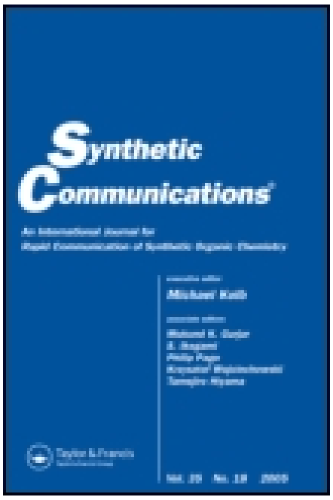
This article was downloaded by: [University of Oklahoma Libraries]
On: 28 October 2014, At: 00:38
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Mercuric Nitrate-Mediated Deprotection of Oximes, Hydrazones, and Semicarbazones

Surya Kanta De [a]
[a] Department of Chemistry , University of Washington , Box 351700, Seattle, Washington, 98195, USA

Published online: 17 Aug 2006.

To cite this article: Surya Kanta De (2004) Mercuric Nitrate-Mediated Deprotection of Oximes, Hydrazones, and Semicarbazones, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 34:12, 2289-2294, DOI: 10.1081/SCC-120038512

To link to this article: http://dx.doi.org/10.1081/SCC-120038512

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®
Vol. 34, No. 12, pp. 2289–2294, 2004

Mercuric Nitrate-Mediated Deprotection of Oximes, Hydrazones, and Semicarbazones

Surya Kanta De*

Department of Chemistry, University of Washington,
Seattle, Washington, USA

ABSTRACT

Mercuric nitrate in wet silica gel is found to be an excellent reagent for the regeneration of carbonyl compounds from oximes, hydrazones, and semicarbazones.

Key Words: Mercuric nitrate; Oximes; Hydrazones; Semicarbazones.

INTRODUCTION

Oximes, hydrazones, and semicarbazones are useful as preferred derivatives for the identification and characterization of carbonyl compounds.[1] Since oximes can be prepared from non-carbonyl compounds,

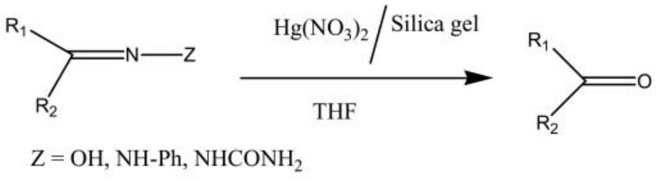
---

*Correspondence: Surya Kanta De, Department of Chemistry, University of Washington, Box 351700, Seattle, WA 98195, USA; E-mail: suryakd@hotmail.com or skd125@yahoo.com.

DOI: 10.1081/SCC-120038512 0039-7911 (Print); 1532-2432 (Online)

www.dekker.com

the regeneration of carbonyl compounds from oximes provides an alternative method for the preparation of aldehydes and ketones.[2] Furthermore, they play an important role by protecting[3] and selectively α-activating groups[4] in organic chemistry. Therefore, there has been a continued interest in the development of procedures for the effective regeneration of carbonyl compounds from the corresponding stable and readily prepared oximes, hydrazones, and semicarbazones. As a result, several methods have been reported for the regeneration of carbonyl compounds from their oximes such as pyridinium chlorochromate,[5] pyridinium chlorochromate-hydrogen peroxide,[6] triethyl ammonium-chlorochromate,[7] chromic-anhydride-chlorotrimethylsilane,[8] dinitrogen tetraoxide,[9] titanium silicate,[10] *N*-haloamide,[11] manganese triacetate,[12] Dess-Martin periodane,[13] tetrabutylammonium peroxydisulfate,[14] clay supported ammonium chlorochromate,[15] and clayfen.[16] Although some of these methods are carried out under mild reaction conditions, most of them require strong acidic media, a strong oxidizing agent (which causes over oxidation), and expensive, and not readily available reagents. Additionally, they can require long reaction times for the regeneration of carbonyl compounds from oximes. Recently, some microwave techniques have been reported,[17] which are valuable methods from the synthetic standpoint, but extreme precautions have to be taken as these reactions were performed under microwave irradiation or ultrasonic irradiation with an oxidant. Little attention has been paid to the regeneration of carbonyl compounds from hydrazones and semicarbazones.[9,13,18,19] Thus, there is still a need to develop a new and facile procedure for the regeneration of carbonyl compounds from oximes, hydrazones, and semicarbazones.



1 (see Table 1) **2**

2a. $R_1 = R_2 = C_6H_5$; **2b.** $R_1 = C_6H_5$, $R_2 = Me$; **2c.** $R_1 = p\text{-}MeOC_6H_4$, $R_2 = H$; **2d.** $R_1 = p\text{-}BrC_6H_4$, $R_2 = H$; **2e.** $R_1 = R_2 = -(CH_2)_5-$; **2f.** $R_1 = R_2 = -(CH_2)_4-$; **2g.** $R_1 = C_6H_5$, $R_2 = H$; **2h.** $R_1 = p\text{-}ClC_6H_4$, $R_2 = Me$; **2i.** $R_1 = p\text{-}MeOC_6H_4$, $R_2 = Me$.

Mercuric nitrate is an inexpensive reagent, which has been used extensively as an oxidizing agent.[20] I believe this is the first report using mercuric nitrate as the reagent for the deprotection of oximes, hydrazones, and semicarbazones. Several oximes were deoximated using mercuric nitrate in silica gel in the presence of a small amount of water under reflux condition in tetrahydrofuran. Semicarbazones and hydrazones were deprotected the same way (Table 1). The conversions were clean and no undesirable side products

Table 1. Deprotection of oximes, hydrazones, and semicarbazones with mercuric nitrate in wet silica gel.

Entry	Substrate (**1**)	Product (**2**)	Time (hr)	Yield (%)	M.p./b.p. (°C) Lit[a]/obs
1	Benzophenone oxime	**2a**	6	94	48–49/46–47
2	Acetophenone oxime	**2b**	8	91	202/200–202
3	4-Methoxybenzaldehyde oxime	**2c**	5	86	248/245–247
4	4-Bromobenzaldehyde oxime	**2d**	5	89	55–58/55–57
5	Cyclohexanone oxime	**2e**	4	93	155/150–152
6	Cyclopentanone oxime	**2f**	5	88	130–131/128–129
7	Benzaldehyde oxime	**2g**	5	83	178–179/179–180
8	4-Chloroacetophenone oxime	**2h**	6	92	232/229–231
9	Benzophenone semicarbazone	**2a**	8	91	
10	4-Bromobenzaldehyde semicarbazone	**2d**	7	82	
11	4-Chloroacetophenone semicarbazone	**2h**	8	90	
12	Cyclohexanone semicarbazone	**2e**	5	88	
13	Acetophenone semicarbazone	**2b**	7	86	
14	Benzophenone phenylhydrazone	**2a**	8	83	
15	4-Chloroacetophenone phenylhydrazone	**2h**	4	89	
16	4-Bromobenzaldehyde phenylhydrazone	**2d**	7	91	
17	4-Methoxyacetophenone phenylhydrazone	**2i**	5	88	36–38/34–35

[a] Available from Aldrich Chemical Company.

were observed. A few drops of water and silica gel were found to be essential for the success of the reaction. Without silica gel support, the reaction is sluggish with mercuric nitrate even after prolonged reaction periods.

In conclusion, a facile method has been developed for the regeneration of carbonyl compounds from their respective oximes, hydrazones, and semicarbazones using mercuric nitrate in wet silica gel.

EXPERIMENTAL

All the products are known compounds and were checked by comparison of their spectral data (IR, ^{1}H NMR) and physical properties with an authentic sample. The reaction was monitored by thin layer chromatography on silica gel because overoxidation may occur in some cases after cleavage of protecting groups. All yields refer to isolated products.

General Procedure for the Regeneration of Carbonyl Compounds from Oximes, Hydrazones, and Semicarbazones with Mercuric Nitrate

A mixture of substrate (oxime or hydrazone or semicarbazone, 1 mmol), mercuric nitrate monohydrate (1 mmol), silica gel (1 g), and water (1 mL) in THF (10 mL) was refluxed for the specified time (Table 1). After completion of the reaction, the reaction mixture was filtered. Then the filtrate was extracted with ethyl acetate and washed with sodium bicarbonate and water. The organic layer was dried over magnesium sulfate then concentrated and filtered through short silica gel column to afford a pure product in good to excellent yield.

REFERENCES

1. Cheronis, N.D.; Entrikin, J.B. *Identification of Organic Compounds*; Interscience: New York, 1963; 318–320.
2. Barton, D.H.R.; Beaton, J.M.; Gelker, L.E.; Pechet, M.M. A new photochemical reaction. J. Am. Chem. Soc. **1961**, *83*, 4076–4083.
3. Greene, T.W.; Wuts, P.G. *Protective Groups in Organic Synthesis*, 3rd Ed.; Wiley: New York, 1999; 352–358.
4. Whitesell, J.K.; Whitesell, M.K. Alkylation of ketones and aldehydes via their nitrogen derivatives. Synthesis **1983**, 517–536.

5. Maloney, J.R.; Lyle, R.E.; Saavedra, J.E.; Lyle, G.G. Oxidative deoximation with pyridinium chlorochromate. Synthesis **1978**, 212–213.
6. Drabowicz, J. Rapid deoximation with pyridinium chlorochromate/hydrogen peroxide system. Synthesis **1980**, 125–126.
7. Rao, C.G.; Radhakrishna, A.S.; Singh, B.B.; Bhatnagar, S.P. Oxidative cleavage of oximes with triethylammonium chlorochromate. Synthesis **1983**, 808.
8. Azipura, J.M.; Juaristi, M.; Lecea, B.; Palomo, C. Reagents and synthetic methods-40: halosilanes/chromium trioxide as efficient oxidizing reagents. Tetrahedron **1985**, *41*, 2903–2911.
9. Shim, S.B.; Kim, K.; Kim, Y.H. Direct conversion of oximes with dinitrogen tetroxide. Tetrahedron Lett. **1987**, *28*, 645–648.
10. Joseph, R.; Sudalai, A.; Ravindranathan, T. Selective catalytic oxidative cleavage of oximes to carbonyl compounds with H_2O_2 over TS-1. Tetrahedron Lett. **1994**, *35*, 5493–5496.
11. Bangar, B.P.; Kunde, L.; Thote, J.L. Deoximation with *N*-haloamides. Synth. Commun. **1997**, *27*, 1149–1152.
12. Ayhan, H.D.; Tanyeli, E.A.; Altinel, E. Manganese triacetate mediated regeneration of carbonyl compounds from oximes. Tetrahedron Lett. **1997**, *38*, 7267–7270.
13. Bose, D.S.; Narraiah, A.V. A facile method for the conversion of oximes and tosylhydrazones to carbonyl compounds with Dess-Martin periodane. Synth. Commun. **1999**, *29*, 937–941.
14. Chen, F.; Liu, A.; Yan, Q.; Liu, M.; Zhang, D.; Shao, L. Tetrabutylammonium peroxydisulfate in organic synthesis-IV. An efficient, highly selective oxidative deoximation by tetrabutylammonium peroxydisulfate. Synth. Commun. **1999**, *29*, 1049–1056.
15. Heravi, M.M.; Beheshtiha, Y.S.; Ghassemzadeh, M.; Hekmatshoar, R.; Sarmad, N. Solid state deoximation with clay supported ammonium chlorochromate: regeneration of carbonyl compounds using microwave in a solventless system. Monatsh Chem. **2000**, *131*, 187–190.
16. Heravi, M.M.; Ajami, D.; Mojtahedi, M.M. Regeneration of carbonyl compounds from oximes on clayfen under conventional heating and microwave irradiation. J. Chem. Res. **2000**, 126–127.
17. (a) Varma, R.S.; Dahiya, R.; Saini, R.K. Solid state regeneration of ketones from oximes on a wet silica supported sodium periodate using microwaves. Tetrahedron Lett. **1997**, *38*, 8819–8820; (b) Boruah, A.; Boruah, B.; Prajapati, D.; Sandhu, J.S. Regeneration of carbonyl compounds from oximes under microwave irradiation. Tetrahedron Lett. **1997**, *38*, 4267–4268.

18. Shirini, F.; Azadbar, M.A. $[(NO_3)_3Ce]_3 \cdot H_2IO_6$: as a versatile and efficient reagent for cleavage of carbon–nitrogen double bonds under heterogeneous and non-aqueous conditions. Synth. Commun. **2001**, *31*, 3775.
19. Shirini, F.; Zolfigo, M.A.; Azadbar, M.R. Efficient solvent free deoximation and dehydrazonation with HIO_3 in the presence of wet SiO_2. Synth. Commun. **2002**, *32*, 315–318.
20. Nishiguchi, T.; Asano, F. Oxidation of alcohols by metal nitrates supported on silica gel. Tetrahedron Lett. **1988**, *29*, 6265–6266.

Received in the USA March 3, 2004

Downloaded by [University of Oklahoma Libraries] at 00:38 28 October 2014

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/ Order Reprints" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Request Permission/Order Reprints

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081SCC120038512