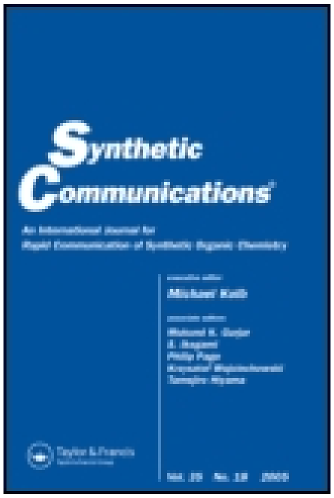
This article was downloaded by: [Laurentian University]
On: 07 December 2014, At: 01:54
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Oxidative Deoximation with Catalytic Sodium Tungstate

A. Manjula [a], G. Narsimha Reddy [a] & B. Vittal Rao [a]
[a] Organic Division II , Indian Institute of Chemical Technology , Hyderabad, India

Published online: 15 Aug 2006.

To cite this article: A. Manjula , G. Narsimha Reddy & B. Vittal Rao (2003) Oxidative Deoximation with Catalytic Sodium Tungstate, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 33:19, 3455-3459

To link to this article: http://dx.doi.org/10.1081/SCC-120024008

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

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SYNTHETIC COMMUNICATIONS®
Vol. 33, No. 19, pp. 3455–3459, 2003

Oxidative Deoximation with Catalytic Sodium Tungstate[#]

A. Manjula, G. Narsimha Reddy, and B. Vittal Rao*

Organic Division II, Indian Institute of Chemical
Technology, Hyderabad, India

ABSTRACT

A simple and mild method of oxidative deoximation based on catalytic amount of sodium tungstate is described. This method is effective for deprotection of ketones and aldehydes.

A number of carbonyl functional group equivalents are routinely employed in organic synthesis. Oximes are readily available and highly stable derivatives of carbonyl compounds that have been regarded both as protective[1] as well as activating groups. Oximes have been used extensively for purification and characterization of carbonyl compounds.[2] They also provide a viable route to amides from carbonyl

---

[#] IICT Communication No. 021201.

*Correspondence: B. Vittal Rao, Organic Division II, Indian Institute of Chemical Technology, Hyderabad 500 007, India; E-mail: vittalrao@iict.ap.nic.in.

DOI: 10.1081/SCC-120024008
0039-7911 (Print); 1532-2432 (Online)
www.dekker.com

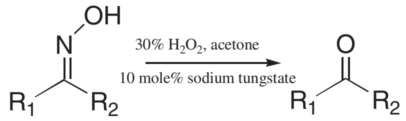
equivalents via Beckmann rearrangement.[3] However, the utility of oximes as carbonyl equivalents is limited by the methods employed for their regeneration. Classically they are regenerated by acid hydrolysis under suitable conditions.[4] This process removes hydroxylamine from the equilibrium. There are limits to the scope of this reaction since compounds containing acid sensitive groups cannot be subjected to this hydrolysis. Recently there has been a lot of stress on the oxidative,[5] reductive[6] and microwave irradiation[7] methods for cleavage of deoximation. It has been found that most of the oxidative methods use non catalytic amount of corrosive and carcinogenic metals such as chromium or expensive catalysts or mostly involve microwave techniques. In view of the recent stress on the catalytic processes towards the development of clean and green chemical processes, investigation of new, less hazardous chemical oxidants has become a priority for the synthetic organic chemists. Herein, we report the use of a combination of catalytic amount sodium tungstate and hydrogen peroxide as a novel reagent system for the oxidative deoximation.

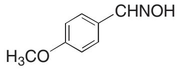
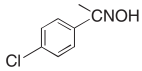
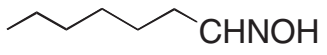
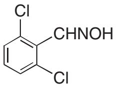
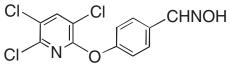
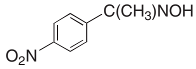
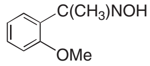
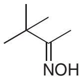
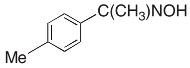
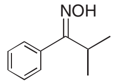
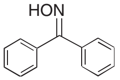
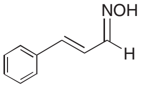
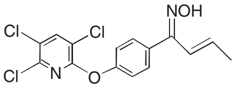
Treatment of oxime (both ketoximes and aldoximes) with 30% hydrogen peroxide in acetone, in the presence of catalytic amount (10 mol%) of sodium tungstate at ambient temperature afforded the corresponding carbonyl compound.[8] In order to test the generality of the deoximation various types of oximes were subjected to the oxidation in the presence of catalytic amount of sodium tungstate and 30% hydrogen peroxide to yield the corresponding carbonyl compounds in moderate to good yields. The reaction conditions are mild. Moreover the method is a general one applicable to all classes of aldehydes and ketones. The reaction times and the yield of deoximation are presented in Table 1.

The deoximation was applicable for enolisable carbonyl compounds also. The yields for the deprotection of ketoximes were of the higher order compared to those of the aldoximes. It is noteworthy that when the oxidation was done with a mixture of the oxime and an alcohol, the alcohol remained unaffected while the oxime was completely converted to the corresponding ketone (as represented in the Sch. 1). The deprotections with the aldoximes gave lesser yields of the product because of the oxidation to the corresponding acid. It was found that with the aldoximes when the oxidation times were shorter the deoximation was incomplete and small amount of acid was formed at the end of deoximation.

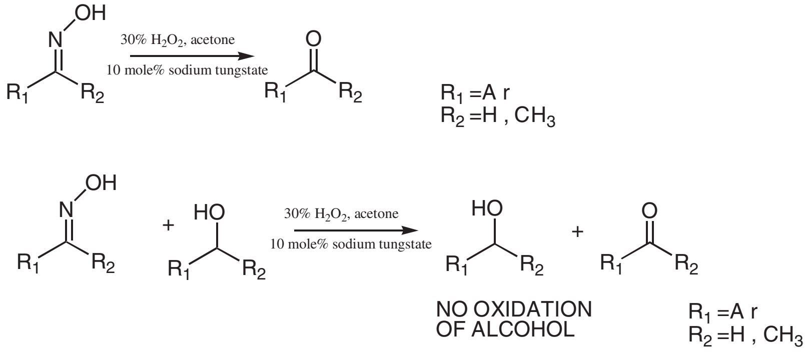
In conclusion, an efficient and inexpensive protocol for regeneration of carbonyl compounds has been realized using catalytic amount of sodium tungstate. The significant features being (a) operational simplicity; (b) use of inexpensive reagent for performing the reaction; (c) does

Table 1.[a]



Entry	Substrate	Time (h)	Yield (%)
1	 	4	78
2	 	5	98
3	 	4	70
4	 	12	85
5	 	4	60
6	 	5	96
7	 	10	92
8	 	5	70
9	 	5	95
10	 	6	95
11	 	6	90
12	 	6	80
13	 	6	60

[a] Unoptimized yields of pure products exhibited physical and spectral properties in accordance with the assigned structures.



Scheme 1.

not involve any additives for promoting the reaction; (d) a variety of functional groups remain unaffected during the transformation.

REFERENCES

1. Greene, T.G.; Wuts, P.G.M. *Protective Groups in Organic Synthesis*, 2nd Ed.; John Wiley & Sons: New York, 1991.
2. Shriner, R.L.; Fuson, R.C.; Curtin, D.Y.; Morrill, T.C. *The Systematic Identification of Organic Compounds*, 6th Ed.; Wiley: New York, 1980.
3. Donaruma, L.G.; Heldt, W.Z. Org. React. **1960**, *11*, 1.
4. (a) Hershberg, E.B. J. Org. Chem. **1948**, *13*, 542; (b) Bandgar, B.P.; Shaikh, S.I.; Iyer, S. Synth. Commun. **1996**, *26*, 1163.
5. Ganguly, N.C.; De, P.; Sukai, A.K.; De, S. Synth. Commun. **2002**, *32*, 1, and references cited therein.
6. Firouzabadi, H.; Jamalian, A.; Babak, K. Bull. Chem. Soc. Jpn. **2002**, *75*, 1761, and references cited therein.
7. Heravi, M.M.; Ajami, D.; Mohajerani, B.; Tabar-Hydar, K.; Ghassemzadeh, M. Synth. Commun. **2002**, *32*, 3325 and references cited therein.
8. In a typical experiment, the oxime (3 mmols) was dissolved in acetone 5 mL and sodium tungstate (10-mol%) was added to it. The reaction mixture was cooled to $-5°C$ in ice-salt mixture. To a stirred mixture of the above 1.5 mL of H_2O_2 was added dropwise. The reaction was monitored by TLC and the solvent was removed and water added to the residue. The mixture was extracted with ether,

combined ether extracts were washed with 5% $Na_2S_2O_3$, water and dried over anhydrous sodium sulfate. Evaporation of the solvent gives crude carbonyl compound, which is further purified by crystallization/distillation.

Analytical data for new compounds is given below:

5. Oxime: M.p. 234–236°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.15 (d, $J = 6$ Hz, 2H, ArH); 7.65 (d, $J = 6$ Hz, 2H, ArH), 7.85 (s, 1H, ArH); 8.10 (s, 1H, $C\underline{H}$=NH). EIMS *m*/*z*: 318 (M+).

Aldehyde: M.p. 123–124°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.3 (d, $J = 6$ Hz, 2H, ArH), 7.8 (s, 1H, ArH), 7.9 (d, $J = 6$ Hz, 2H, ArH), 10.0 (s, 1H, $C\underline{H}O$). IR (KBr) $\nu = 1413$, 1698 cm^{-1}. EIMS: 303 (M^+).

13. Oxime ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.0 (s, 3H, CH_3), 6.75 (s, 1H, CH=CH), 7.1 (d, $J = 6$ Hz, 2H, ArH), 7.5 (m, 3H, ArH & CH=CH), 7.8 (s, 1H, ArH). IR (KBr) $\nu = 3286$, 3124, 2897, 1536, 1406, 1167 cm^{-1}.

Ketone. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.4 (s, 3H, CH_3), 6.70 (d, $J = 10$ Hz, 1H, CH=CH), 7.2 (d, $J = 6$ Hz, 2H, ArH), 7.5 (d, 1H, $J = 10$ Hz, CH=CH), 7.6 (d, $J = 6$ Hz, 2H, ArH), 7.85 (s, 1H, ArH). IR (KBr) $\nu = 3102$, 1654, 1502, 1403, 1178 cm^{-1}. EIMS: 343 (M^+).

Marcel Dekker, Inc. • 270 Madison Avenue • New York, NY 10016