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Silica Chloride (SiO₂-Cl), a New Heterogeneous Reagent, for the Selective and Efficient Conversion of Benzylic Alcohols to Their Corresponding Chlorides and Iodides

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Silica Chloride (SiO₂-Cl), a New Heterogeneous Reagent, for the Selective and Efficient Conversion of Benzylic Alcohols to Their Corresponding Chlorides and Iodides

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ABSTRACT

Structurally different benzylic alcohols were efficiently converted to their corresponding chlorides by silica chloride (SiO₂-Cl) in CHCl₃ at room temperature. Silica chloride is also able to convert benzylic alcohols to their iodides in the presence of NaI in a mixture of CH₃CN/CHCl₃ in excellent yields.

Key Words: Silica chloride; Benzylic alcohols; Benzylic chlorides; Benzylic iodides.

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INTRODUCTION

Generation of halides from corresponding alcohols^[1,2] is an important transformation in organic synthesis. The important role of halides in the carbon-carbon bond formation by organometallic and free radical reactions as well as nucleophilic substitution has been well documented.^[3] One of the most commonly used reagent for this purpose is thionyl chloride that can be applied alone or in combination with bases. However, the reactions are invariably slow and often require reflux conditions.^[4] Recently a modified procedure is reported in which thionyl chloride has been used in the presence of benzotriazole at room temperature for this purpose.^[5] It is also reported that iodine in petroleum ether at 60–80°C can directly convert alcohols to their corresponding iodides with rather low yields.^[6] It has also been established that alcohols can be converted to the corresponding iodides or bromides by the reaction of TMSI or TMSBr respectively.^[19,20] However, similar reaction does not occur with the less reactive TMSCl alone, although, it has been shown that the transformation can be accomplished with TMSCl when a catalytic amount of SeO_{2} ,^[2] BiCl₃,^[7] or DMSO^[8] has been employed. In recent years, we have paid attention to the preparation of the high capacity silica chloride and to explore its synthetic utilities as a catalyst and as a reagent in organic reactions.^[9-13]

RESULTS AND DISCUSSIONS

In continuation of this study we have found that in contrast to TMSCl alone, silica chloride can be simply applied specifically for the conversion of aryl alcohols to their corresponding chlorides (Sch. 1).

Compounds under this study were primary, secondary, allylic, propargylic, and benzylic alcohols. Among different solvents such as; CHCl₃, CH₃CN, THF, and CH₂Cl₂, chloroform turned out to be a suitable solvent for this transformation. Our preliminary observations showed that, except benzyl alcohol (Table 1, Entry 1), chlorination of



 R^1 , R^2 = Aryl or R^1 , R^2 = Activated aryl and H

Scheme 1.

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Entry	R^1	R	Time (h)	Yield ^{a,b} (%)
1	Ph	Н	24	27 ^{c,[14]}
2	p-MeC ₆ H ₄	Н	5	88 ^[15]
3	<i>p</i> -MeOC ₆ H ₄	Н	0.75	93 ^[1]
4	Ph	Et	4	90 ^[6]
5	Ph	Ph	5	89 ^[15]
6			4.5	89 ^{d,[16]}
7			5	87 ^{d,[17]}
8	PhCH ₂ CH ₂ CH ₂	Н	24	NR
9	$CH_3 (CH_2)_5$	Me	24	NR
10	$CH_3 (CH_2)_4$	HC≡C	24	20 ^{c,[15]}
11	CH ₃ (CH ₂) ₄	$H_2C=CH$	24	23 ^{c,[18]}

Table 1. Chlorination of alcohols using silica chloride (SiO₂-Cl).

^aIsolated yields.

 $^{b1}\text{H}\,\text{NMR}$ and $^{13}\text{C}\,\text{NMR}$ of some of the halides are given in the Ref. $^{[13]}$

°GC yields.

^dLess than 10% of the reaction mixture was composed of the corresponding benzylic alkenes.

substituted benzyl alcohols with electron-donating groups such as $-CH_3$ and $-OCH_3$ proceeded very well in high yields at room temperature in the presence of this reagent (Table 1, Entries 2, 3). Conversion of a variety of secondary benzylic alcohols to the corresponding chlorides was also achieved in good to excellent yields under similar reaction conditions (Table 1, Entries 4–7). Moreover, we have found that primary and secondary aliphatic alcohols remained intact in the presence of this reagent in CHCl₃ at room temperature (Table 1, Entries 8, 9). However, we also noticed that the presented procedure was not satisfactory for the efficient conversion of allylic and propargylic alcohols to their corresponding chlorides (Table 1, Entries 10,11).

The earlier works of Jung^[19] and Olah^[20] showed the effective use of TMSI and TMSBr for the conversion of alcohols to the corresponding halides. Moreover, it has been shown that chlorosilanes in combination with iodide and bromide anions convert alcohols to iodides and bromides via in situ generation of iodo- and bromosilanes respectively. These

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$$R^{1} \xrightarrow{OH} R^{2} \xrightarrow{SiO_{2} \longrightarrow Cl(NaI)} R^{1} \xrightarrow{I} R^{2}$$

$$R^{1} = aryl, alkyl \quad R^{2} = aryl, alkyl, H$$
Scheme 2.

results prompted us to study the possibility of the in situ formation of inorganic solid analogs of iodo- and bromosilanes by the reaction of silica chloride with iodide and bromide anions. We first examined in situ generation of silica iodide by the reaction of silica chloride with a solution of molar excess of NaI in a CH₃CN/CHCl₃ solvent system. After 120 min, the reaction of benzyl alcohol with the resulting silica iodide was studied. We have observed that, in contrast to silica chloride, in this case, the reaction proceeded well to afford benzyl iodide in 89% isolated yield (Sch. 2, Table 2, Entry 1).

This result encouraged us to investigate the ability of the in situ generated silica iodide for the conversion of the other structurally different alcohols to their iodides. We have found that different types of primary benzylic alcohols with electron-donating and electron-withdrawing substituents and also secondary benzylic alcohols were converted to the corresponding iodides in good to excellent yields (Table 2, Entries 2-6). Surprisingly, iodination of the alcohol (Table 2, Entry 7) was accompanied with the elimination reaction and the corresponding alkene was obtained in 92% yield. Interestingly, allylic and propargylic alcohols were converted to the corresponding iodides in moderate to good yields upon treatment with the in situ generated silica iodide (Table 2, Entries 8, 9). However, this method was not suitable for the conversion of primary and secondary aliphatic alcohols to their iodides (Table 2, Entries 10, 11). Unfortunately, our efforts for the preparation of alkyl and benzyl bromides using in situ generated silica bromide (silica chloride treated with an excess of LiBr) were not satisfactory, and in most cases, a mixture of the chloride and bromide was formed in the reaction mixture.

EXPERIMENTAL

General. Silica chloride (SiO₂-Cl) was prepared according of the reported procedure.^[8] IR spectra were recorded on a Perkin-Elmer 781

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Table 2.	Iodination	of alcohols	using	silica	chloride	(SiO ₂ -Cl)/NaI	in	а
mixture of	f CHCl ₃ /CH	I ₃ CN.						

Entry	R^1	\mathbb{R}^2	Time (h)	Yield ^{a,b,ref} (%)
1	Ph	Н	2	89 ^[5]
2	$p-MeC_6H_4$	Н	1.3	91 ^[17]
3	<i>p</i> -MeOC ₆ H ₄	Н	1	90 ^[17]
4	$p-\mathrm{ClC}_6\mathrm{H}_4$	Н	3	88 ^[17]
5	Ph	Et	1.5	89 ^[17]
6	Ph	Ph	2	86 ^[17]
7	and a second sec		1.5	92 ^{d,[15]}
8	9-(Hydroxymethyl) anthracene		4	80 ^[21]
9	1,4-Benzenedimethanol		5	88 ^[15]
10	Cinnamyl alcohol		2	89 ^{b,[22]}
11	$CH_3 (CH_2)_4$	HC≡C	2	NR ^c
12	$CH_3(CH_2)_4$	H ₂ C=CH	2	NR ^c
13	PhCH ₂ CH ₂ CH ₂	Н	2	NR ^c
14	CH ₃ (CH ₂) ₅ Me	Me	2	NR ^c

^aIsolated yields.

^bReactions were performed at room temperature with the ratio of substrates: silica chloride: NaI 1mmol/1g/3 mmol.

^c4 mmol NaI was used.

^dGC yields.

spectrophotometer.¹H NMR and ¹³C NMR spectra were run on a Bruker Avance DPX 250 MHz instrument. Mass spectra were run on a Shimadzu GC MS-QP 1000 EX. Products are known and they were identified by the comparison of their spectra and physical constants with authentic samples.

Conversion of 4-methoxybenzyl alcohol to 4-methoxybenzyl chloride, a typical procedure. To a solution of 4-methoxybenzyl alcohol (0.69 g, 5 mmol) in CHCl₃ (25 mL), silica-chloride (5 g) was added and the resulting mixture was stirred at room temperature for 0.75 h. After completion of the reaction (TLC, *n*-hexane/EtOAc, 5/1), the mixture was filtered through a silica gel pad (3 cm thick). Evaporation of the solvent afforded liquid 4-methoxybenzyl chloride in 93% yield (Table1, entry 3).

Conversion of benzyl alcohol to benzyl iodide. To a solution of sodium iodide (2.25 g, 15 mmol) in CHCl₃/CH₃CN (15/10 mL), silica chloride (5g) was added and stirred for 5 min. To the resulting mixture, benzyl

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alcohol (0.54 g, 5 mmol) was added and the resulting mixture was stirred at room temperature for 2 h. After completion of the reaction (TLC, *n*-hexane/EtOAc, 5/1), Na₂S₂O₃ powder (0.5 g) was added to the mixture and the solvent was evaporated under reduced pressure. The resulting solid mixture was added on a silica gel pad (5 cm thick) and was washed with petroleum ether (200 mL). After filteration, the solvent was evaporated to dryness to afford pure benzyl iodide in 89% yield as a low melting yellow crystalline compound (Table 2, Entry 1).

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REFERENCES

- Carey, F.A.; Soundberg, R.S. Advanced Organic Chemistry; A plenum/Rosetta Ed.: New York, 1980; (b) Larock, R.C. Comprehensive Organic Transformation: A Guide to Functional Group Preparation; VCH Publishers: New York, 1989, 358 pp; Lee, J.G.; Kang, K.K. J. Org. Chem. 1988, 53, 3634.
- 2. Naso, F.; Marchese, G. *The Chemistry of Halides, Pseudi-Halides and Azides*; Patai, S., Rappoport, Z.J., Eds.; Wiley: New York, 1983.
- Giese, B. Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds; Pergamon Press: Oxford, 1986.
- (a) Hwang, Y.C.; Fowler, F.W. J. Org. Chem. 1985, 50, 2719;
 (b) Brown, G.W. *The Chemistry of the Hydroxyl Group*; Patai, S., Ed.; Interscience: London, 1971; Part 1, 592–622 pp; (c) Wolfe, S.; Godfrey, J.C.; Holdrege, C.T.; Perron, Y.G. Can. J. Chem. 1968, 46, 2549; (d) Ansell, M.F.; In *The Chemistry of Acyl Halides*, Patai, S., Ed.; Interscience: London, 1972; Chapter 2, 35–68 pp; (e) Lee, J.B.; Nolan, T.J.; Can. J. Chem. 1966, 44, 1331.
- 5. Chaudhari, S.S.; Akamanchi, K.G. Synlett **1999**, 1763 and the references cited therein.
- 6. Joseph, R.; Pallan, P.S.; Sudalai, A.; Ravindranathan, T. Tetrahedron Lett. **1995**, 609 and the references cited therein.
- 7. Labrouiilere, M.; Roux, K.K.; Gaspard-Iloughmane, H.; Dubac, J. Synlett **1994**, 723 and the references cited therein.
- 8. Snyder, D.C. J. Org. Chem. **1995**, *60*, 2638 and the references cited therein.

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Conversion of Benzylic Alcohols

- Firouzabadi, H.; Iranpoor, N.; Karimi, B.; Hazarkhani, H. Synlett 2000, 163.
- Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. Phosphorus, Sulfur and Silicon 2002, 177, 2847.
- 11. Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. Phosphorus, Sulfur and Silicon **2001**, *176*, 165.
- (a) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. Tetrahedron Lett. 2002, 43, 7139; (b) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. Phosphorus, Sulfur and Silicon 2003, 178, 149.
- Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. J. Org. Chem. 2002, 67, 2572.
- 14. Ort, O. Org. Synth. 1987, 65, 203.
- 15. *Handbook of Chemistry and Physics*, 80th Ed.; CRC Press: 1999–2000.
- Bellesia, F.; Ghelfi, F.; Pagnoni, U.M.; Pinetti, A. Gazz. Chem. Ital. 1992, 122, 437.
- 17. Aizipurua, J.A.; Lecea, B.; Palomo, C. Can. J. Chem. 1986, 64, 2342.
- Matveeva, E.D.; Evin, A.S.; Mitroshin, D.B.; Kurts, S.A.L. Zh. Org. Chem. 1995, 31, 1121 (Russ); Chem. Abst. 1996, 124, 342584h.
- (a) Jung, M.E.; Ornstein, P.L. Tetrahedron Lett. 1977, 2659; (b) Jung, M.E.; Hatfield, G.L. Tetrahedron Lett. 1978, 4483.
- (a) Olah, G.A.; Narang, S.C.; Gupta, B.G.B.; Malhotra, R. J. Org. Chem. 1980, 9, 1638.
- Yoa, J.H.; Chiang, H.L.; Chiang, P.C. Zhongguo Huanging Gongcheng Xuekan. 1995, 5, 291 (Ch); Chem. Abst. 1996, 124, 240565k.
- (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.

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