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THE PREPARATION AND PROPERTIES OF SILYL METHYL SULPHIDE*

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Abstract—The new compound, SiH₃SCH₃, has been prepared from SiH₃I·N(CH₃)₃ and CH₃SH. Its physical properties have been studied. Using B_2H_6 as a reference Lewis acid, SiH₃SCH₃ has been found to be a weaker Lewis base than (CH₃)₂S. Diborane was not a sufficiently strong Lewis acid to differentiate between the relative base strengths of SiH₃SCH₃ and (SiH₃)₂S.

IN a previous paper⁽¹⁾ it was shown that $(CH_3)_2O$ was a stronger Lewis base than both SiH_3OCH_3 and $(SiH_3)_2O$ when B_2H_6 was used as the reference Lewis acid. The base strength of SiH_3OCH_3 relative to $(SiH_3)_2O$ could not be determined since neither compound formed an addition compound with B_2H_6 . Since B_2H_6 generally forms stronger addition compounds with sulfides than with ethers,⁽²⁾ it was hoped that if the analogous series of sulphides was investigated that the relative base strengths of the silvl methyl and disilyl compounds could be determined.

EXPERIMENTAL

Apparatus and reagents. The apparatus, techniques and reagents were identical to those used in previous work.⁽¹⁾

Methanethiol. Commercial CH₃SH (99 per cent minimum purity) was distilled in the vacuum system, the first and last portions to distil being rejected.

Preparation of SiH₃SCH₃. A slight excess of $(CH_3)_3N$ was mixed with SiH₃I(0.7098 g) in a 500 ml bulb at -196° and after warming to room temperature, the excess $(CH_3)_3N$ was distilled from the solid SiH₃I·N(CH₃)₃. CH₃SH(0.2024 g) was then added and the reaction vessel was held at 0° for 7 hr. Materials volatile at -78° were then allowed to distil from the reaction vessel for a period of 85 min. Fractionation of the volatile materials yielded crude SiH₃SCH₃ as a condensate in a trap at -96° . Slow distillation from a trap at -78° yielded pure SiH₃SCH₃(0.1782 g, 54 per cent yield;

mol. wt. found, 78·0, calcd., 78·22). Analyses and all experimental work with SiH₃SCH₃ were carried out using material whose vapor pressure at 0° was in the range 105·1–105·4 mm (calcd., 105·2 mm).

A sample of the material (0.0886 g) was hydrolysed in 35% aqueous NaOH containing ethanol (2 ml) and piperidine (2 ml). Silicon was determined as $SiO_2^{(3)}$ (Found, 35.8. Calcd., 35.91%). Another sample was analysed for carbon and hydrogen.[‡] (Found: C, 15.6; H, 7.9. Calcd. C, 15.35; H, 7.7%). SiH₃SCH₃ melts sharply at --116.7 \pm 0.4%.

Vapour-pressure of SiH₃SCH₃. The vapour-pressures of SiH₃SCH₃ were measured at a number of temperatures using a mercury manometer. They are recorded in Table 1.

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 $[\]ddagger$ Analyses performed by Micro-Analysis, Inc., Wilmington, Del. Since SiH_3SCH_3 decomposes slowly at room temperature, the sample was transported in Dry-ice.

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The above data for SiH₃SCH₃ are represented by the equation

$$\log P(\mathrm{mm}) = \frac{-1604}{T} + 7.893$$

which gives an extrapolated boiling point of $46.8 \pm 0.2^\circ$, a molar heat of vaporization of 7.34 kcal and a Trouton's constant of 22.9. Since no decomposition of the compound occurred during the vapour-pressure determinations, the true boiling point should not differ greatly from the extrapolated value.

$T(^{\circ}\mathbf{C})$	<i>P</i> (mm)(expt.)	P (mm)(calcd.)
-45.2	6.9	7.2
-37.6	11.8	12.2
-30·2	19.6	19.6
-24.9	27.1	27.1
-17.2	42.3	42.4
-11.6	57.8	57.8
- 5.8	78.8	78.3
- 0.2	104.0	104.2
0.0	105-1†	105.2
0.0	105.4‡	105-2
2.4	118.2	118-3

* Duration of experiment approximately 11 hrs.

† Pressure before experiment.

‡ Pressure after experiment.

cm ⁻¹	Designation	Analogy (cm ⁻¹)
2910 w)*	C-H stretch ⁽⁴⁾	
2840 v.w)		
2160 s	Si—H stretch	2210 in SiH_3SCF_3 ; ⁽⁵⁾
1		2180 in $(SiH_3)_2S^{(6)}$
1440 w)	CUL deformation(4)	
1320 w	CH ₃ deformation.	
959 sh. m	SiH ₃ deformation	940 in SiH ₃ SCF ₃
		956 in (SiH ₃) ₂ S
915 s	SiH_a deformation	910, 906, 762 in SiH ₃ SCF ₃
		907 in (SiH ₃) ₂ S
695 w	C—S stretch	694 in $(CH_3)_2 S^{(7)}$
645 m	SiH ₃ rock	625 in SiH_3SCF_3 ;
	-	635 in (SiH ₃) ₂ S

* w = weak, s = strong, v.w. = very weak, m = medium, sh. m. = shoulder medium

Infra-red spectrum of SiH₃SCH₃. This was made with a Perkin-Elmer Model 21 double beam recording spectrophotometer, employing a sodium chloride optical system and a 10 cm cell fitted with 30 mm potassium bromide windows cemented with glyptal resin. The measurement was made at 20° on a gaseous sample at 16 mm pressure.

Thermal stability of SiH₃SCH₃.SiH₃SCH₃(0.0517 g) was allowed to stand at room temperature,

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partly in the liquid phase and partly in the vapour phase in a 12 ml all-glass container, in normal laboratory lighting, for four days. Only 94 per cent of the SiH_3SCH_3 was recovered as volatile material. The more volatile half of the material was removed by distillation and the remaining half was found to have a vapour-pressure at 0° of 101.6 mm (calcd. 105.2 mm). Hence some thermal decomposition had occurred.

Interaction of SiH₃SCH₃ with B_2H_6 .(i) SiH₃SCH₃(0.434 mmole) and B_2H_6 (0.217 mmole) were combined at -196° in a small tube connected to a mercury manometer. The tube was surrounded by a -80° bath for 15 min and then cooled to -196° . This was repeated six times in order to facilitate mixing. After cooling to -130.5° the mixture exerted a pressure of 37.0 mm. The sum of the vapourpressures of the individual compounds at this temperature is $48.2 \text{ mm}^{(8)}$; 81.6 per cent of the original B_2H_6 used was found to distil from the mixture at -130.5° during 4-5 min. The remainder of the material, on fractionation, yielded B_2H_6 , which, when combined with that first removed, amounted to 0.215 mmole, (mol. wt. found, 26.6, calcd., 27.69; infra-red spectrum identical to that of pure B_2H_6). The other fraction consisted of SiH₃SCH₃(0.438 mmole; mol. wt. found, 77.9, calcd., 78.22; vapourpressure at 0°, found 105.0 mm, calcd., 105.2 mm).

(ii) A second experiment was performed in which an excess of B_2H_6 was employed. SiH₃SCH₃ (0·438 mmole) and B_2H_6 (0·831 mmole) were treated as previously described. A constant pressure of 38·5 mm was measured after 80 min at $-130\cdot6^\circ$. The sum of the vapour-pressures of the individual components at this temperature is 47·8 mm. Ninety-nine per cent of the original B_2H_6 used was found to distil from the mixture at $-130\cdot5^\circ$ during 1 hr. Upon fractionation, the remainder of the material yielded a trace of B_2H_6 , which, when combined with that first removed, amounted to 0·827 mmole, (mol. wt. found 27·5, calcd., 27·69, infra-red spectrum identical to that of pure B_2H_6). The other fraction consisted of SiH₃SCH₃(0·441 mmole; mol. wt., found 77·8, calcd., 78·22, vapour-pressure at 0°, found 105·3 mm, calcd., 105·2 mm).

It is believed that all the B_2H_6 did not distil from the $-130\cdot5^{\circ}$ mixture in the first experiment because the time allowed was not sufficiently long. The low vapour-pressures of the SiH₃SCH₃-B₂H₆ mixture at $-130\cdot5^{\circ}$ and $-130\cdot6^{\circ}$ are probably due to solubility effects or to some form of weak interaction.⁽¹⁾

RESULTS AND DISCUSSION

The reaction of the addition compound formed from SiH_3I and $(CH_3)_3N$ with CH_3SH at 0° gave good yields of the new compound SiH_3SCH_3

$$SiH_3I \cdot N(CH_3)_3 + CH_3SH \rightarrow SiH_3SCH_3 + (CH_3)_3N \cdot HI$$

No evidence was obtained for the formation of an addition compound between SiH_3SCH_3 and B_2H_6 under conditions suitable for the formation of $(CH_3)_2S\cdot BH_3$.⁽⁹⁾ It has been reported that under similar experimental conditions there is no adduct formation between $(SiH_3)_2S$ and B_2H_6 .⁽¹⁰⁾ Both SiH_3SCH_3 and $(SiH_3)_2S$ are therefore weaker Lewis bases than $(CH_3)_2S$ but B_2H_6 is not a sufficiently strong acid to differentiate between the relative base strengths of SiH_3SCH_3 and $(SiH_3)_2S$. It is highly likely that the unexpectedly small base strength of SiH_3SCH_3 observed is due at least in part, to the energy required to convert B_2H_6 to BH_3 units.⁽¹⁾

The relative electronegativity values of silicon (1.8) and carbon (2.5) would lead one to expect that the base strength of the sulphides would increase as silyl groups were substituted for methyl groups. The fact that $(SiH_3)_2O$ is a much weaker base than $(CH_3)_2O^{(10)}$ has been attributed to the fact that considerable $p_{\pi}-d_{\pi}$ bonding occurs between the oxygen and the silicon. This is consistent with the fact that the Si—O—Si

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bond angle in $(SiH_3)_2O$ is 155° ,⁽¹¹⁾ whereas the C—O—C angle in $(CH_3)_2O$ is 111° .⁽¹²⁾ The oxygen bonds in $(SiH_3)_{2}O$ therefore have considerable SP character. If an exactly analogous explanation were to be given to explain the low base strength of $(SiH_3)_{2}S$ then one would expect that the Si-S-Si angle would be large. However, it has been found to be only 100°.⁽¹³⁾ This. therefore, suggests that the bonding in the sulphur linkages has very little s character and is primarily pure p in character with the $p_{\pi} - d_{\pi}$ bond involving principally the remaining 3p sulphur electrons. This is consistent with the observations that in simple sulphur compounds such as $H_{2}S$ and $(CH_{3})_{2}S$ there is less s character in the sulphur bonds than in the oxygen bonds in the analogous species H_2O and $(CH_3)_2O$. This is exhibited in the observed bond angles $H_2O = 104^{\circ}31^{2}(14)$. $H_2S = 92^{\circ}6'^{(15)}$, $(CH_3)_2O = 111^{\circ(12)}$, $(CH_3)_2S = 104^{\circ}28'$.⁽¹⁶⁾

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