

This article was downloaded by:

On: 28 January 2011

Access details: Access Details: Free Access

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



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

OXIDATIVE DEPROTECTION OF TRIMETHYL SILYL ETHER TO CARBONYL COMPOUNDS USING SILICA GEL SUPPORTED DESS-MARTIN PERIODINANE

Hossien Abdi Oskooie^a; Mehrnoosh Khalilpoor^a; Akbar Saednia^b; Nooshin Sarmad^a; Majid. M. Heravi^a

^a Department of Chemistry, School of Science, Azzahra University, Tehran, Iran ^b School of Chemistry, Tabriz University, Tabriz, Iran

To cite this Article Oskooie, Hossien Abdi , Khalilpoor, Mehrnoosh , Saednia, Akbar , Sarmad, Nooshin and Heravi, Majid. M.(2000) 'OXIDATIVE DEPROTECTION OF TRIMETHYL SILYL ETHER TO CARBONYL COMPOUNDS USING SILICA GEL SUPPORTED DESS-MARTIN PERIODINANE', Phosphorus, Sulfur, and Silicon and the Related Elements, 166: 1, 197 – 200

To link to this Article: DOI: 10.1080/10426500008076541

URL: <http://dx.doi.org/10.1080/10426500008076541>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

OXIDATIVE DEPROTECTION OF TRIMETHYL SILYL ETHER TO CARBONYL COMPOUNDS USING SILICA GEL SUPPORTED DESS-MARTIN PERIODINANE

HOSSIEN ABDI OSKOOIE^{a*}, MEHRNOOSH KHALILPOOR^a,
AKBAR SAEDNIA^b, NOOSHIN SARMAD^a and MAJID.M. HERAVI^a

^aDepartment of Chemistry, School of Science, Azzahra University, Vanak, Tehran,
Iran and ^bSchool of Chemistry, Tabriz University, Tabriz, Iran

(Received June 29, 2000)

Direct oxidative deprotection of different trimethylsilyl ether to their corresponding carbonyl compounds has been achieved using silica gel supported Dess-Martin periodinane in non-aqueous conditions.

Keywords: Oxidative deprotection; carbonyl compounds; supported reagent; Dess-Martin periodinane

In 1991 B.D Dess and J.C. Martin reported a periodinane compound as a versatile oxidizing agents¹. Dess-Martin periodinane is an efficient and selective agent for producing aldehydes and ketones from primary and secondary alcohols. A large numbers of imino derivatives such as oximes have been oxidatively cleaved by this reagent².

The protection of functional groups is a useful and important method in organic synthesis. One of the most useful and convenient methods for protection of hydroxy groups is their transformation to trialkylsilyl ethers³.

Direct oxidation of trimethylsilyl ethers to the corresponding aldehydes and ketones is of great relevance to organic synthesis. Although various methods have been reported for such a transformation⁴ some of them show limitations such as the requirement for aqueous reaction conditions, use of

* Corresponding Author.

expensive reagents, long reaction times, tedious work up and low yields of products. Therefore presentation of new methods and inexpensive and environmentally friendly reagents for such functional group transformation is still in much demand.

In recent years, the organic reactions on solid supports have gained special attention because of their enhanced selectivity, milder conditions and associated ease of manipulation⁵. Recently we have demonstrated the use of supported reagents for an efficient and mild method in organic methodologies⁶. Following the above findings we have investigated the possibility of extending the oxidation ability of Dess-Martin periodinane reagent to oxidative deprotection of trimethylsilyl ethers.

Dess-Martin periodinane (DMP) 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1H)-one] has received wide recognition as a mild, selective reagent for oxidation of primary and secondary alcohols to the corresponding carbonyl compounds. However, a literature survey showed no references concerning the use of this reagent as a reagent of oxidative deprotection of trimethylsilyl ether. Since Dess-Martin periodinane is no longer commercially available, it was prepared according to literature procedure⁷.

The supported reagent was prepared by mixing equal amount of Dess-Martin periodine with silica gel(mesh 60–100). The reaction is conducted by refluxing 2 equivalents of this silica gel supported Dess-Martin periodinane with silyl ether in CH_2Cl_2 . The corresponding carbonyl compounds can be easily separated by filtration and evaporation of the solvent in high yield. In this reaction no traces of benzoic acid were observed even after prolonged reflux of benzyl trimethylsilyl ether with excess of the supported reagent. Cinnamyl trimethylsilyl ether was also oxidatively deprotected to cinnamyl aldehyde in high yield. No benzaldehyde was detected in this reaction showing that benzylic double bonds are not prone to cleavage by this method, (table).

It is worthwhile to mention that in the absence of silica gel the reactions in all cases are sluggish and a considerable amount of ethers and alcohols were recovered unchanged in the reaction solvent at elevated temperature.

TABLE I Oxidative deprotection of trimethylsilyl ether with Dess-Martin periodinane supported onto silica gel under non- aqueous conditions

Entry	Substrate	Time(sec)	Product	Yield(%)
1	PhCH ₂ OSiMe ₃	20	PhCHO	98
2	5-Me-2-NO ₂ C ₆ H ₃ CH ₂ OSiMe ₃	20	5-Me-2-NO ₂ C ₆ H ₃ CHO	88
3	PhCH=CHCH ₂ SiOMe ₃	30	PhCH=CHCHO	85
4	Cyclohexyltrimethylsilyl ether	30	Cyclohexanone	88
5	Mentholtrimethylsilyl ether	30	Menthone	82
6	Pentylsilyl ether	40	Pentanal	90
7	Cholestroltrimethylsilyl ether	40	Cholestenone	82

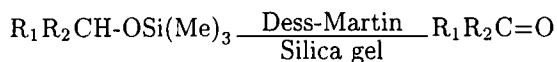
Yields refer to isolated produced

EXPERIMENTAL

All products were known compounds and identified by comparison with authentic samples. Yields refer to isolated products. Dess-Martin reagent was prepared according to a reported procedure¹.

GENERAL PROCEDURE FOR OXIDATIVE DEPROTECTION OF TRIMETHYLSILYL ETHERS

In a round bottomed flask(50 ml) equipped with a magnetic stiner and a condenser a solution of trimethylsilyl ether(1.2 mmol), Dess-Martin periodinane supported onto silica gel(2.4 mmol) were refluxed in CH₂Cl₂(50 ml) for specified time. The progress of the reaction was monitored by T.L.C(eluent ether- ethyl acetate 80–20), the mixture was filtered and solid was washed with CH₂Cl₂(10 ml). The filtrate was evaporated under reduced pressure and the crude was passed through silica gel pad for further purification to afford the corresponding carbonyl compounds.



Acknowledgements

Financial supports of this projects from research concil of Azzahra University is gratefully appreciated.

References

1. B.D. Dess, J.C. Martin, *J. Am. Chem. Soc.* **113**, 7277(1991).
2. D.S. Base, A.V. Narsaiah, *Synth Commun.* **29**(6), 937(1999).
3. T.W. Green, P.G.M. Wuts, *Protective Groups in Organic Synthesis*, New York, 2nd edn 1991.
4. a) M.M. Heravi, D. Ajami, K. Tabar Hydar, M.M., Mojtahedi, *J. Chem. Res.*, 620(1998).
b) M.M. Heravi, D. Ajami, Ghassemzadeh, *Synthesis*, **3**, 393(1999).
c) M.M. Heravi, D. Ajami, K. Tabar hydar, *Synth Commun*, **29**, 1009(1999).
d) M.M. Heravi, M. Tajbakhsh, B. Mohajirani, M. Ghassemzadeh, *Z., Naturforsch.*, **54b**, 394(1999).
5. a) M. Balogh, P. Laszlo, *Organic Chemistry Using Clays*. Springer-Verlag, Berlin(1993).
b) A. Comelis, P. Laszlo, *Synthesis*, 849(1980).
c) A. Mc Killop, D.W. Young, *Synthesis*, 401(1979).
6. a) M.M. Heravi, D. Ajami, K. Aghapoor, M., Ghassemzadeh, *J. Chem. Soc. Chem. Commun.*, 833(1999) and references cited therein.
b) M.M. Heravi, D., Ajami, *J. Chem. Res.*, 718(1998).
c) M.M. Heravi, D. Ajami, M.M. Mojtahedi, M. Ghassemzadeh, *Tetrahedron Lett.* **40**, 561(1999).
7. R.E. Ireland, L., Longlin, *J. Org. Chem* **58**, 2899(1993).