



USE OF TRANSITION METAL SALTS FOR SELECTIVE OXIDATION OF TRIETHYLSILANE TO TRIETHYLSILANOL IN THE PRESENCE OF *tert*-BUTYLHYDROPEROXIDE

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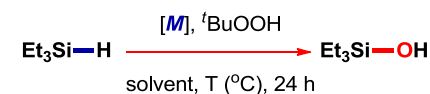
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Abstract

The use of transition metal chlorides for the oxidation of triethylsilane to triethylsilanol in the presence of *tert*-butylhydroperoxide is reported. It is shown that the process is sensitive to the type of a metal catalyst and the reaction conditions. Among the metal salts explored, CuCl₂ is found to be the most selective and, therefore, the most suitable catalyst for the process described. An appreciable level of activities observed in the case of other transition metal salts, in particular, MnCl₂ renders further studies in this area very promising.

Key words: silanols, peroxides, metal-catalyzed oxidation, hydrosilanes, silanes, homogeneous catalysis.



[M] = CuCl₂, FeCl₃, NiCl₂, CAN, CoCl₂, MnCl₂

Introduction

The versatile properties of silanols (analogs of organic alcohols) promote their extensive use in different fields of chemistry and related sciences, ranging from fine organic synthesis and catalysis to the chemistry of high-molecular compounds and biology [1]. For example, investigation of the biological activity of this class of organosilicon compounds [2] revealed their considerable potential as bactericide and antiseptic materials [3]. Furthermore, silanols were shown to be useful building blocks in the construction of high-molecular compounds with predefined structures [4], including dendrimers [5]. In recent years, increasing attention has been drawn to the catalytic activity of these compounds and their application in organic synthesis [6].

Despite the wide application scope of silanols, the development of approaches to their synthesis remains an urgent problem. The main method in use, namely, the hydrolysis of chlorosilanes does not meet the modern principles of green chemistry. It is also limited by the choice of the starting compounds due to their low availability and the high sensitivity of the method to various functional groups. Another challenge resides in the low stability of silanols in the reaction medium, which leads to the formation of disiloxanes as the main by-products.

A rising alternative to the conventional synthesis of silanols from chlorosilanes is the catalytic oxidation of hydrosilanes in the presence of oxidizing agents and various catalysts [7]. Although this method is advantageous in terms of functional group tolerance, even the use of hardly accessible or noncommercial oxidants and catalysts often fails to solve the condensation problem.

Results and discussion

Recently we have suggested a preparative method for the synthesis of alkyl- and siloxysilanols based on the oxidation of the corresponding hydrosilanes in the presence of inexpensive commercially available reagents, namely, copper carbonate as a catalyst and *tert*-butylhydroperoxide as an oxidizing agent in acetonitrile at 80 °C [8].

In view of the discovery of an efficient catalytic system, it seemed interesting to screen the related types of metal catalysts in order to extend the potential of the method. In this context, we decided to estimate the catalytic performance of other 3d metal salts (MnCl₂, CuCl₂, NiCl₂, CoCl₂, and FeCl₃) and cerium(IV) ammonium nitrate (CAN) (Table 1). The latter is a rare-earth metal catalyst that is widely used in oxidative processes in combination with *tert*-butylhydroperoxide [9]. The salts of these metals were selected owing to their lower cost compared to the platinum group metal derivatives ([Ru], [Rh], [Pd], [Re], [Os], [Ir], and [Pt]).

First, the activities of the metal salts were evaluated upon heating in benzene at 100 °C. None of the compounds provided the complete conversion of triethylsilane **1** under these conditions (Table 1, entry 1). The most active catalyst appeared to be MnCl₂ which afforded the highest conversion of **1** and 87% yield of triethylsilanol **2**. NiCl₂, CAN and CoCl₂ were slightly less active and provided comparable conversions of the starting silane with good yields of product **2** (82–83%). The high level of selectivity was observed almost in all cases (except for FeCl₃): the content of disiloxane **3** in the resulting mixtures did not exceed 10%.

- Kakimoto, Y. Imai, *Macromolecules*, **1991**, *24*, 3469–3474. DOI: 10.1021/ma00012a001
6. (a) S. E. Denmark, A. Ambrosi, *Org. Process Res. Dev.*, **2015**, *19*, 982–994. DOI: 10.1021/acs.oprd.5b00201; (b) C. Huang, B. Chattopadhyay, V. Gevorgyan, *J. Am. Chem. Soc.*, **2011**, *133*, 12406–12409. DOI: 10.1021/ja204924j; (c) K. M. Diemoz, J. E. Hein, S. O. Wilson, J. C. Fettinger, A. K. Franz, *J. Org. Chem.*, **2017**, *82*, 6738–6747. DOI: 10.1021/acs.joc.7b00875
7. (a) V. Chandrasekhar, R. Boomishankar, S. Nagendran, *Chem. Rev.*, **2004**, *104*, 5847–5910. DOI: 10.1021/cr0306135; (b) Y. Kawakami, Y. Sakuma, T. Wakuda, T. Nakai, M. Shirasaka, Y. Kabe, *Organometallics*, **2010**, *29*, 3281–3288. DOI: 10.1021/om901120m; (c) K. Valliant-Saunders, E. Gunn, G. R. Shelton, D. A. Hrovat, W. T. Borden, J. M. Mayer, *Inorg. Chem.*, **2007**, *46*, 5212–5219. DOI: 10.1021/ic062468u; (d) D. Limnios, C. G. Kokotos, *ACS Catal.*, **2013**, *3*, 2239–2243. DOI: 10.1021/cs400515w; (e) M. Aliaga-Lavrijsen, M. Iglesias, A. Cebollada, K. Garcés, N. García, P. J. Sanz Miguel, F. J. Fernández-Alvarez, J. J. Pérez-Torrente, L. A. Oro, *Organometallics*, **2015**, *34*, 2378–2385. DOI: 10.1021/om5011726; (f) T. Mitsudome, S. Arita, H. Mori, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Angew. Chem., Int. Ed.*, **2008**, *47*, 7938–7940. DOI: 10.1002/anie.200802761; (g) K. Motokura, D. Kashiwame, A. Miyaji, T. Baba, *Org. Lett.*, **2012**, *14*, 2642–2645. DOI: 10.1021/ol301034j; (h) A. K. L. Teo, W. Y. Fan, *RSC Adv.*, **2014**, *4*, 37645–37648. DOI: 10.1039/C4RA05669H; (i) R. A. Corbin, E. A. Ison, M. M. Abu-Omar, *Dalton Trans.*, **2009**, 2850–2855. DOI: 10.1039/B822783G; (j) B. P. S. Chauhan, A. Sarkar, M. Chauhan, A. Roka, *Appl. Organomet. Chem.*, **2009**, *23*, 85–390. DOI: 10.1002/aoc.1528; (k) T. Mitsudome, A. Noujima, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Chem. Commun.*, **2009**, 5302–5304. DOI: 10.1039/B910208F; (l) T. Liu, F. Yang, Y. Li, L. Ren, L. Zhang, K. Xu, X. Wang, C. Xu, J. Gao., *J. Mater. Chem. A*, **2014**, *2*, 245–250. DOI: 10.1039/C3TA13693; (m) R. Ishimoto, K. Kamata, N. Mizuno, *Angew. Chem., Int. Ed.*, **2009**, *48*, 8900–8904. DOI: 10.1002/anie.200904694; (n) S. Nojima, K. Kamata, K. Suzuki, K. Yamaguchi, N. Mizuno, *ChemCatChem*, **2015**, *7*, 1097–1104. DOI: 10.1002/cctc.201402975
8. A. V. Arzumanyan, I. K. Goncharova, R. A. Novikov, S. A. Milenin, A. M. Muzafarov, *Synlett.*, **2017**, *29*, 489–492. DOI: 10.1055/s-0036-1591512
9. (a) S. D. McCann, S. S. Stahl, *Acc. Chem. Res.*, **2015**, *48*, 1756–1766. DOI: 10.1021/acs.accounts.5b00060; (b) T. Punniyamurthy, L. Rout, *Coord. Chem. Rev.*, **2008**, *252*, 134–154. DOI: 10.1016/j.ccr.2007.04.003; (c) I. Bauer, H.-J. Knölker, *Chem. Rev.*, **2015**, *115*, 3170–3387. DOI: 10.1021/cr500425u; (d) M. S. Kharasch, P. Pauson, W. Nudenberg, *J. Org. Chem.*, **1953**, *18*, 322–327. DOI: 10.1021/jo01131a016; (e) R. T. Gephart III, C. L. McMullin, N. G. Sapiezynski, E. S. Jang, M. J. B. Aguilera, T. R. Cundari, T. H. Warren, *J. Am. Chem. Soc.*, **2012**, *134*, 17350–17353. DOI: 10.1021/ja3053688; (f) J. Christoffers, *J. Org. Chem.*, **1999**, *64*, 7668–7669. DOI: 10.1021/jo9909094; (g) J. W. Brown, Q. T. Nguyen, T. Otto, N. N. Jarenwattananon, S. Glöggler, L.-S. Bouchard, *Catal. Commun.*, **2015**, *59*, 50–54. DOI: 10.1016/j.catcom.2014.09.040; (h) T. Yamada, T. Takai, O. Rhode, T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **1991**, *64*, 2109–2117. DOI: 10.1246/bcsj.64.2109