Partially Fluorinated Derivatives of Disiloxane

By EDWARD W. KIFER and CHARLES H. VAN DYKE*

(*Department of Chemistry and the Mellon Institute of Carnegie-Mellon University, Pittsburgh, Pennsylvania* 15213)

Summary The synthesis of $FSiH_2OSiH_3$ and $(FSiH_2)_2O$ has been achieved by the reaction of $(SiH_3)_2O$ with PF_5 at low temperatures.

THE silicon–oxygen bond of siloxanes is readily cleaved by a variety of covalent halides. Schmutzler[1] reports that the interaction of $(Me_3Si)_2O$ with $PhPF_4$ produces Me_3SiF and $PhPOF_2$ in high yield; thus the expected reaction of siloxanes with PF_5 is:

$$\equiv Si\text{–}O\text{–}Si\equiv + PF_5 \rightarrow 2\equiv Si\text{–}F + POF_3 \qquad (1)$$

We have observed that the room temperature reaction of $(Me_3Si)_2O$ with PF_5 produces Me_3SiF and POF_3 quantitatively; however, the reaction of $(SiH_3)_2O$ with PF_5 under identical conditions produces an appreciable quantity of SiH_2F_2 and smaller amounts of H_2, PF_3, $HPOF_2$, and SiF_4 in addition to the expected SiH_3F and POF_3. Other experiments indicate that SiH_2F_2 is not formed by the decomposition of SiH_3F in the presence of PF_5 under the same conditions.

When the reaction of $(SiH_3)_2O$ and PF_5 was carried out at −78°, mass spectral analyses indicated that the products included two partially fluorinated siloxanes. The latter are most likely formed according to equation (2).

$$(SiH_3)_2O + PF_5 \xrightarrow{-78^\circ} FSiH_2OSiH_3 \text{ [and } (FSiH_2)_2O] + HPF_4 \text{ and/or } H_2PF_3 \qquad (2)$$

The HPF_4 or H_2PF_3 in the above equation could not be characterized directly owing to their ready decomposition; however, the H_2, PF_3, $HPOF_2$, and SiF_4 which were observed are products of the known decomposition of HPF_4 and H_2PF_3 in the presence of glass.[2,3] The cleavage of the silicon–oxygen bond of the partially fluorinated siloxanes by PF_5 would account for the formation of SiH_2F_2 in the reactions at higher temperatures.

By adjusting the ratio of reactants and the reaction time, the two new fluorosiloxanes could be selectively obtained in reasonably good yields, although some cleavage of the silicon–oxygen bond took place in all experiments. Monofluorodisiloxane, $FSiH_2OSiH_3$, (b.p. −7·6°) was obtained in 65% yield by using a 1 : 1 molar ratio of reactants and allowing a 15 min. reaction time. Difluorodisiloxane, which was shown to be exclusively $(FSiH_2)_2O$ by its ^1H n.m.r. spectrum (b.p. 17·5°) was obtained in 31% yield by using a 1 : 2 $(SiH_3)_2O : PF_5$ ratio and allowing a 60 min. reaction time. The syntheses were carried out with liquid phase present at −78° in all-glass break-seal tubes. Standard vacuum-line techniques were used throughout.

The two fluorosiloxanes are difficult to separate by conventional low-temperature vacuum fractionation; however, $FSiH_2OSiH_3$ will pass through a trap maintained at −116°, whereas $(FSiH_2)_2O$ essentially does not. It is difficult to ascertain when the above separation is complete by i.r. techniques, owing to the similarity of the spectra for the two compounds. In this work, the final purification of the fluorosiloxanes was achieved by using preparative-scale g.l.c. An 18 ft. column packed with a 20% silicone oil (710)/Chromosorb W (60–80 mesh) is satisfactory for the separation. The best purity check is by g.l.c. or mass spectrometry. The compounds, once purified, are reasonably stable thermally and can be handled routinely in normal vacuum-line operations.

The mass, i.r., and n.m.r. spectral patterns of the compounds all show the expected features. The calculated/observed precise mass values for the parent ions less one hydrogen (the most intense ions in the mass spectra) are 94·9787/94·9784 and 112·9692/112·9691 for Si_2H_4FO and $Si_2H_3F_2O$, respectively. Major i.r. absorption bands for the two compounds are listed below.

$FSiH_2OSiH_3$: 2207(s); 1720(w); 1225(w) 1123(s); 970(s); 948,936(vs); 883,868(w); 731(m)

$(FSiH_2)_2O$: 2212(s); 1740(w); 1231(w); 1134(s); 978(s); 937,927(vs); 883,872(w) 723(m).

The absorptions in the 927—948 cm.$^{-1}$ region are readily assigned to the silicon–fluorine stretch.[4] Most of the remaining frequency assignments can be made from the assignments given for $(SiH_3)_2O$.[5]

^1H n.m.r. data for the compounds (10% by volume in $FCCl_3$; Me_4Si internal standard) are:

$FSiH_2OSiH_3$: τ $FSi\mathit{H}_2 = 5{\cdot}36$; $Si\mathit{H}_3 = 5{\cdot}28$; J(HSiF) 61·2 Hz; J ($^{29}SiH_3$) = 224·7 Hz

$(FSiH_2)_2O$: τ $FSiH_2 = 5{\cdot}25$; J(HSiF) 61·2 Hz.

The normal effect of fluorine substitution in $(SiH_3)_2O$ would be to cause a down-field shift of the remaining protons attached to silicon. However, in $FSiH_2OSiH_3$ the protons in the $FSiH_2$ group are not changed as much from $(SiH_3)_2O$ (τ 5·39)[6] as the SiH_3 protons, several bonds removed from the fluorine. It is difficult to establish whether this unusual trend is due to some factor associated with the Si–O–Si linkage or whether the effect is peculiar to fluorine substitution. The carbon analogue of the compound has not been studied; however, the available data for $ClCH_2OMe$ and Me_2O show the expected trends based on simple electronegativity concepts [for $ClCH_2OMe$, τ $ClC\mathit{H}_2$ 4·72, $C\mathit{H}_3$ = 6·62; for Me_2O 7, τ $C\mathit{H}_3$ 6·79].

Fluorination of the silicon–hydrogen bonds of $(SiH_3)_2S$ or SiH_3OMe could not be achieved by this method. With the latter compound, the silicon–oxygen bond is quantitatively cleaved at −78°, producing SiH_3F and an unstable compound tentatively identified as $MeOPF_4$.[8] The reaction of PF_5 with $(SiH_3{\cdot}SiH_2)_2O$ at −78°, produces $SiH_3{\cdot}SiH_2F$ and POF_3, with no evidence whatsoever of the formation of any partially fluorinated siloxanes.

The abnormally wide Si–O–Si bond angle observed in $(SiH_3)_2O$ (144.1°)[9] and other siloxanes has usually been attributed to $(p\rightarrow d)\pi$ bonding in this linkage involving the filled p-orbitals of oxygen and silicon's vacant d-orbitals. The new fluorosiloxanes described here offer excellent systems for observing whether the magnitude of the Si–O–Si bond angle and possibly the degree of π-bonding in the Si–O–Si linkage can be altered appreciably by introducing atoms on silicon which possess strong σ-withdrawing yet strong π-donor properties all the while keeping steric effects to a minimum.

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