

Short communication

# Catalytic oxidative cleavage of C=N bond in the presence of mixed-addenda vanadomolybdophosphate, $H_6PMo_9V_3O_{40}$ as a green and reusable catalyst

Majid M. Heravi<sup>a,\*</sup>, Leila Ranjbar<sup>a</sup>, Fatemeh Derikvand<sup>a</sup>,  
Hossine A. Oskooie, Fatemeh F. Bamoharram<sup>b</sup>

<sup>a</sup> Department of Chemistry, School of Science, Azzahra University, Vanak, Tehran, Iran

<sup>b</sup> Department of Chemistry, Islamic Azad University-Mashhad Branch, Mashhad, Iran

Received 13 September 2006; accepted 2 October 2006

Available online 7 October 2006

## Abstract

An efficient and improved procedure for oxidative cleavage of C=N bond is developed in the presence of  $H_6PMo_9V_3O_{40}$  as a green and reusable catalyst in refluxing acetic acid.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Phenylhydrazones; Semicarbazones; Oxime; Deprotection; Heteropolyacids; Oxidative cleavage

## 1. Introduction

Oximes, hydrazones and semicarbazones are useful protecting groups [1] and are widely used for purification and characterization of carbonyl compounds, as they are highly crystalline and stable compounds. Their synthesis from non-carbonyl compounds [2] provides an alternative way to aldehydes and ketones. There has been great interest in the development of mild techniques for the conversion of oximes into their corresponding carbonyl compounds [3–5], but only a little attention has been paid for the regeneration of carbonyl compounds from hydrazones and semicarbazones [6–8]. In addition most of the known methods require drastic conditions, high temperature, long reaction times, expensive, toxic or not readily available reagents, freshly preparation of the reagents and tedious work-up procedure [9–11].

The problems associated with both the handling and disposal of conventional inorganic acids have raised the interest in the development of alternative clean processes and technologies involving the use of solid acid catalysts.

Heteropolyacids (HPAs) are transition metal oxygen anion clusters that exhibit a wide range of molecular sizes, composi-

tions and architectures [12]. Among them, the Keggin-type [13] HPAs have long been known to be good catalysts for oxidation reactions [14,15]. They exhibit great advantages: for example, their catalytic properties can be tuned by changing the identity of charge-compensating countercations, heteroatoms and framework metal atoms [16].

In continuation of our work on catalytic properties of heteropolyacids [17–25], and cleavage of C=N bonds [26] in this paper we wish to report a convenient and efficient method for the regeneration of carbonyl compounds from semicarbazones, hydrazones and oximes using  $H_6PMo_9V_3O_{40}$  as a green, reusable and superior catalyst in refluxing acetic acid.

## 2. Experimental

All compounds were known and their physical and spectroscopic data were compared with those of authentic samples and found to be identical. Yields were obtained using GC analysis. The oximes, hydrazones and semicarbazones were prepared by standard procedures [27].

### 2.1. Oxidative cleavage of C=N: general procedure

Protected carbonyl compound (1 mmol) in acetic acid (3 mL) was treated with a catalytic amount of heteropolyacid (1 mol%)

\* Corresponding author. Fax: +98 2188047861.

E-mail address: [mmh1331@yahoo.com](mailto:mmh1331@yahoo.com) (M.M. Heravi).

at 118 °C. The progress of reaction was monitored by thin layer chromatography (TLC) and gas chromatography (GC) using petroleum ether: ethyl acetate as eluent. After completion of the reaction the catalyst was filtered off and diethylether (5 mL) was added to the mixture. The obtained solution washed with 5% NaHCO<sub>3</sub> (10 mL) and brine (10 mL) successively and dried over MgSO<sub>4</sub>. The solvent was evaporated under reduced pressure to yield the crude products. Further purification was obtained by flash chromatography.

### 3. Results and discussion

To optimize the catalytic system, the cleavage of benzaldehyde phenylhydrazone in the presence of a catalytic amount of H<sub>6</sub>PMo<sub>9</sub>V<sub>3</sub>O<sub>40</sub> was used as a model and efficiency of a variety of solvents and heteropolyacids was studied in this reaction.

The effect of solvent on the model reaction was studied by carrying out the reaction in a solvent-free system and in a variety of solvents including water, chloroform, dichloromethane, ethanol, acetonitrile and acetic acid at different temperatures. As shown in Table 1 the best results in terms of yield and time have been achieved in acetic acid. Thus it was applied as solvent of choice. It is noteworthy to mention that in the absence of the catalyst and just refluxing the substrate in neat acetic acid, no reaction took place. One of the important factors affecting the oxidation capacity of polyanions is the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO). The effect of solvent is attributed to the effect on the LUMO levels.

The heteropoly anions are easily reducible chemical species, thus the energy of the LUMO must be sufficiently low. The solvent molecules can stabilize these anions and place molecular orbitals at the appropriate level. Therefore both yields and reaction times can be affected by solvent.

The efficiency of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>, H<sub>4</sub>PMo<sub>11</sub>VO<sub>40</sub>, H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>, and H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> were also studied in the model reaction (Table 2) in refluxing acetic acid, which were unsatisfactory even after long reaction times. The obtained results by H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> with Dawson structure are similar to Keggin types. Thus the structure of the anion (Keggin or Dawson) cannot affect the yield. Among the Keggin heteropolyacids, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> and Keggin-type vanadium-substituted heteropolymolybdates: H<sub>4</sub>PMo<sub>11</sub>VO<sub>40</sub>, H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> and H<sub>6</sub>PMo<sub>9</sub>V<sub>3</sub>O<sub>40</sub>, the last one gave the best results in the model reaction. Keeping in mind that the model

Table 1  
Oxidative cleavage of benzaldehyde phenylhydrazone, in the presence of catalytic amount of H<sub>6</sub>PMo<sub>9</sub>V<sub>3</sub>O<sub>40</sub> in different solvents

Entry	Solvent	Temperature (°C)	Time (min)	Yield (%)
1	Dichloromethane	40	360	25
2	Chloroform	61	360	30
3	Ethanol	78.3	360	40
4	Acetonitrile	82	360	45
5	Water	100	360	40
6	Acetic acid	118	20	95
7	Solvent free	80	360	33

Table 2  
Oxidative cleavage of benzaldehyde phenylhydrazone, using different heteropolyacids (1 mol%) in refluxing acetic acid

Entry	Heteropolyacid	Time (min)	Yield (%)
1	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	360	5
2	H <sub>6</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub>	360	10
3	H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	360	15
4	H <sub>4</sub> PMo <sub>11</sub> VO <sub>40</sub>	360	30
5	H <sub>5</sub> PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub>	360	39
6	H <sub>6</sub> PMo <sub>9</sub> V <sub>3</sub> O <sub>40</sub>	20	95

reaction has an oxidative nature, this result is expected. The introduction of vanadium (V) into the Keggin framework is beneficial for redox catalysis [28], shifting its reactivity from acid-dominated to redox-dominated. In addition the number of introduced vanadium (V) has a dramatic effect on the yields. One of the difficulties encountered in interpreting data obtained from reactions of vanadomolybdophosphate anions is that in solution, a mixture of heteropoly anions are usually present. In addition positional isomers of the polyvanadium anions are also apparent. Another complication inherent in the study of multi electron oxidations by polyvanadium-containing anions is the capacity of these oxidants to be reduced by one or more electrons (reduction of each V(V) ion to V(IV) [29,30].

However it is difficult to clarify the different activity between these catalysts in this reaction. We believe there is a complex relationship between the activity and structure of polyanion. Transition metal cations have an important effect on the catalytic properties of these compounds when they substitute molybdenum cations in the Keggin units. The case of vanadium, which can occupy both anionic and cationic positions, is more complex.

It is suggested that the interactions of the polarized polyanion with substrate and the number of vanadium atoms are important factors in catalytic activity in our reaction.

To show the generality of this method a variety of protected carbonyl compounds including phenylhydrazones semicarbazones and oximes were subjected to this reaction and all products were obtained in good yields (Table 3). As expected,

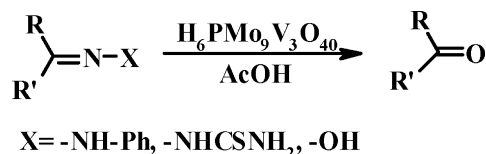
Table 3  
Oxidative cleavage of phenylhydrazone, semicarbazone and oximes in the presence of catalytic amount of H<sub>6</sub>PMo<sub>9</sub>V<sub>3</sub>O<sub>40</sub> in refluxing acetic acid

Entry	Substrate	Time (min)	Yield (%) <sup>a</sup>
1	Benzaldehyde semicarbazone	20	95
2	3-Nitrobenzaldehyde semicarbazone	30	94
3	Cinnamaldehyde semicarbazone	5	93
4	Cyclohexanone semicarbazone	35	97
5	Camphor semicarbazone	18	96
6	Benzaldehyde phenylhydrazone	20	95
7	4-Methylbenzaldehyde phenylhydrazone	35	98
8	2-Methoxybenzaldehyde phenylhydrazone	5	97
9	4-Nitrobenzaldehyde phenylhydrazone	90	94
10	4-Chlorobenzaldehyde phenylhydrazone	5	96
11	4-Methylbenzaldehyde oxime	10	97
12	Cinnamaldehyde oxime	5	95
13	Cyclohexanone oxime	10	94

<sup>a</sup> Yields refer to GC analysis.

the presence of electron-withdrawing groups on the aromatic ring of precursors increases the reaction times.

We also investigate the reusability of the catalyst. For this purpose after completing the model reaction, the catalyst was removed and washed with diethyl ether and subjected to a second run of the reaction process with the same substrate. The results of the first experiment and subsequent experiments were almost consistent in yields after three runs (86%, 84%, 81%).



#### 4. Conclusion

$\text{H}_6[\text{PMo}_9\text{V}_3\text{O}_{40}]$ , a Keggin-type heteropolyacid, is a highly efficient solid acid catalyst for oxidative cleavage of C=N bond. The method has advantages in terms of yield, heterogeneous nature, expenses, availability of reagents and reusability of the green catalyst, short reaction times and easy work-up procedure.

#### References

- [1] T.W. Greene, P.G. Wuts, *Protective Groups in Organic Synthesis*, 3rd ed., Wiley, New York, 1999.
- [2] D.H.R. Barton, J.M. Beaton, *J. Am. Chem. Soc.* 83 (1961) 4083.
- [3] (a) R. Hosseinzadeh, M. Tajbakshsh, M.Y. Niaki, *Tetrahedron Lett.* 43 (2002) 9413;  
(b) M.M. Hashemi, M. Akhbari, Z.K. Jaber, *LOC* 3 (2) (2006) 121.
- [4] P. Salehi, M.M. Khodaei, M. Goodarzi, *Synth. Commun.* 32 (2002) 1259.
- [5] A. Khazaei, R. Ghorbani, Vaghei, *Tetrahedron Lett.* 43 (2002) 3073.
- [6] D.H.R. Barton, D.J. Lester, S.V. Ley, *J. Chem. Soc. Perkin Trans. 1* (1980) 1212.
- [7] S.B. Shim, K. Kim, Y.H. Kim, *Tetrahedron Lett.* 28 (1987) 645.
- [8] D.S. Bose, A.V. Narraiah, *Synth. Commun.* 29 (1999) 937.
- [9] B.A. Nattier, K.J. Eash, R.S. Mohan, *Synthesis* (2001) 1010.
- [10] B.P. Bandgar, S.I. Shaikh, S. Iyer, *Synth. Commun.* 26 (1996) 1163.
- [11] G.A. Olah, M. Aravanaghi, G.K.S. Parakash, *Synthesis* (1980) 220.
- [12] C.L. Hill (Guest Ed.), *Chem. Rev.* 98 (1998) 1.
- [13] J.F. Keggin, *Nature* 131 (1933) 908.
- [14] M. Misono, *Catal. Rev. Sci. Eng.* 29 (1987) 269.
- [15] I.V. Kozhevnikov, *Catal. Rev. Sci. Eng.* 37 (1995) 311.
- [16] T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* 41 (1996) 113.
- [17] M.M. Heravi, F. Derikvand, F.F. Bamoharram, *J. Mol. Catal. A: Chem.* 242 (2005) 173.
- [18] M.M. Heravi, Kh. Bakhtiari, F.F. Bamoharram, *Catal. Commun.* 7 (2006) 499.
- [19] M.M. Heravi, Kh. Bakhtiari, F.F. Bamoharram, *Catal. Commun.* 7 (2006) 373.
- [20] F.F. Bamoharram, M.M. Heravi, M. Roshani, A. Gharib, M. Jahangir, *J. Mol. Catal. A: Chem.* 252 (2006) 90.
- [21] M.M. Heravi, R. Motamedi, N. Seifi, F.F. Bamoharram, *J. Mol. Catal. A: Chem.* 249 (2006) 1.
- [22] F.F. Bamoharram, M.M. Heravi, M. Roshani, M. Jahangir, A. Gharib, *J. Appl. Catal. A: Gen.* 302 (2006) 42.
- [23] F.F. Bamoharram, M.M. Heravi, M. Roshani, M. Akbarpour, *J. Mol. Catal. A: Chem.* 255 (2006) 193.
- [24] M.M. Heravi, G. Rajabzadeh, F.F. Bamoharram, N. Seifi, *J. Mol. Catal. A: Chem.* 256 (2006) 238.
- [25] (a) M.M. Heravi, K. Farahnaz, F.F. Behbahani, Bamoharram, *J. Mol. Catal. A: Chem.* 253 (2006) 16;  
(b) F.F. Bamoharram, M.M. Heravi, M. Roshani, N. Tavakoli, *J. Mol. Catal. A: Chem.* 252 (2006) 219.
- [26] (a) M.M. Heravi, A.J. Sabaghian, K. Bakhtiari, M. Ghassemzadeh, *J. Br. Chem. Soc.* 17 (2006) 614;  
(b) M.M. Heravi, F. Derikvand, M. Ghassemzadeh, *Synth. Commun.* 36 (2006) 581;  
(c) Sh. Khaleghi, M.M. Heravi, F. Drikvand, *Phosphorus Sulfur* 181 (2006) 227;  
(d) M.M. Mojtahedi, M.M. Heravi, *Indian. J. Chem. B* 44 (2005) 831;  
(e) M.M. Heravi, D. Ajami, R. Hekmat Shoar, N. Sarnad, F. Faridbod, *Phosphorus Sulfur* 179 (2004) 2423.
- [27] A.I. Vogel, *A Text Book of Practical Organic Chemistry*, 3rd ed., ELBS Longman, 1975.
- [28] N. Mizuno, M. Misono, *J. Mol. Catal.* 86 (1994) 319.
- [29] I.V. Kazhevnikov, V.E. Tarabanko, K.I. Matveev, *Kinet. Katal.* 22 (1981) 619.
- [30] R. Neumann, M. Lissel, *J. Org. Chem.* 54 (1989) 4607.