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# TRIFLUOROMETHYLSILANE, $CF_3SiH_3$

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## SUMMARY

$CF_3SiH_3$ (I) has been obtained in ~90 % yield from the reaction of $CF_3SiF_3$ or $CF_3SiF_2I$ with $LiAlH_4$ in dibutyl ether at -78°. (I) has been characterized by its $^1H$, $^{19}F$, $^{13}C$ and $^{29}Si$ NMR-, mass-, IR- and Raman spectra. It is thermally stable up to 180° and not attacked by $O_2$, $H_2O$ and $H_3PO_4$, but cleaved by aqueous alkali. From a rovibrational analysis, $B_o = 0.09769(2)$ $cm^{-1}$ is deduced, and a long SiC bond, 1.95(1)Å, is predicted.

## INTRODUCTION

Among the few $CF_3Si$ compounds reported so far [1], $CF_3SiF_3$ (II), which has been obtained via the reaction of $CF_3I$ with $SiF_2$ and subsequent fluorination of $CF_3SiF_2I$ with $SbF_3$, has been characterized most thoroughly [2]. In contrast to the behaviour of the tetramethyl derivatives of C, Ge and Sn, the direct fluorination of $(CH_3)_4Si$ under mild conditions does not afford $(CF_3)_4Si$ but gives incompletely fluorinated compounds, e.g. $Si(CF_3)(CF_2H)(CFH_2)(CH_3)$ [3].

The simplest trifluoromethylsilane, namely $CF_3SiH_3$ (I), has not been reported. Both its chemical behaviour and its

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physical properties are of interest since its SiC bond is expected to be unusually long and weak [4], and efforts directed towards its synthesis seemed to be justified.

## RESULTS AND DISCUSSION

We have been able to obtain (I) with good yield, 90 and 85 %, respectively, by reacting (II) or $CF_3SiF_2I$ with $LiAlH_4$ in dibutyl ether at -78° for 15 minutes. The reduction of the $SiF_3$ and $SiF_2I$ groups is selective, no attack of the $CF_3$ group being observed under these conditions. Only $SiH_4$ (ca. 5 %) and $HCF_3$ (in traces) have been detected as side products On prolonged contact with dibutyl ether, $CF_3SiF_2I$ decomposes to form (II), $SiF_4$, cyclo-$C_3F_6$ and cleavage products of the ether. A similarly selective reduction of a fluoroalkyl fluorosilane with $LiAlH_4$ has been recently reported, only $[H(CH_3)_2Si]_2CF_2$ being obtained from $[F(CH_3)_2Si]_2CF_2$ [5].

The physical properties of (I) have been determined. At room temperature, (I) is a colourless, monomeric gas, mp. -124 °C, $bp._{760}$ -38.3 °C, vapour pressure (-88 to -37 °C) log p [torr] = 7.632 - 1115 $T^{-1}$ [K]. $^1H$, $^{19}F$, $^{13}C$ and $^{29}Si$ NMR spectra have been recorded. Chemical shifts and coupling constants are set out in Table 1. The mass spectrum of (I), Table 1, is in agreement with the proposed constitution. Formation of SiF bonds by fluorine migration is important in the fragmentation process. Several ions with intact SiC bonds have been observed, ($M^+$ - HF) (~10 % relative intensity) being the most abundant of these. The mass spectrum of $CF_3SiD_3$ is fully analogous and confirms that m/e = 31 is ($SiH_3^+$) rather than ($CF^+$).

TABLE 1

Spectroscopic data of $CF_3SiH_3$

Vibrational Spectra

| Assignment | $a_1$ | IR[a]/Raman[b] | e | IR/Raman |
|---|---|---|---|---|
| $\nu(SiH_3)$ | $\nu_1$ | 2209/2205 | $\nu_7$ | 2223/2220 |
| $\delta(SiH_3)$ | $\nu_2$ | 899/896 | $\nu_8$ | 936/931 |
| $\rho(SiH_3)$ | | - | $\nu_9$ | 646/648 |
| $\nu(CF_3)$ | $\nu_3$ | 1223/1218 | $\nu_{10}$ | 1110/1085 |
| $\delta(CF_3)$ | $\nu_4$ | 733/731 | $\nu_{11}$ | 501/502 |
| $\rho(CF_3)$ | | - | $\nu_{12}$ | 217/227 |
| $\nu(SiC)$ | $\nu_5$ | 405/402 | | - |

NMR Data

$^1H$[c] $\delta$ = 3.92 (q), $^3J(HF)$ = 7.5 Hz, $^1J(H^{29}Si)$ = 223 Hz

$^{19}F$[d] $\delta$ = -56.1, $^3J(FH)$ = 7.5 Hz, $^2J(F^{29}Si)$ = 48.8 Hz, $^1J(F^{13}C)$ = 314.3 Hz

$^{13}C$[e] $\delta$ = 129.9, $^1J(^{13}CF)$ = 316 Hz

$^{29}Si$[f] $\delta$ = -71.1, $^2J(^{29}SiF)$ = 46 Hz

Mass Spectrum, 70 eV, E.I., in order of decreasing intensity

m/e 31 ($SiH_3^+$, 100%), 49 ($H_2SiF^+$, 85 %), 47 ($SiF^+$, 77 %), 67 ($HSiF_2^+$, 67 %), 33 ($H_2CF^+$, 28 %) ... 100 ($M^+$, 3 %)

[a]Gas phase, ± 1 $cm^{-1}$. [b]Liquid phase, ± 2 $cm^{-1}$. [c]90 MHz, in $TMS/CFCl_3$. [d]84.67 MHz, in $TMS/CFCl_3$. [e]20.0 MHz, in $C_6D_6$, against external TMS. [f]15.8 MHz, in $C_6D_6$, against external TMS.

Medium resolution IR and Raman spectra of (I) have been recorded, Table 1. They are assigned to the eleven active fundamentals, IR band contours, Raman polarization states and a normal coordinate analysis incorporating $CF_3SiD_3$ data unambiguously confirming the given assignment. The inactive $a_2$ torsion $\nu_6$ may be estimated, ~110 $cm^{-1}$. Previous reports [6] of this vibration are erroneous because $CF_3SiH_3$ and the well-known $CH_3SiF_3$ have been confused.

High resolution (0.04 $cm^{-1}$) IR spectra of (I) in the $\nu_2$* and $\nu_3$ regions have been recorded, and rotational J structure has been resolved up to J = 90. A polynomial analysis, $\sigma(J) = 5 \times 10^{-3}$ $cm^{-1}$, provides the ground state rotational constant $B_0$ = 0.09769(2) $cm^{-1}$. This may be used to estimate the SiC bond length if resonable assumptions are made for the geometry of the $CF_3$ (d CF 1.335 Å, ∠ FCF 108.5°) and $SiH_3$ part (d SiH 1.478 Å, ∠ HSiH 108.7°). The predicted SiC distance, 1.95(1) Å, is more than 0.06 Å longer than the standard value, cf. 1.867 Å in $CH_3SiH_3$ [7]. Despite its long and weak SiC bond, (I) shows surprisingly high chemical and thermal stability. In the gas phase, (I) is not attacked by $O_2$ and $H_2O$. It is not decomposed by $H_3PO_4$ (1:1), but rapidly cleaved by aqueous NaOH (10 %) according to eqn. (1):

$$CF_3SiH_3 + 4OH^- \rightarrow CF_3H + SiO_4^{4-} + 3\ H_2 \qquad (1)$$

Thermal decomposition of (I) begins at 180 °C and is complete after 15 hours at 210°. Among minor amounts of additional

*The rotational structure of $\nu_2$ is systematically perturbed for high J values due to Coriolis-x,y resonance with $\nu_8$.

products the following volatile decomposition products were identified: $SiH_2F_2$, $HSiF_3$, $HCF_3$ and traces of $SiF_4$, $H_3SiF$ and cyclo-$C_3F_6$. $SiH_4$ was definitely absent. In an independent experiment it was shown that, under the chosen conditions, $H_3SiF$ does not decompose to form $H_2SiF_2$ and $HSiF_3$. From the composition of the thermolysis products we conclude that $CF_2$ elimination is the first step of the thermal cleavage. Homolytic SiC fission, subsequent transfer of F to Si and H to C and recombination of radicals may also account for the observations.

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