

Thermolysis of trifluoromethylsilanes. Novel fluoromethylsilanes by insertion of CF_2 and CHF into Si–H bonds

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(Received September 20th, 1989)

Abstract

The thermal decomposition in the gas phase of CF_3SiH_3 and $(\text{CF}_3)_2\text{SiH}_2$ begins at -200 and -100°C , respectively. It is catalyzed by KF , and involves as initial step a clean CF_2 elimination with an α -fluorine shift. Reactive species such as HBr trap CF_2 quantitatively (to give in this case CHF_2Br), while addition to the less reactive cyclohexene (to give 7,7-difluorobicycloheptane) is accompanied by secondary reactions. These dominate in the absence of an efficient CF_2 trapping agent, and spectroscopic product analyses reveal that they mainly arise from insertion of the carbenes $\text{CH}_n\text{F}_{2-n}$ into Si–H bonds followed by $\text{CH}_{n+1}\text{F}_{1-n}$ elimination ($n = 0, 1$). This sequence corresponds to H/F exchange at the Si atom. Insertion of CF_2 (generated by thermolysis of CF_3SiF_3 below 100°C) into an Si–H bond of H_3SiF to give $\text{CHF}_2\text{SiH}_2\text{F}$ in good yield is the first example of such a reaction and demonstrates its usefulness for the selective synthesis of CHF_2Si compounds. In addition, some dismutation of $\text{SiH}_n\text{F}_{3-n}$ moieties accompanies the carbene elimination/insertion reactions and the resulting novel fluoromethylsilanes were characterized by ^1H and ^{19}F NMR and (in part) IR spectroscopy. The synthesis of $(\text{CF}_3)_2\text{SiHBr}$ by cleavage of $(\text{CF}_3)_2\text{Si}(\text{H})\text{N}(\text{i-Pr})_2$ with BBr_3 and its conversion with LiAlH_4 to $(\text{CF}_3)_2\text{SiH}_2$ are reported. The mechanism of the CF_2/SiH insertion reaction is discussed.

Introduction

The development of trifluoromethylsilicon chemistry was delayed by the difficulties associated with the formation of Si– CF_3 bonds. Sharp and Coyle [1] prepared the first such compound by inserting the short-lived SiF_2 into a C–I bond, but recently more general routes have become available which involve nucleophilic trifluoromethylation with the reagents $(\text{Et}_2\text{N})_3\text{P}/\text{CF}_3\text{Br}$ [2–4] and $(\text{Me}_2\text{N})_2\text{C}=\text{C}-(\text{NMe}_2)_2/\text{CF}_3\text{I}$ [5]. The applicability of the nucleophilic trifluoromethylation of

electropositive main group elements such as Si is, however, severely curtailed by the ease of formation and oligomerization of CF_2 as well as the strength of the concomitantly formed element-fluorine bond, effects which strongly favour thermal decomposition of the desired products. Thus, the silicon compounds belong to the family of trifluoromethyl derivatives of electropositive elements which are generally regarded as convenient sources of CF_2 [6-8]; they are mostly used in solution, but reactions in the gas phase have been reported [9]. Thermal decomposition of CF_3SiF_3 (I), which has a lifetime of ca. 7 min at 100°C in the gas phase, yields SiF_4 and CF_2 quantitatively, the latter oligomerizing in the absence of suitable trapping agents to C_2F_4 and cyclo- C_3F_6 [10].

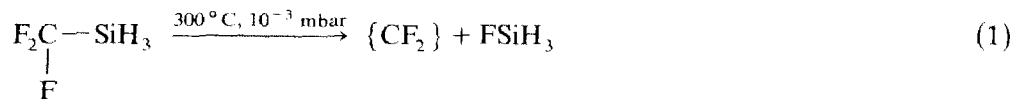
Although CF_2 is a powerful insertion reagent, to our knowledge no such insertions have been reported for Si-H [10], Si-F, Si-Cl and Si-Br bonds [11,12]. On the other hand, CF_2 is known to insert into Si-Si [13] and Si-O bonds [14], as well as into Ge-H and Sn-H bonds, with formation of GeCHF_2 [15] and SnCHF_2 compounds [6]. Insertion of plasma-generated CF_2 into Si-H bonds probably plays an important role in the production by chemical vapour deposition of amorphous Si:C(H,F) alloy films that show promising properties as photosensitive diodes [16].

The thermal decomposition of CF_3SiH_3 (II) is reported to start at ca. 180°C . In the absence of carbene trapping agents, H_2SiF_2 and HSiF_3 were formed [17]. These cannot be primary decomposition products but must come from secondary reactions. In order to identify these secondary reactions, we have investigated the thermal decomposition of II and $(\text{CF}_3)_2\text{SiH}_2$ (III) in the gas phase, in the absence and in the presence of various carbene trapping agents. We have also studied the secondary reactions of II with CF_2 generated from I under mild conditions, and the results are reported below.

Thermal decomposition of CF_3SiH_3

Primary products

The composition of the products obtained by thermolysis of II depends greatly on the conditions employed. While numerous volatile species are obtained at elevated temperature and pressure (see below), a simple and clean decomposition is observed in the presence of an efficient CF_2 trapping agent or at low pressure under collision-free conditions, C_2F_4 then being formed by dimerization of CF_2 . The process may be represented as an elimination of CF_2 according to eq. 1:



However, even at 300°C the decomposition of II in a flow experiment was incomplete, and at 10^{-3} mbar more than 95% was recovered. The decomposition is strongly accelerated by KF, more than 95% being decomposed at 160°C under otherwise similar conditions. The near quantitative formation of H_3SiF rules out the elimination of HF according to eq. 3.



Table 1

Thermolysis of CF_3SiH_3 (II) in the presence of cyclohexane and HBr

| | | |
|--------------------------------------|---|--|
| Conditions of thermolysis | 1.4 mmol II 6.8 mmol C_6H_{10} 5 h, 210 °C, 3 bar | 1.4 mmol II 7.0 mmol HBr 5.3 h, 210 °C, 3 bar |
| Decomposition (%) | 95 | 100 |
| Volatile thermolysis products (mol%) | H_3SiF (51) H_2SiF_2 (47) | H_3SiF (35) H_3SiBr (13) CHF_2Br (50) $\text{HSiF}_3, \text{SiF}_4$ (2) |
| Less volatile products | traces: $\text{HSiF}_3, \text{SiF}_4, \text{HCF}_3$ | |
| | | |
| | 1 / 0.52 / 0.65 | |

The reaction products similarly rule out as the initial step both a decomposition according to eq. 4

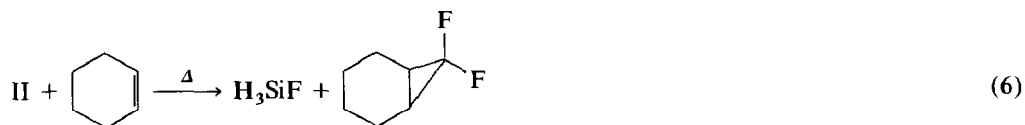


as well as a homolytic fission of the C–Si bond according to eq. 5.

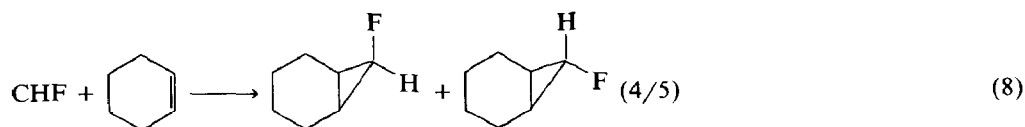


When II and an excess of HBr, an efficient CF_2 trap [18], were heated together at 210 °C in a glass cylinder at a pressure of 3 bar for 6 h, CHF_2Br was quantitatively formed and various silane derivatives were identified in the gaseous thermolysis products (Table 1), which were made up of 70% of H_3SiF , 26% of H_3SiBr and 4% of ($\text{SiF}_4 + \text{HSiF}_3$). We confirmed independently that H_3SiBr is formed from H_3SiF and HBr under these conditions.

Thermolysis of II in the presence of the carbene trapping agent cyclohexene under the same conditions is less specific (Table 1). Approximately half of the reaction products, H_3SiF and 7,7-difluorobicycloheptane [4.1.0], are formed by a process similar to that mentioned above, eq. 6:



The other products arise from secondary reactions, eqs. 7 and 8,



the formation of *endo*- and *exo*-7-fluorobicycloheptane[4.1.0] proving the occurrence of monofluorocarbene CHF as intermediate [19]. No other products were

observed, except for traces of HSiF_3 , SiF_4 and HCF_3 (Table 1). Evidently, secondary reactions of CF_2 with H_3SiF compete with the trapping of CF_2 by the olefin, which is apparently a slower process than trapping by HBr [18.20].

Thermal decomposition of II: secondary products

In order to throw light on the mechanism of formation of the secondary products, we thermally decomposed II completely at pressures of 0.2 and 40 bar, Table 2. In qualitative terms the product distribution is fairly independent of the pressure and temperature although under more vigorous conditions the products undergo substantial subsequent decomposition. In contrast to the flow experiment, neither H_3SiF nor C_2F_4 were observed among the products. H_2SiF_2 , which is a major product at lower pressure, was absent at higher pressure, while substantial amounts of HSiF_3 were identified in both experiments. No SiF_4 was found. In an independent experiment we confirmed that H_3SiF does not decompose under the thermolysis conditions and so the H_2SiF_2 and HSiF_3 must be formed by complex processes; e.g. as in eqs. 7 and 9.



Only small amounts of the CF_2 oligomer cyclo- C_3F_6 were found, and no C_2F_4 or other fluorocarbons were detected.

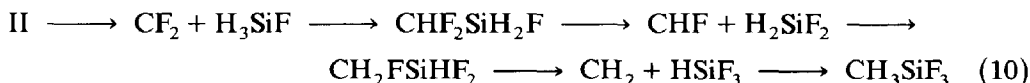
All other products, which were fully characterized by NMR and, in part, vibrational spectroscopy (see below), can be interpreted in terms of insertion of CHF and CH_2 into the Si-H bonds of H_2SiF_2 and HSiF_3 . Inspection of Table 2 reveals that CH_3Si species resulting from CH_2 insertion are more abundant at higher pressure and temperature. The insertion of CH_2 into Si-H bonds has been

Table 2
Thermolysis of CF_3SiH_3 (II)

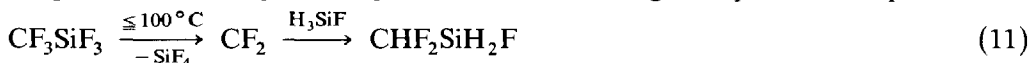
| Conditions of thermolysis | 0.5 mmol II 15 h, 210 °C, 200 mbar (5 h, 180 °C, 200 mbar) | 0.9 mmol II 6 h, 240 °C, 40 bar | 2.4 mmol II 300 °C, 10^{-3} mbar flow system | 0.9 mmol II 160 °C, 10^{-3} mbar flow over KF |
|--|--|---------------------------------------|---|--|
| Decomposition (%) | 100 (5-10) | 97 | 3-4 | 95 |
| Volatile products identified (mol%) | | | | |
| H_3SiF | | | 67 | 63 |
| H_2SiF_2 | 29.4 | | | |
| $\text{CH}_2\text{FSiHF}_2$ | 17.6 | 3.7 | | |
| $(\text{CH}_2\text{F})\text{CH}_3\text{SiF}_2$ | | 16.6 | | |
| CH_3SiHF_2 | 7.4 | 19.2 | | |
| $(\text{CH}_3)_2\text{SiF}_2$ | | 2.2 | | |
| HSiF_3 | 17.6 | 19.2 | | |
| CH_2FSiF_3 | 14.7 | 20.4 | | |
| CH_3SiF_3 | 5.9 | 9.4 | | |
| HCF_3 | 4.4 | 0.7 | | |
| C_2F_4 | | | 33 | 35 |
| cyclo- C_3F_6 | 1.5 | 2.1 | | SiH_4 2 |

reported to be one of the fastest reactions of methylene [21–23], whereas to our knowledge, insertion of CHF into Si–H bonds has not yet been observed.

More vigorous conditions increase the proportion of CH₂-insertion products at the expense of those from CHF. This is in agreement with a stepwise increase in thermal stability on going from CF₃SiH₃ to CH₃SiF₃ in the sequence shown in eq. 10.

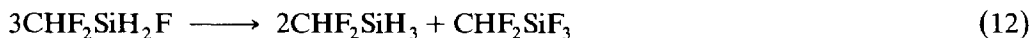


Since we could not detect CHF₂SiH₂F (IV), or any other product which could have come directly from insertion of CF₂ into H₃SiF, we generated CF₂ by low temperature thermolysis at $\leq 100^\circ\text{C}$ of I according to eq. 11 in the presence of



H₃SiF. Under these conditions the expected insertion product IV should be sufficiently stable to allow its detection or even isolation. The gas phase thermolysis $\leq 100^\circ\text{C}$ of I in the presence of H₃SiF indeed yielded $\geq 63\%$ IV, along with $\leq 1\%$ C₂F₄ and traces of CHF₂SiHF₂ and CHF₂SiF₃, the insertion products of CF₂ with H₂SiF₂ and HSiF₃ being formed as shown in the sequence in eq. 10. This is the first unambiguous proof that CF₂, which is considerably less reactive than CHF and CH₂, does in fact insert into Si–H bonds. It is known that CF₂ does not insert into the Si–H bonds of either (CH₃)₃SiH [10] or II upon co-thermolization with I in the gas phase below 100°C, C₂F₄ and cyclo-C₃F₆ being the only detectable products arising from the elimination of CF₂.

Our failure to detect any of the species IV in the course of the decomposition of II suggests that IV undergoes thermolysis at least as readily as II. In order to substantiate this we co-thermolized a 50/50 mixture of II and IV for 1 h at 120 and 150°C and monitored the reaction by ¹⁹F NMR spectroscopy. At 120°, II acts only as a solvent, whereas IV undergoes almost quantitative dismutation according to eq. 12.



The co-thermolysis experiment performed at 150°C yielded, along with CHF₂SiH₃, the decomposition products of CHF₂SiHF₂, namely HSiF₃ and CHF trapped by insertion into II (\rightarrow CF₃(CH₂F)SiH₂), HSiF₃ (\rightarrow CH₂FSiF₃) and CHF₂SiH₃ (\rightarrow CHF₂(CH₂F)SiH₂). The silane CHF₂SiHF₂ is likely to be an intermediate in the reaction represented by eq. 12. Thus it is almost certain that all the steps of the observed hydrogen/fluorine exchange involve either an elimination/insertion process or dismutation.

Thermal decomposition of (CF₃)₂SiH₂

The thermal stability of trifluoromethylsilanes (CF₃)_nSiX_{4-n} decreases as the electronegativity of the X atom and the number *n* of the CF₃ groups bonded to silicon are increased. This behaviour is in line with that reported for 2,2-difluoroethylsilanes CHF₂CH₂SiX₃ [24] and perfluoroether derivatives (R_f-O-R_f)_n SiMe_{4-n} [25]. In spite of the lower temperature the decomposition of III proceeds in

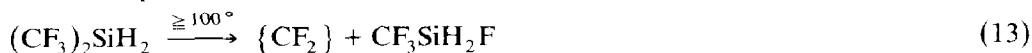
Table 3

Thermolysis of $(CF_3)_2SiH_2$ (III)

| Conditions of thermolysis | 0.5 mmol III 1 h, 99 °C, 14 bar | 0.5 mmol III 30 min, 210 °C, 14 bar | Co-thermolysis with cyclohexene 1 mmol III/ 1 mmol C_6H_{10} 30 min, 110 °C ^a | Co-thermolysis with HBr 1 mmol III/ 2 mmol HBr 92 min, 123 °C, 1.4 bar |
|---|---------------------------------------|---|--|--|
| Decomposition (%) | 5 | 100 | 60 | 66 |
| Volatile products of thermolysis (mol%) | | | | |
| CF_3SiH_2F | 4 | | 32 | 38 |
| $CHF_2(CF_3)SiH_2$ | 4 | | 14 | |
| H_2SiF_2 | 2 | 3 | 6 | 7 |
| CHF_2SiHF_2 | 28 | | 31 | |
| CHF_2SiF_3 | 15 | | 4 | |
| $HSiF_3$ | 2 | 11 | | |
| SiF_4 | <1 | 5 | | |
| CH_2FSiF_3 | | 32 | | CHF_2Br 55 |
| CH_2FSiHF_2 | | 8 | | |
| $(CH_2F)_2SiF_2$ | | 7 | | |
| C_2F_4 | 3 | 5 | 4 | |
| cyclo- C_3F_6 | 17 | 22 | 4 | |

^a 7,7-difluorobicycloheptane[4.1.0] identified as less-volatile material.

an analogous way to that outlined above for II although the CF_2 insertion products CHF_2SiHF_2 and CHF_2SiF_3 are now present in the complex mixture of decomposition products, the CHF_2SiF_3 appearing when the thermolysis is taken to completeness at high temperature (Table 3). Above 150 °C, the CHF_2Si derivatives slowly decomposed to yield CH_2FSiF_3 and eventually SiF_4 , whereas only $HSiF_3$ and SiF_4 were observed from thermolysis at or above 200 °C. The primary product of the thermal decomposition beginning at about 100 °C is CF_3SiH_2F , which can be isolated if the concomitantly eliminated CF_2 is trapped with cyclohexene or HBr. Table 3, eq. 13.



CF_3SiH_2F slowly decomposes at $\sim 120^\circ C$ with further elimination of CF_2 to yield H_2SiF_2 . The rate of the insertion of CF_2 into an Si-H bond and that of its addition to cyclohexene are comparable under these conditions. In contrast with the behaviour of II, no 7-fluorobicycloheptane[4.1.0] was formed when III was thermolyzed at 110 °C in the presence of cyclohexene. At room temperature the liquefied thermolysis products of II and III react, presumably by SiH/SiF dismutation processes according to eq. 12, to form novel hydrogen-rich fluoromethylsilanes, e.g. CH_2FSiH_3 and $(CH_2F)_2SiH_2$ from II and $(CHF_2)_2SiH_2$ and CH_2FSiH_3 (traces) from III respectively. Their ^{19}F NMR signals have diagnostic high frequency shifts, with large vicinal FCSiH coupling constants, and appear as singlets in the proton-decoupled spectra.

NMR spectra of the decomposition products

Products arising from the thermal decomposition of II and III were identified by means of their 1H and ^{19}F NMR chemical shifts, and the nature of the observed

multiplets and by decoupling experiments. The NMR data are listed in Table 4. In general, fluoromethylfluorosilanes with X_2CSiX_2 units, $X = H$ or F , possess magnetically non-equivalent geminal F and H nuclei which give rise to two different vicinal couplings. Frequently only mean constants can be derived, as is expected e.g. for species containing an $F_2CSi(H,F)_2$ unit, with $|^2J(FCF)| \approx 340 \text{ Hz}$ [26] $\gg |^3J(FH, FF) - ^3J(FH', FF')|$ [27].

An $AA'XX'$ spin system is however shown by $(CH_2F)(CH_3)SiF_2$, the simulation of which ($M_3AA'XX'Y$ system) yielded $|^2J(AA')| = 23.3 \text{ Hz}$ and $|^2J(XX')| = 21.4 \text{ Hz}$. Although an assignment of AA' and XX' to $FSiF'$ and HCH' could not be made, the values may be compared with the previously reported $FSiF'$ coupling constant of $+21 \text{ Hz}$ for $RR'SiF_2$ species [28], while the sign of $^2J(HCH')$ is probably negative [29]. The 1H and ^{19}F chemical shifts for the $CH_{3-n}F_n$ groups in α -fluoroalkylsilanes $(CH_{3-n}F_n)SiX_3$, $n = 1-3$, depend on n in a specific fashion. Thus, the ^{19}F signal reveals a systematic high frequency shift from -265.0 ppm (CH_2FSiH_3 , $n = 1$) and -128.9 ppm (CHF_2SiH_3 , $n = 2$) to -55.2 ppm (CF_3SiH_3 , $n = 3$), while the geminal FCH coupling constants are less affected, with $|^2J(FCH_2)| > |^2J(F_2CH)|$. On the other hand, $|^2J(HSiF)|$ is smaller in CH_3SiH_2F (48.8 Hz) than in CH_3SiHF_2 (67.5 Hz) [29]. The vicinal $FCSiF$ coupling constants for the fluoromethylfluorosilanes, Table 4, are smaller than those for I, namely 11.0 Hz [10], with a positive sign [30], and likewise $|^3J(HCSiH)|$ is smaller than for CH_3SiH_3 (4.7 Hz) [31].

The $|^3J(HF)|$ coupling constants decrease with increasing fluorination of both the Si and the C atoms. Thus, the largest $|^3J(FCSiH)|$ and $|^3J(HCSiF)|$ constants for fluorinated methylsilanes are observed for CH_2FSiH_3 (14.7 Hz) and CH_3SiH_2F (8.3 Hz) [29], respectively. Four-bond FF and HF coupling, with $|^4J(FF)| \gg |^4J(HF)|$ [32-34], was resolved for bis(fluoromethyl) derivatives. Because of this coupling, the $H(C)$ signals of $(CHF_2)_2SiH_2$ are split into a complex multiplet, while the $H(Si)$ resonance, with a mean vicinal $|^3J(HF)|$ constant of 9.3 Hz and $|^3J(HH)| = 1.8 \text{ Hz}$, reveals a first order multiplet structure. Accordingly the ^{19}F signal consists, in essence, of a doublet of triplets ($N = |^2J(FH) + ^4J(FH')| = 45.9 \text{ Hz}$) accompanied by two ab-type systems ($L = |^2J(FH) - ^4J(FH')| = 45.1 \text{ Hz}$) that can be approximated by an $(AA'X)_2M_2$ system with $|^4J(FF)| = 3.7 \text{ Hz}$, $|^4J(FF')| = 2.1 \text{ Hz}$ and $|^4J(HH')| \approx 0 \text{ Hz}$. For $(CH_2F)_2SiH_2$ the low intensity of the ^{19}F signals only allows identification of the most intense subsystem with a first order splitting ($N = |^2J(FH) + ^4J(FH')| = 46.9 \text{ Hz}$).

Discussion

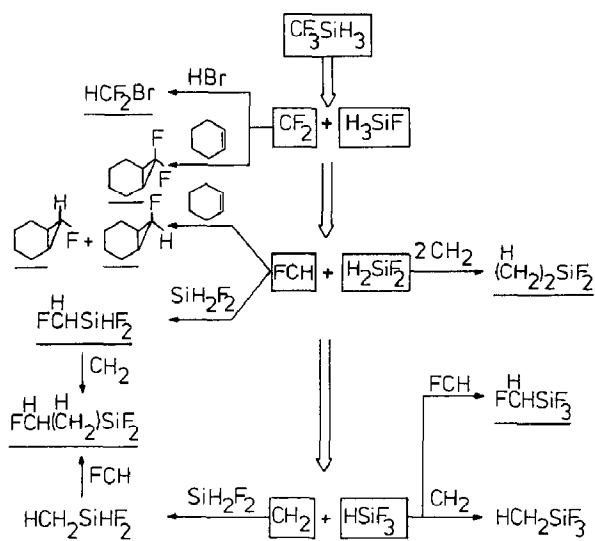
The decomposition mechanism established for II and III and the fall in thermal stability in the order $II > III > I$ are consistent with results of kinetic investigations of α -fluoroalkylsilanes by Haszeldine et al. [35,36]. They reported a unimolecular decomposition with carbene elimination, the activation energy of which decreased as the electronegativity of the Si substituents was increased. In contrast to what one might expect from the presence of long, and therefore presumably weak, Si-C bonds in I ($1.910(5) \text{ \AA}$ [37]) and II ($1.923(3) \text{ \AA}$ [38]), no homolytic Si-C cleavage was detected.

The identities of the thermolysis products have been determined, and their formation can be fully accounted for in terms of secondary reactions involving

Table 4
NMR data for α -fluoromethylsilanes (δ in ppm, J in Hz)

| | $\delta(F(Si))$ | $\delta(F(C))$ | $\delta(H(Si))$ | $\delta(H(C))$ | $ ^2J(HSiF) $ | $ ^2J(FCH) $ | $ ^3J(FCSiF) $ | $ ^3J(HCSiF) $ | $ ^3J(FCSiH) $ | $ ^3J(HCSiH) $ |
|------------------------|-----------------|----------------|-----------------|----------------|---------------|--------------|------------------|-----------------------|-------------------|------------------|
| $CF_3SiF_3^a$ | -150.7 | -66.3 | | | | | 11.0 | | | |
| CF_3SiHF_2 | -150.0 | -70.3 | 4.89 | | 64.8 | | 6.4 | | 3.8 | |
| CF_3SiH_2F | -201.3 | -66.4 | 4.88 | | 47.3 | | < 0.3 | | 5.8 | |
| CF_3SiH_3 | | -55.2 | 3.92 | | | | | | 7.5 | |
| $(CF_3)_2SiH_2^b$ | | -56.7 | 4.41 | | | | | | 6.1 | |
| CHF_2SiF_3 | -147.8 | -142.6 | | 5.86 | | 44.6 | 4.4 | 2.7 | | |
| CHF_2SiHF_2 | -149.1 | -144.9 | 4.65 | 5.71 | 64.6 | 45.1 | 5.1 ^c | 0.7 | 1.5 | 2.0 |
| CHF_2SiH_2F | -203.6 | -142.8 | 4.77 | 6.03 | 47.3 | 45.8 | < 0.1 | 0.4 | 7.1 ^c | 1.7 |
| CHF_2SiH_3 | | -128.9 | 3.85 | 6.14 | | 46.0 | | | 11.0 | 1.8 |
| $(CHF_2)_2SiH_2^d$ | | -131.8 | 4.08 | 6.18 | | 45.5 | | | 9.3 ^c | 1.9 |
| $(CHF_2)(CF_3)SiH_2^e$ | | -132.2 | 4.25 | 6.22 | | 45.5 | | | 8.1 ^f | -1.7 |
| | | -56.4 | | | | | | | 6.5 ^g | |
| CH_2FSiF_3 | -142.8 | -285.0 | | 4.53 | | 46.8 | 5.2 | 3.2 | | |
| CH_2FSiHF_2 | -145.9 | -285.2 | 4.77 | 4.40 | 65.3 | 47.0 | 4.0 | 3.9 ^c | 2.4 | 1.0 |
| $(CH_2F)_2SiF_2$ | -148.3 | -284.5 | | 4.52 | | 47.0 | 3.4 | ^h | | |
| $(CH_2F)CH_2SiF_2^i$ | -140.0 | -281.2 | | 4.37 | | 47.1 | 3.2 | 6.2, 1.7 ^j | | |
| | | | | 0.36 | | | | 6.4 ^k | | |
| $(CH_2F)(CF_3)SiH_2^l$ | | -271.6 | 4.18 | 4.69 | | 46.7 | | | 13.8 ^m | 2.7 ^c |
| | | -57.6 | | | | | | | 6.6 ^g | |
| $(CH_2F)_2SiH_2$ | | -269.5 | 3.9 | 4.66 | | 46.9 | | | 14.4 | 2.9 ^c |
| CH_2FSiH_3 | | -265.0 | 3.63 | 4.61 | | 46.7 | | | 14.7 | 3.5 |
| $CH_2F(CHF_2)SiH_2^n$ | | -271.1 | - | 4.75 | | 46.8 | | | 14.1 | 2.8 ^c |
| | | -132.5 | | - | | 45.9 | | | 9.7 | - |

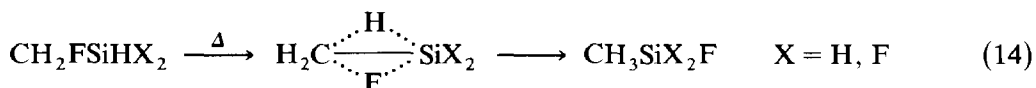
^a Ref. 1a. ^b $|^4J(FCSiCF)|$ 4.1 Hz. ^c Mean coupling constant. ^d $|^3J(FCSiCF)|$ 3.7 Hz. ^e $|^3J(FCSiCF)|$ 3.7 Hz. ^f $|^3J(FCSiCF)|$ 2.1 Hz. ^g $|^3J(HCSiCF)|$ 0.4 Hz. see text. ^h $|^4J(FCSiCF)|$ 3.7 Hz. ⁱ $|^3J(F_2CHSiH)|$. ^j $|^3J(F_2CSiH)|$. ^k $|^3J(F_2CSiH)|$. ^l Coupling constant not determined. ^m $|^4J(FCSiCH)|$ 1.1 Hz. ⁿ $|^3J(CH_2CFSiF')|$. ^o $|^3J(H_2CFSiF')|$. see text. ^p $|^3J(H_3CSiF)|$. ^q $|^4J(FCSiCF)|$ 3.0 Hz. ^r $|^3J(FCH_2SiH)|$. ^s $|^4J(FCSiCF)|$ 1.5 Hz.



Scheme 1. Thermolysis of CF_3SiH_3 , identified species are underlined.

carbene elimination and insertion. The CF_2 insertion into an Si–H bond, which has been established for the first time in the present study, has a key function in the decomposition mechanism; its potential for the selective synthesis of CHF_2Si derivatives is at present under investigation in our laboratory.

The elimination/insertion sequence continues as shown in Scheme 1, and the carbenes CF_2 and CHF have been trapped with cyclohexene, although the thermal instability of difluoromethylsilanes, which lose CHF , prevented their detection from thermolysis at $\geq 210^\circ\text{C}$ (Tables 2 and 3). On the other hand, while there is no evidence for free CH_2 as a reaction intermediate, we do not think that CH_3Si derivatives can be formed by any mechanism other than CH_2 elimination from a CH_2FSi precursor and insertion into an Si–H bond. Formally, a dyotropic rearrangement according to eq. 14, which has been observed as one of two path-

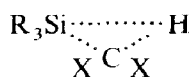


ways in the isomerization of $\text{CH}_2\text{ClSi}(\text{CH}_3)_2\text{H}$ to $(\text{CH}_3)_3\text{SiCl}$ [39], would offer an alternative route.

Insertions of CF_2 have received little attention [40,41,18], while the addition of carbenes to alkenes has been studied in great detail. The selectivity in olefin addition reactions of CF_2 has been compared with that of other dihalocarbenes and $\text{O}(3p)$ atoms [20], and a model for the addition process based on ab initio calculations has been proposed [42]. The experimentally observed electrophilicity of CF_2 is not consistent with the character following from the philicity parameter, which places CF_2 , $m(\text{CF}_2) = 1.47$ [43], between the ambiphilic carbene $\text{C}(\text{OMe})\text{Ph}$, $m = 1.34$, and the nucleophilic $\text{C}(\text{OMe})_2$, $m = 2.22$ [43].

Insertion reactions of the singlet carbenes CCl_2 and CBr_2 into the Si–H bonds of optically active silane have been shown to be stereoselective, and a concerted mechanism with a three-center transition state was postulated [44]. In agreement with their electrophilic character, CCl_2 and CBr_2 [23], as well as $\text{CF}(\text{CHF}_2)$ [45],

react with increasing ease into Si–H as the electron-releasing character of the remaining silicon substituents is increased. In contrast, CF_2 inserts readily into H_3SiF but not into Me_3SiH [10] and II. Operation of a different reaction mechanism for CF_2 could account for this difference. The large singlet/triplet energy separation, $\sim 240 \text{ kJ mol}^{-1}$ [46], makes the participation of triplet- CF_2 in the insertion process unlikely. A two step mechanism, with H abstraction prior to the formation of the above mentioned three-center transition state, would be in agreement with the experimental results. While the Si–H bond dissociation energies of Me_3SiH ($376 \pm 11 \text{ kJ mol}^{-1}$ [47]) and H_3SiF (calc. $375.1 \text{ kJ mol}^{-1}$ [48]) are not significantly different, the greater polarity of the $\text{Si}^{\delta+}\text{--H}^{\delta-}$ bond in H_3SiF would facilitate electrophilic attack on this H atom by CF_2 . Such radical reactions of singlet carbenes have been demonstrated by CIDNP NMR spectroscopy [49]. A two-step process, comprising an initial electrophilic H abstraction and a subsequent phase to form the threecenter transition state, is supported by ab initio calculations



of the insertion of carbenes into E–H bonds (E = Si, Ge) [50]. According to these calculations the higher electronic stability of CF_2 than of the more reactive species CCl_2 and CBr_2 implies that in the transition state there is nucleophilic interaction of the σ HOMO of CF_2 with the σ^* LUMO mostly localized at the Si atom. In accord with this reasoning, the unexpectedly lower reactivity of CF_2 can be attributed to a nucleophilicity greater than that of CCl_2 and $\text{CF}(\text{CHF}_2)$.

An important outcome of the present investigation is the possibility of selectively synthesizing CHF_2Si derivatives, which are difficult to prepare by other routes, by CF_2 insertion into SiH bonds, and to use these species as precursors for CHF, convenient sources of which are still lacking [6].

Experimental

Volatile materials were handled in a vacuum system equipped with greaseless valves. Gas volumes were determined by use of a MKS Baratron pressure gauge. Spectra were recorded with the following instruments: ^1H and ^{19}F NMR: Varian EM 390 operating at 90.00 and 84.67 MHz, Bruker AC 250 operating at 250.00 and 235.36 MHz, IR: Perkin Elmer 580 B, 400–4000 cm^{-1} , 10 cm gas cell.

Starting material

Compounds I and II were synthesized by published methods [3], while III was obtained by reduction of $(\text{CF}_3)_2\text{SiHBr}$.

Bis(trifluoromethyl)bromosilane. To 35.4 g (133 mmol) of $(\text{CF}_3)_2\text{Si}(\text{H})\text{N}(\text{i-Pr})_2$ [4], 33.6 g (133 mmol) of BBr_3 were added dropwise at 0°C . The mixture was kept at room temperature for 2 days, then the more volatile compound $(\text{CF}_3)_2\text{SiHBr}$, b.p. 34°C (160 mmHg) was condensed and in vacuo (yield 92%, purity $\geq 95\%$), and the remaining was identified as $\text{Br}_2\text{BN}(\text{i-Pr})_2$. IR (cm^{-1}): 2247 s, PQR, $\Delta\nu(\text{PR})$ 10 cm^{-1} , 1222 s, 1207 vs, 1177 m, 1133 vs, 1102 s, 770 vs, 732 s, 729 s, 539 m, 494 s, 448 s, 406 s, PQR. NMR: ^{19}F , int. std. CFCl_3 , $\delta(\text{CF}_3)$ -62.5 ppm, $|^3J(\text{FH})|$ 4.8 Hz, $|^2J(\text{F}^{29}\text{Si})|$ 59.3 Hz; ^1H , int. std. TMS, $\delta(\text{SiH})$ 5.06 ppm, $|^1J(\text{H}^{29}\text{Si})|$ 280.9 Hz.

Bis(trifluoromethyl)silane(III). To a suspension of 0.5 g (13.2 mmol) LiAlH_4 in 70 ml di-n-butylether at -78°C , 11.0 g (45 mmol) $(\text{CF}_3)_2\text{SiHBr}$ were added dropwise. The mixture was warmed to 0°C and stirred for 10 min. Volatile products were evaporated off and the material collected in a -150°C trap was distilled through a 50 cm slit tube column to give III, b.p. 5°C (760 mmHg), 28% yield, along with 3.4 g of unchanged $(\text{CF}_3)_2\text{SiHBr}_2$. IR (cm^{-1}): 2249 s, 2233 sh, 1226 s, 1213 vs, PQR, 1167 m, 1127 vs, 1099 s, 1094 s, 917 s, 815 vs, PQR, 735 m, 601 m, 433 m, 417 m. NMR see Table 4.

Thermolysis of II

The low pressure thermolysis was carried out by heating 0.5 mmol of II in a 50 ml glass ampoule for 2–5 h at a temperature which was increased stepwise from 60 to 210°C . At each step the composition of the gaseous products was examined by IR spectroscopy, and a first indication of decomposition products was observed after heating to 180°C for 5 h. Decomposition was complete after 15 h at 210°C . The decomposition in the presence of cyclohexene and HBr was performed similarly; details are given in Tables 1 and 2.

In the high pressure thermolysis 0.9 mmol of II were sealed in a glass tube of 3.2 mm i.d. having a volume of 0.5 ml and heated to 240°C for 6 h. The extrapolated pressure was ca. 40 bar. Gaseous decomposition products were investigated by NMR spectroscopy (Table 2).

Dynamic decomposition of II was studied by passing II slowly through a heated glass tube at a pressure of 10^{-3} mbar; the products (H_3SiF and C_2F_4) were separated from unchanged II by fractional condensation in vacuo. In contrast, II was decomposed almost completely at 160°C , when passed through a glass tube containing dried KF (Table 2).

Reaction of CF_3SiF_3 with H_3SiF : CF_2 insertion

2 mmol of a mixture consisting of 49 mol% H_3SiF and 51 mol% I was sealed in a 35 ml Pyrex ampoule and kept at 82°C for 2 h. The CF_2 insertion products were collected in a -120°C trap and thereby separated from more volatile material. Both fractions were investigated by NMR and IR spectroscopy. The -120°C trap contained IV, purity $> 95\%$, yield 55% (63% with regard to consumed H_3SiF), while the more volatile material consisted of I, H_3SiF , SiF_4 and, with respect to consumed H_3SiF , $\sim 12\%$ H_2SiF_2 and $< 1\%$ HSiF_3 . In a similar reaction carried out at 102°C for 1 h, the yield of insertion products was increased to 67%, and $\sim 1\%$ of C_2F_4 was found in the more volatile fraction.

Difluoromethylfluorosilane (IV). b.p. 45°C (760 mmHg), M , found 102.3, (calcd. 100.12, by gas density) [51]. IR (cm^{-1}) 2934s, 2234vs, 2221vs, PQR, 1400m, 1328m, PQR, $\Delta\nu(\text{PR}) 15 \text{ cm}^{-1}$, 1098s, 1034vs, PR, $\Delta\nu(\text{PR}) 9 \text{ cm}^{-1}$, 956s, PQR, $\Delta\nu(\text{PR}) 16 \text{ cm}^{-1}$, 933sh, 913vs, PQR, $\Delta\nu(\text{PR}) 14 \text{ cm}^{-1}$, 863s, PQR, $\Delta\nu(\text{PR}) 16 \text{ cm}^{-1}$, 721s, PQR, 601s, 502s, PQR. NMR see Table 4.

Thermolysis of IV in the presence of II

Two samples, each consisting of 0.6 mmol IV and 0.6 mmol II, were sealed in 4 mm o.d. glass tubes, volume 1 ml, and kept for 1 h at 120 and 150°C respectively. Analysis by NMR spectroscopy indicated complete decomposition of IV in both cases. At 120°C , 61% of CHF_2SiH_3 and 26% of CHF_2SiF_3 , formed by dismutation,

were found, along with 5% $(\text{CHF}_2)_2\text{SiH}_2$. Thermolysis at 150°C yielded CHF_2SiH_3 (51%), HSiF_3 (17%), $(\text{CHF}_2)_2\text{SiH}_2$ (8%), CHF_2SiF_3 (4%) and, by insertion of CHF , CH_2FSiF_3 (9%) and $\text{CH}_2\text{F}(\text{CHF}_2)\text{SiH}_2$ (4%). In addition, 13% of II was converted into $\text{CH}_2\text{F}(\text{CF}_3)\text{SiH}_2$. $\text{CH}_2\text{F}(\text{CHF}_2)\text{SiH}_2$, ^{19}F NMR: $\delta(\text{CHF}_2) -132.5$ ppm, $|^2J(\text{FH})| 45.9$ Hz, $|^3J(\text{FH})| 9.7$ Hz, $|^4J(\text{FF})| 1.5$ Hz, $\delta(\text{CH}_2\text{F}) -271.1$ ppm, $|^2J(\text{FH})| 46.8$ Hz, $|^3J(\text{FH})| 14.1$ Hz, $|^4J(\text{FF})| 1.5$ Hz; ^1H NMR: $\delta(\text{CH}_2\text{F}) 4.75$ ppm, $|^2J(\text{HF})| 46.8$ Hz, $|^3J(\text{HH})| 2.8$ Hz. CHF_2 and SiH_2 signals were hidden under stronger signals from other compounds.

Thermolysis of III

The thermolysis of III was performed as described for II. Details are given in Table 3. Increase in the time of reaction of III with HBr at 123°C from 92 to 122 min changed the $\text{CF}_3\text{SiH}_2\text{F}/\text{H}_2\text{SiF}_2$ ratio from 5.5/1 to 0.9/1. The $\text{CF}_3\text{SiH}_2\text{F}$ was always contaminated with some CHF_2Br , which could not be separated by repeated fractional condensation. $\text{CF}_3\text{SiH}_2\text{F}$, IR (cm^{-1}): 2248s, PQR, 2240sh, 1238s, PR, 1109vs, 959s, PR, 916vs, PQR, $\Delta\nu(\text{PR}) 13$ cm^{-1} , 871s, PQR, $\Delta\nu(\text{PR}) 13$ cm^{-1} , 718m (CHF_2Br), 641s, 498m, 412s, PQR.

Acknowledgements

We thank Professor R. Eujen for valuable comments and help. Support by the Fonds der Chemie is gratefully acknowledged.

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