# ORGANOSILYLATION: SYNTHESIS AND CHARACTERIZATION OF SILYLMETHYL METHYL ETHER\*

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The synthesis of germyl silane (1), GeH<sub>3</sub>SiH<sub>3</sub>, by the reaction of germyl chloride and potassium silyl (2), KSiH<sub>3</sub>, has been reported. This novel silylation reaction appears to be of general application. The synthesis of the new compound silylmethyl methyl ether, SiH<sub>3</sub>CH<sub>2</sub>OCH<sub>3</sub>, and KSiH<sub>3</sub> is reported. Vapor pressure data, empirical vapor pressure equation, Trouton's constant, melting point, and extrapolated boiling point of the pure compound are presented. Spectroscopic studies confirm the structure of the molecule.

## Physical Properties

Vapor pressure of a pure sample of silylmethyl methyl ether was measured in the range  $-20^{\circ}$  C to  $-64^{\circ}$  C. Data are reported in Table I. Vapor pressures in the range covered are represented by the equation:

$$\log P_{mm} = \frac{-1549.2}{t^{\circ}c + 273.16} + 8.0790$$

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The extrapolated boiling point, the molar heat of vaporization and Trouton's Constant were calculated to be  $-18^{\circ}$  C, 7089 cals. mole<sup>-1</sup>, and 24.3 cals. deg. mole.<sup>-1</sup> respectively.

TABLE I

Temp.	(°C)	Obs.	(mms)	Calcd.	(mms)
-63.9		4.7		4.7	
-64.2		4.7*		4.6	
-57.6		7.8		7.8	
-49.2		14.4		14.5	
-42.4		23.3		23.3	
-37.8		31.5		31.3	
-30.7		49.0		49.0	
-26.4		63.3		63.4	
-23.9		72.6		72.9	

Pressure observed on cooling after measurements on the sample had been completed.

Melting point was measured to be  $-123.0\pm0.2^{\circ}$  C.

The NMR Spectrum of the compound in tetramethylsilane proves its structure. The SiH<sub>3</sub> proton resonance signal appears as a triplet (relative intensity 1:2:1) due to splitting by the CH<sub>2</sub> protons.

Similarly the  $CH_2$  proton resonance signal is split into a quartet (relative intensity 1:3:3:1) due to the splitting by the protons of the SiH<sub>3</sub> group. The  $CH_3$  group gives rise to a single line as expected. The chemical shifts and coupling constants are given in Table II.

Comparing the chemical shifts of silylmethyl methyl ether with those of similar compounds, we note that proton resonance signal (3) in silane (-3.2 ppm) appears close to the signal in our molecule. This establishes the position of the silyl

## TABLE II

	Proto	on Ch	nemical	Shifts		
Compound	Pro	oton	Enviror	ment	Chemi	cal Shift (ppm)
SiH <sub>3</sub> CH <sub>2</sub> OCH <sub>3</sub>						
			$\mathtt{SiH}_3$			-3.54
			CH <sub>2</sub>			-3.33
			CH <sub>3</sub>			-3.27
	Spin-Spi	in Co	oupling	Constants		
Compound	$\mathtt{J}_{\mathrm{HH}}$	, (CPS	5)	J <sub>Si</sub> 29 <sub>H</sub> (CPS)		J <sub>C</sub> 13 <sub>H</sub> (CPS)
$SiH_3 CH_2 OCH_3$						
	CH3					141.0
	SiH <sub>3</sub>	2.55	5	203.3		
	CH <sub>2</sub>	2.55	5			

group in the molecule. The CH<sub>3</sub> proton resonance falls at the same field as that of CH<sub>3</sub> protons (5) in dimethyl ether (-3.27 ppm). The Si<sup>29</sup>H coupling constant (4) in SiH<sub>4</sub> (202.5±0.2 cps) is found to be close to the observed value in our compound.

Major fragments observed in the mass spectrum of  $SiH_3 CH_2 OCH_3$  were, in decreasing order of abundance:  $CH_3 OCH_2^+$ ,  $SiH_3 CH_2 O^+$ ,  $CH_3^+$ ,  $OCH_3^+$ ,  $SiH_3^+$ ,  $CH_3 OCH^+$ , and  $CH_2 OCH^+$ .

The infrared absorption spectrum agreed well with the structure of the molecule. The infrared spectrum showed weak to strong bands  $[cm^{-1}, gas$ phase at: 3000, 2880, 2820 (medium, C-H stretch <sup>(6)</sup>); 2170 (strong, Si-H stretch<sup>(7)</sup>); 1455 (weak, CH<sub>3</sub> deformation <sup>(7,9)</sup>); 1124 (strong, C-O-C assymetric skeletal stretch<sup>(10)</sup>) and 920 (very strong, SiH<sub>3</sub> deformation<sup>(7,8,9)</sup>)].

#### **Experimental**

Materials: Practical grade 1-2 dimethoxyethane was purified by distillation over metallic potassium in dry nitrogen stream. Disilane (10)  $Si_2H_6$  was prepared by the reduction of  $Si_2Cl_6$  in pure dry butylether with  $LiAlH_4$  and purified by low temperature distillations (11).

Preparation and Purification of Silylmethyl Methyl Ether: Phenyl potassium, 0.022 moles (K and K Labs.) as a slurry in normal hexane was treated with pure hydrogen at atmospheric pressure and room temperature for 48 hours to form potassium hydride. About 0.01 moles of hydrogen was absorbed. Disilane (0.006 moles) and 4 mls. of monoglyme were condensed onto the solids in the reaction flask. Reaction was allowed to proceed for 24 hours at room temperature. Pressure of one atmosphere at the beginning of reaction increased slightly towards the end of reaction. The reaction flask was cooled in a slush of  $-126^{\circ}$  C and the products were pumped through three traps cooled in liquid nitrogen. About 0.004 moles of monosilane was collected.

The reaction flask was cooled in  $-78^{\circ}$  C bath and pumped out for 15 minutes. An excess of pure dry monochloromethyl ether was now condensed onto the newly formed potassium silyl solid. The flask was warmed up to room temperature.

The new compound  $SiH_3CH_2OCH_3$  was formed on warming the reaction flask to room temperature. It is believed that the reaction may be represented by the following equation:

> $SiH_3 K + ClCH_2 OCH_3 = SiH_3 CH_2 OCH_3 + KCl$ No cleavage of the C-O-C linkage was observed. The volatile material, cooled at  $-78^\circ$  C was

allowed to distill into two traps cooled in liquid nitrogen, through two traps cooled at -96° C. The fraction collecting at -96° C was further fractionated on a nitrogen cooled low temperature column (12). About 70 mg of the pure compound was obtained. Analysis: Calcd: C, 31.51%; H, 10.58%; found: C, 31.75%; H, 10.30%; mol. wt. Calcd. 76.06; found 76.57.

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