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Graphical Abstract





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Nickel(0) Catalyzed Oxidation of Organosilanes to Disiloxanes by Air as an Oxidant

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ABSTRACT

We report here an efficient non-aqueous route to symmetrical disiloxanes from their corresponding organosilanes using $Ni(COD)_2$ with 3,4,7,8-tetramethyl-1,10-phenanthroline in air. Our methodology is very simple and high yielding. The reaction mechanism is also proposed.

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1

Keywords: Disiloxanes Organosilanes Bis(cyclooctadiene)nickel(0) Aerobic

Siloxanes possessing Si-O linkage are ubiquitous in nature. They have widespread applications in silicone industries,¹ pharmaceutical,² cosmetic industries,³ liquid crystal display element,⁴ microelectronic devices and sensor fabrication.⁵ They are also used as a coupling partner in Hiyama-type reaction.⁶ Siloxane like 1,3-bis(phenylethynyl) tetramethyldisiloxane has also been employed as a building block in the synthesis of novel macrocycles.⁷ 1,3-diphenyl disiloxane (DPDS) has been used for preparing phosphine ligands with extremely diverse scaffolds as well as to recycle phosphine oxides in ambient catalytic phosphine redox reactions.⁸

Many methods have been available in the literature for the preparation of symmetrical disiloxanes like an intermolecular condensation of silanols,⁹ reactions of polysiloxanes with Grignard reagents.¹⁰ Chojnowski's group also used Lewis acid, tris(pentafluorophenyl)borane as a catalyst to produce disiloxanes *via* a coupling reaction of hydrosilanes with alkoxysilanes.¹¹ Transition-metal catalyzed oxidation of hydrosilanes is the most common strategy to prepare disiloxanes.¹² In(III)-catalyzed air oxidation of hydrosilanes has been reported; however, the reaction has limited scope and the generation of a full equivalent of hydrogen gas which is a safety concerned.¹³

Although many transition metals have been reported for these types of transformations, the nickel catalyzed transformation is much less reported. However, nickel due to its relatively electropositive nature readily loss electron density in oxidative addition reaction which allows for the use of cross-coupling electrophiles, its low cost, easy to handle and also due to the readily available oxidation states invoked in development of a broad range of innovative reactions.¹⁴ Normally used traditional oxidants are often toxic and released a considerable amount of by-products. The oxygen in the air is a cost-free oxidant and

produces no waste or water as the sole by-product.¹⁵ Thus, in this report, we are using bis(cyclooctadiene)nickel(0) with 3,4,7,8-tetramethyl-1,10-phenanthroline under aerobic condition to oxidize hydrosilanes (**Scheme 1**).

Scheme 1: Ni(0) catalyzed air oxidation of hydrosilanes to symmetrical disiloxanes.

We initiated our study by testing several nickel compounds using 1,10-phenanthroline for the synthesis of disiloxanes from organosilanes in toluene at 70 °C. Among the tested compounds Ni(COD)₂ was found to be the best catalyst in promoting the reaction giving disiloxane in the highest yield of 89% (Table 1, entry 1). Compounds like Ni(CO)₂(PPh₃)₂, Ni(PPh₃)₄ were with good activity for the oxidation giving the desired product 2a in good yield (Table 1, entries 2 and 3). Nickel powder and Ni(acac)₂ also showed the activities but the results were not appreciable (Table 1, entries 4 and 5). Ni(OH)(OAc), Ni(NO₃)₂.6H₂O, Ni(C₂O₄).H₂O, Ni(OAc)₂.2H₂O were also tested but failed to catalyze the reaction (Table 1, entries 6-9). We did not limit our studies to Ni compounds only. Other metals compounds of Fe and Co were also studied but the results were not appreciable (Table 1, entries 10 and 11). We also investigated the ligand on the reactivity of the reaction using optimal catalyst Ni(COD)₂. Ligands like 1,10-phenanthroline-5,6-dione, 4,7dimethoxy-1,10-phenanthroline, 2,2'-bipyridine and tricyclohexylphosphane gave moderate yield, while 3,4,7,8tetramethyl-1,10-phenanthroline furnished excellent yield (97%) and bathophenanthroline gave a good yield (92%). But with

Tetrahedron Letters

ligand 3,8-dibromo phenanthroline the yield was poor. We next screened different solvents to find that toluene was the bestperforming medium. The reaction was found to proceed with lower efficiency in solvents like 1,4-dioxane and DMF, moderate reactivity in MeCN and no reaction in DCE. We also investigated the effect of temperature on the reactivity by varying the temperature from 30-90 °C. However, the best result was obtained at 70 °C.

Having found the optimal conditions, we investigated the oxidative coupling of an array of organosilanes (Table 2). The oxidative coupling, which is different from the traditional coupling, occurs between two nucleophiles in presence of an appropriate oxidant. Oxidative coupling reactions received great attention for their exemplary potential in carbon-carbon and carbon-heteroatom bond formation.¹⁶ The reaction was found to be very general and not sensitive to the electronic nature of the substituents. It also tolerates various aryldimethylsilanes having activating and deactivating group on the aryl moiety like methyl, ethyl, methoxy, fluoro, chloro, and cyano at *para*position giving the corresponding disiloxanes in excellent yield (Table 2, entries 2, 6-11). Position of substituents has no much

Table 1. Optimization of organosilane oxidation to disiloxane^a

effect on the reactivities of the organosilanes; ortho, meta or para-methyl aryl substituents gave almost comparably excellent yields (Table 2, entries 2-4). It also tolerates the bulky aryl substituents like para-tert-butyl phenyl dimethyl silane and gave excellent yield (Table 2, entry 8). Even the sterically hindered silanes such as diphenyl methyl silane, triphenylsilane can also tolerate the reaction conditions giving the corresponding oxidative coupling product in moderate yields (Table 2, entries 12 and 13). Long chain alkyl substituted silanes like trihexylsilane and triethylsilane also furnished good results (Table 2, entries 16 and 17). The cyclohexylsilane gave the corresponding disiloxane greater than 99% yield. Interestingly, ortho-phenylene bis(dimethylsilane) offered cyclic disiloxane with moderate yield (Table 2, entry 18). The applicability of the reaction condition for the preparation of unsymmetrical disiloxane was tested by coupling aryldimethylsilane 1a with pmethyl aryldimethylsilane 1d, a mixture of the unsymmetrical disiloxane 3 with self-coupling products 2a and 2d was obtained in 84% total yield (Scheme 2). Judged from the ratio of the products, the reaction between two different silanes showed no selectivity.

Si-H	Metal/ Ligand
	Air, Solvent, 70 °C
1a	2a

Entry	Metal	Ligand	Solvent	Time (h)	Yield (%) ^b
1	Ni(COD) ₂	1,10-phenanthroline	Toluene	9	89
2	Ni(CO) ₂ (PPh ₃) ₂	1,10-phenanthroline	Toluene	46	67
3	Ni(PPh ₃) ₄	1,10-phenanthroline	Toluene	9	87
4	Ni(powder)	1,10-phenanthroline	Toluene	72	8
5	Ni(acac) ₂	1,10-phenanthroline	Toluene	72	20
6	Ni(OH)(OAc)	1,10-phenanthroline	Toluene	72	0
7	Ni(NO ₃) ₂ .6H ₂ O	1,10-phenanthroline	Toluene	72	0
8	Ni(C ₂ O ₄).H ₂ O	1,10-phenanthroline	Toluene	72	0
9	Ni(OAc) ₂ .2H ₂ O	1,10-phenanthroline	Toluene	72	0
10 ^c	Fe catalyst	1,10-phenanthroline	Toluene	72	0-18
11 ^d	Co catalyst	1,10-phenanthroline	Toluene	72	0-13
12	Ni(COD) ₂	3,4,7,8-Tetramethyl-1,10-phenanthroline	Toluene	4	97
-13	Ni(COD) ₂	Bathophenanthroline	Toluene	6	92
14	Ni(COD) ₂	3,8-Dibromophenanthroline	Toluene	72	7
15	Ni(COD) ₂	1,10-phenanthroliine-5,6-dione	Toluene	72	58
16	Ni(COD) ₂	4,7-Dimethoxy-1,10-phenanthroline	Toluene	9	75
17	Ni(COD) ₂	2,2'-Bipyridine	Toluene	60	67
18	Ni(COD) ₂	Tricyclohexylphosphane	Toluene	48	48
19	Ni(COD) ₂	3,4,7,8-Tetramethyl-1,10-phenanthroline	1,4-Dioxane	18	92
20	Ni(COD) ₂	3,4,7,8-Tetramethyl-1,10-phenanthroline	DCE	72	NR
21	Ni(COD) ₂	3,4,7,8-Tetramethyl-1,10-phenanthroline	MeCN	5	82
22	Ni(COD) ₂	3,4,7,8-Tetramethyl-1,10-phenanthroline	DMF	4	91
23	Ni(COD) ₂	3,4,7,8-Tetramethyl-1,10-phenanthroline	DMSO	6	32
24	Ni(COD) ₂	3 4 7 8-Tetramethyl-1, 10-phenanthroline	Pentanol	6	57
	1.1(002)2	-,.,.,- recument, i, i phenantinonne		÷	

^aReaction condition: **1a** (0.4mmol), metal (5%), ligand (6%), solvent (1 mL), under air (1 atm); ^bIsolated yields; ^cFe(powder), FeCl₂, FeBr₂, Fel₂, Fe(OTf)₂, FeCl₃, FeBr₃ used. ^dCoF₃, CoCl₂, CoBr₂, Col₂, Co(acac)₃, Co(SCN)₂.(H₂O)₃, Co(OAc)₂.⁴ H₂O, CoCO₃ used.

Table 2: Scope of the substrates for the synthesis of disiloxane^a

R ²	Ni(COD) ₂ / 3,4,7,8-Tetramethy	l-1,10-phenanthro	oline R	³ . Si ⁻ Si ⁻ R ¹
H H	Air, toluene,	R	${}^{2^{\prime}1^{\prime}}$ ${}^{1^{\prime}}$ ${}^{1^{\prime}}$ ${}^{1^{\prime}}$ ${}^{2^{\prime}}$ ${}^{2^{\prime}}$ ${}^{1^{\prime}}$ ${}^{2^{\prime}}$ ${}^{2^{\prime}}$	
1a-r			2a-r	
Entry	Substrate	Product	Time (h)	Yield (%) ^c
1		2a	3	97
2^b	SiH 1b	2b	5	94
3	SiH 1c	2c	3	92
4		2d	3	92
5	SiH 1e	2e	3.5	89
6	,o-√SiH 1f	2f	5	82
7		2g	3	98
8	$\rightarrow \swarrow$ SiH	2h	3.5	>99
9	F-SiH 1i	2i	5	94
10	$Cl \rightarrow SiH$	2ј	6	92
11		2k	8	95
12		21	4	85
13 ^b	$\left(\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	2m	5	69
14	C ^H _{Si} ₁ In	2n	5	82
15 ^b		20	4	>99
16 ^b	SiH 1p	2р	4	82
17 ^b	SiH 1q	2q	8	83
18 ^b	SiH SiH Ir	$\sum_{\substack{i=1\\j \\ 2r}}^{i}$	6	76



Scheme 2: Preparation of unsymmetrical disiloxane

To identify the oxygen source, we investigated the reaction by a set of control experiments (Scheme 3). When the reaction was carried out under O_2 atmosphere, **2a** was obtained in 72% yield. By using 5 equivalents of water instead of other oxygen sources, no product was detected. The reaction was also carried out in presence of MS 4A° giving **2a** in high yield. These control experiments had ruled out the possibility that water served as an oxygen source. Thus, confirmed the current reaction is the aerobic oxidation reaction.





We are tempted to assume the mechanism for the oxidative coupling of organosilane as follows (Scheme 4). A nickel(0) species initially reacts with ligand 3,4,7,8-tetramethyl-1,10-phenanthroline to generate complex A which undergo oxidative addition to the organosilane 1 to form nickel (II) square planer intermediate **B**, followed by addition of molecular oxygen in between Ni and hydrogen bond to form nickel (II) peroxide C.¹⁷ Another molecule of organosilane may enter the catalytic cycle to form ether **D** with the release of water molecule which finally furnished the oxidative coupling product disiloxane **2** and regenerates the nickel complex **A**.



^{*a*}Reaction condition: **1a** (0.4 mmol), Ni(cod)₂ (5%), 3,4,7,8-tetramethyl-1,10phenanthroline (6%), toluene (1 mL), 70 °C, under air (1 atm); ^{*b*}**1a** (0.4 mmol), Ni(COD)₂ (10%), 3,4,7,8-tetramethyl-1,10-phenanthroline (12%), toluene (1 mL), 90 °C, under air (1 atm); ^{*c*}Isolated yields.

Scheme 4: Plausible mechanism of the oxidative coupling reaction

Tetrahedron

In summary, we reported an efficient zero valent nickel catalyzed nonaqueous aerobic oxidation of wide range of organosilanes to furnish disiloxanes. The methodology provided high yield, simple experimental set-up, short reaction time which are ideal for laboratory preparation.

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Highlights

- 1) An efficient zero valent nickel catalyzed nonaqueous aerobic oxidation of organosilanes was reported.
- 2) Various disiloxanes symmetrical disiloxanes were prepared from their corresponding organosilanes.
- The mechanism of the nickel catalyzed aerobic oxidation of organosilane is proposed.

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- 18. General procedure for the synthesis 2a. Ni(COD)₂ (5.5 mg, 0.02 mmol), 3,4,7,8-Tetramethyl-1,10-phenanthroline (5.7 mg, 0.024 mmol), 1.0 mL toluene were added to a Schlenk tube under argon atmosphere. The resulting solution was stirred at room temperature for 30 min, then the organosilane 1a (54.5 mg, 0.4 mmol) was added and the mixture was stirred at 70 °C under atmosphere with GC monitoring until the complete consumption of 1a. The residue was purified by silica gel column chromatography to afford the corresponding disiloxane 2a (55.6 mg, 97% yield).

4