

## Synthesis of Silicon Derivatives of 1,3-Dioxabutylbenzene and 3'-(1,3-dioxabutyl)Pyridine

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**Summary:** Silicon containing compounds, 1,3-dioxabutylbenzene and 3'-(1,3-dioxabutyl) pyridine have been investigated for pseudorotation on pentacoordinated silicon atom.  $^1\text{H}$  and  $^{29}\text{Si}$ -NMR at ambient and different temperatures were recorded and no evidence was found for intramolecular O Si coordinate bond in these compounds.

### Introduction

Trigonal bipyramidal geometry for pentacoordinated silicon derivatives is very well known [1-4]. The strength of the coordinate E Si bond (where E is base containing electron donating atoms such as nitrogen, oxygen, phosphorous or sulphur) is controlled by the electron withdrawing substituents on the silicon atom and their steric factors. The pentacoordination ability of silicon increases in the order H, OR, F, SR, OAc, Cl, Br. Recently much attention has been given on the synthesis of silicon compounds containing different electron-donating atoms. We prepared silicon compounds of 1,3-dioxabutylbenzene and 3'-(1,3-dioxabutyl)pyridine in good yields. The proton NMR at ambient temperature and  $^{29}\text{Si}$  NMR at different temperatures have been recorded in order to investigate the presence of intramolecular O Si coordination and hence pseudorotation in these compounds.

### Experimental

#### Apparatus and Procedure

Proton NMR at ambient temperature in  $\text{CCl}_4$  and  $^{29}\text{Si}$  NMR at variable temperature in dichloromethylene were recorded on Varian EM 390 apparatus using TMS as internal reference.

The elemental analysis were obtained for the investigated derivatives and the results are given in Table 1.

#### Synthesis

1,3-Dioxabutylbenzene (1) and 3'-(1,3-dioxabutyl)pyridine (2) were prepared as the method described by Winkle and Ronald [5]. The silicon derivatives of (1) and (2) were synthesised as follows:

Table-1: Elemental Analysis Results for the Investigated Compounds

No.	Mol. Formula	%Si		%C		%H		%N		%Cl	
		Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
1.	$\text{C}_8\text{H}_{10}\text{O}_2$	-	-	69.55	69.21	7.30	7.22	-	-	-	-
2.	$\text{C}_7\text{H}_9\text{NO}_2$	-	-	60.42	61.01	6.52	7.02	10.06	10.35	-	-
3.	$\text{C}_{10}\text{H}_{16}\text{O}_2\text{Si}$	14.31	14.55	61.18	61.24	8.22	8.54	-	-	-	-
4.	$\text{C}_{10}\text{H}_{15}\text{O}_2\text{ClSi}$	12.17	12.60	52.05	51.89	6.55	6.82	-	-	15.36	14.98
5.	$\text{C}_{11}\text{H}_{18}\text{O}_3\text{Si}$	12.41	12.22	58.37	59.02	8.02	8.31	-	-	-	-
7.	$\text{C}_9\text{H}_{15}\text{NO}_2\text{Si}$	14.23	13.98	54.79	55.11	7.66	7.57	7.10	7.62	-	-

\*Compound 6 was unstable

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*1'-(1,3-Dioxabutyl)-2-(dimethylsilyl) benzene (3)*

A solution of (1) 6.9 g, (50 mmol) in dry ether (50 ml) was treated with n-butyllithium (1.0 mole, 50 ml) under nitrogen atmosphere. The mixture was stirred for three hours at room temperature resulting in the formation of a white precipitate of the ortholithiated derivative of (1) which was filtered, washed with dry ether (2 x 20 ml) and then added to 4.72 g (50 mmol) dimethylchlorosilane in ether solution. After stirring for three hours the reaction mixture was filtered and the ether was removed by vacuum evaporation. The syrupy residue was distilled at 330-331 °K/15 mm to give (3) in 60% yield.

*1'-(1,3-Dioxabutyl)-2-(Chlorodimethylsilyl) benzene (4)*

In to a solution of (3) 1.96 g (0.01 mmol) in 50 ml dry carbontetrachloride at 273°K dry chlorine gas was passed for 20 minutes unit Si H absorption in NMR at 4.5 ppm completely disappeared. The chlorinated solution on evaporation of the solvent under vacuum gave (4) in 100% yield.

*1'-(1,3-Dioxabutyl)-2-(methoxydimethylsilyl) benzene (5)*

A solution of (3) 0.69g (0.5 mmol) in dry benzene was refluxed with 0.16 g (0.15 mmol) of methanol for two hours in the presence of Wilkinson's catalyst, (Ph<sub>3</sub>P)<sub>3</sub> RhCl. The reaction mixture was filtered followed by the removal of the solvent under vacuum. The residual liquid was distilled at 362-363°K/15 mm to give (5) 90% yield.

*1'-(1,3-Dioxabutyl)-2-(dichloromethylsilyl) benzene (6)*

A solution of (1) 1.10 g (8 mmol) in dry ether was treated with 8 ml. of 1.0 molar n-butyllithium in dry ether for three hours at room temperature under nitrogen atmosphere. Ortholithiated derivative of 1 formed was washed with ether and treated with 1.196 g (8 mmol) methyltrichlorosilane in dry ether. After completion of the reaction, solvent was removed under vacuum, the product 6 thus formed was found to decompose on removal of the solvent.

*3'-(1,3-Dioxabutyl)-4-(dimethylsilyl) pyridiene (7)*

1.390 g. (10 mmol) of (2) was taken in 30 ml dry ether and treated with 1.7 molar (10 mmol) ter-

tiarybutyl lithium under argon atmosphere at 351°K for fifteen minutes. The 4-lithiated derivative of 2 was precipitated. The precipitate was filtered, washed with ether and suspended in dry ether and treated with dimethylchlorosilane. Lithium chloride thus formed was filtered off and solvent

Table-2: <sup>1</sup>H NMR Chemical Shifts of Compounds

No	value PPM	Group
3	7.3 - 6.6	4 H (Aromatic Protons)
	5.0 ---	2 H (OCH <sub>2</sub> group)
	4.3 ---	1 H (Si - H group)
	3.3 ---	3 H (O - CH <sub>3</sub> group)
	0.35 ---	6 H (Si(CH <sub>3</sub> ) <sub>2</sub> group)
4	7.7 - 6.5	4 H (Aromatic)
	5.15 ---	2 H (OCH <sub>2</sub> group)
	3.40 ---	3 H (OCH <sub>3</sub> group)
	0.33 ---	6 H (Si (CH <sub>3</sub> ) <sub>2</sub> group)
5	7.3 - 6.6	4 H (Aromatic)
	5.0 ---	2 H (OCH <sub>2</sub> group)
	3.3 ---	3 H (OCH <sub>3</sub> group)
	3.2 ---	3 H (Si-OCH <sub>3</sub> )
	0.35 ---	6 H (Si(CH <sub>3</sub> ) <sub>2</sub> group)
6	7.3 - 6.5	4 H (Aromatic)
	5.15 ---	2 H (OCH <sub>2</sub> group)
	3.4 ---	3 H (OCH <sub>3</sub> group)
	0.30 ---	3 H (Si-CH <sub>3</sub> group)
7	8.3 - 7	3 H (Aromatic)
	5.25 ---	2 H (C-CH <sub>2</sub> group)
	3.5 ---	3 H (O-CH <sub>3</sub> group)
	4.50 ---	1 H (Si-H)
	0.33 ---	6 H (Si(CH <sub>3</sub> ) <sub>2</sub> group)

Table-3: <sup>29</sup>Si-NMR Chemical Shifts of Compounds (3) - (5) at Different Temperatures.

No	Temperature(K°)	Chemical Shift/PPm
3	193	18.7971
	213	18.7410
	243	18.7082
	273	18.7065
	303	18.7119
4	213	21.4011
	243	21.7042
	273	21.9584
	303	22.0288
5	193	8.6407
	213	8.5223
	243	8.2648
	273	8.0529
	303	7.9823

evaporated. Compound (7) was obtained on distillation at 90°/15 mm.

### Results and Discussion

The investigated derivative of (1) and (2) for which structures are given in Fig. 1 were charac-

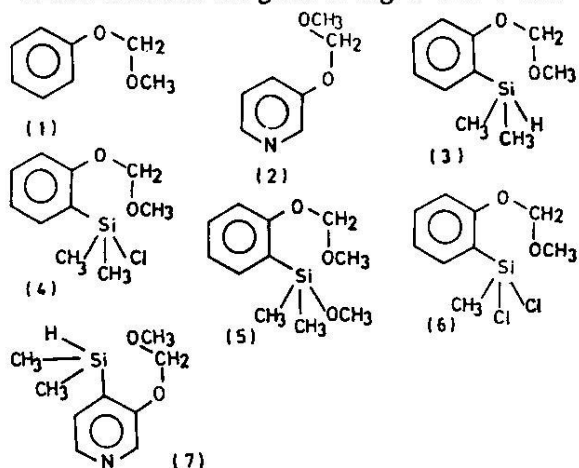


Fig.1: Structures of 1,3-dioxabutylbenzene (1), 3'-(1,3-dioxabutyl)-pyridine (2) and their derivatives (3-7).

terized by elemental analysis, <sup>1</sup>H NMR and <sup>29</sup>Si NMR spectra. The results for the <sup>1</sup>H NMR spectral at room temperature are given in Table 2 where <sup>29</sup>Si NMR results at different temperature are given in Table 3. The <sup>29</sup>Si NMR spectra data confirmed that there is no intramolecular coordinate bond between O---Si in these compounds, where the <sup>1</sup>H NMR data are evident for the synthesis of these compounds.

### References

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