Pergamon

Tetrahedron Letters, Vol. 35, No. 33, pp. 6127-6128, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01211-3

Deoxygenation of Sulfoxides with Silica Chloride.

Farajollah Mohanazadeh*, Ahmad Reza Momeni and Yousef Ranjbar

Institute of Chemistry, Mazandaran University, Babolsar, Iran

Abstract: Deoxygenation of sulfoxides to sulfides has been achieved in a simple procedure using silica chloride.

Deoxygenation of sulfoxide to sulfide is an important synthetic transformation in organic chemistry. Many reagents and methodologies[1-3] are developed for the deoxygenation of sulfoxides. One of the reported reagents for deoxygenation of sulfoxides is iodotrimethylsilane.[4] Its handling does not need special precaution and the work up of reaction mixture is not time consuming. This reagent is however, expensive.

In this paper, we wish to report a new application for silica chloride. We investigate the reaction of sulfoxides with silica chloride. The present method is mild and effective, using an inexpensive reagent, and thus offering significant advantages.

$$\mathrm{RSOR} \xrightarrow{\text{silica chloride}} \mathrm{RSR}$$

Silica chloride is obtained from reaction of silica gel (Art 7731 for TLC from Merck, Darmstadt, FRG) and thionyl chloride according to a literature procedure.[5] The amount of chlorosilyl groups (0.9 mmole of Cl/g silica) is determind by a standard method.[6] The resulting greyish powder is kept in a dessicator.

In a typical procedure the sulfoxide (0.9 mmole) and chlorinated silica (2 g) are mixed in an aprotic solvent, e.g. carbon tetrachloride (10 mL) or dichloromethane, at room temperature with exclusion of atmospheric moisture, for the time period specified in the Table. The corresponding sulfide is isolated in a pure state by simple filtration and evaporation of the solvent. Deoxygenation of both alkyl and aryl sulfoxides takes place very smoothly without any side product formation. In the case of methyl sulfoxide, the product is methyl chloromethyl sulfide, rather than the expected dimethyl sulfide.

A comparison of the results presented in this article with that reported earlier[4] clearly indicates that chlorinated silica is a more effective reagent than iodotrimethylsilane and bromotrimethylsilane. For example, the reaction time for deoxygenation of phenyl sulfoxide is 3 min. (81%). This time for iodotrimethylsilane and bromotrimethylsilane is respectively 2 h (73%) and 48 h (reflux, mixture of products).

Table. Conversion of sulfoxides to corresponding sulfides.

entry	substrate	product	time[a] (min)	yield[b] (%)
1	methyl sulfoxide	methyl chloromethyl sulfide	10	90
2	isopropyl sulfoxide	isopropyl sulfide	10	73
3	*tert* -butyl sulfoxide	*tert* -butyl sulfide	10	67
4	*sec* -butyl sulfoxide	*sec* -butyl sulfide	10	71
5	phenyl sulfoxide	phenyl sulfide	3	81
6	benzyl sulfoxide	benzyl sulfide	10	90
7	*n* -butyl sulfoxide	*n* -butyl sulfide	10	75

[a] The course of reaction was checked by TLC and GC. [b] Yield of isolated pure product.

Also, we prepared silica iodide (0.2 mmole of I/g silica) from reaction of silica gel with triphenylphosphine diiodide.[7] This reagent was not able to convert sulfoxide to sulfide. It seems the amount of iodide attached to the silica, was insufficient to progress the reaction.

In conclusion, silica chloride thus appears to be a mild and efficient reagent for deoxygenation of sulfoxides to the corresponding sulfides in high yield. Moreover, the easy availability of this reagent makes this simple procedure attractive and a practical alternative to the existing methods.

References

1. For a review, Madesclaire, M. *Tetrahedron* **1988**, 44, 6537-6580.
2. Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *Synthesis* **1979**, 61-62.
3. Olah, G. A.; Husain, A.; Singh, B. P.; Mehrotra, A. K. *J. Org. Chem.* **1983**, 48, 3667-3672.
4. Olah, G. A.; Gupta, B. G. B.; Narang, S. C. *Synthesis* **1977**, 583-584.
5. Saunders, D. H.; Barford, R. A.; Magidman, P.; Olszewski, L. T.; Rothbart, H. L. *Anal. Chem.* **1974**, 46, 834-838.
6. Hillebrand, W. F.; Lundell, G. E. F. *Applied Inorganic Analysis* , Wiley, New York, 1953, pp. 590.
7. Wiley, G. A.; Hershkowitz, R. L.; Rein, B. M.; Chung, B. C. *J. Am. Chem. Soc.* **1964**, 86, 964-965.

(*Received in UK* 25 *March* 1994; *revised* 21 *June* 1994; *accepted* 24 *June* 1994)