



An efficient and simple method for the preparation of symmetrical disiloxanes from hydrosilanes by Lewis acid-catalyzed air oxidation

Madabhushi Sridhar*, Beeram China Ramanaiah, Chinthala Narsaiah, Mudam Kumara Swamy, Bellam Mahesh, Mallu Kishore Kumar Reddy

Fluoroorganics Division, Indian Institute of Chemical Technology, Hyderabad 500 607, India

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ABSTRACT

Symmetrical disiloxanes were prepared in high yields by air oxidation of mono, di, and trihydrosilanes under Lewis acid catalysis.

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Symmetrical disiloxanes are important class of compounds in silicon chemistry.¹ Some of the symmetrical disiloxanes are known to have important applications as liquid crystals² and pharmacologically active compounds³ (Fig. 1). Recently, they have drawn more attention as useful intermediates in organic synthesis. For example, the recent reports of Napier et al.⁴ and Sore et al.⁵ show novel applications of aryl disiloxanes and vinyl disiloxanes, respectively, as efficient coupling partners in Hiyama cross-coupling reactions. Mézailles et al.⁶ have employed 1,3-bis(phenylethynyl)tetramethyldisiloxane as a building block in the synthesis of novel macrocycles.

The general methods available in literature for the preparation of symmetrical disiloxanes are intermolecular condensation of silanols,⁷ and reaction of polysiloxanes with Grignard reagents.⁸ Here we report for the first time, a simple, mild, and non-aqueous method for the preparation of Symmetrical disiloxanes in high yields from mono, di, and trihydrosilanes by Lewis acid-catalyzed air oxidation, which proceeds with the evolution of hydrogen gas as shown in Scheme 1.

In our preliminary study, we have investigated aerobic oxidation of triethylsilane to 1,1,1,3,3,3-hexaethyl disiloxane using Lewis acids such as InCl_3 , InBr_3 , SbCl_3 , $\text{Cu}(\text{OTf})_3$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, NbCl_5 , $\text{Bi}(\text{OTf})_3$, TaCl_5 , $\text{BF}_3 \cdot \text{Et}_2\text{O}$, FeCl_3 , $\text{La}(\text{OTf})_3$, and montmorillonite K10 clay as catalysts. The results are shown in Table 1.

In this study, InBr_3 was found to be an excellent catalyst in promoting this reaction, which gave 1,1,1,3,3,3-hexaethyl disiloxane

in 97% yield. This reaction was found to proceed with equal efficiency in solvents such as tetrahydrofuran (THF), dichloromethane, chloroform and no reaction was observed in hexane and under solvent-free conditions. We have studied aerobic oxidation of a variety of mono, di and trihydrosilanes in THF using InBr_3 as a catalyst under similar conditions and obtained⁹ corresponding symmetrical disiloxanes in high yields (85–99%). These results are shown in Table 2. The compounds Me_2SiHCl and $\text{MeHSi}(\text{OEt})_2$, which were substituted with electronegative atom such as Cl and O have, however, remained unreactive under the reaction conditions.

InBr_3 forms a stable solid complex $[\text{InBr}_3 \cdot (\text{THF})_2]$ with THF.¹⁰ In the present study, THF was used as a solvent and the reaction mixture separated into two liquid layers upon removal of the solvent after completion of the reaction, in which, the upper layer was found to be disiloxane and the bottom layer was InBr_3 -THF complex. We have recovered 81% of InBr_3 as THF complex (white powder) from the bottom layer by removal of the solvent under vacuum. The recovered $\text{InBr}_3 \cdot (\text{THF})_2$ complex was also found to be highly active in catalyzing air oxidation of hydrosilane to disiloxane. For example, oxidation of dimethyl-*p*-tolyl silane **11** using InBr_3 as catalyst and THF as solvent gave disiloxane **21** in 98% yield. The recovered catalyst from the first cycle, that is, InBr_3 -THF complex, gave **21** in 92% yield under similar conditions.⁹

Recently, Berberova¹¹ reported intensive evolution of hydrogen when hydrosilanes were subjected to single electron electrochemical oxidation, which was associated with the fragmentation of radical cation of hydrosilane into silyl cation and hydrogen. In the present reaction also, oxidation of hydrosilane was accompanied with the evolution of hydrogen. Since Lewis acids (metal

* Corresponding author. Tel.: +91 040 27191772; fax: +91 040 27160387.
E-mail address: smiict@gmail.com (M. Sridhar).

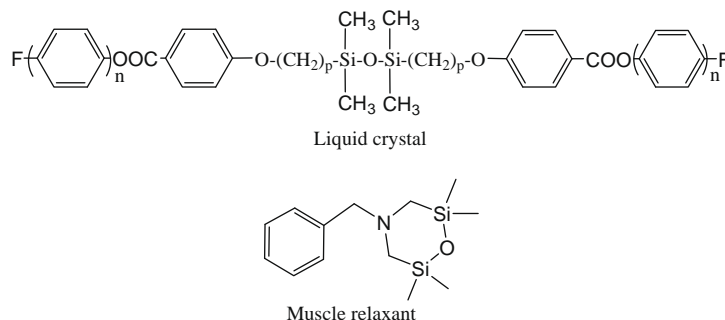
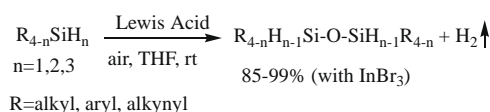


Figure 1.



Scheme 1.

Table 1
Lewis acid-catalyzed air oxidation of triethylsilane to 1,1,1,3,3,3-hexaethyldisiloxane

S.No.	Lewis acid	Reaction time (h)	Yield ^a (%)
1	AlCl ₃	6	N.R.
2	ZnCl ₂	6	20
3	FeCl ₃	6	Trace
4	CuCl ₂ ·2H ₂ O	6	51
5	Cu(OTf) ₃	6	62
6	NbCl ₅	6	55
7	Bi(OTf) ₃	6	70
8	BF ₃ ·Et ₂ O	6	N.R.
9	I ₂	6	Trace
10	K10 clay	6	N.R.
11	SbCl ₃	6	90
12	La(OTf) ₃	6	N.R.
13	InCl ₃	6	90
14	InBr ₃	3	97

^a Isolated yields; all the reactions were carried out using 5 mol % catalyst.

Table 2
InBr₃-catalyzed air oxidation of hydrosilanes to disiloxanes

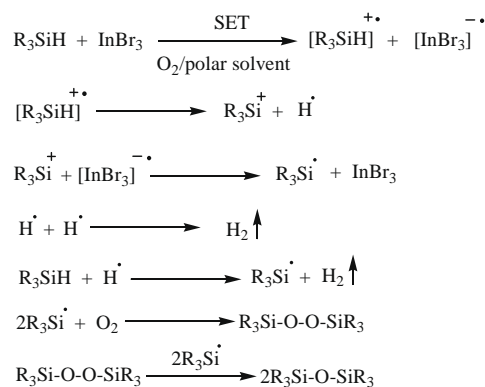
$$R_{4-n}SiH_n \xrightarrow[\text{air, THF, rt}]{\text{InBr}_3} R_{4-n}H_{n-1}Si-O-SiH_{n-1}R_{4-n}$$

n=1,2,3

Entry	Disiloxane	Reaction time (h)	Yield ^a (%)
a	PhMe ₂ Si-O-SiMe ₂ Ph	2	99
b	Ph ₂ MeSi-O-SiMePh ₂	2	92
c	Ph ₃ Si-O-SiPh ₃	5	95
d	Et ₃ Si-O-SiEt ₃	3(3 ^b)	97(90 ^b)
e	(<i>i</i> -Pro) ₃ Si-O-Si(<i>i</i> -Pro) ₃	24	96
f	PhC≡C-Si(Me) ₂ -O-(Me) ₂ Si-C≡CPh	12	85
g	(<i>n</i> -C ₈ H ₁₇) ₃ Si-O-Si(<i>n</i> -C ₈ H ₁₇) ₃	5	87
h	PhMeHSi-O-SiHMePh	4	99
i	Ph ₂ HSi-O-SiHPh ₂	4	97
j	Et ₂ HSi-O-SiHEt ₂	3	98
k	(<i>t</i> -Bu) ₂ HSi-O-SiH(<i>t</i> -Bu) ₂	24	85
l	(<i>p</i> -MeC ₆ H ₄)Me ₂ Si-O-Si(<i>p</i> -MeC ₆ H ₄)Me ₂	4	98
m	(<i>n</i> -C ₆ H ₁₃) ₂ Si-O-SiH ₂ (<i>n</i> -C ₆ H ₁₃)	5	90

^a Isolated yields; all the products gave satisfactory ¹H, ¹³C NMR, IR and Mass spectral data.

^b Corresponds to air oxidation of neat hydrosilane with preformed InBr₃-THF complex.



Scheme 2.

halides) are known to induce single electron transfer (SET) reactions,¹² it appears that Lewis acid-catalyzed air oxidation of hydrosilane to disiloxane involves SET pathway as the initial step of the process as shown in Scheme 2. Polar solvents are favorable to SET reactions and the present reaction was found to proceed well only in polar solvents.

In conclusion, this work describes the first observation of Lewis acid-catalyzed efficient and selective aerobic oxidation of hydrosilanes to symmetrical disiloxanes. We have developed a mild, efficient, and environmentally friendly method for selective preparation of symmetrical disiloxanes from mono, di, and trihydrosilanes by air oxidation using InBr₃ as a catalyst, which is easily recoverable and recyclable.

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 - Typical procedure for Lewis acid-catalyzed air oxidation of hydrosilane to disiloxane*: Dimethyl-*p*-tolyl silane **11** (1.0 g, 6.7 mmol), InBr₃ (118 mg, 0.33 mmol), and tetrahydrofuran (10 ml) were taken in a 25 ml round-bottomed flask and stirred for 4 h at room temperature keeping the reaction open to air. The reaction proceeded with the evolution of hydrogen gas bubbles (The isolated gas gave a positive 'pop' test with lit splinter). After completion of the reaction (TLC), the solvent was removed under reduced pressure. The resulting mixture was separated into two liquid layers. The upper layer was found to be the desired disiloxane, which is miscible in hexane and the bottom layer was InBr₃-THF complex, which is not miscible with hexane. Hence, the crude product was extracted with hexane (4 × 5 ml) from this bi-layer mixture and concentrated under reduced pressure. Purification of the crude product by column chromatography (silica gel 100–200 mesh, hexane) gave 1,3,3-tetramethyl-1,3-di-*p*-tolyl-disiloxane **21** (1.02 g, 98%) as a colorless oil. The spectral data obtained for **21** is as follows: ¹H NMR (CDCl₃, 300 MHz): δ = 7.3–7.4 (d, *J* = 7.6 Hz, 4H), 7.1–7.1(d, *J* = 7.6 Hz, 4H), 2.3 (s, 6H), 0.3 (br s, 12H); ¹³C NMR (CDCl₃, 75 MHz) δ = 139.7, 137.5, 132.6, 128.5, 21.8, 1.0; IR (Neat, cm⁻¹): ν 3056, 2967, 1426, 1245, 1108, 1050, 837, 789; EIMS (*m/z*, %): 314 (M⁺, 23), 299(65), 267(25), 225(20), 223(35), 207(84), 179(24), 149(32), 93(54), 77(23), 57(27), 43(100). Exact mass observed for C₁₈H₂₆O₂Si₂: 314.1514 (calcd: 314.1522).
 - Study of the reusability of the catalyst*: The recovered bottom layer obtained above was InBr₃-THF complex, which was in the form of a viscous liquid. It was thoroughly washed with hexane (3 × 5 ml) and dried under vacuum to obtain [InBr₃·(THF)₂] in the form of a white powder (135 mg). 50 mg of InBr₃·(THF)₂ obtained as above was taken into a 25 ml r.b. flask and to this, dimethyl-*p*-tolyl silane **11** (0.4 g, 2.6 mmol) and THF (5 ml) were added and stirred for 4 h at room temperature keeping open to air. After the completion of the reaction, 0.38 g (92%) of disiloxane **21** was obtained upon purification and its spectral data were identical to that obtained above.
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