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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 NaBrO₃-NH₄CI REAGENT IN AQUEOUS ACETONITRILE

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To cite this article: Ahmad Shaabani & Ali-Reza Karimi (2001) OXIDATION DEPROTECTION OF TRIMETHYLSILYL ETHERS TO CARBONYL COMPOUNDS BY NaBrO₃-NH₄CI REAGENT IN AQUEOUS ACETONITRILE, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:5, 759-765, DOI: <u>10.1081/SCC-100103266</u>

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

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OXIDATION DEPROTECTION OF TRIMETHYLSILYL ETHERS TO CARBONYL COMPOUNDS BY NaBrO₃-NH₄CI REAGENT IN AQUEOUS ACETONITRILE

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ABSTRACT

Primary and secondary benzylic and secondary alkyl trimethlysilyl ethers are efficiently converted into their carbonyl compounds by NaBrO₃-NH₄Cl in aqueous acetonitrile. Primary alkyl silyl ethers give only the corresponding alcohols without further oxidation with NaBrO₃-NH₄Cl.

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.

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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 silvl ethers into carbonyl compounds under mild condition with a variety of silvl ethers is of primary importance in synthetic organic chemistry. Conversion of silvl by Jones reagent (CrO₃, H₂SO₄/acetone),⁴ CrO₃/Py,⁵ PCC,⁶ ethers PDC,^{6b} PFC,⁷ (Ph₃SiO)₂CrO₂/t-BuO₂H,⁸ Ph₃SiOH/CrO₃/t-BuO₂H,⁹ DMSO based reagents,¹⁰ NBS,¹¹ DDQ,¹² Ph₃CBF₄,¹³ Ce(IV)/NaBrO₃,¹⁴ AgBrO₃/AlCl₃¹⁵ and NaBrO₃/AlCl₃¹⁵ 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 NaBrO₃-NH₄Cl is an efficient oxidant for the oxidation of alcohols¹⁶ 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 NaBrO₃-NH₄Cl. We have found that this method of oxidative deprotection is very convenient for conversion of silvl 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, NaBrO₃ 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.

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)°C	Mp of 2,4-DNP (T/°C)	135(130 ^b)	144(142 ^d)	162(162 ^d)	148(148 ^a)	162(163°)
Table 1. Oxidation of Silyl Ethers to Carbonyl Compounds by NaBrO ₃ -NH ₄ Cl in Acetonitril-Water (7/3) at 80°C	Mp of Carbonyl Product (T/°C)	I	I	I	I	I
	Bp of Carbonyl Product or alcohol At 760 Torr (T ^o C)	122(122–124ª)	127–139(131°)	150–155(155°)	181(178–180 ^a)	185–193(195°)
	2,4-DNP Yield (%)	70	06	85	85	88
	Isolated Yield (%)	75	84	80	81	82
	Reaction Time (t/min)	45	30	45	50	50
	Product	\rightarrow	0=	0=	⊂	°
	Reactant	OTMS	OTMS	otms	SMTO	SMTO
L	Entry	-	7	ŝ	4	Ś

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(continued)

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Table 1. Continued	Mp of 2,4-DNP (T/°C)	I	230(237 ^d)	240(250 ^d)	125(125–126 ^h)
	Mp of Carbonyl Product (T/°C)	I	I	I	93-95(94-96ª)
	$ \begin{array}{llllllllllllllllllllllllllllllllllll$	63–64 ^f	175(179°)	199–201(202°)	I
	2,4-DNP Yield (%)	I	87	95	58
	Isolated Yield (%)	55	82	06	60
	Reaction Time (t/min)	50	30	30	30
	Product	-t-Bu	CHO	\sim	$\langle \rangle$
	Reactant	OTMS -t-Bu	CH2OTMS	OTMS	OTMS
	Entry	96	L	×	9 ^g

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172–175(175–177 ^a) –	I	1	- 118(118.5-119.5 ¹)	
I	174(174–176 ^a)	193(193–195 ^a)	I	
Ι	Ι	I	48	
70	90	06	45	532 Pa).
30	15	15	50	Pa). Torr ∼
X	HO	MM	HO	Torr(~101080 it., (24)62.5, 4
A OTMS	HOMO MUCH	Motime Motion	otms otms	^a From ref. 21. ^b From ref. 22. ^c From ref. 23. ^c From ref. 23. At 760 Torr(\sim 101080 Pa). ^c Cis and trans isomers. ^f At 5 Torr(\sim 665 Pa) (lit., (24)62.5, 4 Torr \sim 532 Pa). ^g (+)-endo-Norborneol. ^h From ref. 25. ⁱ From ref. 26.
10	11	12	13	a Fron b Fron c Fron d

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. ¹H NMR spectra were recorded at 90 MHz on a JEOL EX-90 instrument with CDCl₃ as solvent and Me₄Si as an internal standard. Yields reported refer to isolated products or 2,4-dinitrophenyl-hydrazone 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 NaBrO₃ (0.755 g, 5 mmol) and NH₄Cl (0.400 g, 7.5 mmol) in aqueous acetonitrile (CH₃CN-H₂O = 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 MgSO₄. 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

- (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.
- (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.
- (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.
- Mahrwald, R.; Theil, F.; Schick, H.; Schwartz, S.; Palme, H.J.; Weber, G. J. Prakt. Chem. 1986, 77, 328.

TRIMETHYLSILYL ETHERS

- (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.
- 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.
- (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.
- (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.
- (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.
- 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.
- 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.
- 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

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