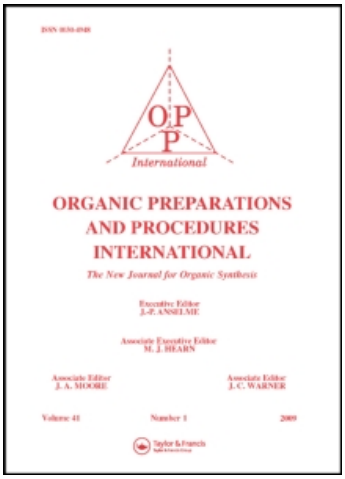

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

CONVERSION OF ALCOHOLS TO ALKYL CHLORIDES WITH SILICA CHLORIDE

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To cite this Article Mohanazadeh, F. and Momeni, A. R.(1996) 'CONVERSION OF ALCOHOLS TO ALKYL CHLORIDES WITH SILICA CHLORIDE', Organic Preparations and Procedures International, 28: 4, 492 — 494
To link to this Article: DOI: 10.1080/00304949609356562
URL: http://dx.doi.org/10.1080/00304949609356562

Acknowledgments.- This work has been supported by the National Natural Science Foundation of China and National Laboratory of Elemento-Organic Chemistry.

REFERENCES

1. F. R. Atherton and A. R. Todd, *J. Chem. Soc.*, 674 (**1947**).

2. D. Houalla, Z. Bounza. S. Skouta, L. Riesel and D. Lindemann, *Tetrahedron Lett.*, **33**, 2817 (1992).

3. L. Z. Liu, G. W. Li, X. Z. Zeng, L. B. Fu and R. Z. Cao, *Heteroatom Chem.*, **7**, 131 (1996).

4. R. Burgada, H. Germa, M.Willson and F. Mathis, *Tetrahedron*, **27**, 5833 (1971).

5. L. Z. Liu, G. W. Li and M. Z. Huang, *Phosphorus, Sulfur, and Silicon*, **69**, 1 (1992).

6. D. Houalla, T. Mouheich, M. Sanchez and R. Wolf, *Phosphorus*, **5**, 229 (1975).

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CONVERSION OF ALCOHOLS TO ALKYL CHLORIDES WITH SILICA CHLORIDE

Submitted by (03/08/96)

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The importance of alkyl halides in the formation of carbon-carbon bonds by nucleophilic substitution is well established. A variety of procedures for converting alcohols, the most common precursors of alkyl halides, have been developed.[1] The choice of the appropriate reagent is usually dictated by the sensitivity of the alcohol and other functional groups present in the molecule. The last two decades have witnessed an explosive growth in the use of organosilicon reagents in organic chemistry.[2,3] For example, alcohols can be converted to alkyl iodides with iodotrimethylsilane.[4] However, the reaction of alcohols with chlorotrimethylsilane generates trimethylsilyl ethers and not alkyl chlorides.[4] We now report a simple and efficient method for the conversion of alcohols into chlorides under mild conditions *via* treatment of the alcohols with silica chloride.

This reagent converts primary, secondary, and tertiary alcohols to corresponding alkyl chlorides in high yield. A racemic mixture of the alkyl chloride was obtained from the reaction of an optically pure (+)-2-butanol with silica chloride. A comparison of the present results with those reported earlier,[7,8] clearly indicates that silica chloride is a more effective reagent than thionyl chloride because

lower temperature and shorter reaction time. For example, the reaction time for chlorination of 1-hexanol is 30 min. (80%) at *room temperature* compared to 3 hrs with thionyl chloride at 76° (63%).[8] Non-polar solvents, such as CCl_4 or CH_2Cl_2 are ideal for the reaction while polar solvents such as DMSO or DMF are not suitable.

TABLE. Conversion of Alcohols to Alkyl Halides

R	Temp. (°C)	Time (min.)	Yield (%)[a] RCl	ROH	bp (torr) (°C)	lit.
Benzyl	25	3	90[a]	10[c]	178-180	179[9]
Benzyl	76	15	85[b]		178-180	179
1-Hexyl	25	30	80[a]	20[c]	132-135	134[10]
1-Hexyl	76	180	65[b]		132-135	134
Cyclohexyl	25	30	85[a]	15[c]	183-186	184-186[11]
Cyclohexyl	76	180	62[b]		183-186	184-186
1-Phenyl-2-propyl	25	30	80[a]	20[c]	202-205 (720)	200-205[12]
1 -Phenyl-2-propyl	76	180	60[b]		202-205	200-205
3-Methyl-1-butyl	25	30	80[a]	20[c]	100-102	98.5[13]
3-Methyl-1-butyl	76	180	40[b]		100-102	98.5
tert-Butyl	25	5	90[a]	10[c]	50-52	51[14]
tert-Butyl	76	180	24[b]		50-52	51
1-Adamantyl	25	30	75[a]	25[c]	165-166[d]	165[1]
(+)-2-Butyl[e]	25	30	80[a]	20[c]	68-69	68[13]

a) Chlorination with silica chloride. b) Chlorination with thionyl chloride in CCl_4. c) Recovered. d) Melting point. e) A racemic mixture of 2-butyl chloride was obtained.

EXPERIMENTAL SECTION

The ^1H NMR were recorded on a Varian EM 360A NMR spectrometer using tetramethylsilane as internal standard. Infrared spectra were taken on a Perkin-Elmer 267 spectrophotometer. Thin layer chromatography was performed on silica gel (Macerey-Nagel Co., Plygram Sil G/uv). Comparison of spectral data (^1H NMR, IR) and thin layer chromatography with authentic samples confirmed structure and purity of the reported halides.

Preparation of Silica Chloride.- Silica chloride was obtained according to a reported procedure.[5] Thus, 6 g silica gel (Art 7731 for TLC from Merck, Darmstadt, FRG) was refluxed with thionyl chloride (50 mL), with exclusion of atmospheric moisture, for 18 hrs. The resulting grayish powder is kept in desiccator. The amount of chlorosilyl groups (0.9 mmole of Cl/g silica) was determined by standard methods.[6]

General Procedure for Conversion of Alcohols to Alkyl Chlorides.- The alcohol (0.9 mmole) and silica chloride (2 g) were mixed in CCl_4 (4 mL) at room temperature, with exclusion of atmospheric moisture, for the time period specified in the Table. The progress of reaction was monitored by TLC and GC. After progress of reaction was complete, the mixture was filtered using suction. Removal of the solvent from the filtrate led to the pure product (GC and NMR). The filter cake was washed with acetone and the wash was evaporated to give the unreacted alcohol.

REFERENCES

1. R. C. Larock, *Comprehensive Organic Transformations: A Guide to Functional Group Preparations,* VCH Publisher, Inc., New York, NY, 353 (**1989**).
2. W. C. Groutas and D. Felker, *Synthesis,* 861 (**1980**).
3. F. Jin, B. Jiang and Y. Xu, *Tetrahedron Lett.*, **33**, 1221 (1992).
4. M. E. Jung and P. L. Ornstein, *ibid.*, 2659 (**1977**).
5. D. H. Saunders, R. A. Barford, P. Magidman, L. T. Olszewski and H. L. Rothbart, *Anal. Chem.*, **46**, 834 (1979).
6. W. F. Hillbrand and G. E. F. Lundell, *Applied Inorganic Analysis,* J. Wiley & Sons, New York, 590 (**1953**).
7. R. H. Clark and H. R. L. Streight, *Trans. Roy. Soc. Can.*, **23**, 77 (1929).
8. A. I. Vogel, *J. Chem. Soc.*, 636 (**1943**).
9. A. I. Vogel, *Practical Organic Chemistry,* Longmans, London, 538 (**1959**).
10. S. A. Mumford and J. W. C. Phillips, *J. Chem. Soc.*, 75 (**1950**).
11. *The Merck Index,* Merck & Co., Inc., Rahway, NJ, 9th Ed., 2739 (**1976**).
12. Z. N. Nazarova and I. P. Tsukervanik, *J. Gen. Chem. USSR*, **14,** 77 (1944).
13. J. F. Norris and H. B. Taylor, *J. Am. Chem. Soc.*, **46**, 756 (1924).
14. W. Gerrard, M. J. D. Isaacs, G. Machell, K. B. Smith and P. L. Wyvili, *J. Chem. Soc.*, 1920 (**1953**).
15. H. Stetter and M. Schwarz and A. Hirschhorn, *Chem. Ber.*, **92**, 1629 (1959).

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