

AIPW₁₂O₄₀ and AIPMo₁₂O₄₀ as Highly Effective and Eco-friendly Catalysts for Aldoximation of Aldehydes Under Solvent-Free Conditions

RAZIEH FAZAELI* and HAMID ALIYAN

Department of Chemistry, Islamic Azad University, Shahreza Branch, Shahreza, Isfahan-86145-311, Iran; E-mail: aliyana@iaush.ac.ir; fazaeli@iaush.ac.ir

The oxime formation of aromatic aldehydes has directly been carried out with hydroxylamine hydrochloride using heteropoly acids (AIPW₁₂O₄₀, AIPMo₁₂O₄₀) as catalysts in the absence of solvent. It is found that these heteropoly acids were effective catalysts for the formation of oxime of aldehydes. This method consistently has the advantage of high yields of the products, short reaction time, mild and solvent-free conditions, cleaner reactions and isolation procedures.

Key Words: E- and Z-Isomer of oximes, Aldoxime, Hydroxylamine hydrochloride, Heteropoly acids.

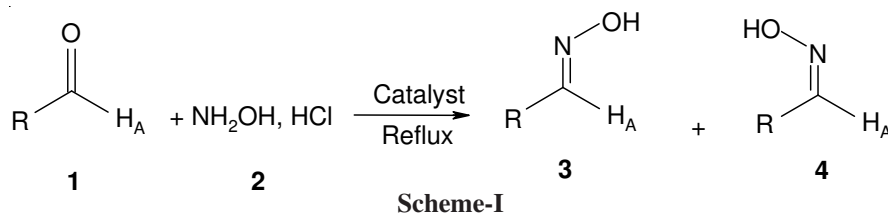
INTRODUCTION

Oximes are extensively used as preferred derivatives for purification and characterization of carbonyl compounds¹. Their synthesis from non-carbonyl compounds, such as nitrosation of an active methylene group², nitrosation of an α -halocarbonyl compound³, condensation of a nitroalkene with an aldehyde⁴, provides a valid alternative pathway to carbonyl compounds. Furthermore oximes play an important role as protecting⁵ and selectively α -activating groups⁶ in synthetic organic chemistry.

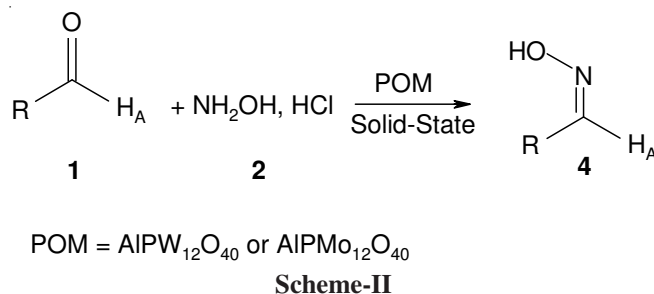
Addition of hydroxylamine hydrochloride to carbonyls to yield oximes is one of the best known examples of nonenzymatic addition-elimination reaction in organic synthesis⁷. These reactions usually produce both isomeric aldoximes (Z and E) (**Scheme-I**), which have biological activities. Until now, very few improved procedures have been reported for the synthesis of Z-isomers of oximes using catalyst such as K₂CO₃⁸. The development of efficient and versatile catalytic systems for selective conversion of aldehydes to oximes is an active ongoing research area and thus, further improvement for better yields and milder reaction conditions is needed.

In recent decades, uses of heteropoly acids (HPAs) as catalysts for fine organic synthetic processes have been developed and are important for industries related with fine chemicals⁹, including flavors, pharmaceuticals and food industries¹⁰. Among heteropoly acids, polytungstic acids are the most widely used owing to their high acid strengths, thermal stabilities and low reducibilities. Catalysts based on heteropoly acids as Bronsted acids have many advantages over liquid catalysts. They are non-corrosive and environmentally benign, presenting fewer disposal problems¹¹. Solid heteropoly acids have attracted much attention in organic owing

to easy work-up procedures, easy filtration and minimization of cost and waste generation due to reuse and recycling of the catalysts¹¹.



In continuation of our work on the catalytic properties of heteropoly acids¹²⁻¹⁶, herein, we wish to report a suitable method for controlling the stereochemistry of the reaction of hydroxylamine hydrochloride with aldehydes in the presence of $\text{AIPW}_{12}\text{O}_{40}$,¹⁷⁻²³ (AITP) and $\text{AIPMo}_{12}\text{O}_{40}$ (AIMP) in solid state (**Scheme-II**).



EXPERIMENTAL

General procedure for preparation of Z-isomer of oximes in the presence of heteropoly acid: Hydroxylamine hydrochloride (1.5 mmol) and heteropoly acid, ($\text{AIPW}_{12}\text{O}_{40}$ or $\text{AIPMo}_{12}\text{O}_{40}$, 0.02 mmol) and aldehyde (1 mmol) were ground together in mortar with a pestle at room temperature for several minutes. Progress of the reaction was monitored by GC and TLC. After complete disappearing of the starting material, the reaction mixture was cooled, washed with cold diethyl ether and filtered to remove heteropoly acid. Then the mixture was poured into ice-water and extracted with cold diethyl ether (25 mL). The organic solution was dried over Na_2SO_4 to give the crude Z-aldoximes. The products were identified by comparison of their physical data with those prepared in accordance with the literature procedures.

RESULTS AND DISCUSSION

At first, for optimization of the reaction conditions, the formation of oxime of some aldehydes, (4-nitrobenzaldehyde, with withdrawing groups and 4-methoxybenzaldehyde with electron donating groups), as model substrates and $\text{AIPW}_{12}\text{O}_{40}$ as a catalyst, were conducted in different solvents. The results show that the efficiency and the yield of the reaction in solutions were much less than these observed under solvent-free conditions (Table-1). According to the results, our method (solvent-free conditions) is suitable for the formation of oxime of aromatic aldehydes.

TABLE-1
ALDOXIMATION OF 4-NITROBENZALDEHYDE AND 4-METHOXYBENZALDEHYDE WITH HYDROXYLAMINE HYDROCHLORIDE IN THE PRESENCE OF ALPW₁₂O₄₀ IN VARIOUS SOLVENTS AFTER 1 h^a

Temp. (°C)	GC Yield (%) ^b					
	CH ₃ CN	CHCl ₃	EtOH	MeOH	CH ₃ COCH ₃	EtOAc
Room temp.	65 ^c (54) ^d	40 (54)	58 (53)	59 (34)	56 (35)	41 (27)
40	72 (58)	55 (58)	64 (68)	71 (68)	65 (56)	49 (38)

^aReaction conditions: aldehyde (1 mmol), hydroxylamine hydrochloride (1.5 mmol) AIPW₁₂O₄₀ (0.02 mmol), solvent (5 mL); ^b4-nitrobenzaldehyde; ^c4-methoxybenzaldehyde.

TABLE-2
CONVERSION OF ALDEHYDES TO Z-ISOMER OF ALDOXIMES BY HPAS (ALTP OR ALMP) AS CATALYSTS, UNDER SOLIDE-STATE CONDITIONS^a

Oximes	Substrate (R)	Type of HPA	Time (min): yield (%) ^b	m.p. (L)	¹ H chemical shifts of H _A
4a	4-(Me)-C ₆ H ₄	AITP	2:98	79 (80 ²⁴)	8.49
		ALMP	5:95		
4b	3-(Me)-C ₆ H ₄	AITP	3:100	61(60 ²⁴)	8.13
		ALMP	4:100		
4c	4-(NO ₂)-C ₆ H ₄	AITP	4:98	(129 ²⁴)	8.20
		ALMP	4:95		
4d	4-(Cl)-C ₆ H ₄	AITP	5:100	(145 ²⁵)	8.12
		ALMP	8:100		
4e	2-(Cl)-C ₆ H ₄	AITP	5:92	(100 ²⁶)	8.38
		ALMP	7:95		
4f	4-(OMe)-C ₆ H ₄	AITP	4:100	(133 ^{25,27})	8.00
		ALMP	7:100		
4g	3-(OMe)-C ₆ H ₄	AITP	5:100	(112 ²⁷)	8.10
		ALMP	5:100		
4h	4-(OH)-C ₆ H ₄	AITP	7:92	75 (72 ²⁸)	8.07
		ALMP	10: 95		
4i	2-(OH)-C ₆ H ₄	AITP	3:100	(63 ²⁸)	8.22
		ALMP	5:92		
4j	3-(OH)-C ₆ H ₄	AITP	6:100	90(90 ²⁸)	8.09
		ALMP	9:89		

^aReaction conditions: Aldehyde (1 mmol), catalyst (0.02 mmol), NH₂OH.HCl (1.5 mmol), room temperature; ^bData based on GC.

Various types of aromatic aldehydes with electron donating and withdrawing groups were rapidly condensed with hydroxylamine hydrochloride, afforded the corresponding Z-isomer of oximes (OH *cis* to aryl) in excellent yields in the presence of AITP or ALMP which are cheap, reusable and available catalysts. The generality and scope of the reaction is summarized in **Scheme-II** and Table-2.

Furthermore, the use of just 2 mol % of heteropoly acid is sufficient to promote the reaction and no additives are required for this conversion. There are no improvements in the reaction rates and yields by increasing the amount of the heteropoly acid from 2 mol % to 5 mol %.

In this study, we have introduced aluminium dodecatungstophosphate (AITP) and aluminum dodecamolybdophosphate (AIMP) as new highly effective non-hygroscopic, non-corrosive, heterogeneous and environmentally benign catalysts for the preparation of aldoxime from aldehyde under solvent free condition. The procedure offers several advantages including short reaction times, mild and solvent-free conditions, cleaner reactions and high yields of the products as well as simple experimental and isolation procedures.

ACKNOWLEDGEMENTS

The authors are grateful to the Center of Excellence of Chemistry of the University of Isfahan and Islamic Azad University, Shahreza branch, for financial support of this work.

REFERENCES

1. N.D. Cheronis and J.B. Entrikin, Identification of Organic Compounds Interscience, New York (1963).
2. R.H. Barry and W.M. Hartune, *J. Org. Chem.*, **12**, 460 (1947).
3. W.M. Hartung and F. Crossley, *Org. Synth. Coll.*, **2**, 263 (1943).
4. H.B. Hasi, A.G. Susie and R.L. Heider, *J. Org. Chem.*, **15**, 8 (1950).
5. J.G. Greene and P.G.M. Wuts, Protective Groups in Organic Synthesis, John Wiley and Sons New York, edn. 2, 175 (1991).
6. J.K. Whitesell and M.A. Whitesell, *Synthesis*, 54 (1983).
7. W.P. Jencks, *J. Am. Chem. Soc.*, **81**, 475 (1959).
8. H. Sharghi and M. Hosseini Sarvari, *Synlett.*, **1**, 99 (2001).
9. I.V. Kozhevnikov, in ed.: E. Derouane, Catalysts for Fine Chemical Synthesis, Catalysis by Polyoxometalates 2, Wiley, New York (2002).
10. T. Okuhara, N. Mizuno and M. Misono, *Adv. Catal.*, **41**, 221 (1996).
11. M. A. Schwegler, H. van Bekkum and N. Munck, *Appl. Catal. A.*, **74**, 191 (1991).
12. R. Fazaeli, S. Tangestaninejad, H. Aliyan and M. Moghadam, *Appl. Catal. A*, **309**, 44 (2006).
13. R. Fazaeli, S. Tangestaninejad and H. Aliyan, *Can. J. Chem.*, **84**, 812 (2006).
14. R. Fazaeli, S. Tangestaninejad and H. Aliyan, *Cat. Commun.*, **8**, 205 (2007).
15. R. Fazaeli, S. Tangestaninejad and H. Aliyan, *Appl. Catal. A.*, **318**, 218 (2007).
16. R. Fazaeli, H. Aliyan and S. Tangestaninejad, *Heterocycles*, **71**, 805 (2007).
17. H. Firouzabadi, N. Iranpoor and A.A. Jafari, *J. Mol. Catal.*, **244**, 168 (2006).
18. H. Firouzabadi, N. Iranpoor and A.A. Jafari, *J. Mol. Catal.*, **227**, 97 (2005).
19. H. Firouzabadi, N. Iranpoor and A.A. Jafari, *Tetrahedron Lett.* **46**, 2683 (2005).
20. H. Firouzabadi, N. Iranpoor, F. Nowrouzi and K. Amani, *Tetrahedron Lett.* **44**, 5343 (2003).
21. H. Firouzabadi, N. Iranpoor and A.A. Jafari, *Lett. Org. Chem.*, **3**, 25 (2006).
22. H. Firouzabadi, N. Iranpoor and F. Nowrouzi, *Tetrahedron*, **60**, 10843 (2004).
23. H. Firouzabadi and A. A. Jafari, *J. Iran. Chem. Soc.*, **2**, 85 (2005).
24. L. Brehm, *Acta Cryst.*, **28B**, 3646 (1972).
25. J. Smolkova, O. Exner, G. Barbaro, D. Macciantelli and A. Dondoni *J. Chem. Soc. Perkin II*, 1051 (1980).
26. O.L. Brady and S.G. Jarrett, *J. Chem. Soc.*, 1227 (1950).
27. R.J. Crawford and C. Woo, *Can. J. Chem.*, **43**, 1534 (1965).
28. CRC Handbook of Tables for Organic Compound Identification, edn. 3 and 54 (1981).