

Preyssler's anion, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$, as an efficient catalyst for the selective synthesis of geminal diacetates

Fatemeh F. Bamoharram,^{a*} Majid M. Heravi,^{a,b} Jalal Sh. Emampour,^c Mina Roshani,^a Tayebeh Mirghafari^a

^aDepartment of Chemistry, Islamic Azad University, Mashhad Branch, Mashhad, Iran

^bDepartment of Chemistry, School of Sciences, Azzahra University, Vanak, Tehran, Iran

^cDepartment of Chemistry, School of Sciences, Ferdowsi University, Mashhad, Iran

Abstract: The highly selective catalytic synthesis of gem-bis (acyloxy)-alkanes has been studied using Preyssler catalyst, $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ at room temperature and under solventless conditions. Comparison of Preyssler catalyst with the other heteropoly anions showed that, in all cases, maximum of product yields was observed by using $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ as catalyst. The effects of catalyst moles and time of reaction were studied.

Keywords: Heteropolyacid; Preyssler; Catalyst; 1,1-Diacetates; Acylal

Introduction

Geminal-Diacetates (acylals) or gem-bis (acyloxy)-alkanes are important starting materials for the preparation of dienes and chiral allylic esters [1,2]. In addition, these compounds are one of the important protecting groups because of their stability under various reaction conditions including neutral, basic and aqueous acids media [3-5]. Acylals have also been used as precursors for Diels-Alder reactions [6] and a cross-linking reagents for cellulose in cotton [7]. The most common method for the preparation of acylals is the reaction of an aldehyde with acetic anhydride in the presence of an acid catalyst. At this area, strong protonic acids such as sulfuric, methane sulfonic or phosphoric acids have been used [8,9]. Use of Lewis acids such as PCl_3 , ZnCl_2 , TMSCl-NaI , I_2 , FeCl_3 , NBS, anhydrous ferrous sulfate, LiBr , InCl_3 , WCl_6 , CAN, LiBF_4 are also reported [10-21]. Other catalysts for this conversion including clays, zeolites, Nafion-H, graphite, ZrCl_4 , $\text{Zn}(\text{BF}_4)_2$, $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{AlPW}_{12}\text{O}_{40}$, $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 24\text{H}_2\text{O}$, $\text{Sc}(\text{OTf})_3$, $\text{Cu}(\text{OTf})_2$, $\text{Bi}(\text{OTf})_3$ and LiOTf have also been used [22-32].

Even though a wide variety of catalysts were used for the synthesis of 1,1-diacetates, but there is a good new scope for research towards finding green and eco-friendly catalysts and new reports are still being

published, using new catalysts. However, many of the reported methods, involve strongly acidic conditions, high temperature, long reaction times, expensive catalysts along with high catalyst loadings, excess amounts of reagents, and generation of significant quantities of waste. For these reasons, there is a demand for a methodology that is mild, efficient, environmentally benign, site selective, with using green and reusable solid acids as catalysts.

Heteropoly acids are a class of molecularly defined inorganic metal-oxide clusters, possess intriguing structures and diverse properties and in recent years have been studied extensively for use as solid acid and redox catalysts [33,34]. They are used in solution as well as in the solid state as acid and oxidation catalysts. Therefore, it appears to be an interesting challenge to obtain new catalysts based on heteropoly compounds with special properties. However, among the used heteropolyacids, there is a special interest in catalytic applications of Keggin structure and catalytic behavior of other heteropolyacids, specially Preyssler structure has been largely overlooked. We have recently initiated studies into catalytic properties of heteropoly acids [35], specially sodium-30-tungsto pentaphosphate, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$, the so-called Preyssler's anion [36].

*Corresponding author. Fax: +(98) 511 8424020; E-Mail: fbamoharram@mshdiau.ac.ir; abamoharram@yahoo.com

Reasons for selecting this catalyst as a catalyst of choice, are its high hydrolytic stability (pH=0-12), high thermal stability, reusability, safety, quantity of waste, separability, corrosiveness, high oxidation potential and greenness.

In this paper, in continuation of our researchs on acylals preparation [37], we wish to report an efficient method for the preparation of acylals from a series of aldehydes catalyzed by Preyssler's anion, with outstanding properties. Also we compared the catalytic efficiencies

of the Preyssler catalyst with other heteropolyacids.

Results and Discussion

Initially, under a systematic study we examined the catalytic performance of Preyssler in the synthesis of acylals and compared the catalytic activities of a wide variety of heteropolyacids with this anion. The results are shown in Table 1.

Table 1. Comparison of the Preyssler catalyst with other heteropoly anions for acylal synthesis from aromatic aldehydes under solventfree conditions

Entry	Catalyst	% yield with 4-nitro benzaldehyde	% yield with 4-methyl benzaldehyde	% yield with 4-bromo benzaldehyde	% yield with 4-chloro benzaldehyde	% yield with 3-hydroxy benzaldehyde
1	H ₁₄ NaP ₅ W ₃₀ O ₁₁₀	99.6	90.0	88.2	95.4	90.3
2	H ₃ PMo ₁₂ O ₄₀	86.5	89.4	79.3	82.3	74.4
3	K ₁₀ P ₂ W ₁₈ Co ₄ (H ₂ O) ₂ O ₆₈ .20H ₂ O	40.0	40.6	Trace	Trace	Trace
4	H ₄ SiW ₁₂ O ₄₀	85.2	56.9	54.8	81.4	84.1
5	Na ₃ PMo ₁₂ O ₄₀	38.9	85.3	17.2	24.6	64.6
6	K ₇ Na ₃ P ₂ W ₁₈ Cu ₄ (H ₂ O) ₂ O ₆₈ .20H ₂ O	38.9	58.4	Trace	25.9	Trace
7	HN ₂ PW ₁₂ O ₄₀	44.3	72.7	72.7	78.1	66.07
8	H ₁₄ NaP ₅ MoW ₂₉ O ₁₁₀	77.8	8.2	24.1	20.5	Trace
9	H ₅ PMo ₁₀ V ₂ O ₄₀	65.7	Trace	8.0	61.3	36.8
10	K ₁₀ P ₂ W ₁₈ Zn ₄ (H ₂ O) ₂ O ₆₈ .20H ₂ O	38.9	40.6	39.6	43.6	Trace
11	H ₆ PMo ₉ V ₃ O ₄₀	58.3	Trace	72.0	82.3	22.02
12	H ₆ P ₂ W ₁₈ O ₆₂	84.8	81.3	42.4	65.0	88.1
13	H ₄ PMo ₁₁ VO ₄₀	50.9	Trace	82.7	83.5	22.02
14	Na ₃ PW ₁₂ O ₄₀	89.4	75.6	58.6	66.6	71.8
15	H ₄ SiMo ₁₂ O ₄₀	80.1	24.3	46.8	72.0	65.6

The results show that H₁₄[NaP₅W₃₀O₁₁₀] is more effective than the other heteropoly anions and the highest yields are obtained when the reaction is carried out with H₁₄[NaP₅W₃₀O₁₁₀]. A significant interpretation for observed different activities of tested heteropoly anions is very difficult. Their properties can be varied by their constitutive elements as heteroatom, polyatom, and counter-cation. However, because one of the important factors that affect the oxidation capacity and activity of poly anions which is the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO), it is suggested that the energy and composition of the LUMOs have significant effects on the redox properties and activity of the studied poly anions as catalyst. The highest activity for H₁₄[NaP₅W₃₀O₁₁₀] is attributed to the energy and composition of the LUMO, strong acidic properties, and higher acidic protons. The larger number of protons may lower the activation barrier and the large anion can provide many sites on the oval-shaped

molecule that are likely to render the catalyst effective. At the other stage the effects of concentration of catalyst on the yields of acylals were studied.

For all of the aldehydes, the experiments were carried out at room temperature, with 0.01 mol acetic anhydride and varying the given amounts of the Preyssler catalyst. The results are shown in Table 2. The reaction was studied with various moles of Preyssler catalyst from 2.3×10^{-6} mole to 8.04×10^{-6} mole.

In all cases, with 9.4×10^{-6} mole catalyst (Table 1, first row) the higher yield of acylals was obtained at 30 min at room temperature and shorter times gave lower yields. The reaction progress was followed by TLC and GC and the results indicate that the yields were affected by changing the catalyst moles. The yields increases with that of the catalyst moles up to 9.4×10^{-6} mole and any further increasing of the catalyst moles does not have any effect on the yields.

Table 2. Yields of 1,1-diacetates in the presence of different moles of Peryssler catalyst

Entry	Moles of $H_{14}[NaP_5W_{30}O_{110}]$	% yield with 4-boromo benzaldehyde	% yield with 4-methyl benzaldehyde	% yield with 4-chloro benzaldehyde	% yield with 4-nitro benzaldehyde	% yield with 3-hydroxy benzaldehyde
1	$10^{-6} \times 8.04$	78.6	72.3	68.7	73.2	85.4
2	$10^{-6} \times 6.7$	68.9	64.3	86.0	24.0	76.2
3	5.36×10^{-6}	45.6	80.2	45.6	32.0	73.1
4	4.02×10^{-6}	57.5	88.6	54.3	40.0	81.3
5	2.68×10^{-6}	45.2	68.6	49.1	65.2	50.6
6	2.3×10^{-6}	57.9	79.6	47.7	65.0	71.8

Finally, under optimum conditions, the effect of reaction times on the percentage yield of products was studied. The results in Table 3 indicate that at the earlier hours of the reaction times, there is considerable amount of formed product. However, there is an increase in the

yields with increase reaction times and formation of significant 1,1-diacetates observes at 30 min. Any further increasing of the time does not have any effect on the yields.

Table 3. Yields of 1,1-diacetates in different times

Entry	Time (min)	% yield with 4-boromo benzaldehyde	% yield with 4-methyl benzaldehyde	% yield with 4-choloro benzaldehyde	% yield with 4-nitro benzaldehyde	% yield with 3-hydroxy benzaldehyde
1	5	52.4	40.6	56.7	72.8	44.05
2	10	57.5	58.5	58.02	74.0	66.07
3	15	77.5	66.6	72.0	75.6	77.97
4	20	78.6	73.9	86.4	76.0	78.85
5	25	83.1	81.3	88.0	76.8	78.85
6	30	88.2	90.0	95.4	99.6	90.3

To show the high selectivity of the method, we studied competitive reactions for acylation of aldehydes in the presence of ketones. Ketones did not produce any acylal under the same conditions; this suggested that chemoselective protection of aldehydes in the presence of ketones could be achieved with this process. Also we used the Preyssler catalyst in the deprotection of acylals to the corresponding aldehydes by treatment of acylals with a catalytic amount of this catalyst in acetone as solvent. Under this condition, aldehydes were obtained in quantitative yields.

Experimental Section

All of the chemicals were obtained from commercial sources and used as received. Some of the catalysts were obtained from commercial sources and the others were synthesized according to literature[36h,38]. All products were known compounds and identified by comparison of their spectra and physical data on the base of literature description. All the yields were calculated from crystallized products and their purity

was established by GLC, being better than 98%. 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 egilent Mass spectra were obtained with a Massens POEKTRO METER CH-7A VARIN MAT BREMEN spectrometer. H NMR spectra were recorded on a FT NMR Bruker 100 MHZ Aspect 3000 spectrometer.

General procedure

In a typical reaction, a mixture of aldehyde (1 mmole), acetic anhydride (10 mmole) and catalyst (9.4×10^{-6} mole) was stirred at room temperature for 30 min and then ethyl ether (10 mL) was added to the reaction mixture. The resulting solution was successively washed with 1 M NaOH and water, dried over anhydrous Na_2SO_4 , and filtered. The solution was then concentrated, and the solid crude product was recrystallized from petroleum ether yielding each of the pure acylals.

Conclusions

In conclusion, $H_{14}[NaP_5W_{30}O_{110}]$ with high hydrolytic (pH=0-12) and thermal stability compared with the other heteropoly anions has been found to be a highly efficient catalyst for acylals formation. Low cost of the catalyst, simple experimental set-up and procedure, high yields with excellent chemoselectivity, demonstrates the applicability of this catalyst for various reactions that require strong solid acid catalysts with highly thermal and hydrolytic stability. This catalyst is considered to provide a versatile catalytic system for other synthetic methods in organic reactions.

References

- [1] (a) Snider, B. B.; Amin, S. G. *Synthetic Commun.* **1978**, 8, 117. (b) Saucy, G.; Marbet, R.; Lindlar, H.; Isler, O. *Helv. Chim. Acta.* **1959**, 42, 1945.
- [2] Trost, B. M.; Lee, B. C. *J. Am. Chem. Soc.* **2001**, 123, 3687.
- [3] Pinnick, H. W.; Kochhar, K. S.; Bal, B. S.; Deshpande, R. P.; Radhakrishna, S. N. *J. Org. Chem.* **1983**, 48, 1765.
- [4] Greene, T. W.; Wuts, P. G. M. *Protective Groups in organic synthesis*, 3rd ed.; John Wiley and Sons: New York (1999)
- [5] Gregory, M. J. *J. Chem. Soc. B* **1970**, 1201.
- [6] Banks, R. E.; Miller, J. A.; Nunn, M. J.; Stanley, P.; Weakly, T. R.; Ullah, J. *J. Chem. Soc. Perkin Trans.* **1981**, 1, 1096.
- [7] Frick Jr., J. G.; Harper Jr, R. J. *J. Appl. Polym. Sci.* **1984**, 29, 1433.
- [8] Kumar, P.; Hedge, V. R.; Kumar, T. P. *Tetrahedron Lett.* **1995**, 36, 601, and references cited therein.
- [9] Lieberman, S. M.; Connor, R. *Org. Synthetic Coll.* **1951**, 2, 441.
- [10] Michie, J. K.; Miller, J. A. *Synthesis.* **1981**, 824.
- [11] Scriabine, I. *Bull. Soc. Chem. Fr.* **1961**, 1194.
- [12] Deka, N.; Borah, R.; Kalita, D. J.; Sarma, J. C. *J. Chem. Res. S* **1998**, 94.
- [13] Deka, N.; Kalita, D. J.; Borah, R.; Sarma J. C., *J. Org. Chem.* **1997**, 62, 1563.
- [14] Kochhar, K. S.; Bal, B. S.; Deshpande, R. P.; Rajadh Yaksha, S. N.; Pinnick, H. W. *J. Org. Chem.* **1983**, 48, 1765.
- [15] Karimi, B.; Seradj, H.; Ebrahimian, R. G. *Synlett.* **2000**, 623.
- [16] Jin, T. S.; Du, Y.; Li, T. S. *Indian J. Chem. Sect. B* **1998**, 37, 939.
- [17] Kumar, H. M. S.; Reddy, B. V. S.; Reddy, P. T.; Yadav, J. S. *J. Chem. Res. S* **2000**, 86.
- [18] Yadav, J. S.; Reddy, B. V. S.; Srinivas, C. *Synthetic Commun.* **2002**, 32, 1175.
- [19] Karimi, B.; Ebrahiman, G. R.; Seradj, H. *Synthetic Commun.* **2002**, 32, 669.
- [20] Roy, S. C.; Banerjee, B. *Synlett.* **2002**, 1677.
- [21] Yadav, J. S.; Reddy, B. V. S.; Venugopal, C.; Ramalingam, T. *Synlett* **2002**, 604.
- [22] (a) Bandgar, B. P.; Mahajan, N. P.; Mulay, D. P.; Thote, J. L.; Wadagaonkar, P. P. *J. Chem. Res. S* **1995**, 86. (b) Kumar, P.; Hegde, V. R.; Kumar, P. T. *Tetrahedron Lett.* **1995**, 36, 601. (c) Olah G. A.; Mehrotra, A. K. *Synthesis* **1982**, 962. (d) Jin, T. S.; Du, G. Y.; Zhage, G. Y.; Li, T. S. *Synthetic Commun.* **1997**, 27, 2261. (e) Li, Y. Q. *Synthetic Commun.* **2000**, 30, 3913.
- [23] Smitha, G.; Reddy, C. S. *Tetrahedron* **2003**, 59, 9571.
- [24] Ranu, B. C.; Dutta, A. *J. Chem. Lett.* **2003**, 32, 366.
- [25] Zhang, X.; Li, L.; Zhang, G. *Green Chem.* **2003**, 5, 646.
- [26] Aggen, D. H.; Arnold, J. N.; Hayes, P. D.; Smoter, N. J.; Mohan, R. S. *Tetrahedron* **2004**, 60, 3675.
- [27] Firouzabadi, H.; Iranpoor, N.; Nowrouzi, F.; Amani, K. *Tetrahedron Lett.* **2003**, 44, 3951.
- [28] Romanelli, G. P.; Thomas, H. J.; Baronetti, G. T.; Autino, J. C. *Tetrahedron Lett.* **2003**, 44, 1301.
- [29] Aggarwal, V. K.; Fonquerna, S.; Vennall, G. P. *Synlett* **1998**, 849.
- [30] Chandra, K. L.; Saravanan, P.; Singh, V. K. *Synlett* **2000**, 359.
- [31] Carrigan, M. D.; Eash, K. J.; Oswald, M. C.; Mohan, R. S. *Tetrahedron Lett.* **2001**, 42, 8133.
- [32] Karimi, B.; Maleki, J. *J. Org. Chem.* **2003**, 68, 4951.
- [33] Timofeeva, M. N. *Appl. Catal.* **2003**, 256, 19.
- [34] Mizuno, N.; Misono, M. *Chem. Rev.* **1998**, 98, 199.
- [35] (a) Bamoharram, F. F. *Molecules*, **2009**, in press. (b) Bamoharram, F. F.; Heravi, M. M.; Ardalan, T.; Ardalan P. *Chin. Chem. Lett.* **2009**, 20, 1005. (c) Heravi, M. M.; Bakhtiari, Kh.; Bamoharram, F. F. *Catal. Commun.* **2006**, 7, 373. (d) Heravi, M. M.; Derikvand, F.; Bamoharram, F. F. *J. Mol. Catal.* **2005**, 242, 173. (e) Alizadeh, M. H.; Razavi, H.; Bamoharram, F. F.; Daneshvar, K. *J. Mol. Catal.* **2003**, 206, 89. (f) Heravi, M. M.; Rajabzadeh Gh.; Bamoharram, F. F.; Seifi, N. *J. Mol. Catal.* **2006**, 256, 238.
- [36] (a) Bamoharram, F. F.; Heravi, M. M.; Roshani, M.; Ghangir, M.; Gharib, A. *Appl. Catal. A Gen.* **2006**, 302, 42. (b) Bamoharram, F. F.; Heravi, M. M.; Roshani, M.; Tavakoli, N. *J. Mol. Catal. A*

- Chem.* **2006**, 252, 219. (c) Bamoharram, F. F.; Heravi, M. M.; Roshani, M.; Gharib, A.; Gahangir, M. *J. Mol. Catal. A Chem.* **2006**, 252, 90. (d) Bamoharram, F. F.; Heravi, M. M.; Roshani, M.; Akbarpour, M. *J. Mol. Catal. A Chem.* **2006**, 255, 193. (e) Bamoharram, F. F.; Heravi, M. M.; Heravi, M. M.; Meraji, M. *Int. J. Green Nanotech.* **2009**, in press. (f) Bamoharram, F. F.; Heravi, M. M.; Roshani, M.; Toosi, M. *Green Chem. Lett. Rev.* **2009**, 2, 35. (g) Bamoharram, F. F.; Heravi, M. M.; Roshani, M.; Gahangir, M.; Gharib, A. *J. Mol. Catal. A Chem.* **2007**, 271, 126. (h) Bamoharram, F. F.; Roshani, M.; Alizadeh, M. H.; Razavi, H.; Moghayadi, M. *J. Braz. Chem. Soc.* **2006**, 17, 505.
- [37] Heravi, M. M.; Bakhtiari, Kh.; Bamoharram, F. F. *Catal. Commun.* **2006**, 7, 499.
- [38] (a) Tsigdinos, G. A.; Hallada, C. J. *Inorg. Chem.* **1968**, 7, 437. (b) Kozhevnikov, I. V. *Catalysts for fine chemical synthesis, Catalysis by polyoxometalates*. Vol.2. Wiley & Sons: England, 2002.