CLEAVAGE OF ESTERS AND ETHERS WITH SILICA CHLORIDE

F. Mohanazadeh and A.R. Momeni

Department of Chemistry, University of Mazandaran, Babolsar, Islamic Republic of Iran

Abstract

Silica chloride converted benzyl or *tert*-butyl esters to the corresponding acid chlorides and alkyl chlorides. It also converted benzyl or *tert*-butyl phenyl ethers to the corresponding alkyl chlorides and phenol.

Introduction

The chlorination of silanol groups on silica with thionyl chloride is reported [1,2]. This reactive polymer is used in graft polymerization of methyl methacrylate [3]. It is also used as a substrate in Grignard reaction [1,2] and deoxygenation of sulfoxides to sulfides [4]. The similarity of chlorosilyl groups on the surface of silica with Si-Cl bond in chloromethylsilane encouraged us to compare the chemical properties of this reagent with trimethyl iodosilane.

Results and Discussion

Chloro silica is obtained according to the reported procedure [4]. In a typical procedure, the ester (2 mmole) and chlorinated silica (2 g) are refluxed in CCl_4 (10 ml), with exclusion of atmospheric moisture, for the time period specified in Table 1. The progress of reaction is monitored by TLC and GC. After completion of the reaction, the mixture is filtered. Solvent and products are separated from each other by distillation of the filtrate. Under this condition, the ester is converted to corresponding acid chloride and alkyl chloride.

This reactive polymer is a useful reagent for mild cleavage of benzyl and *tert*-butyl esters under neutral conditions. Carboxylic acid is obtained from the reaction of ester with iodotrimethylsilane [5-7], but acid chloride is prepared by use of this reagent. It should be mentioned that when ester is treated with excess of $(CH_3)_3SiI$ in 75°C over a long period (3 days), the initially formed trimethylsilyl carboxylate is slowly converted into acyl iodide. The reaction of benzyl esters with dry silica gel in the presence of HCl gas in CCl_4, however, was not successful. This provides sufficient grounds for concluding that the reaction of HCl in the presence of silica gel is not playing a major role.

Table 1. Conversion of RCO_2R' to RCOCl and R'Cl

No.	R	R'	Time (h)	Yield [a] (%)
1	phenyl	benzyl	4.0	72
2	phenyl	*tert*-butyl	3.5	64
3	methyl	benzyl	0.5	90
4	methyl	*tert*-butyl	0.5	90
5	phenyl	methyl	4.0	0
6	3-chlorophenyl	benzyl	1.5	90
7	3-methylphenyl	benzyl	5.5	85
8	phenyl	*iso*-propyl	5.0	0
9	methyl	*iso*-propyl	5.0	0

[a]Yield of isolated pure alkyl halides

Low polar solvents, such as carbon tetrachloride or dichloromethane, are ideal for reaction. High polar solvents, e.g. CH_3CN and DMF, are not suitable for reaction.

Aromatic aliphatic ethers are also cleaved by silica chloride, although in low yield. From the data in Table 2,

Table 2. Cleavage of PhOR to PhOH and RCl

No.	R	Time (h)	Yield[a] (%)
1	benzyl	5.5	51
2	*tert*- butyl	4.5	45
3	*iso*-propyl	5.0	0
4	methyl	5.0	0

[a]Yield of isolated pure alkyl halides

Keywords: Esters; Ethers; Silica chloride

it is obvious that *tert*-butyl phenyl ether and benzyl phenyl ether are cleaved by silica chloride in CCl_4. Methyl phenyl ether and *iso*-propyl ether are stable under these conditions.

References

1. Lock, D.C., Schmermund, J.T. and Banner, B. *Anal. Chem.*, **44**, 90, (1972).
2. Saunders, D.H., Barford, R.A., Magidman, P., Olszewski, L.T. and Rothbar, H.L. *Anal. Chem.*, **46**, 834, (1974).
3. Tsubokawa, N. and Ishida, H. *J. Poly. Sci. Part A: Poly. Chem.*, **30**, 2241, (1992).
4. Mohanazadeh, F., Momeni, A,R. and Ranjbar, Y. *Tetrahedron Lett.*, **35**, 6127, (1994).
5. Jung, M.E. and Lyster, M. A. *J. Am. Chem. Soc.*, **99**, 968, (1977).
6. Ho, T. L. and Olah. G. A. *Angew. Chem. Int. Ed. Engl.*, **15**, 774, (1976).
7. Ho, T. L. and Olah, G. A. *Synthesis*, 417, (1977).