

CHLOROFLUORINATION AND CHLORINATION OF BIS(TRIFLUOROMETHYLTHIO)ALKANES

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SUMMARY

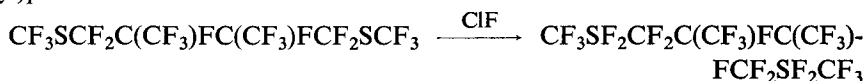
The reactions between $\text{CF}_3\text{SCF}_2\text{C}(\text{CF}_3)\text{FC}(\text{CF}_3)\text{FCF}_2\text{SCF}_3$, $\text{CF}_3\text{SC}(\text{CF}_3)\text{FCF}_2\text{SCF}_3$ and $\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$ and chlorine monofluoride are described. New compounds identified are $\text{CF}_3\text{SF}_2\text{CF}_2\text{C}(\text{CF}_3)\text{FC}(\text{CF}_3)\text{FCF}_2\text{SF}_2\text{CF}_3$, $\text{CF}_3\text{SCH}_2\text{CHClSCF}_3$ and $\text{CF}_3\text{SCH}_2\text{CCl}_2\text{SCF}_3$. Evidence is also presented for the formation of a series of $\text{R}_t\text{SF}_4\text{Cl}$ derivatives.

INTRODUCTION

Chlorine monofluoride is an effective agent for the fluorination or chlorofluorination of lower oxidation state sulphur derivatives: sulphur tetrafluoride gives SF_5Cl ¹, bis(perfluoroalkyl)sulphides give sulphur(IV) derivatives², $(\text{R}_t)_2\text{SF}_2$, and sulphur(VI) derivatives³, $(\text{R}_t)_2\text{SF}_4$, and sulphoxides give sulphur(VI) derivatives⁴, $(\text{R}_t)_2\text{S}(\text{O})\text{F}_2$. We wish to report on the reactions between chlorine monofluoride and some bis(trifluoromethylthio)alkanes.

RESULTS AND DISCUSSION

1,4-Bis(trifluoromethylthio)-2,3-bis(trifluoromethyl)perfluorobutane reacts with chlorine monofluoride to give traces of HCl , SiF_4 , CF_4 , CF_3Cl , SF_4 and SOF_2 but 75% conversion to 1,4-bis(trifluoromethyldifluorothio)-2,3-bis(trifluoromethyl)perfluorobutane.



The monosulphur(IV) derivative is not observed and under the conditions used there is no oxidation to sulphur(VI). This appears to be the first bis(sulphur(IV) fluoride) to be described although other examples should be capable of being

prepared by similar reactions to that described above. The compound is stable in air for short periods but there is slight decomposition at its boiling point (561–563°K). The IR spectrum compares well with those of $(R_f)_2SF_2$ derivatives¹; compared with the spectrum of $CF_3SCF_2C(CF_3)FC(CF_3)FCF_2SCF_3$, the main extra features are the strong bands at between 600 and 700 cm^{-1} due to S–F modes. The mass spectrum does not show the parent ion. In the ^{19}F NMR spectrum the SF_2 and CF_2 fluorines show magnetic non-equivalence, the molecule has two asymmetric centres and the geometry about each sulphur atom is likely to be complex although the fluorines should be essentially axial in trigonal-bipyramids. $CF_3SF_2CF_2CF_3$ also shows similar non-equivalence⁴.

1,2-Bis(trifluoromethylthio)hexafluoropropane, $CF_3SC(CF_3)FCF_2SCF_3$, does not give isolable sulphur(IV) derivatives with chlorine monofluoride but in addition to the volatile products CF_4 , CF_3Cl , SiF_4 , Cl_2 , CF_3SF_5 and *trans*- CF_3SF_4Cl resulting from breakdown of the molecule, two fractions containing *trans*- $(CF_3)_2CFSF_4Cl$, *trans*- $CF_3SF_4CF_2CFCICF_3$, *trans*- $CF_3CFCICF_2SF_4Cl$, $CF_3SCF_2CFCICF_3$, $CF_3SCF(CF_3)CF_2Cl$, $(CF_3)_2CFSCl$, $CF_3CFCICF_2SCl$, $(CF_3)_2CFCl$ and $CF_3(CF_2Cl)CFSCl$ resulted. Individual compounds could not be isolated and identification is by NMR spectroscopy only; similar products have been reported from the reaction between $R_fSR'_f$ and chlorine monofluoride³.

The major products of the reaction between hydrogen-containing 1,2-bis(trifluoromethylthio)ethane and chlorine monofluoride are the chlorination products $CF_3SCHClCH_2SCF_3$ and $CF_3SCCl_2CH_2SCF_3$. The former compound is clearly identified from its mass spectrum and from its NMR spectrum. The latter compound is identified as the 1,1-dichloro derivative rather than $CF_3SCHClCHClSCF_3$ by the mass spectrum which shows CCl_2^+ and $SCCl_2^+$ ions, by the 1H NMR spectrum which shows a signal ($\delta = 3.44$ ppm) indicative of a CH_2 rather than CH groups⁵ and by the ^{19}F NMR spectrum which shows two types of CF_3S group. $CF_3SCHClCH_2SCF_3$ can also be prepared in poor yield from $CF_3SCH_2CH_2SCF_3$ and chlorine.

From the reactions reported here, it is clear that chlorine monofluoride can react with bis(trifluoromethylthio)alkanes in a variety of ways including oxidation to sulphur(IV) fluorides and oxidation to sulphur(VI) derivatives—often after C–S bond cleavage. However, hydrogen-containing species appear to undergo chlorination rather than fluorination. There is always major breakdown of the molecules.

EXPERIMENTAL

Bis(trifluoromethylthio)alkanes were prepared by photolytic addition of CF_3SSCF_3 to olefins⁶. Chlorine monofluoride (Ozark-Mahoning) was handled in an all-metal vacuum line, reactions were carried out in a 75 ml Monel Hoke bomb.

Reaction of CF₃SCF₂C(CF₃)FC(CF₃)FCF₂SCF₃ and ClF

CF₃SCF₂C(CF₃)FC(CF₃)FCF₂SCF₃ (6.51 mmol) and ClF (28 mmol) were allowed to react at room temperature. The volatile products under static vacuum were CF₄, CF₃Cl, SF₄, HCl, SiF₄ and SOF₂ and the remaining products were unreacted CF₃SCF₂C(CF₃)FC(CF₃)FCF₂SCF₃ (1.5 mmol) and CF₃SF₂CF₂C(CF₃)FC(CF₃)FCF₂SF₂CF₃ (nc) (4.5 mmol). Analysis: Found: C, 16.5; F, 72.5; S, 10.9%. C₈F₂₂S₂ requires C, 16.6; F, 72.3; S, 11.1%; b.p. 561–563°K/760 mmHg. ¹⁹F NMR data: chemical shifts; δ(CF₃S), +55.8; δ(CCF₃), +69.3; δ(CF₂), +80.8, +87.7; δ(CF), +169.8; δ(SF₂), +9.5, +13.1 ppm w.r.t. CCl₃F: coupling constants; *J*(SFF'), 113.0; *J*(F₃CSF₂), 20.3; *J*(CFF'), 191.8; *J*(F₃CSF₂-CF₂), 7.9 Hz. Other coupling constants could not be derived from the complex spectrum.

IR data: 1322 (w), 1278 (vs), 1255 (vs), 1227 (vs), 1201 (s), 1163 (m), 1143 (m), 1129 (m), 1101 (vs), 1026 (w), 1014 (m), 934 (w), 899 (m), 855 (m), 842 (m), 809 (s), 785 (m), 752 (s), 681 (s), 649 (s), 619 (s) cm⁻¹.

Mass spectrum (*m/e*, relative abundance, ion): 401[†], C₇F₁₅S⁺; 389[†], C₆F₁₃SF₂⁺; 370[†], C₆F₁₄S⁺; 351, 1, C₆F₁₃S⁺; 332[†], C₆F₁₂S⁺; 313[†], C₆F₁₁S⁺; 301[†], C₅F₁₁S⁺; 281[†], C₆F₁₁⁺; 263, 1, C₅F₉S⁺; 251[†], C₄F₉S⁺; 250[†], C₅F₁₀⁺; 232[†], C₄F₈S⁺; 231, 2, C₅F₉⁺; 225[†], C₅F₇S⁺; 213[†], C₄F₇S⁺; 212[†], C₅F₈⁺; 201, 1, CF₃SF₂CF=CF⁺ and CF₃SF-CF=CF₂⁺; 182, 1, C₃F₆S⁺; 181, 7, C₄F₇⁺; 175[†], C₄F₅S⁺; 169[†], C₃F₇⁺; 163[†], C₃F₅S⁺; 162[†], C₄F₆⁺; 151, 1, C₂F₅S⁺; 150, 8, C₃F₆⁺; 144[†], C₃F₄S⁺; 143[†], C₄F₅⁺; 139, 4, CF₃SF₂⁺; 132[†], C₂F₄S⁺; 131, 3, C₃F₅⁺; 124[†], C₄F₄⁺; 120, 4, CF₄S⁺; 113, 2, C₂F₃S⁺; 112, 1, C₃F₄⁺; 101, 6, CF₃S⁺; 100, 10, C₂F₄⁺; 93, 5, C₃F₃⁺; 82, 3, CF₂S⁺; 81, 2, C₂F₃⁺; 70, 10, SF₂⁺; 69, 100, CF₃⁺; 63, 5, CFS⁺; 51, 7, SF⁺; 50, 51, CF₂⁺; 44, 3, CS⁺; 32, 5, S⁺; 31, 12, CF⁺.

The metastable transitions observed in this spectrum are listed in Table 1.

TABLE 1

<i>m</i> ₁	Transition	<i>m</i> ₂	<i>m</i> [*]	
			Calc.	Found
231	C ₅ F ₉ ⁺ → C ₄ F ₇ ⁺ + •CF ₂	181	141.9	141.9
101	CF ₃ S ⁺ → CF ₂ S ⁺ + F•	82	66.6	66.7
69	CF ₃ ⁺ → CF ₂ ⁺ + F•	50	36.2	36.2
131	or			
	C ₃ F ₅ ⁺ → CF ₃ ⁺ + FC≡CF	69	36.3	

Reaction of CF₃SC(CF₃)CFCF₂SCF₃ and ClF

CF₃SCF(CF₃)CF₂SCF₃ (4.50 mmol) and ClF (20 mmol) were allowed to react at room temperature. Volatile products under static vacuum were CF₄,

† Denotes important ions of less than 1% abundance.

TABLE 2
 ^{19}F NMR DATA FOR PRODUCTS OF REACTION BETWEEN $\text{CF}_3\text{SC}(\text{CF}_3)\text{CFCF}_2\text{SCF}_3$ AND ClF

Compound	Chemical shifts (ppm)†			Coupling constants (Hz)
	$\delta(\text{SF}_4)$	$\delta(\text{CF}_3\text{S})$	$\delta(\text{CF})$	
<i>trans</i> -(CF_3) ₂ CFSE ₄ Cl	-122.0	+74.7	+156.9	$J(\text{CFSE}_4) = 4.5$; $J(\text{CF}_3\text{CSE}_4) = 12.4$; $J(\text{CF}_3\text{CF}) = 5.6$
<i>trans</i> -CF ₃ SF ₄ CF ₂ CFCICF ₃	-22.9	+68.1	+143.9	$J(\text{CFSE}_4) = 23.0$
<i>trans</i> -CF ₃ CFCICF ₂ SF ₄ Cl	-124.4	+77.4	+147.6	$J(\text{CF}_2\text{SE}_4) = 23.6$; $J(\text{CF}_3\text{CFSE}_4) = 11.4$; $J(\text{CF}_3\text{CCSF}_4) = 5.6$
CF ₃ SCF ₂ CFCICF ₃ ††	+39.0	+75.1	+141.6	$J(\text{CF}_3\text{SCE}_2) = 10.2$; $J(\text{CF}_3\text{SCCF}) = 4.8$; $J(\text{CF}_3\text{SCCCE}_3) \sim 0$; $J(\text{CF}_3\text{CF}) = 10.1$; $J(\text{CF}_3\text{CCF}_2) = 10.1$; $J(\text{CF}_2\text{CF}) = 14.7$
CF ₃ SCF(CF ₃)CF ₂ Cl††	+37.6	+71.9	+165.7	$J(\text{CF}_3\text{CF}) = 10.2$
(CF ₃) ₂ CFSCl		+76.8	+167.1	$J(\text{CF}_3\text{CF}) = 39.6$; $J(\text{CF}_3\text{CF}) = 10.4$;
CF ₃ CFCICF ₂ *SCl		+80.0	+138.8	$J(\text{CF}_3\text{CF}) = 11.3$; $J(\text{CF}_3\text{CF}_3) = 7.2$; $J(\text{CF}_3\text{CF}_3) = 6.0$; $J(\text{CF}_3\text{CF}_3) = 10.8$
(CF ₃) ₂ CFCI		+82.2	+145.8	$J(\text{CF}_3\text{CF}) = 6.2$
CF ₃ (CF ₂ O)CFSCl		+73.0	+152.7	$J(\text{CF}_3\text{CCF}_2) = 9.0$; $J(\text{CF}_3\text{CF}_2) = 9.0$; $J(\text{CF}_3\text{CF}) = 16.9$

* Denotes non-equivalence. † Relative to external CCl_3F . †† Agrees with published spectrum⁸.

CF_3Cl , Cl_2 , SiF_4 , CF_3SF_5 and $\text{CF}_3\text{SF}_4\text{Cl}$. The remainder of the products formed two fractions (volatile at 251°K, involatile at 228°K; volatile at 228°K, involatile at 193°K) which could not be further separated. Identification of the products was attempted by ^{19}F NMR spectroscopy (see Table 2 and compare ref. 7).

Reaction of $\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$ and ClF

$\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$ (4.70 mmol) and ClF (20 mmol) were allowed to react at room temperature. Volatile products were HCl , CF_4 , CF_3Cl , Cl_2 and SiF_4 . The remaining material was unchanged $\text{CF}_3\text{SCH}_2\text{CH}_2\text{SCF}_3$ (3.50 mmol), $\text{CF}_3\text{SCCl}_2\text{CH}_2\text{SCF}_3$ (nc) and $\text{CF}_3\text{SCHClCH}_2\text{SCF}_3$ (nc) (trace only).

Mass spectrum of $\text{CF}_3\text{SCCl}_2\text{CH}_2\text{SCF}_3$ (m/e , relative abundance, ion; ions quoted for ^{35}Cl only): 298, 8, M^+ ; 263, 8, $(\text{M}-\text{Cl})^+$; 261, 3, $\text{C}_4\text{F}_6\text{ClS}_2^+$; 229, 46, $\text{C}_3\text{H}_2\text{F}_3\text{Cl}_2\text{S}_2^+$; 228, 26, $\text{C}_3\text{HF}_3\text{Cl}_2\text{S}_2^+$ and $\text{C}_4\text{H}_2\text{F}_6\text{S}_2^+$; 226, 3, $\text{C}_4\text{F}_6\text{S}_2^+$; 197, 3, $\text{C}_3\text{H}_2\text{F}_3\text{Cl}_2\text{S}^+$; 196, 4, $\text{C}_3\text{HF}_3\text{Cl}_2\text{S}^+$; 195, 4, $\text{C}_3\text{F}_3\text{Cl}_2\text{S}^+$; 194, 6, $\text{C}_3\text{H}_2\text{F}_3\text{ClS}_2^+$; 192, 4, $\text{C}_3\text{F}_3\text{ClS}_2^+$; 177, 3, $\text{C}_3\text{HF}_2\text{Cl}_2\text{S}^+$; 176, 2, $\text{C}_3\text{F}_2\text{Cl}_2\text{S}^+$; 162, 10, $\text{C}_3\text{H}_2\text{F}_3\text{ClS}^+$; 161, 8, $\text{C}_3\text{HF}_3\text{ClS}^+$; 159, 4, $\text{C}_3\text{H}_2\text{F}_3\text{S}_2^+$; 157, 4, $\text{C}_3\text{F}_3\text{S}_2^+$; 127, 67, $\text{C}_3\text{H}_2\text{F}_3\text{S}^+$; 125, 59, $\text{C}_3\text{F}_3\text{S}^+$; 115, 54, $\text{CF}_3\text{SCH}_2^+$; 114, 14, $\text{C}_2\text{HF}_3\text{S}^+$ and CCl_2S^+ ; 101, 4, CF_3S^+ ; 92, 9, C_2HClS^+ ; 91, 10, C_2ClS^+ ; 82, 38, CCl_2^+ and CF_2S^+ ; 79, 39, CClS^+ ; 77, 3, $\text{C}_2\text{H}_2\text{FS}^+$; 69, 100, CF_3^+ ; 63, 8, CFS^+ ; 60, 6, C_2HCl^+ ; 59, 12, C_2Cl^+ ; 58, 8, $\text{C}_2\text{H}_2\text{S}^+$; 56, 2, C_2S^+ ; 50, 5, CF_2^+ ; 47, 85, CCl^+ ; 46, 10, CH_2S^+ ; 45, 3, CHS^+ ; 44, 16, CS^+ ; 32, 2, S^+ ; 31, 1, CF^+ ; 26, 11, C_2H_2^+ .

The metastable transitions observed in this spectrum are listed in Table 3.

TABLE 3

m_1	Transition	m_2	m^*	
			Calc.	Found
298	$\text{M}^+ \rightarrow \text{C}_3\text{H}_2\text{F}_3\text{ClS}_2^+ + \text{CF}_3\text{Cl}$	194	126.4	126.5
298	$\text{M}^+ \rightarrow \text{C}_3\text{H}_2\text{F}_3\text{ClS}^+ + \text{CF}_3\text{Cl}$	162	88.1	88.2
115	$\text{CF}_3\text{SCH}_2^+ \rightarrow \text{CFS}^+ + \text{CF}_2\text{H}_2$	63	34.5	34.5

Mass spectrum of $\text{CF}_3\text{SCHClCH}_2\text{SCF}_3$ (m/e , relative abundance, ion; ions quoted for ^{35}Cl only): 264, 6, M^+ ; 229, 10, $(\text{M}-\text{Cl})^+$; 195, 1, $\text{C}_3\text{H}_3\text{F}_3\text{ClS}_2^+$; 163, 9, $\text{C}_3\text{H}_3\text{F}_3\text{ClS}^+$; 160, 2, $\text{C}_3\text{H}_3\text{F}_3\text{S}_2^+$; 159, 2, $\text{C}_4\text{H}_2\text{F}_3\text{S}_2^+$; 149, 9, $\text{CF}_3\text{SCHCl}^+$; 128, 9, $\text{C}_3\text{H}_3\text{F}_3\text{S}^+$; 127, 3, $\text{C}_3\text{H}_2\text{F}_3\text{S}^+$; 115, 58, $\text{CF}_3\text{SCH}_2^+$; 101, 15, CF_3S^+ ; 94, 3, $\text{C}_2\text{H}_3\text{ClS}^+$; 93, 3, $\text{C}_2\text{H}_2\text{ClS}^+$; 91, 10, C_2ClS^+ and $\text{C}_2\text{H}_3\text{S}_2^+$; 90, 3, $\text{C}_2\text{H}_2\text{S}_2^+$; 82, 11, CF_2S^+ ; 77, 9, $\text{C}_2\text{H}_2\text{FS}^+$; 69, 100, CF_3^+ ; 63, 36, CFS^+ ; 62, 20, $\text{C}_2\text{H}_3\text{Cl}^+$; 61, 13, $\text{C}_2\text{H}_2\text{Cl}^+$; 60, 1, C_2HCl^+ ; 59, 17, $\text{C}_2\text{H}_3\text{S}^+$; 58, 16, $\text{C}_2\text{H}_2\text{S}^+$; 57, 5, C_2HS^+ ; 50, 9, CF_2^+ ; 47, 88, CCl^+ ; 35, 23, Cl^+ ; 32, 19, S^+ ; 31, 19, CF^+ ; 27, 45, C_2H_3^+ ; 26, 51, C_2H_2^+ .

The metastable transitions observed in this spectrum are listed in Table 4.

TABLE 4

m_1	Transition	m_2	m^*	
			Calc.	Found
264	$M^+ \rightarrow C_4H_3F_6S_2^+ + Cl\bullet$	229	198.6	198.6
115	$CF_3SCH_2^+ \rightarrow CFS^+ + CF_2H_2$	63	34.5	34.5

The NMR spectrum of $CF_3SCCl_2CH_2SCF_3$ gave the following chemical shifts; 1H spectrum: $\delta(\underline{CH_2})$, +3.44; ^{19}F spectrum: $\delta(\underline{CF_3SCCl_2})$, +43.6; $\delta(\underline{CF_3SCH_2})$, +40.8.

Reaction of $CF_3SCH_2CH_2SCF_3$ and Cl_2

The reaction between $CF_3SCH_2CH_2SCF_3$ (1.27 mmol) and Cl_2 (20.2 mmol) was carried out in the same manner as the reactions with chlorine monofluoride. The products were unreacted Cl_2 , HCl , unreacted $CF_3SCH_2CH_2SCF_3$ (0.90 mmol) and $CF_3SCHClCH_2SCF_3$ (0.20 mmol) fractionated between traps at 228°K and 208°K. The mass spectrum was identical with that of the sample prepared by use of chlorine monofluoride. The ^{19}F NMR spectrum gave shifts $\delta(\underline{CF_3SCH_2})$, +39.5; $\delta(\underline{CF_3SCHCl})$, +38.4. The 1H spectrum was analysed as an ABX system to give parameters δ_X , +5.17; δ_B , +3.37; δ_A , +3.26 ppm; $J(AB)$, 7.7; $J(AX)$, 7.4; $J(BX)$, 5.4 Hz.

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