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DOI: 10.1039/C8GC00424B

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Aerobic Co or Cu / NHPI - catalyzed oxidation of hydride siloxanes: synthesis of siloxanols

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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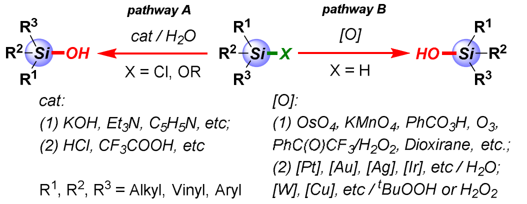
A highly efficient preparative method for synthesis of siloxanols based on aerobic $Co(OAc)_2$ or $Cu(OAc)_2$ / NHPI - catalyzed oxidation of hydride siloxanes using "green", commercially available, simple inexpensive reagents and mild reaction conditions has been proposed. This is a general reaction for the synthesis of mono-, oligo- and polymeric siloxanols with various structures (linear, branched and cyclic).

Siloxanols and silanols (organosilanols) are an important class of organosilicon compounds that attract considerable attention of researchers due to unique physicochemical properties and high potential of applicability in various areas of chemistry.

For example, silanols are widely used in organic synthesis: in cross coupling reactions (Hiyama-Denmark reaction, conjugate addition),[1] in C–H-functionalization (Si–OH as the directing group),[2] as catalysts (hydrogen-bonding catalysts),[3] etc. It has also been shown that the amphiphilic nature of silanols underlies their surface activity[4] and microbial activity.[5]

A classical approach to the synthesis of silanols involves the hydrolysis of chloro- and alkoxysilanes (Scheme 1, *pathway A*).[6-7] In this case, it is important to strictly observe the process conditions (primarily, the *pH* medium) in order to avoid the formation of siloxanes as the main side products. Yet another drawback of this method lies in the limited mutual solubility of the starting silanes and water, which leads to the necessity to study three-component systems (water-solvent-silane) in order to find the optimum conditions.

Another general approach to the synthesis of silanols involves the oxidation of the corresponding hydride silanes. They are preferable as precursors (Scheme 1, *pathway B*) in comparison with chloro- and alkoxy-derivatives due to the following reasons: they are more "green" reagents than chloro- and alkoxy-derivatives; they do not form chloro- and alkoxy-containing side products; a desired silanol can be synthesized selectively by choosing the structure of the starting hydride silane.[7] Two groups of processes can be distinguished here: the processes using organic or inorganic oxidants in stoichiometric or excessive amounts;[8] metal-catalyzed oxidation.[9] These processes are usually based on expensive, toxic and commercially unavailable oxidants and catalysts. Furthermore, in the majority of these studies, the products (silanols) are not isolated in the individual form but, instead, they are just identified in the reaction mixture using GLC and NMR methods.



Scheme 1. The main approaches to the synthesis of silanols

It is important to note that both of these approaches (Scheme 1) are primarily applicable to the synthesis of alkyl-, vinyl- and arylsilanols.

As to siloxanols, they are usually obtained by hydrolysis of di-, tri- and tetra-(chloro- or alkoxy-)silanes (Scheme 1, *pathway A*) to give a mixture of oligomeric and polymeric siloxanols with various structures. To date, studies on the synthesis of siloxanols from the corresponding hydride siloxanes are represented only by a few examples (Scheme 1, *pathway B*),[13a] which, on the one hand, confirm the capability of this

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Electronic Supplementary Information (ESI) available: Materials and methods, screening of **2a** oxidation conditions, optimization of synthesis, characterization data and spectra for **2a-i**, optimization of **2a, 4h-j** silylation, synthesis of **1d-i**. See DOI: 10.1039/x0xx00000x

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approach, and on the other hand, show the limited scope of the real synthetic techniques.[7]

However, siloxanols are a more practically important class of compounds than silanols. They can be used as monomers in heterofunctional polycondensation with alkoxy- or chlorosilanes and allow one to obtain polymers with high molecular mass and with predetermined structures and properties.[10] Siloxanols are also important building blocks in sol-gel processes,[11] in supramolecular chemistry[12] as well as in the synthesis of dendrimers and other structures with well-defined architecture.[13] Furthermore, one of the most popular examples of practical application of siloxanols is their use in RTV (Room-Temperature-Vulcanizing) silicone compositions based on polydimethylsiloxane with terminal Si–OH groups.[14] Yet another, no less important field of use of siloxanols is in organosilicon resins that are usually cured via residual Si–OH groups.[15]

As mentioned above, the second approach (Scheme 1, *pathway B*) to the synthesis of compounds with a Si–OH group is preferable, but to be used as a preparative method for synthesizing mono-, oligo- and polymeric siloxanols it has to comply with the following requirements: possess an inexpensive, commercially available and nontoxic (or low-toxic) oxidative system, relatively mild process conditions, and possibility to easily isolate the target product from the reaction mixture in order to avoid side processes of condensation to give siloxanes.

These requirements are met by aerobic oxidation processes, in particular, taking into consideration the results obtained in the oxidation of C–H and Si–H groups with the TM/NHPI system.[16]

In recent years there have been an increasing number of studies on the oxidation of organic compounds with participation of molecular oxygen allowing one to obtain valuable products that are widely used in science, technology and medicine. Furthermore, aerobic oxidation serves as the basis for a number of industrially important processes (the Wacker process, preparation of *tert*-butyl hydroperoxide and terephthalic acid, oxidation of alkenes, arenes, alkanes, etc.).[17]

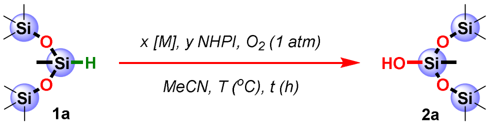
Thus, the purpose of this study was to develop methods of aerobic oxidation of hydride siloxanes under mild conditions in order to obtain siloxanols with various structures.

At the first step of our study, we performed a thorough optimization of conditions for aerobic oxidation of hydride siloxane **1a** to siloxanol **2a**. After that, the optimum conditions were applied to the other substrates **1b-j** (Table 1 & Scheme 2; *Supp. Inf.*).

To determine the most reactive oxidative system ([M]/NHPI/O_2) for the conversion of hydride siloxane **1a** to siloxanol **2a**, first, we performed screening by the type of metal catalyst. The yield of product **2a** in acetonitrile medium with $Cr(OAc)_3$, $Fe(OAc)_2$, $Ni(OAc)_2$ and $Mn(OAc)_2$ was 1 – 3 % in 24 h at 25 ^oC. CAN ($(NH_4)_2Ce(NO_3)_6$) was slightly more reactive – up to 15%, whereas the yields in the case of $Cu(OAc)_2$ and $Co(OAc)_2$ were 57 and 60%, respectively (Table 1, *a*; *Supp. Inf.)*.

Estimation of the efficiency of oxidative systems based on [Co]- ($Co(OAc)_2$/NHPI/O_2) and [Cu]-catalysts ($Cu(OAc)_2$/NHPI/O_2) has shown that the system based on the [Co]-catalyst is more reactive but considerably less selective in the oxidation of hydride siloxane **1a** to siloxanol **2a** than the system based on the [Cu]-catalyst (Table 1, *b*, *c*; *Supp. Inf.)*.

Table 1. Study of the effect of aerobic oxidation conditions of **1a** on the yield of **2a**[a]



[M]	$Co(OAc)_2$	$Cu(OAc)_2$
1a/**2a**/Siloxanes, %	3/60/37,	43/57/0,
	16/82/2,[b]	89/11/0,[b]
	0/16/84,[c]	12/80/8,[c]
	3/90/7[d]	2/95/3,[e] 70[f]

[a] **1a** (0.452 mmol, 1 eq.), NHPI (0.0905 mmol, 0.2 eq.), [M] (2.26 µmol, 0.005 eq.), MeCN (1 mL), 25 °C, 24 h, O_2 (1 atm). The yield of **2a** was determined by GLC. [b] 8 h. [c] 3 days. [d] $Co(OAc)_2$ (0.01 eq.), 25 °C, 8 h. [e] $Cu(OAc)_2$ (0.01 eq.), 60 °C, 6 – 9 h. [f] Isolated yield of **2a** after distillation under reduced pressure.

Since both parameters of the oxidative system (reactivity and selectivity) are important, we continued the optimization of the oxidation conditions of hydride siloxane **1a** to siloxanol **2a** using two independent oxidative systems: $Co(OAc)_2$/NHPI/O_2 and $Cu(OAc)_2$/NHPI/O_2.

First, consider the system based on the [Co]-catalyst. A detailed study of the effect of the starting reagent ratio, solvent nature, organic catalyst, anion in the starting metal catalyst, temperature and process time allowed us to determine the optimum conditions for the synthesis of siloxanol **2a** from hydride siloxane **1a** in 90% yield: $0.01Co(OAc)_2/0.2NHPI/O_2$, MeCN, 25 ^oC, 8 h (Table 1, *d*; *Supp. Inf.*).

The optimum [M]/NHPI ratio for the [Cu]-system, similarly to the [Co]-system, is 0.01/0.2. It allows to obtain siloxanol **2a** in 83% yield at 25 ^oC in 72 h (3 days) (*Supp. Inf.*).

An important feature of the oxidative system based on the [Cu]-catalyst was that the temperature increase from 25 to 60 ^oC made it possible to shorten the time required for the oxidation of hydride siloxane **1a** to siloxanol **2a** from 72 h to 6 – 9 h, respectively, while the yield of the target product increased from 83 to 95% and the fraction of the formed side products slightly decreased from 9 to 3%, respectively (Table 1, *e*; *Supp. Inf.*). The yield of siloxanol **2a** after distillation under reduced pressure was 70% (Table 1, *f*; *Supp. Inf.*).

Thus, the oxidative system based on the [Cu]-catalyst is somewhat more efficient in the oxidation of hydride siloxane **1a** to siloxanol **2a** than the system based on the [Co]-catalyst.

It can be summarized from the results obtained that there are three main parameters having the strongest effect on the overall process efficiency (activity/selectivity): the type of the metal catalyst ($Co(OAc)_2$ and $Cu(OAc)_2$), temperature (25 – 60 ^oC) and the time of the process. Accordingly, we assumed that varying these parameters would allow us to adapt the

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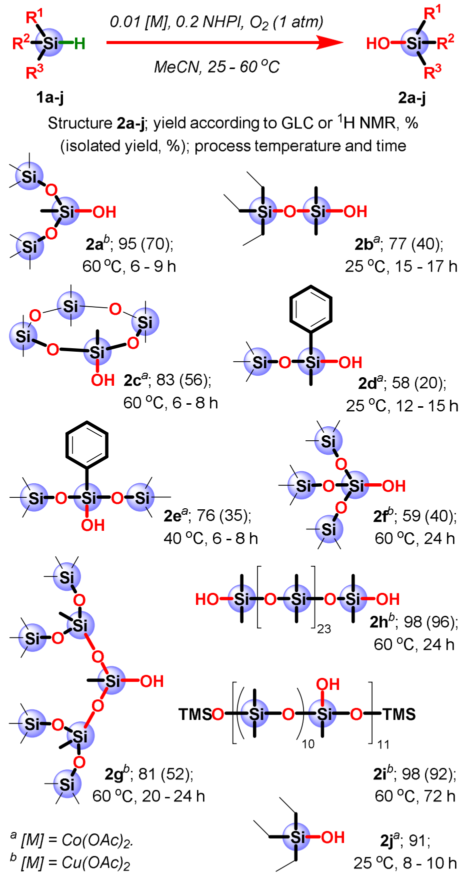
conditions of aerobic oxidation to the other substrates **1b**-j (Scheme 2; *Supp. Inf.*).

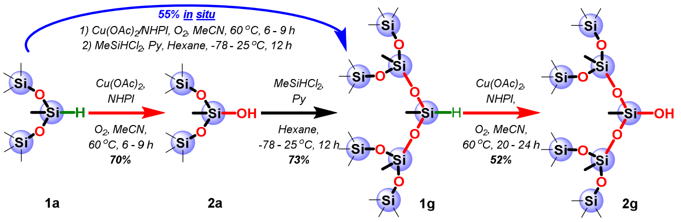


Scheme 2. Synthesis of **2a-j** from **1a-j**

The conditions of [Co]-catalyzed oxidation were found to be applicable not only to acyclic substrates **1b** (obtained from **2j**; *Supp. Inf.*) and **1j**, but also to cyclic ones that are important building blocks in the synthesis of oligo- and polysiloxanes. In fact, hydride siloxane **1c** is selectively converted to the corresponding siloxanol **2c** at 60 °C with retention of the cyclic core; the yield is 95% according to GLC and 56% after isolation. Furthermore, *gem*-phenylsiloxanols **2d-e** that are important reagents in cross-coupling reactions[1] were obtained under [Co]-catalyzed oxidation conditions in 58%, 76% yields according to GLC and in 20%, 35% yields after isolation.

As concerns hydride siloxanes **1f-i**, the oxidative system based on the [Cu]-catalyst was found to be more efficient in their oxidation to siloxanols **2f-j**. For example, the important sterically hindered siloxanol **2f** was obtained in 59% yield according to GLC and 40% after isolation.

To estimate the potential of applying the aerobic oxidation conditions for the synthesis of siloxanes with well-defined structures, dendrimers in particular, we optimized the technique for synthesizing monodendron **2g** from hydride siloxane **1a** by the three-stage or two-stage *in situ* (without isolation of **2a**) method (Scheme 3; *Supp. Inf.*).



Scheme 3. Synthesis of siloxanol **2g**

It was found that hydride siloxane **1g** is also selectively oxidized under [Cu]-catalyzed aerobic oxidation conditions at 60 °C in 12 h to the corresponding siloxanol **2g** in 81% yield according to GLC and 52% after isolation.

This approach can be quite promising in the syntheses of complex molecular systems with well-defined structures.

Since siloxanols are components of such industrially important products as RTV compositions and organosilicon resins, it appears important to estimate the applicability of aerobic oxidation conditions for the conversion of oligo- and polymeric hydride siloxanes **1h-i**. Siloxanols **2h-i** were obtained in 98% yield according to ^{1}H NMR and 96%, 92% yields, respectively, after isolation.

One can suggest that siloxanol **2h** can be obtained by the hydrolysis of dichlorodimethylsilane. However, this reaction produces water that creates serious problems when this compound is used in the areas mentioned above.[6-7] On the other hand, the aerobic oxidation of hydride siloxanes is a method of choice for the preparation of "dry" siloxanols. Thus, siloxanols of type **2i** cannot be obtained selectively by existing methods. By setting the ratio of (Me_2SiO) / (*H*MeSiO) units in the starting hydride siloxane **1i** one can obtain siloxanol **2i** with the same ratio of (Me_2SiO) / ((*HO*)MeSiO) units without the condensation of the Si–*OH* groups that are formed. This is a unique route to the synthesis of oligo- and polysiloxanols with Si–*OH* groups distributed along the chain, which may be of considerable interest for making hydrophobic coatings, self-healing polymers and can be used as components of various formulations.

The reaction conditions of aerobic [Co] or [Cu] / NHPI - catalyzed oxidation are easily scalable and allow siloxanols **2a-i** to be obtained in gram amounts (0.5 – 11 g).

Siloxanols **2a-i** are transparent oily liquids at 25 °C. The structures of **2a-i** were confirmed by ^{1}H, ^{13}C, ^{29}Si and ^{1}H, ^{29}Si-HMBC NMR spectroscopy, IR spectroscopy, ESI-HRMS for **2a-g**, GPC for **2h-i** and single crystal X-ray diffraction with *in situ* crystallization for **2a** (Fig. 1; *Supp. Inf.*).

At room temperature, siloxanol **2a** is a viscous liquid. To measure X-ray diffraction, we crystallized **2a** *in situ* in a thin glass capillary near the melting point. Upon cooling there was a phase transition because changes in the diffraction pattern were clearly visible. The molecules of siloxanol **2a** form O-H¨O bonded tetramers around the -4 axis at 230 K (Fig. 1B). Separation of the polar and nonpolar parts of the structure typical of diphilic siloxane systems with formation of polyhydroxyl domains was observed.[7] In our case, since the nonpolar shell is much larger, hydroxyl groups form isolated clusters (tetramers) rather than layers. Thus, using *in*

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situ crystallization for siloxanol **2a** we demonstrated for the first time the single crystal X-ray analysis of siloxanols that are liquid at room temperature.

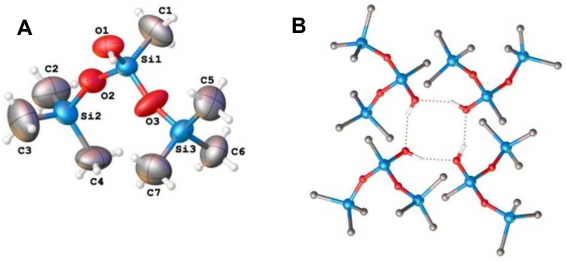

Figure 1. A) Molecular structure of **2a** presented in the form of thermal ellipsoids (50% probability). B) Tetramers formed in the crystal structure of **2a** via O-H¨O bonds.

Studies on the conditions of aerobic [Co] or [Cu] / NHPI - catalyzed oxidation of hydride siloxane **1a** to siloxanol **2a** allowed us to find the most efficient conditions for the oxidation of mono-, oligo- and polymeric siloxanols hydride siloxanes **1a-i** with various structures (linear, branched and cyclic) in gram amounts (0.5 – 11 g).

Thus, considering the simplicity and efficiency of the catalytic reaction and taking into account the commercial availability and the low cost of the reagents used, this method has considerable prospects for application in the synthesis of complex molecular systems with desired structures as well as new organosilicon monomers, oligomers and polymers.

Conflicts of interest

There are no conflicts to declare

Acknowledgments

This work was supported by the grant of the Russian Science Foundation (RSF grant № 14-23-00231).

Siloxanol **2i** was synthesized as a part of work supported by the grant of the Russian Science Foundation (RSF grant № 17-73-10462).

Dr. Alexander F. Smol'yakov thanks the RUDN University Program "5-100" for support of structural (X-ray) studies.

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View Article Online
DOI: 10.1039/C8GC00424B