This article was downloaded by: [University of Illinois at Urbana-Champaign] On: 19 September 2013, At: 04:10 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

Deprotection Chemistry Mediated by $ZrOCI_2 \cdot 8H_2O$: An Efficient, Mild, and Green Method for the Conversion of Oximes to Carbonyl Compounds in Aqueous Acetone

Lakhinath Saikia^a, Subrata Das^a & Ashim Jyoti Thakur^a ^a Department of Chemical Sciences, Central University, Napaam, Tezpur, Assam, India Published online: 03 Mar 2011.

To cite this article: Lakhinath Saikia , Subrata Das & Ashim Jyoti Thakur (2011) Deprotection Chemistry Mediated by $ZrOCI_2 \cdot 8H_2O$: An Efficient, Mild, and Green Method for the Conversion of Oximes to Carbonyl Compounds in Aqueous Acetone, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 41:7, 1071-1076, DOI: 10.1080/00397911003797783

To link to this article: http://dx.doi.org/10.1080/00397911003797783

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions



Synthetic Communications[®], 41: 1071–1076, 2011 Copyright © Taylor & Francis Group, LLC ISSN: 0039-7911 print/1532-2432 online DOI: 10.1080/00397911003797783

DEPROTECTION CHEMISTRY MEDIATED BY ZrOCI₂ · 8H₂O: AN EFFICIENT, MILD, AND GREEN METHOD FOR THE CONVERSION OF OXIMES TO CARBONYL COMPOUNDS IN AQUEOUS ACETONE

Lakhinath Saikia, Subrata Das, and Ashim Jyoti Thakur

Department of Chemical Sciences, Central University, Napaam, Tezpur, Assam, India

GRAPHICAL ABSTRACT



Abstract Less-toxic, moisture-stable, inexpensive, and ecofriendly zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) in aqueous acetone (1:1) mediates the conversion of oximes to carbonyl compounds in moderate to good yields. This green methodology is applicable to both aldoximes and ketoximes with tolerance to >C=C<, $-NO_2$, -OH, and -Cl groups. The reaction and workup are simple.

Keywords Carbonyl compounds; deprotection; green; protection; zirconium oxychloride octahydrate

INTRODUCTION

Continuing our interest in protection and deprotection chemistry,^[1] we were curious about oximes, which constitute one of the most useful protecting groups,^[2,3] especially in multistep organic synthesis, and are extensively used for purification and characterization of carbonyl compounds.^[4] The oxime family not only represents a convenient series of derivatives of carbonyl compounds, but also,

Received December 7, 2009.

Address correspondence to Ashim Jyoti Thakur, Department of Chemical Sciences, Central University, Napaam, Tezpur 784028, Assam, India. E-mail: ashim@tezu.ernet.in

importantly, noncarbonyl compounds can be converted to the carbonyl derivatives via oxime formation.^[5] In addition, oximes may be used as intermediates for the preparation of amides by Beckmann rearrangement.^[6] These requirements and demands for oximes has inspired the development of several deoximation reagents such as trimethylammonium chlorochromate,^[7] dinitrogen tetroxide,^[8] pyridinium chloroformate,^[9] trimethylsilyl chloroformate,^[10] titanium silicate-1,^[11] zirconium sulfophenyl phosphonate,^[12] and N-haloamides.^[13] Photosensitized reaction also finds application in the regeneration of carbonyl compounds from oximes.^[14,15]

As far as the application of zirconium oxychloride octahydrate $(ZrOCl_2 \cdot 8H_2O)$ in organic synthesis is concerned, it has recently attracted attention because of its high water tolerance, ready commercial availability, low cost, and low toxicity $(LD_{50} = 2950 \text{ mg/Kg}, \text{ oral rat}).^{[16]}$ To the best of our knowledge, oxidative cleavage of oximes to parent carbonyl compounds using $ZrOCl_2 \cdot 8H_2O$ has not been reported so far.

RESULTS AND DISCUSSION

Herein, we divulge an experimentally simple, facile deoximation method of oximes 1 using $ZrOCl_2 \cdot 8H_2O$ in aqueous acetone (1:1) under refluxing conditions as depicted in Scheme 1. In fact, this is the first example of deprotection chemistry mediated by $ZrOCl_2 \cdot 8H_2O$. Choice of acetone as one reaction medium was crucial. Other common solvents (CHCl₃, CH₂Cl₂, tetrahydrofuran, etc.) failed to carry out the conversion. Moreover, the presence of acetone is essential, established by the fact that water alone could not bring about the conversion. Acetone probably serves a dual role. First, it dissolves the organic reactants, providing a homogeneous aqueous system, and second, it drives the reaction toward the right-hand side, acting as an exchange reagent.

To start with a simple model reaction, we preferred to select benzaldoxime (Table 1, entry **1a**) as the substrate. The reaction was complete within 2 h with 80% yield. This preliminary observation encouraged us to extend the procedure to other oximes as well. Several optimized examples illustrating the scope and limitations of this new procedure for the conversion of a variety of other oximes **1** (entries **1b–o**) to their parent carbonyl compounds **2** in moderate to good yields (60–87%) are summarized in Table 1. This methodology is equally applicable to ketoximes (entries **1g, h**, and **i**, Table 1) and aldoximes (entries **1a–f** and **j**, Table 1). It was pleasing to



Scheme 1. Deoximation of acyalic oximes 1 using zirconium oxychloride octahydrate.

Entry	R ₁	R ₂	Reaction time (h)	Yield (%) ^{<i>b,c</i>}
a	$-C_6H_5$	-H	2	80
b	$p-ClC_6H_4$	-H	4	76
с	p-BrC ₆ H ₄	-H	4	78
d	p-OHC ₆ H ₄	-H	2.5	85
e	$p-MeC_6H_4$	-H	1	84
f	$p-NO_2C_6H_4$	-H	5	82
g	$m-NO_2C_6H_4$	-H	5	78
h	p-OMeC ₆ H ₄	-H	4	73
i	-CH ₂ =CH-C ₆ H ₅	-H	4	74
j	-Thiophenyl	-H	4.1	70
k	-Furfuryl	-H	4.2	71
1	-3-Formylchromone	-H	3	80
m	$p-MeC_6H_4$	-Me	4.5	87
n	-C ₆ H ₅	$-C_6H_5$	4	71
0	$-C_6H_5$	-Me	2	77

Table 1. Deprotection of acyclic oximes $1a-o^a$ via Scheme 1

^aOximes 1 were synthesized according to the standard procedure and characterized by comparison of their reported spectroscopic and physical data.

^bIsolated yield.

^cAll compounds gave satisfactory IR, ¹H NMR, and ¹³C NMR spectroscopic data, and finally their meeting and boiling points were compared with those of authentic samples.

observe that no Beckmann rearrangement products were found. The -NO₂, -OH, -Cl groups were found to be tolerated under the reaction conditions. Interestingly, the presence of electron-withdrawing groups in the oxime tends to increase the reaction time. The α , β -unsaturated aldoxime, cinnamaldehyde oxime (entry **1k**, Table 1), also afforded the aldehyde smoothly without affecting the carbon–carbon double bond. Notably, aldehydes regenerated from aldoxime did not undergo further oxidation under the reaction conditions. At room temperature, conversion was very poor and required a longer time. The best results were obtained when the amount of ZrOCl₂ · 8H₂O used was twofold with respect to the oximes. In the case of cyclic oximes (entries **3a–e**, Table 2), such as cyclopentanone (entry **3a**, Table 2) and cyclohexanone (entry **3b**, Table 2) conversions and yields were very poor (40–45%) (Scheme 2). We did not notice any polymerization product(s), which was observed in the case of photolysis of oximes^[14] in acetonitrile. Further increasing the reaction time gave no significant improvement in yields.

CONCLUSION

In conclusion, we have developed a mild and efficient new procedure for cleavage of oximes using $ZrOCl_2 \cdot 8H_2O$ in nontoxic aqueous solvent system of acetone-water (1:1) under refluxing conditions.

EXPERIMENTAL

Melting points and boiling points were determined on a Büchi 504 apparatus and are uncorrected. Infrared (IR) spectra were recorded in KBr pallets on a Nicolet

L. SAIKIA, S. DAS, AND A. J. THAKUR

Entry	Oxime 3	Carbonyl compound 4	Reaction time (h)	Yield (%) ^{b,c}
a	он		7	42
Ь	N OH		8	45
С	ОН		8	47
d	OH OH	°	7.5	48
e	OH NOH		8	43

Table 2. Deprotection of cyclic oximes $3\mathbf{a}-\mathbf{e}^a$ via Scheme 2

^aOximes 3 were synthesized according to the standard procedure and characterized by comparison of their reported spectroscopic and physical data.

^bIsolated yield.

^cAll compounds gave satisfactory IR, ¹H NMR, and ¹³C NMR spectroscopic data, and finally their melting and boiling points were compared with those of authentic samples.

(Impact 410) Fourier transform (FT)–IR spectrophotometer. ¹H NMR spectra were recorded on a Varian Mercury Plus 400-MHz NMR spectrophotometer. All the chemicals were used as received. Acetone and water were distilled before use.

Typical Procedure for the Deoximation

The benzaldoxime **1a** (200 mg, 1.65 mmol) along with $ZrOCl_2 \cdot 8H_2O$ (1.06 g, 3.3 mmol) were taken in 40 ml of acetone and water (1:1) in a round-bottomed flask and allowed to reflux for 2 h. Progress of the reaction was monitored by thin-layer chromatography (TLC), and iodine was used as a visualizing agent. After completion of the reaction as indicated by TLC, acetone was evaporated in



Scheme 2. Deoximation of cyclic oximes 3 using zirconium oxychloride octahydrate.

vacuum; the organic content was extracted with ethyl acetate $(3 \times 20 \text{ ml})$, washed with brine, dried over Na₂SO₄, and concentrated down in a rotary evaporator; and finally column chromatography was performed to afford the pure product, benzaldehyde **2a** (140 mg, 80% yield). Similarly, other oximes (**1b–o** and **3a–e**) were subjected to the same reaction conditions to get the deoximation products.

ACKNOWLEDGMENTS

LNS and AJT are grateful to the Council of Scientific and Industrial Research (CSIR), New Delhi, India, for financial support. SD thanks Tezpur University for the institutional fellowship. The support to record NMR spectra at the Indian Institute of Technology (IIT), Guwahati, is gratefully acknowledged.

REFERENCES

- 1. Das, S.; Bora, R.; Devi, R. R.; Thakur, A. J. Molecular iodine in protection and deprotection chemistry. *Synlett.* **2008**, *18*, 2744.
- Sandler, S. R.; Karo, W. In Organic Functional Group Preparations, Academic Press: London, 1989; p. 430.
- Greene, T. W.; Wuts, P. G. M. Protective Groups in Organic Synthesis; Wiley: New York, 1991; p. 214.
- Shriner, R. L.; Fusion, R. C.; Curtin, D. Y.; Morril, T. C. The Systematic Identification of Organic compounds, 6th ed.; Wiley: New York, 1980.
- Barton, D. H. R.; Beaton, J. M.; Geller, L. E.; Pechet, M. A new photochemical reaction. J. Am. Chem. Soc. 1961, 83, 4076.
- Donaruma, L. G.; Heltd, W. Z. The Beckmann rearrangement. In *Organic Reactions*; A. C. Cope (Ed.); John Wiley and Sons: New York, 1960; vol. 11, p. 1.
- Rao, C. G.; Radhakrishna, A. S.; Singh, B. B.; Bhatnagar, S. P. Oxidative cleavage of oximes with triethylammonium chlorochromate. *Synthesis* 1983, 10, 808.
- Shim, S. B.; Kim, K.; Kim, Y. Direct conversion of oximes and hydrazones into their ketones with dinitrogen tetroxide. *Tetrahedron Lett.* 1987, 28, 645.
- Meloney, J. R.; Liyle, R. E.; Saavedra, J. E.; Lyle, G. G. Oxidative deoximation with pyridinium chlorochromate. *Synthesis* 1978, 212.

- Aizpurua, J. M.; Juaristi, M.; Lecea, B.; Palomo, C. Reagents and synthetic methods, 40: Halosilanes/chromium trioxide as efficient oxidising agents. *Tetrahedron* 1985, 41, 2903.
- Joseph, R.; Sudalai, A.; Ravindranathan, T. Selective catalytic oxidative cleavage of oximes to carbonyl compounds with H₂O₂ over TS-1. *Tetrahedron* 1994, 35, 5493.
- Curini, M.; Roasti, O.; Pisani, E. Heterogeneous catalysis in carbonyl regeneration from oximes, semicarbazones, and tosylhydrazones by zirconium sulphenyl phosphonate. *Synlett.* 1996, 333.
- Bandgar, B. P.; Kunde, L. B.; Thote, J. L. Synthetic methods, 6: Deoximation with N-haloamides. Synth. Commun. 1997, 27, 1149.
- de Lijser, H. J. P.; Fardoun, F. H.; Sawyer, J. R.; Quant, M. Photosensitised regeneration of carbonyl compounds from oximes. *Org. Lett.* 2002, 4(14), 2325.
- Tang, Y.; Zhang, D.; Wu, L.-Z.; Chen, B.; Zhang, L.-P.; Tung, C.-H. Photosensitised oxidative protection of oximes to their corresponding carbonyl compounds by platinum(II) terpyridyl acetylide complex. J. Org. Chem. 2004, 69, 4788.
- Reddy, C. S.; Nagaraj, A. Zirconium oxychloride as a new and efficient catalyst for the synthesis of 3,4-dihydropyrimidine-2(1H)-thione/one under solvent-free microwave irradiation conditions. *Heterocycl. Commun.* 2007, 13, 67.