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UCRL-51965

**THE CHEMISTRY OF ALIPHATIC SULFURPENTAFLUORIDE  
DERIVATIVES**

Eugene R. Bissell

November 20, 1975

Prepared for U.S. Energy Research & Development  
Administration under contract No. W-7405-Eng-48



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Printed in the United States of America

Available from

National Technical Information Service

U. S. Department of Commerce

5285 Port Royal Road

Springfield, Virginia 22151

Price: Printed Copy \$     \*; Microfiche \$2.25

<u>*Pages</u>	<u>NTIS Selling Price</u>
1-50	\$4.00
51-150	\$5.45
151-325	\$7.60
326-500	\$10.60
501-1000	\$13.60



**LAWRENCE LIVERMORE LABORATORY**  
University of California, Livermore, California, 94550

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# THE CHEMISTRY OF ALIPHATIC SULFURPENTAFLUORIDE DERIVATIVES

## Abstract

This report summarizes the literature through 1974 on aliphatic sulfurpentafluoride compounds. Methods of preparation and methods of

transforming one pentafluorothio compound into another are briefly discussed. The physical properties of all known derivatives are tabulated.

## Introduction

Aliphatic derivatives of sulfurpentafluoride are currently of interest as potential high-energy compounds and as possible fluorine sources for chemical lasers. We have attempted, therefore, to assemble what is known about them from the literature. First, we briefly discuss two methods of forming pentafluorothio compounds from starting materials that do not contain the pentafluorothio group. Next, we examine fifteen chemical reactions that have been used to transform one pentafluorothio compound into another. Each method is keyed by a letter to the appropriate entries in the tables of derivatives that follow. The tables list all known aliphatic pentafluorothio compounds with their method of preparation, yield, physical properties, and references. The tables are arranged according to functional

groups; i.e., Table 1 lists SF<sub>5</sub> compounds that only contain hydrogen (halogens may be present as additional substituents). A derivative containing double or triple bonds is listed in Table 2 unless there is an additional functional group present, in which case it will be listed under that functional group. Table 3 lists all ethers including unsaturated ethers. Table 4 lists aldehydes and ketones, while carboxylic acids, acyl halides, anhydrides, esters and amides are in Table 5. Table 6 lists amines. No alcohols have been reported. Within each table, the compounds are arranged by empirical formula, according to the accepted Chemical Abstracts order. An attempt has been made to include all the references in the literature to preparative methods and physical properties, not merely to select the few that appear most applicable to

Table 1. Alkanes.

Empirical	Formula Structural	MW (g/mole)	Method	Yield (%)	mp (°C)	bp/P (°C/mm) <sup>a</sup>	np/temp (/°C) <sup>b</sup>	d/temp (g/cm <sup>3</sup> /°C)	References
CClF <sub>7</sub> S	CF <sub>2</sub> C1SF <sub>5</sub>	212.534	B	1		16.5			8
CF <sub>7</sub> IS	CF <sub>2</sub> ISF <sub>5</sub>	303.987	P	54		61-2			18
CF <sub>8</sub> S	CF <sub>3</sub> SF <sub>5</sub>	196.077	B	25	-87	-21 to -20			10
			B	90	-87			11	
CF <sub>12</sub> S <sub>2</sub>	SF <sub>5</sub> CF <sub>2</sub> SF <sub>5</sub>	304.143	B	5		59.6-59.7			11
C <sub>2</sub> ClF <sub>9</sub> S	CF <sub>2</sub> C1CF <sub>2</sub> SF <sub>5</sub>	262.545	A	24	-113	47 <sup>c</sup>			2, 5
C <sub>2</sub> Cl <sub>2</sub> F <sub>8</sub> S	CFC1 <sub>2</sub> CF <sub>2</sub> SF <sub>5</sub>	279.002	A	3		80-3			2
			A	low		79.5-82		2	
C <sub>2</sub> F <sub>10</sub> S	CF <sub>3</sub> CF <sub>2</sub> SF <sub>5</sub>	246.088	C	28		11.3			2
			B	4		13.2-14.2		10, 19	
			B	2		20.5		8, 11	
C <sub>2</sub> F <sub>14</sub> S <sub>2</sub>	CF <sub>3</sub> SF <sub>4</sub> CF <sub>2</sub> SF <sub>5</sub>	354.154	B			88	1.3010/25		8
C <sub>2</sub> HClF <sub>8</sub> S	CHFC1CF <sub>2</sub> SF <sub>5</sub>	244.553	A	12		56.5 <sup>d</sup>			3, 4, 5
			A	80		59		3, 4, 5	
			A	62		59-61		2	
C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub> C1F <sub>5</sub> S	CHC1BrCHBrSF <sub>5</sub>	348.393	C	60		70/13	1.4610/25		6
C <sub>2</sub> H <sub>2</sub> Br <sub>3</sub> F <sub>5</sub> S	CH <sub>2</sub> BrCBr <sub>2</sub> SF <sub>5</sub>	427.301	C	88		42/0.5	1.4973/27		13
C <sub>2</sub> H <sub>2</sub> C1F <sub>7</sub> S	CF <sub>2</sub> C1CH <sub>2</sub> SF <sub>5</sub>	224.737	A						5
			A						5
C <sub>2</sub> H <sub>3</sub> Br <sub>2</sub> F <sub>5</sub> S	CH <sub>2</sub> BrCHBrSF <sub>5</sub>	313.944	C	82		50-2/20	1.4433/25		13
C <sub>2</sub> H <sub>3</sub> C1F <sub>10</sub> S	SF <sub>5</sub> CH <sub>2</sub> CHC1SF <sub>5</sub>	284.569	A			110-120			24

Table 1. Alkanes (continued).

Empirical	Formula Structural	MW (g/mole)	Method	Yield (%)	mp (°C)	bp/P (°C/mm) <sup>a</sup>	np/temp (/°C) <sup>b</sup>	d/temp (g/cm <sup>3</sup> /°C)	References
C <sub>2</sub> H <sub>3</sub> Cl <sub>2</sub> F <sub>5</sub> S	CH <sub>2</sub> ClCHClSF <sub>5</sub>	225.026	C	8		111			2
	CHCl <sub>2</sub> CH <sub>2</sub> SF <sub>5</sub>					108			1.3840/20
C <sub>2</sub> H <sub>4</sub> ClF <sub>5</sub> S	CH <sub>2</sub> ClCH <sub>2</sub> SF <sub>5</sub>	190.577	A	47		92	1.3590/20	1.64/20	6, 20
C <sub>3</sub> F <sub>12</sub> S	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> SF <sub>5</sub>	296.099	B			42	1.2594/25	1.80/25	8
	CF <sub>3</sub> CF <sub>2</sub> SF <sub>4</sub> CF <sub>3</sub>					47.1	1.2674/25	1.803/25	8, 10
C <sub>3</sub> F <sub>16</sub> S <sub>2</sub>	CF <sub>3</sub> SF <sub>4</sub> CF <sub>2</sub> CF <sub>2</sub> SF <sub>5</sub>	404.165	B	1		112			10
	SF <sub>5</sub> CF(CF <sub>3</sub> )CF <sub>2</sub> SF <sub>5</sub>					96			24
C <sub>3</sub> F <sub>18</sub> S <sub>3</sub>	(CF <sub>2</sub> SF <sub>4</sub> ) <sub>3</sub>	474.231	B	2	<-80	144.1-144.5	1.3258/25		10
C <sub>3</sub> H <sub>5</sub> Cl <sub>2</sub> F <sub>5</sub> S	CH <sub>3</sub> CHClCHClSF <sub>5</sub>	239.053	C	93		67/40	1.4191/20	1.6400/20	12
C <sub>3</sub> H <sub>6</sub> ClF <sub>5</sub> S	CH <sub>3</sub> CHClCH <sub>2</sub> SF <sub>5</sub>	201.580	A	78		109	1.3686/20		6, 8
C <sub>4</sub> ClF <sub>13</sub>	CF <sub>2</sub> Cl(CF <sub>2</sub> ) <sub>3</sub> SF <sub>5</sub>	362.567	A		-90	99	1.3052/20		2, 8
C <sub>4</sub> F <sub>12</sub> S	CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> SF <sub>4</sub>	308.110	B			70	1.2766/25		23
C <sub>4</sub> F <sub>14</sub> S	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>3</sub> SF <sub>5</sub>	346.110	B			71	1.2710/25	1.8541/25	8, 11
	CF <sub>3</sub> CF <sub>2</sub> SF <sub>4</sub> CF <sub>2</sub> CF <sub>3</sub>					70	1.2753/25	1.875/25	8, 10
C <sub>4</sub> F <sub>16</sub> S	$\begin{array}{c} \text{CF}_2\text{CF}_2 \\ \diagup \quad \diagdown \\ \text{SF}_4 \quad \text{SF}_4 \\ \diagdown \quad \diagup \\ \text{CF}_2\text{CF}_2 \end{array}$	416.176	B	1	76- 76.5	82/61			10
C <sub>4</sub> H <sub>6</sub> Cl <sub>3</sub> F <sub>5</sub> S	CHCl <sub>2</sub> CH <sub>2</sub> CHClCH <sub>2</sub> SF <sub>5</sub>	287.530	A	15		72/9	1.4269/20		6, 8
C <sub>4</sub> H <sub>8</sub> ClF <sub>5</sub> S	CH <sub>2</sub> Cl(CH <sub>2</sub> ) <sub>3</sub> SF <sub>5</sub>	218.631	A	18		171-2	1.3900/20		6, 8
	(CH <sub>3</sub> ) <sub>2</sub> CClCH <sub>2</sub> SF <sub>5</sub>								
C <sub>6</sub> ClF <sub>17</sub> S	CF <sub>2</sub> Cl(CF <sub>2</sub> ) <sub>5</sub> SF <sub>5</sub>	462.583	A		-5	142	1.3079/20		2, 8
C <sub>6</sub> F <sub>16</sub> S	(CF <sub>2</sub> ) <sub>5</sub> CFSF <sub>5</sub>	408.132	B	4		110	1.3041/25	1.9530/25	9

Table 1. Alkanes (continued).

Empirical	Formula Structural	MW (g/mole)	Method	Yield (%)	mp (°C)	bp/P (°C/mm) <sup>a</sup>	n <sub>D</sub> /temp (/°C) <sup>b</sup>	d/temp (g/cm <sup>3</sup> /°C)	References
C <sub>6</sub> F <sub>18</sub> S	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>5</sub> SF <sub>5</sub>	446.132	B	17	-31	118.2	1.2829/25	1.8910/25	9
	(CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> SF <sub>4</sub>					116	1.2856/25	1.865/25	8
C <sub>6</sub> H <sub>10</sub> ClF <sub>5</sub> S	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> CH SF <sub>5</sub>	244.669	A	16		188-90	1.4320/20	1.4783/20	6
C <sub>8</sub> F <sub>22</sub> S	(CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> SF <sub>4</sub>	546.154	B			154	1.2943/25	1.903/25	8
C <sub>8</sub> H <sub>8</sub> ClF <sub>5</sub> S	PhCHClCH <sub>2</sub> SF <sub>5</sub>	218.631	A	nil					6
C <sub>12</sub> F <sub>26</sub> S	(cycloC <sub>6</sub> F <sub>11</sub> ) <sub>2</sub> SF <sub>4</sub>	670.198	B		90-1	126/37			8, 9
C <sub>12</sub> F <sub>30</sub> S	(CF <sub>3</sub> (CF <sub>2</sub> ) <sub>5</sub> ) <sub>2</sub> SF <sub>4</sub>	746.198	B	3	71-2	65/1			9

<sup>a</sup>If no pressure is given, the boiling point was measured at 1 atm.

<sup>b</sup>The index of refraction is dimensionless.

<sup>c</sup> $\log_{10} P$  (mm) = 7.494 - 1479/T(°C), H<sub>vap</sub> = 6770 kcal/mole, Trouton constant = 21.1.




<sup>d</sup> $\log_{10} P$  (mm) = 6.676 - 1580/T(°C), H<sub>vap</sub> = 7230 kcal/mole, Trouton constant = 21.9.



Table 2. Alkenes and alkynes.

Empirical	Formula		MW (g/mole)	Method	Yield (%)	mp (°C)	bp/P (C/mm)	n <sub>D</sub> /temp ( / °C)	d/temp (g/cm <sup>3</sup> /°C)	References
	Structural									
C <sub>2</sub> F <sub>8</sub> S	CF <sub>2</sub> =CFSF <sub>5</sub>		208.088	E	82		19 <sup>a</sup>			2, 3, 14
C <sub>2</sub> HBrClF <sub>5</sub> S	CHCl=CBrSF <sub>5</sub> <sup>b</sup>		267.469	E	90		50/52			13
	cis-CHCl=CBrSF <sub>5</sub>							1.4150/25	2.06/25	13
	trans-CHCl=CBrSF <sub>5</sub>							1.4250/25	2.06/25	13
C <sub>2</sub> HF <sub>5</sub> S	HC≡CSF <sub>5</sub>		152.096	D	90		6			13
C <sub>2</sub> H <sub>2</sub> BrF <sub>5</sub> S	CH <sub>2</sub> =CBrSF <sub>5</sub>		233.020	E	80		86	1.3814/25		13
C <sub>2</sub> H <sub>2</sub> ClF <sub>5</sub> S	CHCl=CHSF <sub>5</sub>		188.561	A	40		65-7			6, 13, 14
		E		63		66			6	
		E		93		72			16	
		E		85		41 <sup>c</sup>			6, 14	
C <sub>3</sub> H <sub>3</sub> F <sub>5</sub> S	CH <sub>3</sub> C≡CSF <sub>5</sub>		166.123	E	2.5		65-70			1, 6, 14
		A		"nearly quant"	202.588	91-93			1	
							A	24.7		92
C <sub>3</sub> H <sub>5</sub> F <sub>5</sub> S	CH <sub>3</sub> CH=CHSF <sub>5</sub>		168.139	E	32.3		80-2			6, 14
	CH <sub>2</sub> =CHCH <sub>2</sub> SF <sub>5</sub>		186.139	E	3.7		80-2			6, 14
C <sub>4</sub> H <sub>6</sub> Cl <sub>2</sub> F <sub>5</sub> S	CH <sub>2</sub> =CHCHClCH <sub>2</sub> SF <sub>5</sub>		252.072	A	22		78-80/26			6

Table 2. Alkenes and alkynes (continued).

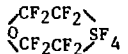
Empirical	Formula Structural	MW (g/mole)	Method	Yield (%)	mp (°C)	bp/P (C/mm)	n <sub>D</sub> /temp (°C)	d/temp (g/cm <sup>3</sup> /°C)	References
C <sub>6</sub> H <sub>7</sub> F <sub>5</sub> S		206.188	G	78		48-50/10	1.4109/25		13
C <sub>6</sub> H <sub>9</sub> F <sub>5</sub> S		208.204	E	79		161/760 112-5/100	1.4282		6
C <sub>8</sub> H <sub>11</sub> F <sub>5</sub> S		234.242	G	50.5		65/4			13

<sup>a</sup>log<sub>10</sub>P(mm) = 6.36 - 1310/T(°C), H<sub>vap</sub> = 5990, Trouton constant = 20.5

<sup>b</sup>1/4 mixture of cis and trans isomers by GC.

<sup>c</sup>log<sub>10</sub>P(mm) = 13.68 - 3420/T(°C), H<sub>vap</sub> = 6800 cal/mole, Trouton constant = 21.6

Table 3. Ethers.

Empirical	Formula Structural	MW (g/mole)	Method	Yield (%)	mp (°C)	bp/P (°C/mm)	n <sub>D</sub> /temp ( /°C)	d/temp (g/cm <sup>3</sup> /°C)	References
C <sub>3</sub> H <sub>3</sub> ClF <sub>8</sub> OS	CH <sub>3</sub> OCFC1CF <sub>2</sub> SF <sub>5</sub>	274.580	A	92		102-3			18
C <sub>3</sub> H <sub>5</sub> F <sub>5</sub> OS	CH <sub>3</sub> OCH=CHSF <sub>5</sub>	184.139	E	33		120-2			15
			H	82		115			17
	<i>cis</i> -CH <sub>3</sub> OCH=CHSF <sub>5</sub>		H	65		50/20	1.3633/25	a	13
	<i>trans</i> -CH <sub>3</sub> OCH=CHSF <sub>5</sub>		H	40		115	1.3572/25	b	13
C <sub>4</sub> F <sub>12</sub> OS		324.110	B		17.1-17.3	80.3	1.3041/25	1.9031/25	10
C <sub>4</sub> F <sub>14</sub> OS	CF <sub>3</sub> CF <sub>2</sub> OCF <sub>2</sub> CF <sub>2</sub> SF <sub>5</sub>	362.110	B			65	1.2598/25	1.772/25	8, 10
C <sub>4</sub> H <sub>5</sub> ClF <sub>8</sub> OS	CH <sub>3</sub> CH <sub>2</sub> OCFC1CF <sub>2</sub> SF <sub>5</sub>	288.139	A	67		117-8			18
C <sub>4</sub> H <sub>5</sub> Cl <sub>2</sub> F <sub>7</sub> OS	CH <sub>3</sub> CH <sub>2</sub> OCFC1CFC1SF <sub>5</sub>	305.064	A	nil					18
C <sub>4</sub> H <sub>9</sub> F <sub>5</sub> O <sub>2</sub> S	(CH <sub>3</sub> O) <sub>2</sub> CHCH <sub>2</sub> SF <sub>5</sub>	216.182	H			63/50	1.3613/25		13

<sup>a</sup>Dipole moment = 5.13 D

<sup>b</sup>Dipole moment = 3.94 D

Table 4. Aldehydes and ketones.

Empirical	Formula Structural	MW (g/mole)	Method	Yield (%)	mp (°C)	bp/P (°C/mm)	n <sub>D</sub> /temp (/°C)	d/temp (g/cm <sup>3</sup> /C)	References
C <sub>2</sub> H <sub>3</sub> F <sub>5</sub> OS	OHCCH <sub>2</sub> SF <sub>5</sub>	170.112	I	53.4		80			15
			K	55.3					7
			I	89	a	79-82			17
C <sub>2</sub> H <sub>5</sub> F <sub>5</sub> O <sub>2</sub> S	H <sub>2</sub> O·OHCCH <sub>2</sub> SF <sub>5</sub>	186.125	L		35-41/100				7
C <sub>3</sub> H <sub>5</sub> F <sub>5</sub> OS	CH <sub>3</sub> COCH <sub>2</sub> SF <sub>5</sub>	200.139	A	15	b	126,53-4/47			7

<sup>a</sup>2,4-dinitrophenylhydrazone, mp 133

<sup>b</sup>2,4-dinitrophenylhydrazone, mp 143-5

Table 5. Acids and their derivatives.

Empirical	Formula Structural	MW (g/mole)	Method	Yield (%)	mp (°C)	bp/P (°C/mm)	$n_D$ /temp (/°C)	d/temp (g/cm <sup>3</sup> /°C)	References
C <sub>2</sub> F <sub>8</sub> OS	SF <sub>5</sub> CF <sub>2</sub> COF	224.088	B						8
C <sub>2</sub> H <sub>7</sub> F <sub>7</sub> O <sub>2</sub> S	SF <sub>5</sub> CF <sub>2</sub> COOH	222.096	L	79		70/60			18
C <sub>2</sub> H <sub>2</sub> ClF <sub>5</sub> OS	SF <sub>5</sub> CH <sub>2</sub> COCl	204.561	N			110-2			15
			N			115			17
			A	57.8		102,47-8/27			7
C <sub>2</sub> H <sub>2</sub> F <sub>7</sub> NOS	SF <sub>5</sub> CF <sub>2</sub> CONH <sub>2</sub>	221.112	O	65	111-2				18
C <sub>2</sub> H <sub>3</sub> F <sub>5</sub> O <sub>2</sub> S	SF <sub>5</sub> CH <sub>2</sub> COOH	186.112	M	69.1	62-4	35-46/0.3			7
			J	49.2	64				15
			J	20	66 <sup>a</sup>	45/2			17
C <sub>3</sub> H <sub>3</sub> F <sub>7</sub> O <sub>2</sub> S	SF <sub>5</sub> CF <sub>2</sub> COOCH <sub>3</sub>	236.123	I	78.5		92.5-93.5			18
C <sub>4</sub> H <sub>5</sub> F <sub>7</sub> O <sub>2</sub> S	SF <sub>5</sub> CF <sub>2</sub> COOCH <sub>2</sub> CH <sub>3</sub>	250.150	I	78		111-3			18
C <sub>4</sub> H <sub>6</sub> ClF <sub>5</sub> O <sub>2</sub> S	SF <sub>5</sub> CH <sub>2</sub> CHC10CCH <sub>3</sub>	248.615	A	47.3		36/27			7
C <sub>4</sub> H <sub>7</sub> F <sub>5</sub> O <sub>2</sub> S	SF <sub>5</sub> CH <sub>2</sub> COOCH <sub>2</sub> CH <sub>3</sub>	214.166	M	54.6		60/41			7
C <sub>6</sub> H <sub>9</sub> F <sub>5</sub> O <sub>4</sub> S	SF <sub>5</sub> CH <sub>2</sub> CH(OOCCH <sub>3</sub> ) <sub>2</sub>	272.204	R	98		49/0.15	1.2793/25		13
C <sub>8</sub> H <sub>8</sub> F <sub>5</sub> NOS	SF <sub>5</sub> CH <sub>2</sub> CONePh	261.226	O	92	114-6				7

<sup>a</sup>pK<sub>a</sub> = 3.9 × 10<sup>-3</sup>, p-bromophenacyl ester, mp 82.

Table 6. Amines.

Empirical	Formula		MW (g/mole)	Yield Method (%)	mp (°C)	bp/P (°C/mm)	n <sub>D</sub> /temp ( /°C)	d/temp (g/cm <sup>3</sup> /°C)	References
	Structual								
CF <sub>9</sub> NS	NF <sub>2</sub> CF <sub>2</sub> SF <sub>5</sub>		229.085	B	-153	9.5			22
C <sub>6</sub> F <sub>19</sub> NS	(CF <sub>3</sub> CF <sub>2</sub> ) <sub>2</sub> NCF <sub>2</sub> CF <sub>2</sub> SF <sub>5</sub>		479.140	B		124	1.2921/25	1.86/25	8

laboratory syntheses. Conflicting values for physical properties are reported without attempting to determine which ones are correct. A considerable body of spectral data, particularly nmr, is available but was not included. It can usually be readily found by consulting the references. The one available report dealing with toxicity is mentioned in Appendix A.

#### A. ADDITION OF SF<sub>5</sub>Cl TO AN OLEFIN OR ACETYLENE

The most generally used method for preparing aliphatic derivatives of SF<sub>5</sub> is to add SF<sub>5</sub>Cl to either an olefin or acetylene under free radical conditions. The method was first reported by H. L. Roberts in 1960.<sup>1</sup> SF<sub>5</sub>Cl behaves as a pseudo-halogen, with SF<sub>5</sub>• as the attacking radical. Markownikov's Rule is obeyed, but in many cases the other isomer (resulting from Cl• attack) is also formed in lesser amounts. The reaction is carried out either photochemically in the gas phase or thermally in the condensed phase in the presence of free radical initiators such as benzoyl peroxide. The thermal method is said to be more satisfactory for fluoroolefins.<sup>2</sup> However, only one useful comparison of the two techniques is available, namely

comparing the yields of the addition to trifluoroethylene. In that case the yield by photochemical addition was 80%<sup>3,4,5</sup> while that from the thermal reaction was 62%.<sup>2</sup> Hexafluoropropene does not undergo addition in the presence of benzoyl peroxide at 150°C but does react under the influence of UV light to give a complex mixture of products.

The reaction fails with olefins that are too readily polymerized (i.e., isobutylene or styrene). In many other instances, telomers are formed in addition to the main product (i.e., ethylene and tetrafluoroethylene). Butadiene adds only one mole of SF<sub>5</sub>Cl even when the latter is in excess.<sup>6,5</sup> Acetylenes also add only one mole.<sup>6</sup> Addition does occur with vinyl ethers and ketene.<sup>7</sup> A limited amount of kinetic data is available.<sup>4,5</sup>

#### B. ELECTROCHEMICAL FLUORINATION<sup>8-11</sup>

Electrochemical fluorination has been used to produce a relatively large number of SF<sub>5</sub> compounds, but in most cases the yields are too small to be of much use. The sulfur-containing compound to be fluorinated is dissolved in anhydrous hydrofluoric acid and electrolyzed under conditions that will produce hydrogen but not fluorine. All of the hydrogens

of the compound being fluorinated are replaced by fluorine; the sulfur is oxidized and fluorinated. Alkyl thiols are converted to perfluoro-alkylsulfurpentafluorides, alkyl sulfides to bis(perfluoroalkyl)sulfurtetrafluorides, carboxylic acids to acyl fluorides. Tertiary nitrogens and ether linkages are retained intact.

#### C. ADDITION OF HALOGEN TO UNSATURATION<sup>2,6,12,13</sup>

Chlorine or bromine will add to unsaturated derivatives of sulfurpentafluoride in the usual way. Four olefins have been treated:  $CF_2=CFSF_5$ ,  $CHCl=CHSF_5$ ,  $CH_2=CHSF_5$ , and  $CH_3CH=CHSF_5$ . Yields are usually good.

#### D. DEHALOGENATION<sup>13</sup>

Only one example of dehalogenation has been reported among sulfurpentafluoride derivatives, but there is no reason to suppose that it would not be a fairly general reaction. In the one case reported, treatment of 1-bromo-2-chlorovinylsulfurpentafluoride with zinc dust in diethyleneglycol dimethyl ether led in 90% yield to pentafluorothioacetylene.

#### E. DEHYDROHALOGENATION<sup>1-3,14,15</sup>

Aliphatic pentafluorosulfur compounds containing a halogen other than fluorine and a hydrogen on adjacent carbons can be dehydrohalogenated by treatment with a suitable base to yield olefins or acetylenes. Where formation of cis and trans isomers is possible, both are produced, although the trans isomer predominates.<sup>13</sup> Where a hydrogen can be abstracted either  $\alpha$  or  $\gamma$  to the  $SF_5$  group, both abstractions occur with  $\alpha$  predominating.<sup>6</sup> Four base-solvent combinations have been used:

- sodium or potassium hydroxide in water or ethanol or mixtures of water and ethanol<sup>6,14</sup>
- Anhydrous potassium hydroxide in ligroin,<sup>2,6</sup>
- Potassium carbonate in acetone<sup>13</sup>
- Cyclohexylamine in toluene<sup>16</sup>

A number of examples are given in Table 2. Yields range from very poor for acetylene formation and  $\gamma$ -hydrogen extraction to as high as 93% for formation of  $CHCl=CHSF_5$ . Unfortunately, no comparisons between the various methods of carrying out the reaction have been made.



## F. DEHYDROGENATION<sup>13</sup>

Only two examples of dehydrogenation of aliphatic pentafluorothio derivatives have been reported. Pyrolysis of (pentafluorothio)-1,4-cyclohexadiene in the presence of a platinum catalyst produced pentafluorothio benzene, and treatment of 4,5-dimethyl-1-pentafluorothio-1,4-cyclohexadiene with chloranil in refluxing xylene produced 1,2-dimethyl-4-pentafluorothio benzene (in 71% yield).

## G. DIELS-ALDER REACTION<sup>13</sup>

Pentafluorothioacetylene reacts as a dienophile with butadiene (78%) or 2,3-dimethylbutadiene (51%) to yield the expected cyclohexadiene derivatives.

## H. OTHER ADDITION REACTIONS

Besides the reactions discussed in A, C, and G there are three reactions involving addition to olefinic or acetylenic unsaturation that have been used to prepare aliphatic pentafluorosulfur compounds:

- Methanol will add to pentafluorothioacetylene, the stereospecificity depending on the reaction conditions. Dry alcoholic potassium hydroxide produces the cis isomer (65%) with only a trace of trans, while addition of a little water to the reaction mixture leads to essentially all trans isomer (40%).<sup>13</sup> Treatment of 2-chlorovinylsulfurpentafluoride with sodium methoxide in anhydrous methanol results in both addition and dehydrohalogenation.<sup>17</sup> The product is apparently the trans isomer judging from its boiling point. A second mole of methanol can be added, but the rate is much slower.<sup>13</sup>
- Diazomethane also adds to pentafluorothioacetylene in the conventional way to produce a 60/40 mixture of 3- and 4-pentafluorothiopyrazole. The total yield is 85%.<sup>13</sup>
- Bis(trifluoromethyl)nitrogen oxide will add (in 93% yield) to pentafluorothioethylene. The product is 1,2-bis(bis(trifluoromethyl)aminooxy)-1-pentafluorothioethane.<sup>12</sup>

I. ACID HYDROLYSIS OF AN  $\alpha$ -CHLORO  
OR VINYL ETHER<sup>15,17</sup>

Treatment of methyl or ethyl 1-chloro-2-pentafluorothiotrifluoroethyl ether with concentrated sulfuric acid at 80-85°C for 45 min yields about 78% of the methyl or ethyl ester of difluoro(pentafluorothio)acetic acid.<sup>18</sup> These are the only examples of this reaction reported with a pentafluorothio group present, but the reaction is quite general for ethers containing the  $-\text{CF}_2\text{O}$  and  $-\text{CFClO}$ -groups.<sup>11</sup> Hydrolysis of 2-methoxyvinylsulfurpentafluoride with phosphoric or hydrochloric acids yields pentafluorothioacetaldehyde.

J. OXIDATION<sup>15,17</sup>

Only one oxidation of a functional group in an aliphatic pentafluorothio compound has been reported. Treatment of pentafluorothioacetaldehyde with cold (0°C) aqueous sodium permanganate produced a 20% yield of pentafluorothioacetic acid.

K. DEHYDRATION<sup>7</sup>

Hydrated pentafluorothio compounds can be dehydrated by treatment with phosphorous pentoxide without altering the pentafluorothio group. The only example reported so far is dehydration of pentafluorothioacetaldehyde hydrate.

L. BASE HYDROLYSIS OF AN ESTER<sup>7,18</sup>

Only two pentafluorothio esters have been hydrolyzed. Ethyl difluoro(pentafluorothio)acetate when titrated with alcoholic sodium hydroxide affords a good yield of the corresponding acid (after acidification). It is necessary to avoid an excess of alkali. 1-Chloro-2-pentafluorothioethyl acetate yields pentafluorothioacetaldehyde hydrate on treatment with potassium hydroxide in methanol at 15-28°C. Treatment of any pentafluorosulfur derivative with strong bases under drastic hydrolytic conditions would be expected to destroy the pentafluorothio group.

M. HYDROLYSIS OR ALCOHOLYSIS OF AN  
ACID HALIDE OR ANHYDRIDE<sup>7</sup>

The only reported examples of this method are with pentafluorothioacetyl chloride. Reaction with water produces the free acid in 69% yield and with ethanol produces the ethyl ester in 55% yield. Other acyl halides and anhydrides should behave similarly.

N. TREATMENT OF AN ACID WITH THIONYL  
CHLORIDE<sup>15</sup>

Of the many widely used agents for forming acyl halides, only thionyl chloride has been tried on

compounds containing a pentafluorothio group. It has been used to convert pentafluorothioacetic acid to the acid chloride.

O. TREATMENT OF AN ESTER OR ACID CHLORIDE WITH AMMONIA OR AN AMINE<sup>7,18</sup>

An ester or acid chloride can be treated with ammonia or an amine without attacking the pentafluorothio group. The treatment results in amides. Only two examples have been reported: reaction of ammonia with ethyl difluoro(pentafluorothio)acetate and reaction of aniline with pentafluorothioacetyl chloride.

P. THE HUNSDIEKER REACTION<sup>18</sup>

Application of the Hunsdiecker reaction to silver difluoro(pentafluorothio)acetate gave a 54% yield of difluoroiodo(pentafluorothio)-methane.

Q. ACYLATION<sup>13</sup>

Pentafluorothioacetaldehyde has been acylated in 90% yield by the sulfuric acid catalysed reaction of the aldehyde with acetic anhydride. No other examples have been reported.

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## Appendix A. Toxicity

Practically nothing is known about the toxicity of aliphatic pentafluorothio compounds.  $SF_5Cl$  is reported to be about as toxic as

phosgene; vinylsulfurpentafluoride is a lung irritant and is toxic to the liver and kidneys.<sup>21</sup>