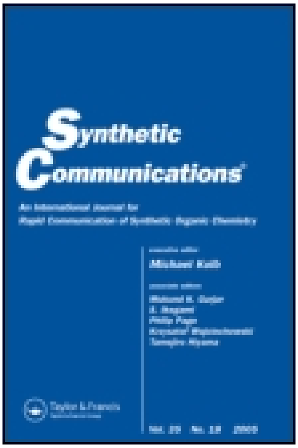


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

OXIDATION DEPROTECTION OF TRIMETHYLSILYL ETHERS TO CARBONYL COMPOUNDS BY $NaBrO_3$-NH_4Cl REAGENT IN AQUEOUS ACETONITRILE

Ahmad Shaabani [a] & Ali-Reza Karimi [a]
[a] Chemistry Department, Shahid Beheshti University, P.O. Box 19396 - 4716, Tehran, Iran

To cite this article: Ahmad Shaabani & Ali-Reza Karimi (2001) OXIDATION DEPROTECTION OF TRIMETHYLSILYL ETHERS TO CARBONYL COMPOUNDS BY $NaBrO_3$-NH_4Cl REAGENT IN AQUEOUS ACETONITRILE, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:5, 759-765, DOI: 10.1081/SCC-100103266

To link to this article: http://dx.doi.org/10.1081/SCC-100103266

SYNTHETIC COMMUNICATIONS, 31(5), 759–765 (2001)

OXIDATION DEPROTECTION OF TRIMETHYLSILYL ETHERS TO CARBONYL COMPOUNDS BY $NaBrO_3$-NH_4Cl REAGENT IN AQUEOUS ACETONITRILE

Ahmad Shaabani* and Ali-Reza Karimi

Chemistry Department, Shahid Beheshti University,
P.O. Box 19396 – 4716, Tehran, Iran

ABSTRACT

Primary and secondary benzylic and secondary alkyl trimethlysilyl ethers are efficiently converted into their carbonyl compounds by $NaBrO_3$-NH_4Cl in aqueous acetonitrile. Primary alkyl silyl ethers give only the corresponding alcohols without further oxidation with $NaBrO_3$-NH_4Cl.

Protection of functional groups is of vital importance in the total synthesis of complex organic compounds.[1] The alcohol function is one of the most important groups in organic molecules and its controlled manipulation during the synthesis is of great value to synthetic organic chemists. The transformation of alcohols into corresponding silyl ethers is a very common way to protect hydroxy groups.[1,2] Such a protection can be used to prevent their oxidation, but sometimes it is necessary to achieve the transformation of the silyl ether to the corresponding carbonyl compound.

---

* Corresponding author.

www.dekker.com

A great number of oxidative deprotection agents can effect the conversion of a silyl ether to a carbonyl compound,[2,3] and a synthetic chemist is faced with an amazing choice of methods for this reaction. However, the susceptibility of aldehydes to further oxidation narrows the choice of reagent for the oxidative deprotection of silyl ethers to aldehydes in good yields.

The discovery of new reagents for the transformation of silyl ethers into carbonyl compounds under mild condition with a variety of silyl ethers is of primary importance in synthetic organic chemistry. Conversion of silyl ethers by Jones reagent (CrO_3, H_2SO_4/acetone),[4] CrO_3/Py,[5] PCC,[6] PFC,[7] PDC,[6b] $(Ph_3SiO)_2CrO_2$/t-BuO_2H,[8] Ph_3SiOH/CrO_3/t-BuO_2H,[9] DMSO based reagents,[10] NBS,[11] DDQ,[12] Ph_3CBF_4,[13] Ce(IV)/$NaBrO_3$,[14] $AgBrO_3/AlCl_3$[15] and $NaBrO_3/AlCl_3$[15] have been reported. Most of the reactions mentioned above suffer more or less serious drawbacks such as: dry media and nonaqueous reaction conditions, poor availability of the reagents, long reaction times and low yields of products, and sometimes they involve a tedious work up. Recently, we have found that the mixture $NaBrO_3$-NH_4Cl is an efficient oxidant for the oxidation of alcohols[16] and sulfides.[17] Herein, we report our subsequent studies on oxidative deprotection of benzylic and secondary silyl ethers to the corresponding aldehydes and ketones and conversion of primary alkyl silyl ethers only into corresponding alcohols without further oxidations using $NaBrO_3$-NH_4Cl. We have found that this method of oxidative deprotection is very convenient for conversion of silyl ethers into carbonyl compounds, because of simplicity and use of mild reaction conditions.

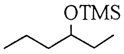
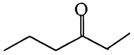
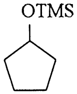
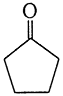
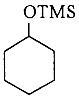
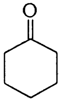
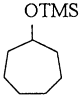
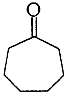
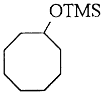
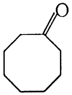
Furthermore, NH_4Cl and $NaBrO_3$ are both cheap and easily available compounds relative to most other oxidizing deprotecting agents that have so far been employed. As shown in Table 1, a wide variety of benzylic and secondary alcohols could be easily converted into the corresponding carbonyl compounds. However, saturated primary alcohols (Table 1, entries 11–13) were only converted to corresponding alcohols.

In conclusion, $NaBrO_3$ in the presence of NH_4Cl provides a new and efficient reagent which promises to be economical for the one-pot oxidation deprotection of benzylic and secondary trimethylsilyl ethers to their corresponding carbonyl compounds in high yields and also conversion of primary alkyl silyl ethers to the corresponding alcohols under mild reaction conditions.

EXPERIMENTAL

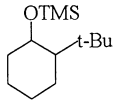
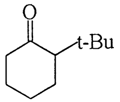
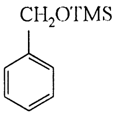
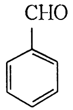
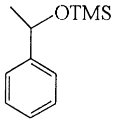
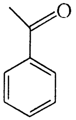
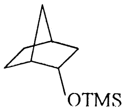
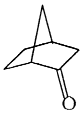
All products are known compounds and were identified by comparison of their physical and spectral data with those of authentic samples.

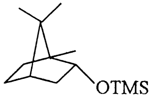
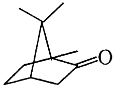
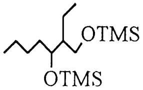
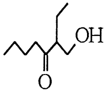
Table 1. Oxidation of Silyl Ethers to Carbonyl Compounds by $NaBrO_3$-NH_4Cl in Acetonitril-Water (7/3) at 80°C

Entry	Reactant	Product	Reaction Time (t/min)	Isolated Yield (%)	2,4-DNP Yield (%)	Bp of Carbonyl Product or alcohol At 760 Torr (T/°C)	Mp of Carbonyl Product (T/°C)	Mp of 2,4-DNP (T/°C)
1			45	75	70	122(122–124[a])	–	135(130[b])
2			30	84	90	127–139(131[c])	–	144(142[d])
3			45	80	85	150–155(155[c])	–	162(162[d])
4			50	81	85	181(178–180[a])	–	148(148[a])
5			50	82	88	185–193(195[c])	–	162(163[c])

(continued)

Table 1. Continued

Entry	Reactant	Product	Reaction Time (t/min)	Isolated Yield (%)	2,4-DNP Yield (%)	Bp of Carbonyl Product or alcohol At 760 Torr (T/°C)	Mp of Carbonyl Product (T/°C)	Mp of 2,4-DNP (T/°C)
6[e]			50	55	–	63–64[f]	–	–
7			30	82	87	175(179[c])	–	230(237[d])
8			30	90	95	199–201(202[c])	–	240(250[d])
9[g]			30	60	58	–	93–95(94–96[a])	125(125–126[h])

10			30	70	–	–	172–175(175–177^{a})	–
11			15	90	–	174(174–176^{a})	–	–
12			15	90	–	193(193–195^{a})	–	–
13			50	45	48	–	–	118(118.5–119.5^{i})

---

[a] From ref. 21.
[b] From ref. 22.
[c] From ref. 23. At 760 Torr(~101080 Pa).
[d] From ref. 23.
[e] Cis and trans isomers.
[f] At 5 Torr(~665 Pa) (lit., (24)62.5, 4 Torr ~ 532 Pa).
[g] (+)-endo-Norborneol.
[h] From ref. 25.
[i] From ref. 26.

Melting points were determined in open capillaries using an oil-bath and are uncorrected. IR spectra were recorded as neat films or as KBr pellets on a Shimadzu 470 spectrometer. ^{1}H NMR spectra were recorded at 90 MHz on a JEOL EX-90 instrument with $CDCl_3$ as solvent and Me_4Si as an internal standard. Yields reported refer to isolated products or 2,4-dinitrophenylhydrazone derivatives (2,4-DNP)[18,19] of the carbonyl compounds. Trimethyl silyl ethers were prepared according to published procedures.[20]

General Procedure

Trimethylsilyl ether (5 mmol) was added to a mixture of $NaBrO_3$ (0.755 g, 5 mmol) and NH_4Cl (0.400 g, 7.5 mmol) in aqueous acetonitrile (CH_3CN-H_2O = 7:3, v:v; 10 ml). The mixture was stirred at 80°C for 15 to 50 minutes. When the reaction was complete, the resulting solution was extracted with methylene dichloride (20 ml). The combined organic layers were dried over $MgSO_4$. After filtration, the solution was evaporated on a rotary evaporator and the resulting crude material was purified on a silica gel column with appropriate eluent.

ACKNOWLEDGMENT

Financial support by the Research Council of Shahid Beheshti University is acknowledged.

REFERENCES

1. (a) Greene, T.W.; Wutz, P.G.M. *Protective Groups in Organic Synthesis*, 2nd ed., Wiley, New York, 1991. (b) Nelson, T.D.; Crouch, R.D. *Synthesis* **1996**, 1031.
2. (a) Colvin, E.W. *Chem. Soc. Rev.* **1978**, *7*, 15. (b) Lalonde, M.; Chan, T.H. *Synthesis* **1985**, 817.
3. Muzart, J. *Synthesis* **1993**, 11.
4. (a) Bowden, K.; Heilbron, I.M.; Jones, E.R.H.; Weedon, B.C.L. *J. Chem. Soc.* **1946**, 39. (b) Baker, R.; Rao, V.B.; Ravenscroft, P.D.; Swain, C.J. *Synthesis* **1983**, 572. (c) Paquette, L.A.; Lin, H.S.; Gunn, B.P.; Coghlan, M.J. *J. Am. Chem. Soc.* **1988**, *110*, 5818.
5. Mahrwald, R.; Theil, F.; Schick, H.; Schwartz, S.; Palme, H.J.; Weber, G. *J. Prakt. Chem.* **1986**, *77*, 328.

6. (a) Hart, T.W.; Metcalfe, D.A.; Scheinmann, F. *J. Chem. Soc. Chem. Commun.* **1979**, 155. (b) Denmark, S.E.; Hammer, R.P.; Weber, E.J.; Habermas, K.L. *J. Org. Chem.* **1987**, *52*, 165.
7. Nonaka, T.; Kanemoto, S.; Oshima, K.; Nazaki, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2019.
8. Muzart, J.; N'Ait Ajjou, A. Synlett. **1991**, 497.
9. Muzart, J.; N'Ait Ajjou, A. *Synth. Commun.* **1992**, *22*, 1993.
10. (a) Afonso, C.M.; Barros, M.T.; Maycock, C.D. J. Chem. Soc. Perkin *Trans. I* **1987**, 1221. (b) Tolstikov, G.A.; Miftakhov, M.S.; Alder, M.E.; Komissarova, N.G.; Kuznetsov, O.M.; Vostrikov, N.S. Synthesis **1989**, 940.
11. Marko, I.E.; Mekhalifia, A.; Ollis, W.D. Synlett. **1990**, 345.
12. (a) Narasimham, N.S.; Bapat, C.P. *J. Chem. Soc. Perkin Trans. I* **1984**, 1435. (b) Piva, O.; Amougay, A.; Pete, J.P. *Tetrahedron Lett.* **1991**, *32*, 3993.
13. (a) Jung, M.E. *J.Org. Chem.* **1976**, *41*, 1479. (b) Jung, M.E.; Speltz, L.M. *J. Am. Chem. Soc.* **1976**, *98*, 788.
14. Olah, G.A.; Gupta, B.G.B.; Fung, A.P. *Synthesis* **1980**, 897.
15. Firouzabadi, H.; Mohammadpoor-Baltork, I. *Synth. Commun.* **1994**, *24*, 1065.
16. Shaabani, A.; Ameri, M. *J. Chem. Research(S)* **1998**, 100.
17. Shaabani, A.; Safaei, H.R.; Bazgir, A. *Iran. J. Chem. & Chem. Eng.* Submitted.
18. Roberts, R.M.; Gilbert, J.C.; Rodwald, L.B.; Wingrove, A.C. *Modern Experimental Organic Chemistry*, 4th ed. Saunders: Philadelphia; 1985, pp. 700–701.
19. Zhang, J.; Hertzler, R.L.; Eisenbraun, E.J. *J. Chem. Educ.* **1992**, *69*, 1037.
20. Firouzabadi, H.; Karimi, B. *Synth. Commun.* **1993**, 1633.
21. *Fluka Catalogue*/Handbook of Fine Chemicals, **1999–2000**.
22. Allen, C.F.H. *J. Am. Chem. Soc.* **1930**, *52*, 2955.
23. Criddle, W.J.; Ellis, G.P. *Spectral and Chemical Characterization of Organic Compounds, A Laboratory Handbook*, Wiley: Chichester, 3rd ed.; 1990.
24. Zhang, J.; Hertzler, R.L.; Eisenbraun, E.J. *J. Chem. Educ.* **1992**, *69*, 1037.
25. Yavari, I.; Shaabani, A. *J. Chem. Research(S)* **1994**, 274.
26. Wear, R.L. *J. Am. Chem. Soc.* **1951**, *73*, 2390.

Received in the U.K. November 11, 1999