

OXIDATIVE DEPROTECTION OF TRIMETHYLSILYL ETHERS WITH TETRABUTYLAMMONIUM PERIODATE (TBAPI) IN THE PRESENCE OF $AlCl_3$ AND BF_3 IN APROTIC SOLVENTS[☆]

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ABSTRACT: Structurally different trimethyl silyl ethers are oxidized with Bu_4NIO_4 in the presence of $AlCl_3$ and BF_3 as catalysts in CH_3CN and $CHCl_3$ under reflux conditions. The corresponding carbonyl compounds are isolated in good yields.

KEY WORDS: Oxidative deprotection, Trimethylsilyl ethers, Tetrabutylammonium periodate, Aluminum chloride, Boron trifluoride.

Protection of functional groups plays a vital role in the total synthesis of complex organic molecules [1]. One of the most encountered functionality in organic molecules is alcohol hydroxy group. The protection of this functionality can be achieved by its conversion to a silyl ether by trimethylsilyl chloride (TMSC) and hexamethyldisilazane (HMDS) [2,3].

In recent years, much attention has been paid to direct oxidations of trimethylsilyl ethers [4]. Some of the methods are; Jones reagent [5,6], CrO_3/Py [7], PCC [7-9], PFC [10], PDC [9], $(Ph_3SiO)_2CrO_2/t-BuO_2H$ [11], $Ph_3SiOH/CrO_3/t-BuO_2H$ [12], DMSO/ $COCl_2$, DMSO/ SO_3Py , DMSO/ $ClSO_3H$, DMSO/ Ac_2O and DMSO/ P_2O_5 [13-15] reagents, NBS [16], DDQ [17, 18], Ph_3CBF_4 [19,20], Ce(IV)/ $NaBrO_3$ [21], $NaBrO_3$ or $AgBrO_3$ in the presence of $AlCl_3$ or BF_3 [22],

$[(NO_3)_3Ce]_2CrO_4$ [23,24] and $[(NO_3)_3Ce]_3H_2IO_6$ [25,26]. Some of the mentioned reagents encounter drawbacks such as; strong protic and aqueous media, unavailability of the reagent, long reaction times and low yields of the products.

Recently, we have paid attention to reactions which are catalyzed by Lewis acids, e.g. oxidations of different functionalities with sodium and silver bromates [27a], and tetrabutylammonium periodate [27b].

Now, we wish to report that tetrabutylammonium periodate; Bu_4NIO_4 (TBAPI) is also able to perform selective transformation of trimethylsilyl ethers to their corresponding carbonyl compounds in the presence of $AlCl_3$ and BF_3 , as catalysts, in dry CH_3CN and $CHCl_3$ under reflux conditions. Our experiments

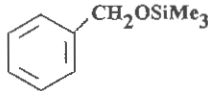
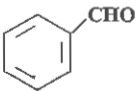
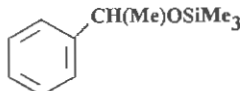
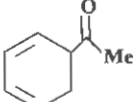
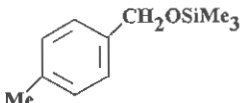
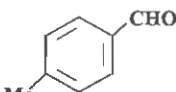
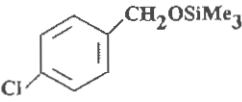
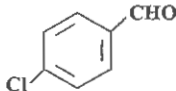
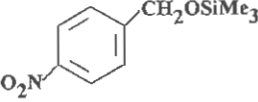
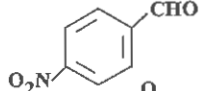
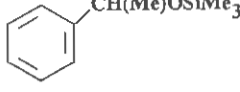
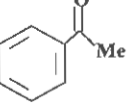
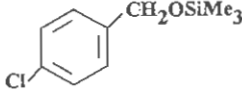
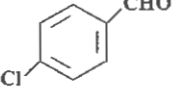
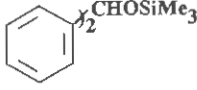
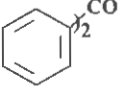
[☆] Dedicated to Professor Abbas Shafiee on the occasion of his 60th birthday.

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Table 1: Oxidative deprotection of benzylic trimethylsilyl ethers with TBAPI / AlCl₃ in refluxing CHCl₃

Entry	Substrate	Product	Subs./TBAPI/AlCl ₃	Reaction time(h)	Yield (%)
1			1 : 0.5 : 0.3	2	80
2			1 : 0.5 : 0.3	2	90
3			1 : 0.5 : 0.3	1.5	95
4			1 : 0.5 : 0.3	1.75	89
5			1 : 1 : 0.5	3	70
6			1 : 0.5 : 0	2	0 ^a
7			1 : 0.5 : 0	1.5	0 ^a
8			1 : 0.5 : 0.3	2	94

a: Without catalyst.

show that benzylic silyl ethers are oxidized in the presence of AlCl₃ in dry CHCl₃. The nature of the catalyst and the solvent is important for this purpose. Non-benzylic and saturated trimethylsilyl ethers are also oxidized with TBAPI but only in the presence of BF₃ in dry CH₃CN. Surprisingly, AlCl₃ is not an effective catalyst for this purpose and the starting materials are isolated from the reaction mixture intact.

Our results are tabulated in Tables 1 and 2. We have also compared the results of our experiments with some other methods reported in the literature, Table 3 [5,11,12].

In conclusion, our observations show that Bu₄NIO₄

is a selective reagent for the oxidative deprotection of trimethylsilyl ethers. This selectivity is effected by the nature of the Lewis acids and the solvents.

EXPERIMENTAL

All yields refer to isolated products, unless otherwise indicated. The purity of the compounds was determined by TLC or GC and the products were identified by the comparison of their IR, NMR and mp with authentic samples.

The oxidizing agent; tetrabutylammonium periodate was prepared according to the reported procedure [27].

Table 2: Oxidative deprotection of non-benzylic and saturated trimethylsilyl ethers with TBAPI/BF₃ in refluxing CH₃CN.

Entry	Substrate	Product	Subs./TBAPI/BF ₃	Reaction time(h)	Yield (%)
1			1:1:0.3	4	78
2			1:1:0.3	4	70
3			1:1:0.3	4	67 ^a
4			1:1:0.3	4	73 ^a
5			1:1:0.3 ^b	4	0
6			1:1:0.3 ^b	4	0

a : GC yield.

b : In the presence of AlCl₃

Oxidation of 4-methylbenzylsilyl ether to 4-methylbenzaldehyde as a typical procedure for conversion of benzylic trimethylsilyl ethers with TBAPI in the presence of AlCl₃

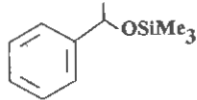
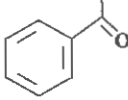
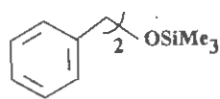
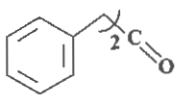
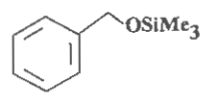
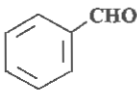
In a round-bottomed flask (50 mL) equipped with a condenser and a magnetic stirrer, a solution of 4-methylbenzylsilyl ether (0.194 g, 1 mmol) in CHCl₃ (15 mL) was prepared. TBAPI (0.217 g, 0.5 mmol) and AlCl₃ (0.04 g, 0.3 mmol) were added to the solution and the resulting mixture was refluxed for 2 hours. The reaction progress was followed by TLC (eluent: CCl₄/Et₂O:5/1). The reaction mixture was filtered through a short pad of silica gel (Type 60, Merck) and the filter cake was washed with CCl₄ (30 mL). The filtrate was evaporated and the residue was redissolved in ether (20 mL). The resulting brown solution was treated with sodium thiosulfate (20%, 20 mL) in order to reduce iodine. The aqueous layer was separated and the organic phase was washed with H₂O (2×20 mL). The ethereal phase was dried over

MgSO₄ and evaporated. The resulting crude material was purified on a silica gel plate or a silica gel column with appropriate eluent. Pure 4-methylbenzaldehyde was obtained, yield 0.114 g, 95% (Table 1).

Oxidation of 2-phenylethylsilyl ether to 2-phenylethanal as a typical procedure for conversion of alkyltrimethylsilyl ethers with TBAPI in the presence of BF₃

A solution of 2-phenylethylsilyl ether (0.194 g, 1 mmol), and BF₃ in Et₂O (0.1 mL, 0.3 mmol) and CH₃CN (10 mL) in a round-bottomed flask (50 mL) was prepared and was refluxed for 4 hours. The progress of the reaction was monitored by TLC (eluent: CCl₄/Et₂O: 5/1). The resulting reaction mixture was filtered from a short pad of silica gel (Type 60, Merck), and the filter cake was washed with CCl₄ (30 mL). The combined filtrates were evaporated and the resulting crude material was redissolved in ether (25 mL). The resulting brown solution was treated with

Table 3: Comparison of some of the results obtained with TBAPI and (1) $(\text{Ph}_3\text{SiO}_2)\text{CrO}_2$ [11], (2) $\text{CrO}_3/\text{H}_2\text{SO}_4/\text{acetone}$ [5] and (3) $\text{Ph}_3\text{SiOH}/\text{CrO}_3/t\text{-BuO}_2\text{H}$ [12].

Entry	Substrate	Product	TBAPI yield(h)	Other methods, yield % (h)		
				(1)	(2)	(3)
1			90(2)	97(14)	76(—)	98(15)
2			94(2)	98(14)	82(—)	99(24)
3			80(2)	42(14)	—	—

sodium thiosulfate (20%, 20 mL) in order to reduce iodine. The aqueous layer was separated and the ethereal phase was washed with H_2O (2×20 mL). The organic layer was separated and was dried over MgSO_4 . The solvent was evaporated and the resulting crude material was purified on a silica gel column with appropriate eluent to afford pure 2-phenylethanal, yield 0.094 g, 78% (Table 2).

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REFERENCES

- [1] Greene, T. W., "Protective Groups in Organic Synthesis", John Wiley and Sons, N.Y. (1981).
- [2] Lalonde, M. and Chan, T. H., *Synthesis*, 817 (1985) and references cited therein.
- [3] a) Firouzabadi, H. and Karimi, B., *Synthetic Commun.*, **12**, 1663(1993) and references cited therein.
b) Firouzabadi, H., Khayat, Z., Sardarian, A. R. and Tangestaninejad, S., *Iranian J. Chem. & Chem. Eng.*, **15**(2), 54(1996).
- [4] Muzart, J., *Synthesis*, **11**(1993), and references cited therein.
- [5] Baker, R., Rao, V. B., Ravenscroft, P. D. and Swain, C. J., *Synthesis*, 572(1983).
- [6] paquette, L. A., Lin, H. S., Gunn, B. P. and Coghlan, M. J., *J. Am. Chem. Soc.*, **110**, 5818 (1988).
- [7] Mahrwald, R., Theil, F., Schick, H., Schwart, S., Palme, H. J. and Weber, G., *J. Prakt. Chem.*, **77**, 328(1986).
- [8] Hart, T. W., Metcalfe, D. A. and Scheinmann, F., *J. Chem. Soc., Chem. Commun.*, 155(1979).
- [9] Denmark, S. E., Hammer, R. P., Weber, E. J. and Habermas, K. L., *J. Org. Chem.*, **52**, 165(1987).
- [10] Nonaka, T., Kanemoto, S., Oshima, K. and Nazaki, H., *Bull. Chem. Soc. Jpn.*, **57**, 2019(1984).
- [11] Muzart, J. and N'Ait Ajjou, A., *Synlett*, 497 (1991).
- [12] Muzart, J. and N'Ait Ajjou, A., *Synthetic Commun.*, **22**, 1993(1992).
- [13] Afonso, C. M., Barros, M. T. and Maycock, C. D., *J. Chem. Soc., Perkin Trans. I*, 1221(1987).
- [14] Tolstikov, G. A., Miftakhov, M. S., Vostrikov, N. S., Komissarova, N. G., Alder, M. E. and Kuznetsov, O. M., *Zh. Org. Khim.*, **24**, 224(1988); *Chem. Abst.*, **110**, 7162C(1989).
- [15] Tolstikov, G. A., Miftakhov, M. S., Alder, M. E., Komissarova, N. G., Kuznetsov, O. M. and Vostriko, N. S., *Synthesis*, 940(1989).
- [16] Marko, I. E., Mekhalfia, A. and Ollis, W. D., *Synlett*, 345(1990) and reference cited therein.
- [17] Narasimhan, N. S. and Bapat, C. P., *J. Chem. Soc., Perkin Trans. I*, 1435(1984).
- [18] Piva, O., Amougay, A. and Pete, J. P., *Tetrahed-*

- ron Lett., **32**, 3993(1991).
- [19] Jung, M. E., *J. Org. Chem.*, **41**, 1479(1976).
- [20] Jung, M. E. and Speltz, L. M., *J. Am. Chem. Soc.*, **98**, 7882(1978).
- [21] Olah, G. A., Gupta, B. G. B. and Fung, A. P., *Synthesis*, 897(1980).
- [22] Firouzabadi, H. and Mohammadpoor-Baltork, I., *Synthetic Commun.*, **24**, 1065(1994).
- [23] Firouzabadi, H., Iranpoor, N., Parham, H. and Toofan, J., *Synthetic Commun.*, **14**, 631(1984).
- [24] Firouzabadi, H. and Shiriny, F., *Synthetic Commun.*, **26**, 423(1996).
- [25] Firouzabadi, H., Iranpoor, N., Kiaeezadeh, F. and Toofan, J., *Synthetic Commun.*, **14**, 973(1984).
- [26] Firouzabadi, H. and Shiriny, F., *Synthetic Commun.*, **26**, 649(1996).
- [27] a) Firouzabadi, H. and Mohammadpoor-Baltork, I., *Bull. Chem. Soc., Jpn.*, **68**, 2319(1995) and references cited therein.
b) Firouzabadi, H., Sardarian, A. R. and Badparva, H., *Bull. Chem. Soc. Jpn.*, **68**, 2595(1996).
- [28] Santaniello, E., Manzochi, A. and Farachi, C., *Synthesis*, 563(1980).