This article was downloaded by: [McMaster University] On: 25 December 2014, At: 21:20 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.tandfonline.com/loi/gpss20

ZINC CHLOROCHROMATE NONAHYDRATE [Zn(CICrO<sub>3</sub>)<sub>2</sub>.9H<sub>2</sub>O] IS A USEFUL REAGENT SOLUTION OXIDATIVE DEPROTECTION FOR THE SOLVENT-FREE AND IN OF TRIMETHYL- AND TERT-BUTYLDIMETHYLSILYL ETHERS

Habib Firouzabadi<sup>a</sup>, Mostafa Gholizadeh<sup>a</sup> & Mahmood Fakourpour<sup>a</sup>

<sup>a</sup> Department of Chemistry , Shiraz University , Shiraz, 71454, Iran Published online: 04 Oct 2006.

To cite this article: Habib Firouzabadi , Mostafa Gholizadeh & Mahmood Fakourpour (1999) ZINC CHLOROCHROMATE NONAHYDRATE [Zn(CICrO<sub>3</sub>)<sub>2</sub>.9H<sub>2</sub>O] IS A USEFUL REAGENT SOLUTION OXIDATIVE DEPROTECTION FOR THE SOLVENT-FREE AND IN OF TRIMETHYL- AND TERT-BUTYLDIMETHYLSILYL ETHERS, Phosphorus, Sulfur, and Silicon and the Related Elements, 155:1, 81-87, DOI: <u>10.1080/10426509908044972</u>

To link to this article: <u>http://dx.doi.org/10.1080/10426509908044972</u>

## 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 Phosphorus, Sulfur and Silicon, 1999, Vol. 155, pp. 81-87 Reprints available directly from the publisher Photocopying permitted by license only © 1999 OPA (Overseas Publishers Association) Amsterdam N.V. Published under license by the Gordon and Breach Science Publishers imprint. Printed in Malaysia

# ZINC CHLOROCHROMATE NONAHYDRATE [Zn(ClCrO<sub>3</sub>)<sub>2</sub>.9H<sub>2</sub>O] IS A USEFUL REAGENT FOR THE SOLVENT-FREE AND IN SOLUTION OXIDATIVE DEPROTECTION OF TRIMETHYL- AND TERT-BUTYLDIMETHYLSILYL ETHERS

HABIB FIROUZABADI<sup>\*</sup>, MOSTAFA GHOLIZADEH and MAHMOOD FAKOURPOUR

Department of Chemistry, Shiraz University, Shiraz 71454, Iran

(Received February 26, 1999)

Primary and secondary tert-butyldimethylsilyl and trimethylsilyl ethers are oxidized to their corresponding carbonyl compounds with zinc chlorochromate nonahydrate (ZCCNH) in dichloromethane or under solvent free conditions in good yields. For comparison, we have also studied the reactions with pyridinium chlorochromate (PCC) under similar reaction conditions.

Keywords: Zinc chlorochromate nonahydrate; Pyridinium chlorochromate; Oxidative deprotection; Oxidation; Silyl ethers; Solvent-free

#### INTRODUCTION

Direct oxidative deprotection of silyl ethers is of practical importance and varieties of methods are available in the chemical literature.<sup>[1]</sup> TMS and TBDMS groups are the two most encountered silyl moieties which are used for masking hydroxyl groups in the course of the total synthesis of complex organic molecules.<sup>[2]</sup> Literature search shows that oxidative cleavage of the TBDMS ethers even under harsh reaction conditions is difficult<sup>[1a,3]</sup>.

<sup>\*</sup> Correspondence Authors.

In this report we have paid attention to the oxidative deprotection of TBDMS and TMS ethers using zinc chlorochromate nonahydrate  $(ZCCNH)^{[1b]}$ , a newly developed oxidizing agent, in  $CH_2Cl_2$  or under neat condition .Through this study, we have also compared the results of the oxidative deprotection of the silyl ethers with ZCCNH with those obtained by pyridinium chlorochromate (PCC) oxidation.<sup>[4]</sup>

#### **RESULTS AND DISCUSSION**

Both reagents are effective oxidants for the transformation of TMS ethers  $(1_{a-i})$  to the corresponding carbonyl compounds under solvent-free conditions (Table I). Oxidation of some TMS ethers in solutions are reported earlier with ZCCNH and PCC<sup>[1a,b,1,3]</sup> or we have investigated in our laboratories during the progress of this work. For comparison, we have also summarized the results in solution in Table I.

TABLE I Comparison of Oxidative Deprotection of TMS Ethers to Their Corresponding Carbonyl Compounds with Zinc Chlorochromate Nonahydrate (ZCCNH) and Pyridinium Chlorochromate (PCC) under Solvent-Free Conditions and in Solution

	Substrate	Solvent-Free Oxid/Subst(h) Yield <sup>a</sup>		In Solution Oxid/Subst(h) Yield <sup>a</sup>	
		(ZCCNH)	(PCC)	(ZCCNH)	(PCC)
1	CH2OTMS	0.5(-) <sup>b</sup> 80	4(0.25)95	0.5(0.25)85	4(1.5)90
2	O2N CH2OTMS	1(-) <sup>b</sup> 85	6(1)10	2(3.4)87 <sup>20</sup>	6(2)77
3	OOTMS	1(-) <sup>b</sup> 84	10(0.5)80	1(0.25)80	10(2)86

		Solvent-Free		In Solution	
	Substrate	Oxid/Subst(h) Yield <sup>a</sup>		Oxid/Subst(h) Yield <sup>a</sup>	
		(ZCCNH)	(PCC)	(ZCCNH)	(PCC)
4	OTMS	1.2(-) <sup>b</sup> 74 <sup>c</sup>	10(0.7)80 <sup>c</sup>	1.2(0.25)95	10(1)71
5	OTMS O O	0.8(-) <sup>b</sup> 95	5(0.3)93	1(0.25)93	5(0.5)87
6	MeO CH2OTMS	0.4(-) <sup>b</sup> 95	3(0.17)98	0.4(0.8)89	4(0.5)88
7	ОТМЯ	1.2(-) <sup>b</sup> 76 <sup>c</sup>	10(0.5)75 <sup>c</sup>	1.2(0.8)93	10(1)87
8	CH <sub>2</sub> OTMS	0.8(-) <sup>b</sup> 85	5(0.08)70	0.8(0.2)73	5(0.2)57
9	TMSO OTMS	1.5(-) <sup>b</sup> 100	6(0.2)89	1(1)90 <sup>20</sup> .	-(2)99

a) Isolated yields after column chromatography or as 2,4-dinitrophenylhydrazone derivative.
b) Reactions occurred immediately.

c) GC yield.

Direct oxidation of tert-butyldimethylsilyl (TBDMS) ethers is a difficult  $task^{[11]}$  and we have studied the use of ZCCNH, as an oxidant, for this purpose in CH<sub>2</sub>Cl<sub>2</sub>. Surprisingly, the transformation proceeded smoothly in less than lh and the corresponding carbonyl compounds were isolated in good to high yields. *tert-Butyldimethylsilyl* ethers are stable to PCC in

solution even in the presence of added potassium fluoride.<sup>[3]</sup>Oxidation of tert-butyldimethylsilyl ethers with ZCCNH and PCC under neat conditions was also studied. ZCCNH is an effective oxidant in the absence of solvent for this purpose and the carbonyl compounds are produced in 70–88% yields in a few minutes at room temperature (Table II).

TABLE II Comparison of Oxidative Deprotection of tert-Butyldimethylsilyl (TBDMS) Ethers with Zinc Chlorochromate Nonahydrate (ZCCNH) and Pyridinium Chlorochromate (PCC) under Solvent-Free Conditions and in Solution

		Solvent-Free Oxid/Subst(h) Yield <sup>a</sup>		In Solution Oxid/Subst(h) Yield <sup>a</sup>	
	Substrate				
		(ZCCNH)	(PCC)	(ZCCNH)	(PCC)
1	CH OTBDMS	5.5(0.17)83	8.5(0.8)85	7(0.5)80	10(5)- <sup>b</sup>
2	NO2 CH_OTBDMS	6.5(0.1785	10(2)-Ь	10(0.5)78	15(3)90
3	OTBDMS	6(-) <sup>b</sup> 74	10(1)10	8(0.5)80	15(3)84
4	OTEDMS	6.2(0.17)73 <sup>c</sup>	10(3)10 <sup>c</sup>	8(0.6)75 <sup>c</sup>	10(3)90 <sup>c</sup>
5		7.2(0.17)87	10(1)80	9(-)76	10(4)70
6	MeO CH_OTBDMS	4.5(-) <sup>b</sup> 88	7(0.7) <del>9</del> 0)	5.5(0.3)90	10(5)90

.



a) Isolated yields after column chromatography or as 2,4-dinitrophenylhydrazone derivative. b) Reactions occurred immediately.

c) GC yield.

Generally, ZCCNH is a more effective reagent than PCC for conversion of TBDMS ethers to their corresponding carbonyl compounds either in solution or in the absence of solvent (Table II).

#### Conclusion

Zinc chlorochromate nonahydrate (ZCCNH) an easily prepared and a cheap reagent is a useful oxidant for the efficient oxidative deprotection of highly stable tert-butyldimethylsilyl ethers to their corresponding carbonyl compounds in good yields. The reactions proceed under mild reaction conditions in solution and also in the absence of solvent. Generally, ZCCNH is a more effective reagent than PCC for the oxidative transformation of TBDMS ethers. Both ZCCNH and PCC transform TMS ethers to the carbonyl compounds effectively in the absence of solvents and in solution. Over-oxidation of the products is not observed by the presented methods.

#### **EXPERIMENTAL**

General: Products were characterized by comparison of their physical data with those of authentic samples. All yields refer to isolated products unless otherwise indicated. IR spectra were recorded on a Perkin Elmer 781. Mass spectra were recorded on a Shimadzu GCMC-QP 1000 EX. TLC accomplished the purity determination of the products on silica gel polygram SILG/UV 254 plates or GLC on a Shimadzu GC-14A instrument.  $CH_2Cl_2$  was dried and predistilled. The yields of the partially volatile carbonyl compounds were determined by both GLC or as their 2,4-dinitrophenylhydrazone derivatives.

## Oxidative Deprotection of 4-Nitrobenzyl-tert-butyldimethylsilyl Ether with Zn(ClCrO<sub>3</sub>)<sub>2</sub>.9H<sub>2</sub>O (ZCCNH) in CH<sub>2</sub>Cl<sub>2</sub> to 4-Nitrobenzaldehyde: a Typical Precedure for the Direct Oxidation of TBDMS Ethers to Their Corresponding Carbonyl Compounds

To a solution of 4-nitrobenzyl-tert-butyldimethylsilyl ether (0.267 g, 1 mmol) in  $CH_2Cl_2$  (10 ml) in a round-bottom flask (25 ml) equipped with a magnetic stirrer,  $Zn(ClCrO_3)_2.9H_2O$  (4.98 g, 10 mmol) was added and the resulting mixture was stirred vigorously for 0.5 h. The progress of the reaction was monitored by TLC. Solvent was evaporated on a rotary evaporator and the residue was applied on a silica gel pad and was eluted with petroleum ether/acetone (8/1). The solvent was evaporated and to the resulting residue,  $CH_3OH$  (3×5 ml) was added and the resulting mixture was isolated in 78% yield, 0.118 g, mp 105–106°C [lit, mp 106°C] (entry 2, Table II).

## Oxidative Deprotection of 4-Nitrobenzyltrimethylsilyl Ether with Pyridinium Chlorochromate (PCC) to 4-Nitrobenzaldehyde Under Solvent-Free Conditions: a Typical Procedure for the Direct Oxidation of TMS Ethers to their Corresponding Carbonyl Compounds

A mixture of 4-nitrobenzyltrimethylsilyl ether (0.226 g, 1 mmol) and PCC (1.3 g, 6 mmol) was prepared and was magnetically agitated for 1h. at room temperature. To the resulting mixture  $Et_2O$  (30 ml) was added and filtered through a silica gel pad (4 g). The filter cake was washed further

with an extra amount of  $Et_2O$  (20 ml). The combined filtrates were evaporated and the resulting residue was further purified by column chromatog-raphy on silica gel and eluted with petroleum ether/acetone (8/1) to afford the desired aldehyde in a quantitative yield, mp 105–106°C [Lit.<sup>[24]</sup> 106°C] (entry 2, Table I).

#### Acknowledgements

The authors are grateful for the support of this work by National Research Council of I.R. Iran (NRCI) by grant no.464.

#### References

- a) Firouzabadi, H., Sharifi, A., Karimi, B. Iran. J. Chem. & Chem. Eng. 1993, 12, 32.,
   b) Firouzabadi, H., Sharifi, A. Synthesis 1992, 999 and the references cited therein.
  - c) Olah, G. A., Ho, T.L. Synthesis 1976, 609.
  - d) Olah, G.A., Gupta, B.G.B., Fung, A.P. Synthesis 1980, 897.
  - e) Tolstikov, G.A., Moftikhov, M.S., Komissorova, N.G., Alder, M.E., Kutsnetsov, O.M., Vostrikov, N.S. Synthesis **1989**, 940.
  - f) Marko, I.E., Mekhalfia, A., Ollis, W.D. Synlett, 1990, 354.
  - g) Narasimhan, N.S., Bapat, C.P., J. Chem. Soc. Perkin Trans. 1984, 1435.
  - h) Aizpurua, J.M., Carrick, W.L. Tetrrahedron 1983, 24, 4367.
  - i) D' Auria, M., D'Onofrio, Piacatteli, G. Scettri, A. Synthetic Commun. 1982, 12, 1127.
  - j) Sansbury, F. H., Warren, S. Tetrahedron Lett. 1991, 32, 3425.
  - k) Firouzabadi, H. Mohammadpour-Baltork, I. Synthetic Commun. 1994, 24, 1065.
    1) Muzart, J., Synthesis, 1993, 11.
  - m) Mohammadpour- Baltourk, I., Pouranshirvani, S, Synthesis 1997, 756.
- [2] Lalonde, M., Chan, T.H., Synthesis, 1985, 817, and references cited therein. Greene, T.W., Wutz, P.G.M., "Protective Groups in Organic Synthesis", 2nd ed., John Wiley and Sons, New York, 1981.
- [3] Liu, H., Han, I.S. Synthetic Commun. 1985, 15, 759.
- [4] Piancatelli, G., Scettri, A., D'auria, M., Synthesis, 1982, 245.
- [5] Aldrich Catalog/Handbook of Fine Chemicals, 1992-1993.