⁷⁻ as catalyst in chloroform produce the highest yield of lactone.

Keywords: Catalyst, Keggin, Heteropolyanion, Lactonization, Lactone

Introduction

Lactones have deserved great interest in synthetic and natural products chemistry. These structures occur extensively in the natural world and their biological and pharmacological activities have been widely studied [1-5]. They can be also used for the synthesis of polyesters [6,7]. Several catalytic synthetic methods for lactones have been developed and reported during recent years [1,8,9]. Catalytic technology has supported chemical industry and assisted to solve environmental issues. Green/sustainable chemistry (GSC) is, in a word, chemistry and chemical technology for environmentally friendly products and processes. When the GSC Network, Japan was launched, a new organization for the promotion of GSC activities, "green and sustainable chemistry" was defined in a slightly broader sense, that is, innovative chemical technologies for sustainable society, including waste treatment and reuse. It is pointed out that easily applicable methods for the evaluation of greenness (or green index) are necessary for the sound development of GSC movement. Then, green/ sustainable aspects of heteropolyacid catalysts are described referring to examples of the achievements of basic studies and successful practical applications: (i) water-tolerant acid catalysis, (ii) catalysis in pseudoliquid phase, (iii) solid-phase catalysis, (iv) bi-

functional catalysis in combination with noble metals, and (v) green processes in bi-phase systems [10]. Also heteropolyacids are green and harmless to the environment with respect to corrosiveness, safety, quantity of waste, and separability with certainly some exceptions [11]. It is well known that the use of heteropolyacid catalysts for organic synthesis reactions can give a lot benefits. In view of green chemistry, the substitution of harmful liquid acids by solid reusable heteropolyacids as catalyst in organic synthesis is the most promising application of these acids.

A heteropolyacid is an oxide cluster, which has a type of phosphorus/silicon oxo acid and oxo acids with molybdenum, tungsten and other elements. The application of heteropolyacids as catalytic materials is growing continuously in the catalytic field [11].

These compounds possess unique properties such as: well-defined structure, Brønsted acidity, possibility to modify their acid-base and redox properties by changing their chemical composition (substituted HPAs), ability to accept and release electrons, high proton mobility, etc [12]. We have worked on heteropolyacids with Keggin, Dawson and Peyssler structures as catalyst [13,14]. In continuation of these attempts, we studied direct esterification of butanol to butylbutanoate [15] and the synthesis of γ -butyrolactone, ϵ -caprolactone and 2-cumarone in the presence of Preyssler catalyst as a green and reusable catalyst [16]. With respect to the

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catalytic activity of transition-metal-substituted, the catalytic activities of Keggin have been largely overlooked. Herein we wish to report an efficient and green method for the synthesis of lactones from the corresponding diols, in the presence of hydrogen peroxide as an oxidizing agent and transition metal substituted Keggin as catalysts. The effect of different reaction parameters such as temperature, catalyst, concentration of diol and oxidant and solvent were studied on the yield of lactonization. The reaction parameters were varied to determine the optimum conditions with respect to yields of the reactions.

Results and Discussion

The catalytic lactonization of 1,4-butane diol, 1,6-hexane diol and 1,2-benzene dimethanol were studied in the presence of $K_7[PW_{11}MO_{40}]$, (M=Co(II), Ni (II), Cu(II), Zn(II), as catalyst and hydrogen peroxide as an oxidant . The structure of this catalyst is shown in

Figure 1: Structure of a transition metal-substituted Keggin

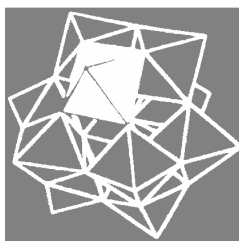


Figure 2: Yields of catalytic oxidation of 1,4-butanediol in $CHCl_3$

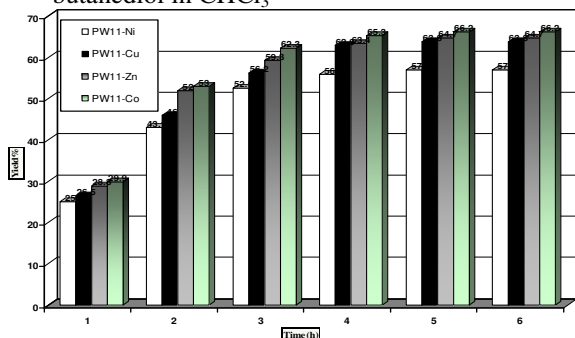


Figure 3: Yields of catalytic oxidation 1,4-butanediol in $1,2-C_2H_4Cl_2$

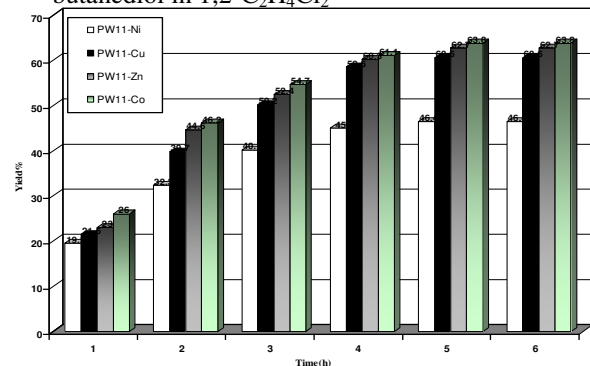


Figure 1. The optimization of the reaction conditions were realized by studying the effects of the amount of hydrogen peroxide, the amount of diol, the types of M, as well as other important factors such as solvent, temperature and time of reactions that control the yield of diols.

Effect of the solvent type

Chloroform, 1,2-dichloromethane, carbon tetrachloride, acetonitrile, dimethylformamide, 2-dimethyl tetrahydrofuran and dimethylsulfoxide were examined as solvents. Among these solvents, chloroform, 1,2-dichloroethane and carbon tetrachloride gave good results. The effect of these solvents on the lactonization of diols is shown in Figures (2-10). Table 7 shows the results for the other solvents (after 6h).

Figure 4: Yields of catalytic oxidation 1,4-butanediol in CCl_4

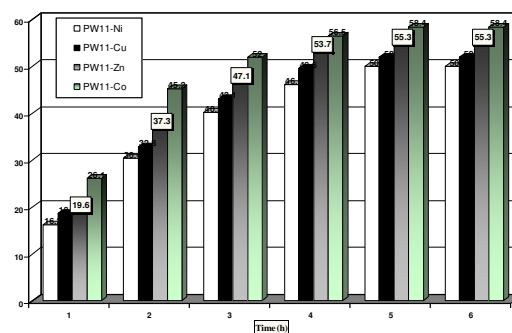


Figure 5: Yields of catalytic oxidation 1,6-hexane diol in $CHCl_3$

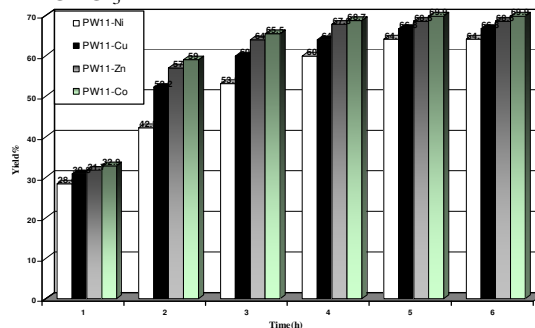


Figure 6: Yields of catalytic oxidation 1,6-hexane diol in $1,2-C_2H_4Cl_2$

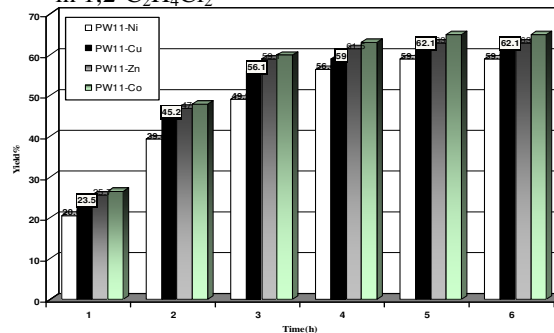
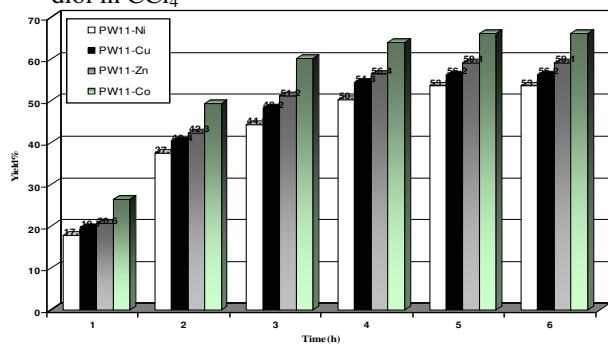
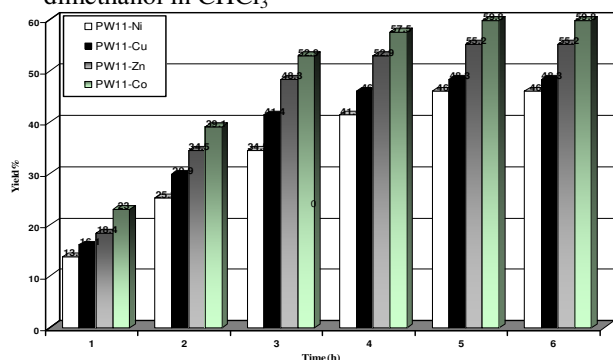
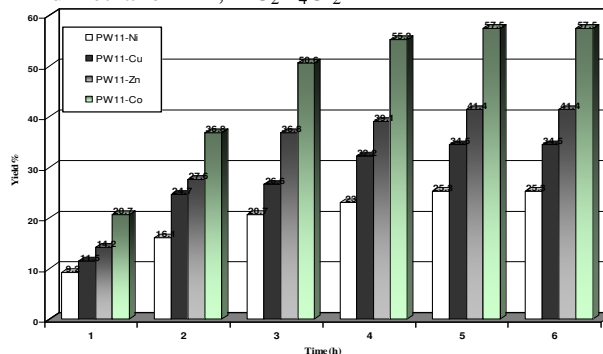
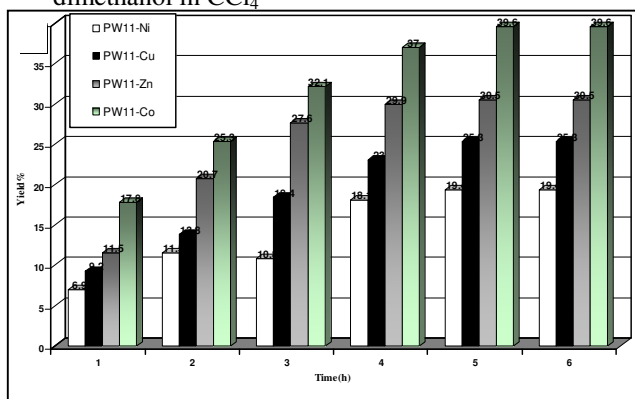


Figure 7: Yields of catalytic oxidation 1,6-hexane diol in CCl_4 **Figure 8:** Yields of catalytic oxidation of 1,2-benzene dimethanol in CHCl_3 **Figure 9:** Yields of catalytic oxidation 1,2-benzene dimethanol in 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ **Figure 10:** Yields of catalytic oxidation 1,2-benzene dimethanol in CCl_4 

However, the maximum isolated yield of lactones was obtained in chloroform as solvent. Interestingly, in all of the solvents the yields are higher with $\text{K}_7[\text{PW}_{11}\text{CoO}_{40}]$. In all cases, the IR spectra showed the absence of alcoholic OH band and appearance of carbonyl band in $1700\text{--}1800\text{ cm}^{-1}$. IR spectra of γ -butyrolactone and ϵ -caprolactone showed, stretching vibration band of carbonyl group in the range of $1770\text{--}1790$ and $1700\text{--}1735\text{ cm}^{-1}$ respectively. IR spectra of 2-cumaranone showed stretching vibration band of carbonyl group in $1700\text{--}1800\text{ cm}^{-1}$. This shift is attributed to conjugation of benzene ring with carbonyl group.

Effect of the catalyst type

Transition-metal-substituted polyoxometalates have attracted much attention as oxidation catalysts because of their unique ensemble of properties, including metal oxide-like structure, thermal and hydrolytic stability, tunable acidities, and redox potentials, and alterable solubilities in various media, etc [17-22]. Keggin type $[\text{XM}_{11}\text{O}_{39}]^{n-}$ so called lacunary heteropolyanions are derived by removing one MO unit from the Keggin heteropolyacids, $[\text{XM}_{12}\text{O}_{40}]^{n-}$. The catalytic properties of Keggin can be tuned by changing the identity of

charge-compensating counter cations, heteroatoms and framework metal atoms [23].

Many transition metals (M') can fit into this octahedral binding site, giving rise to transition metal substituted heteropolyanions, $[\text{XMM}'\text{O}_{40}]^{n-}$ (Figure 1) [20]. In most cases the incorporated metal is the active site for the reactions. By changing the number and the kind of the substituted addenda atoms, the electrochemical character of polyoxometalates and catalytic activity of them can be widely changed.

The results of the lactonization of diols in the presence of transition metal substituted heteropolyanions with Co, Ni, Cu, and Zn ions showed that the presence of Co ion in mixed addenda heteropolyacid, enhances the conversion of diols. This result is expected. It has been established that cobalt compounds, including Co-polyoxometalates, are among the best catalysts for different organic reactions [24-32]. The superior activity of cobalt in these reactions is due to its ability to initiate the catalytic process via interaction with the substrate molecule. In these heteropolyanion types, cobalt(II) is located partially outside of the lacunary hole and, thus, the cation exhibits characteristics both of free cobalt ions and of cobalt-containing heteropolyacids, so the

cobalt(II) cation was simply extracted from the heteropolyacid skeleton. This ease of exchange occurs only for cobalt (II)-containing heteropolyacids and it is not a general feature. This exchange capability is due to the size of these metal ions. The lacunary heteropolyacids can exchange only metal ions of diameter approximately <90 pm. Since cobalt (II) is larger than this critical dimension, as it must remain partially outside the lacunary hole and should be extracted relatively easily [26,33]. It is suggested that in this study, higher activity of $K_7[PW_{11}CoO_{40}]$ is related to the above mentioned conclusion.

Effect of substrate concentration

Experiments on lactonization of diols were carried out

at reflux temperature of the solvents by varying the moles of diols to 1/2 and 1/4, while keeping the concentrations of hydrogen peroxide and catalyst constant. In chloroform (solvent of choice), the relationship of the yield of lactones with the decrease of amount of diol is summarized in tables 1-6. Comparison of Figures (2, 5), and 8 (highest concentration) with results of these tables shows that the yield decreases by decrease of the amount of diol. Since the esterification is a straight forward reaction, the yields of the cyclic ester can be increased by increasing the concentration of diols. Interestingly, in all cases the highest yields were obtained with $K_7[PW_{11}CoO_{40}]$.

Table 1: Yields of catalytic oxidation of 1,4-butanediol in the presence of various transition metal-substituted Keggin catalysts in chloroform

Catalyst	$K_7[PW_{11}CoO_{40}]$	$K_7[PW_{11}ZnO_{40}]$	$K_7[PW_{11}CuO_{40}]$	$K_7[PW_{11}NiO_{40}]$
Time(h)				
1	26.00	24.80	22.10	21.00
2	49.10	46.50	43.00	40.00
3	58.00	55.10	49.50	47.30
4	61.70	58.50	52.30	51.00
5	62.50	60.00	54.00	52.90
6	62.50	60.00	54.00	52.90

^aReaction conditions: substrate: 0.575×10^{-2} mol, Catalyst: 0.15×10^{-4} mol, solvent: 10mL, hydrogen peroxide 30%: 0.046mol, reflux

Table 2: Yields of catalytic oxidation of 1,4-butanediol in the presence of various transition metal-substituted Keggin catalysts in chloroform

Catalyst	$K_7[PW_{11}CoO_{40}]$	$K_7[PW_{11}ZnO_{40}]$	$K_7[PW_{11}CuO_{40}]$	$K_7[PW_{11}NiO_{40}]$
Time(h)				
3	42.00	40.50	38.20	35.00
6	58.70	51.50	47.60	41.10

^aReaction conditions: substrate: 0.287×10^{-2} mol, Catalyst: 0.15×10^{-4} mol, solvent: 10mL, hydrogen peroxide 30%: 0.046mol, reflux

Table 3: Yields of catalytic oxidation of 1,6-hexanediol in the presence of various transition metal-substituted Keggin catalysts in chloroform

Catalyst	$K_7[PW_{11}CoO_{40}]$	$K_7[PW_{11}ZnO_{40}]$	$K_7[PW_{11}CuO_{40}]$	$K_7[PW_{11}NiO_{40}]$
Time(h)				
1	29.50	28.20	26.00	25.10
2	51.20	49.00	46.20	42.50
3	60.00	57.50	52.60	48.70
4	62.20	60.20	58.50	52.20
5	63.80	61.10	59.40	54.00
6	63.80	61.10	59.40	54.00

^aReaction conditions: substrate: 0.434×10^{-2} mol, Catalyst: 0.15×10^{-4} mol, solvent: 10mL, hydrogen peroxide 30%: 0.046mol, reflux

Table 4: Yields of catalytic oxidation of 1,6-hexanediol in the presence of various transition metal-substituted Keggin catalysts in chloroform

Catalyst	K ₇ [PW ₁₁ CoO ₄₀)	K ₇ [PW ₁₁ ZnO ₄₀)	K ₇ [PW ₁₁ CuO ₄₀)	K ₇ [PW ₁₁ NiO ₄₀)
Time(h)				
3	51.30	48.10	42.00	39.20
6	61.20	57.50	50.10	46.00

^aReaction conditions: substrate: 0.217×10^{-2} mol, Catalyst: 0.15×10^{-4} mol, solvent: 10mL, hydrogen peroxide 30%: 0.046mol, reflux

Table 5: Yields of catalytic oxidation of 1,2-benzendimethanol in the presence of various transition metal-substituted Keggin catalysts in chloroform

Catalyst	K ₇ [PW ₁₁ CoO ₄₀)	K ₇ [PW ₁₁ ZnO ₄₀)	K ₇ [PW ₁₁ CuO ₄₀)	K ₇ [PW ₁₁ NiO ₄₀)
Time(h)				
1	17.20	14.10	Trace	Trace
2	32.50	28.30	23.10	17.00
3	44.70	39.60	31.70	26.10
4	46.00	42.30	37.30	34.50
5	47.10	44.00	38.50	36.00
6	47.10	44.00	38.50	36.00

^aReaction conditions: substrate: 0.361×10^{-2} mol, Catalyst: 0.15×10^{-4} mol, solvent: 10mL, hydrogen peroxide 30%: 0.046mol, reflux

Table 6: Yields of catalytic oxidation of 1,2-benzendimethanol in the presence of various transition metal-substituted Keggin catalysts in chloroform

Catalyst	K ₇ [PW ₁₁ CoO ₄₀)	K ₇ [PW ₁₁ ZnO ₄₀)	K ₇ [PW ₁₁ CuO ₄₀)	K ₇ [PW ₁₁ NiO ₄₀)
Time(h)				
3	34.10	28.60	22.20	18.00
6	39.60	37.50	26.30	22.50

^aReaction conditions: substrate: 0.180×10^{-2} mol, Catalyst: 0.15×10^{-4} mol, solvent: 10mL, hydrogen peroxide 30%: 0.046mol, reflux

Table 7: Yields of catalytic oxidation of diols in the presence of various transition metal-substituted Keggin catalysts (time= 6 h)

Diol (Solvent)	K ₇ [PW ₁₁ CoO ₄₀)	K ₇ [PW ₁₁ ZnO ₄₀)	K ₇ [PW ₁₁ CuO ₄₀)	K ₇ [PW ₁₁ NiO ₄₀)
1,2-benzendimethanol (CH ₃ CN)	34.30	32.10	30.50	28.10
1,2-benzendimethanol (DMF)	30.10	28.90	26.50	24.20
1,2-benzendimethanol (THF)	28.50	26.00	23.70	21.70
1,2-benzendimethanol (DMSO)	24.00	21.30	19.90	17.40
1,4-butanediol (CH ₃ CN)	48.50	45.70	44.10	42.50

Table 7. Continued

1,4-butanediol (DMF)	44.80	41.30	40.50	38.10
1,4-butanediol (THF)	41.20	39.30	37.50	35.00
1,6-hexanediol (CH ₃ CN)	56.10	48.50	45.20	42.50
1,6-hexanediol (DMF)	52.20	45.00	42.10	40.50
1,6-hexanediol (THF)	49.70	43.50	41.7	39.50
1,6-hexanediol (DMSO)	45.10	42.00	40.50	39.80

^aReaction conditions: substrate: 0.3 g, catalyst: 0.15×10^{-4} mol, solvent: 10mL, hydrogen peroxide 30%: 0.046mol, reflux

Effect of the mole numbers of hydrogen peroxide

The lactonization of diols was investigated with different molar ratios of substrate: oxidant under optimum conditions. The study of the effects of the amount of hydrogen peroxide is shown in Figures 11-13. Our studies show that, the reaction yields were affected by changing the molar ratio of diol. Interestingly, the yield decreases with increase of the molar ratio of hydrogen peroxide from 0.046 mol to 0.138 mol.

In the absence of catalyst, hydrogen peroxide has poor ability to oxidize the diols with very low yields. Very small amount of product was formed in the absence of hydrogen peroxide with or without addition of the heteropolyacid. The best results were obtained by using 0.046 mol of hydrogen peroxide (Figures 2-10). When the mole numbers of hydrogen peroxide increased to 0.107 mole the yields decreased (Figures 11-13) and with increase of moles to 0.138 the yields decreased dramatically. It can be suggested that with the increase of the mole numbers of hydrogen peroxide both of hydroxyl groups of the diols are oxidized. For expanding of our work we studied, using urea-hydrogen peroxide (UHP-H₂O₂) and DABCO-H₂O₂. In the last few years, several reports appeared on the use of UHP and DABCO-H₂O₂ for different reactions [34-39]. Hence, it was thought that instead of aqueous hydrogen peroxide, anhydrous UHP-H₂O₂ or DABCO-H₂O₂ can be used as the oxidizing agent. A major advantage of UHP lies in its potential for releasing anhydrous hydrogen peroxide into solution in a controlled manner [40]. Literature survey, revealed that UHP and DABCO- H₂O₂ are insoluble in common organic

solvents such as chloroform as solvent of choice in our reactions [41,42].

Figure 11: Yields of catalytic oxidation of 1,4-butanediol in optimum conditions with increase of oxidant amount (H₂O₂: 0.107 mol)

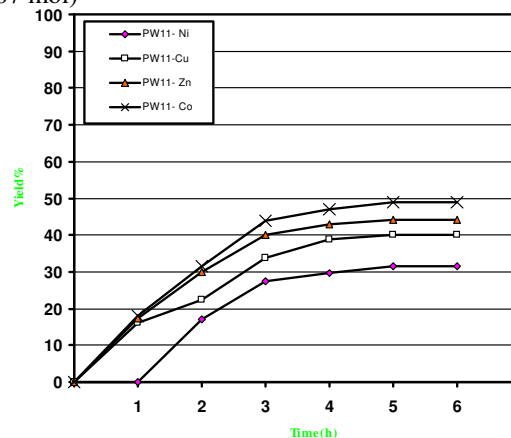


Figure 12: Yields of catalytic oxidation of 1,6-hexanediol in optimum conditions with increase of oxidant amount (H₂O₂: 0.107 mol)

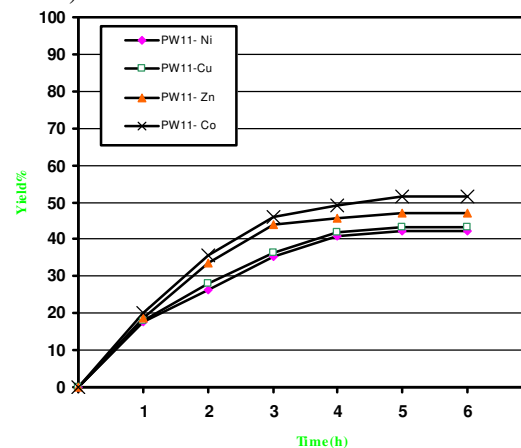
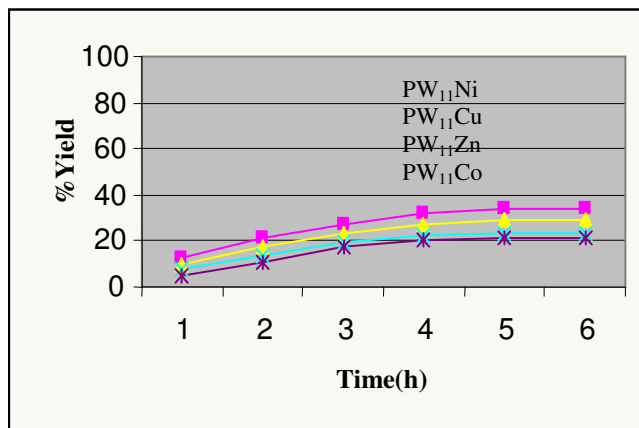


Figure 13: Yields of catalytic oxidation of 1,2-benzene dimethanol in optimum conditions with increase of oxidant amount (H_2O_2 : 0.107 mol)



Effect of temperature

We also observed that this lactonization depends on temperature. In all solvents in the presence of heteropolyanion catalysts, the yields of the lactones were examined at reflux temperature, and lower temperatures.

The results showed that the reaction temperature is an effective factor on the yield of lactonization under the optimized conditions. Thus, the highest yields of lactones were obtained at reflux temperature. The lactonization of diols at lower temperatures is relatively slow reactions and the lower yields of the reaction were obtained when the temperature was further decreased. This result was expected, since increasing the temperature is apparently favorable for the acceleration of the forward reaction.

Effect of reaction time

For all of the diols in the presence of heteropolyanion catalysts, the effect of reaction time on the yield of the lactones was studied. The results in the figures and tables show the effect of the reaction time on the yield of lactones. The best yields were achieved after 5-6 h of reaction and yield increased with the time of the reaction. The maximum of isolated yields were achieved after 6 h.

Experimental section

Chemical and instruments

All solvents, Karl-Fisher reagent and diols were purchased from commercial sources. IR spectra were obtained with a Buck 500 scientific spectrometer. GLC

analysis was performed on a Pu 4500 gas chromatograph with FID detector. $^1\text{H-NMR}$ spectra were recorded on a FT-NMR Bruker 100MHZ Aspect 3000 spectrometer. All catalysts were prepared according to the literature methods [43,44].

Typical procedure for lactonization reaction:

In a typical reaction a mixture of 1,4-butanediol (1.15×10^{-2} mol), catalyst (0.15×10^{-4} mol), solvent (10 mL) and hydrogen peroxide 30% (0.046 mole) were refluxed for 6 h. 1,6-hexane diol and 1, 2- benzene dimethanol were used 0.869×10^{-2} and 0.723×10^{-2} moles respectively. The progress of reaction was followed by measuring the amount of produced water by karl-fisher titration. Then, 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 over magnesium sulfate and evaporated under reduced pressure. The lactones were purified by column chromatography using petroleum ether and diethyl ether as eluent. Yields determined by GC and Karl-Fisher titration.

Conclusions

In summary, we have developed a new method using of mixed addenda Keggin heteropolyacids as inexpensive, easy to handle, non-corrosive and environmentally benign catalysts for the synthesis of cyclic esters known as lactones from the corresponding diols. The advantages of the present procedure are simplicity of operation and work-up and good yields of products. The data reported in this work show that mixed addenda Keggin heteropolyanions exhibit significant and outstanding activity in the lactonization of diols in various solvents and concentration of diols.

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