



Silica chloride in the presence of NaI is a useful system for the efficient and selective conversion of TMS, TBDMS and THP ethers into their corresponding iodides

Habib Firouzabadi,* Nasser Iranpoor* and Hassan Hazarkhani

Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

Received 2 July 2002; revised 3 August 2002; accepted 15 August 2002

Abstract—Direct and highly selective conversion of benzylic, allylic and propargylic TMS, TBDMS and THP ethers into their corresponding iodides with the SiO₂-Cl/NaI system is described. Reactions were conducted in CH₃CN at room temperature. Aliphatic silyl and tetrahydropyranyl ethers remained almost intact under similar reaction conditions. © 2002 Published by Elsevier Science Ltd.

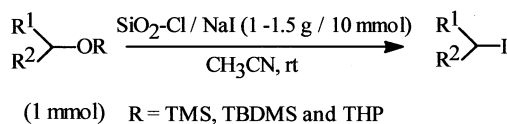
The utility of the trialkylsilyl group and dihydropyran as protecting groups for hydroxy functions during multi step synthesis has been well documented.¹ Direct transformation of silyl and tetrahydropyranyl ethers into the corresponding halides is an attractive^{2a-d} method for the generation of iodides which are important precursors for the preparation of organometallics and also free radical reactions as well as nucleophilic substitutions.^{2d-i} The effective use of TMSI for the conversion of alcohols to the corresponding iodides has been well recognized.³ Moreover, it has been shown that chlorosilanes in combination with iodide anion convert alcohols to the iodides⁴ via in situ generation of iodosilanes. In addition, solid supports have found wide applications in organic reactions.⁵ They mostly facilitate the work-up of the reaction and usually high selectivity accompanied with high yields of the products are observed. Silica gel is one of the extensively used supports for different purposes in organic chemistry.⁶ Modified silica supports for functional group transformation are also of interest. Silica chloride has been reported to be an efficient reagent for the preparation of sulfobenzylsilica,^{7a} the selective thioacetalization of

carbonyl compounds,^{7b} transformation of sulfoxides to thioethers^{7c} and the selective tetrahydropyranlation of symmetrical diols.^{7d} We have used our high capacity silica chloride for transthoacetalization of acetals^{7e} and transformation of acylals into 1,3-dithiolanes, 1,3-dithianes and 1,3-oxathiolanes,^{7f} dehydration of tertiary benzylic alcohols,^{7g} deprotection of thioacetals and ring expansion of cyclic thioacetals.^{7h} We now report that solid silica chloride in the presence of NaI can be efficiently employed for the preparation of iodides under heterogeneous conditions. This system has been successfully used for direct and highly selective conversion of benzylic, allylic and propargylic TMS, TBDMS and THP-ethers into their corresponding iodides in high yields (Scheme 1, Table 1).

As shown in Table 1, primary and secondary benzylic TMS, TBDMS and THP-ethers were easily converted into their benzylic iodides in good to excellent yields. Allylic and propargylic TMS, TBDMS and THP-ethers were smoothly converted to their iodides in good yields. However, aliphatic TMS, TBDMS, THP-ethers survived under similar reaction conditions.

In order to show the high selectivity of the method, we have carried out the successful conversion of a benzylic TMS-ether in the presence of a secondary aliphatic one in a single molecule (Scheme 2). The structure of the product was determined by NMR spectroscopy and chemical reactions.

In summary, this system is efficient, cheap, and easily available and reacts under mild reaction conditions for



Scheme 1.

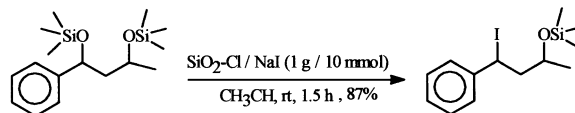
* Corresponding authors.

Table 1. Selective conversion of TMS, TBDMS and THP ethers into their corresponding iodides by the silica chloride/NaI system in CH₃CN

Entry	Substrate	time	Si-Cl / NaI / Sub.	Yield ^{a,b}
		(h)	(g / mmol / mmol)	
1		1	1: 10: 1	90
2		0.75	1: 10: 1	91
3		1.5	1: 10: 1	89
4		0.5	1: 10: 1	92
5		1.5	1: 10: 1	90
6		1	1: 10: 1	89
7		0.75	1: 10: 1	90
8		2	1: 10: 1.8	80
9		2.5	1: 10: 1	76
10		0.75	1: 10: 1	91
11		1	1: 10: 1	90
12		1.5	1: 10: 1	89
13		1	1: 10: 1	90
14		2	1: 10: 1	89
15		1.25	1: 10: 1	91
16		1.5	1: 10: 1	89
17		1	1: 10: 1	90
18		2.5	1: 10: 1	81
19		3	1: 10: 1	79
20		1	1.2: 10: 1	91
21		0.75	1.2: 10: 1	92
22		0.75	1.2: 10: 1	90
23		1	1.2: 10: 1	92
24		0.75	1.2: 10: 1	90
25		1.5	1.5: 10: 1	83
26		2	1.2: 10: 1	80

a) Isolated yields. b) Structures were confirmed by IR, ¹H-NMR, ¹³C-NMR, mp / bp.

the selective preparation of iodides from their silyl and tetrahydropyranyl ethers. The handling of this solid heterogeneous system is much easier than using the expensive, corrosive and highly reactive liquid

**Scheme 2.**

trimethylsilyl iodide (TMSI) with hazardous vapors. This system can also be used at elevated temperatures where required very easily. Work-up of the reaction mixtures is easy and the reactions are not time-consuming.

Typical procedure for the conversion of TMS, TBDMS and THP-ethers into their corresponding iodides: To a solution of sodium iodide (2.25 g, 10 mmol) in CH₃CN (30 mL), silica chloride (1–1.5 g)^{7c} and the ether (2 mmol) were added and the resulting mixture was stirred at room temperature. After completion of the reaction (Table 1, TLC, *n*-hexane/EtOAc, 5/1), powdered Na₂S₂O₃ (0.5 g) was added to the mixture (to destroy the liberated iodine in the reaction mixture) and the solvent was evaporated under reduced pressure. The resulting solid mixture was added to a silica gel pad (5 cm thick) and was washed with petroleum ether (bp 60–80°C, 150 ml). The resulting solution was evaporated to dryness to afford the almost pure iodide in good to excellent yields.

Acknowledgements

The authors are thankful to the Shiraz University Research Council for the support of this work.

References

- (a) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1991; (b) Lalonde, M.; Chan, T. H. *Synthesis* **1985**, 817; (c) Van Boom, J. H.; Herschied, J. D. M.; Reese, C. B. *Synthesis* **1973**, 169.
- (a) Firouzabadi, H.; Iranpoor, N.; Shaterian, H. *Synlett* **2000**, 65–66; (b) Aizpurua, J. M.; Cossio, F. P.; Palomo, C. *J. Org. Chem.* **1986**, *51*, 4941; (c) Mattes, H.; Benezra, C. *Tetrahedron Lett.* **1987**, *28*, 659; (d) Kim, S.; Park, J. H. *J. Org. Chem.* **1988**, *53*, 3111; (e) Tanaka, A.; Oritani, T. *Tetrahedron Lett.* **1997**, *38*, 7223; (f) Hwang, Y. C.; Fowler, F. W. *J. Org. Chem.* **1985**, *50*, 2719; (g) Brown, G. W. In *The Chemistry of the Hydroxyl Group*; Patai, S.; Ed.; Interscience: London, 1971; Part 1, pp. 592–622; (h) Wolfe, S.; Godfrey, J. C.; Holdrege, C. T.; Perron, Y. G. *Can. J. Chem.* **1968**, *46*, 2549; (i) Ansell, M. F. In *The Chemistry of Acyl Halides*; Patai, S., Ed.; Interscience: London, 1972; Chapter 2, pp. 35–68; (j) Lee, J. B.; Nolan, T. J. *Can. J. Chem.* **1966**, *44*, 1331.
- (a) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 612; (b) See also Olah, G. A.; Narang, S. C. *Tetrahedron Lett.* **1982**, *38*, 2225.

4. (a) Morita, T.; Yoshida, S.; Okamoto, Y.; Sakurai, H. *Synthesis* **1979**, 37; (b) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Hussanian, A.; Singh, B. P.; Mehrotra, A. K. *J. Org. Chem.* **1983**, 48, 3667.
5. (a) McKillop, A.; Young, D. W. *Synthesis* **1979**, 401; (b) Cornelis, A.; Laszlo, P. *Synthesis* **1985**, 909.
6. (a) Keinan, E.; Mazur, Y. *J. Org. Chem.* **1978**, 43, 1020; (b) Tal, D. M.; Keinan, E.; Mazur, Y. *Tetrahedron* **1981**, 37, 4327; (c) Onofrio, F. D.; Scettri, A. *Synthesis* **1985**, 1159; (d) Chávez, F.; Suárez, S.; Díaz, E. *Synth. Commun.* **1994**, 24, 2325; (e) Nishiguchi, T.; Kamio, C. *J. Chem. Soc., Perkin Trans. 1* **1989**, 707.
7. (a) Saunders, D. H.; Barford, R. A.; Magidman, P.; Olszewski, L. T.; Rothbart, H. L. *Anal. Chem.* **1974**, 46, 834; (b) Kamitori, Y.; Hojo, M.; Masuda, R.; Kimura, T.; Yoshida, T. *J. Org. Chem.* **1986**, 51, 1427; (c) Mohanazadeh, F.; Momeni, A. R.; Ranjbar, Y. *Tetrahedron Lett.* **1994**, 6127; (d) Ravindranath, N.; Ramesh, C.; Das, B. *Synlett* **2001**, 1777; (e) Firouzabadi, H.; Iranpoor, N.; Karimi, B.; Hazarkhani, H. *Synlett* **2000**, 263; (f) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. *Phosphorus Sulfur Silicon* **2002**, 174, 165; (g) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H.; Karimi, B. *Synth. Commun.*, in press; (h) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H.; Karimi, B. *J. Org. Chem.* **2002**, 67, 2572–2576.