

## Free-radical addition of 2-(perfluoroalkyl)ethanethiols to alkenes, alkadienes, cycloalkenes, alkynes and vinyl monomers

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### Abstract

The free-radical addition of 2-(perfluoroalkyl)ethanethiols ( $R_FCH_2CH_2SH$ ) to alkenes, cycloalkenes, alkadienes and alkynes has been studied to determine: (1) the mode of reaction, i.e. the stereochemistry, regiochemistry and any skeletal changes; (2) the relative reactivity towards unsaturates of differing structures and classes as affected by the presence of the  $R_F$  group; and (3) the influence of the reaction conditions on the rate of addition or selectivity for different products. Adducts from 2-(*F*-hexyl)ethane thiol (**1**) and alkenes have been obtained in high yield, but containing small amounts of regio isomers. For example, compound **1** with 1-heptene gave 1-[2-(*F*-hexyl)ethanethio]heptane (**3**, 96% yield) as well as 2-[2-(*F*-hexyl)ethanethio]heptane (**4**, 0.61%) and 3-[2-(*F*-hexyl)ethanethio]heptane (**5**, 2.22%). 1,6-Hexadiene and 1,7-octadiene gave chiefly linear adducts, i.e.  $R_FCH_2CH_2S(CH_2)_nCH=CH_2$  (**7**,  $n=4$ ; or **12**,  $n=6$ , respectively) and  $R_FCH_2CH_2S(CH_2)_nSCH_2CH_2R_F$  (**8**,  $n=6$ ; or **14**,  $n=8$ , respectively). A small amount (2–3%) of *cis*- and *trans*-1-methyl-[2-(*F*-hexyl)ethanethiomethyl]cyclohexane (**13**) isomers were present in **12**. Compound **1** with 1,6-heptadiene gave 7-[2-(*F*-hexyl)ethanethio]-1-heptene (**9**), the bis adduct, 1,7-bis-[2-(*F*-hexyl)ethanethio]heptane (**11**) and the cyclic adducts, *cis*- and *trans*-1-methyl-2-[2-(*F*-hexyl)-ethanethio]methylcyclopentane (**10**). The relative amounts of cyclic isomers depended on the reactant ratio. Compound **1** added readily with free-radical initiation to vinyl monomers such as styrene and vinyl acetate, and to phenyl acetylene, propargyl acetate and ethyl propynoate. These new addition products are useful as models for further study.

### Introduction

This work had its inception in a study of the free-radical addition of perfluoroalkyl iodides ( $R_FI$ ) to unsaturated compounds [1–4], these early papers and patents giving practical methods, now widely used, for the synthesis of a variety of  $R_F$ -containing organic compounds. Of particular industrial importance are the ethylene adducts  $R_F(CH_2CH_2)_nI$ , where  $n=1, 2, 3$  or higher [4]. Subsequently, many adducts of  $R_FI$ , their unusual chemistry and some practical applications have been described in a series of papers [5–11]. Early on,  $R_FCH_2CH_2CH_2CH_2SH$  and its homologs were synthesized, and free-radical addition to undecylenic acid gave  $R_F(CH_2)_4S(CH_2)_{10}COOH$  [12]. This terminal [(*F*-alkyl)-thia]alkanoic acid and its homologs showed pronounced

surface activity. Later,  $R_FCH_2CH_2SH$  was converted to an interesting group of solid, well-characterized norbornene anhydride derivatives which also provided another series of useful compounds [13]. Though some related chemistry of fluorine-substituted thiols has been reported [14–16], only one paper describes the free-radical reaction of  $R_FCH_2CH_2SH$  and some unsaturated silanes [17].

The present work emphasizes the free-radical chemistry of fluorine-substituted thiols in an attempt to define the scope of the reaction and the structures of the products. This first paper explores the reactions of  $R_FCH_2CH_2SH$  (where  $R_F = C_6F_{13}$  or  $C_8F_{17}$ ) with alkenes, alkadienes, cycloalkenes and certain alkynes or vinyl monomers. The reaction conditions and the isolation and characterization of the products by appropriate methods are described. The quantitative determination of the side-reaction products by capillary GC analysis is demonstrated. A subsequent paper [18] will report a quantitative study of the relative reactivity of thiols with unsaturated compounds, in comparison with similar reactions of perfluoroalkyl iodides. Further papers will describe the preparative reactions of *F*-alkyl-substituted thiols for functional derivatives of typical alcohols, esters and carboxylic acid derivatives.

## Results and discussion

Simple alkenes react readily with  $C_6F_{13}CH_2CH_2SH$  (**1**) in an inert atmosphere when initiated by azo-bis-isobutyronitrile (AIBN) at 70 °C. A certain amount of free-radical reaction occurred with compound **1** and a reactive alkene such as 1-heptene, *even without* an initiator, upon standing at 25 °C if the mixture had been exposed to air (oxygen) during transfer of reactants by pipet. This effect had been observed earlier by Cadogan and Sadler [19] in the reaction of 1-octene with methyl mercaptoacetate. To avoid this difficulty, the transfer of liquids was undertaken by pipet under nitrogen purge into a cooled reaction tube. The tube was sealed, further cooled to –78 °C or –196 °C, then evacuated and filled three times with nitrogen and resealed (see below for experimental details). Reactive alkenes added compound **1** completely in *n*-heptane solution (1 and 2 M) within 2–5 h. Reaction without solvent was advantageous for less reactive compounds or for the preparation of larger amounts of adducts. To control the exothermic reaction, it was convenient to add the alkene slowly to a stirred mixture of compound **1** and AIBN. Tables 1–3 list the reactions of compound **1** with various unsaturated compounds together with the reaction conditions, the code numbers, the names, the physical constants and the yields of the adducts. The results of combustion analysis and the essential NMR spectroscopic parameters are listed in Table 4.

Terminal alkenes add compound **1** regioselectively but not regiospecifically (Table 1). 1-Hexene (Table 1, entry 1) afforded a mixture of 1-[2-(*F*-hexyl)ethanethio]hexane (**2**) in 93.0% distilled yield (93.88% purity by capillary

TABLE 1

Adducts from the reaction of compound 1 with alkenes and alkadienes at 70 °C<sup>a</sup>

Alkene/alkadiene		Adduct						
Entry No.	Name	Weight		Compound No.	Boiling point (°C/mmHg)	$n_D^{25}$	Yield (%)	(GC) <sup>b</sup>
		g	mmol					
1	1-hexene	1.26	15.0	2	70/0.20	1.3704	93.0 <sup>c</sup>	(93.9)
2	1-heptene <sup>d,e</sup>	2.45	25.0	3, 4	1-[2-( <i>F</i> -hexyl)ethanethio]hexane (2) 94/1.05	1.3745	90.9 <sup>f</sup>	(95.7)
3	1-heptene <sup>d,g</sup>	0.52	5.0	3, 4	1-[2-( <i>F</i> -hexyl)ethanethio]heptane (3) 2-[2-( <i>F</i> -hexyl)ethanethio]heptane (4)	—	69 <sup>h</sup>	(95.3)
4	<i>cis</i> -2-heptene <sup>d,e</sup>	2.45	25.0	4, 5	69/0.10 3-[2-( <i>F</i> -hexyl)ethanethio]heptane (5)	1.374	73.6 <sup>i</sup>	
5	1-octene <sup>d,j</sup>	5.61	50.0	6	72/0.10 1-[( <i>F</i> -hexyl)ethanethio]octane (6)	—	81.1	
6	1,5-hexadiene	1.23	15.0	7	44/0.10 6-[2-( <i>F</i> -hexyl)ethanethio]-1-hexene (7)	—	60.5	
7	1,6-heptadiene <sup>e</sup>	1.93	20.0	8	1,6-bis-[2-( <i>F</i> -hexyl)ethanethio]hexane (8)	—	1.25	(26.3) <sup>k</sup>
				9, 10, 11	42/0.05 7-[2-( <i>F</i> -hexyl)ethanethio]-1-heptene (9) <i>cis</i> - and <i>trans</i> -1-methyl-2-[2-( <i>F</i> -hexyl)ethanethio]methylcyclopentane [ <i>cis</i> -(10), <i>trans</i> -(10)]	—	56.3	
8	1,6-heptadiene <sup>d,l</sup>	0.976	10.15	9, 10, 11	1,7-bis-[2-( <i>F</i> -hexyl)ethanethio]heptane (11)	—	37.4 <sup>i</sup>	(52.0; 10.2; 32.8)
					—	—	4.23	

(continued)

TABLE 1 (continued)

Alkene/alkadiene		Adduct		
Entry No.	Name	Weight	Boiling point (°C/mmHg)	Yield (GC) <sup>b</sup>
		g		
9	1,7-octadiene <sup>m</sup>	2.31	20.0	—
			86/0.05	(75) <sup>n</sup>
			8-[2-( <i>F</i> -hexyl)ethanethio]1-octene (12)	
			<i>cis</i> - and <i>trans</i> -1-methyl-[2-( <i>F</i> -hexyl)ethanethiomethyl]cyclohexane [ <i>cis</i> -(13), <i>trans</i> -(13)]	
			1,8-bis-[2-( <i>F</i> -hexyl)ethanethio]octane (14)	21.8 <sup>p</sup>

<sup>a</sup>Procedure A was employed unless stated otherwise: compound 1 (3.80 g, 9.448 mmol), alkene (15 mmol), AIBN (0.0131 g, 0.0800 mmol) in *n*-heptane (10 ml).

<sup>b</sup>GC purity or percentage yield in parentheses.

<sup>c</sup>1-Hexene (20.0 mmol) and compound 1 (14.6 mmol) were employed. In addition to 2, 1-hexene gave the following adducts: GC retention time of 14.74 min (2.287%), probably 2-[2-(*F*-hexyl)ethanethio]hexane; at 14.949 min (0.503%), probably 2-[2-(*F*-octyl)ethanethio]hexane; and at 16.793 min (2.13%), probably 1-[2-(*F*-octyl)ethanethio]hexane.

<sup>d</sup>Procedure B.

<sup>e</sup>See Experimental section for details.

<sup>f</sup>Contained several regio isomers (see Table 5 for GC analyses).

<sup>g</sup>Reaction sample exposed to air (see Experimental section for details).

<sup>h</sup>For GC analyses, see Table 5.

<sup>i</sup>See Table 5 for identity of isomers.

<sup>j</sup>1-Octene (5.61 g, 50.0 mmol; redistilled b.p., 121.5 °C under nitrogen), compound 1 (11.4 g, 30.0 mmol) and AIBN (0.0985 g, 0.600 mmol) at 70 °C for 15 h gave: fraction I, b.p. 72 °C/0.1 mmHg, 3.09 g; fraction II, b.p. 75–77 °C/0.25 mmHg, 8.30 g; and a residue, 0.35 g. GC analysis: (DB-1 and DB-5 columns both 15 m in length): Fraction I (DB-1): isomer, 15.91 min, 1.67%; isomer, 15.98 min, 3.328%; isomer, 16.61 min, 0.216%; 6, 16.93 min, 90.52%; homolog (?), 17.86 min, 1.01%. Fraction II (DB-5): isomer, 16.91 min, 1.01%; isomer, 16.97 min, 2.11%; 6, 17.92 min, 93.60%; and homolog (?), 18.87 min, 2.71%.

<sup>k</sup>Sample contained *c.* 11% of 7 (NMR analysis: CH<sub>2</sub>=CH resonances) and also regio isomers of 8 (NMR analysis: δ 0.90 ppm (d, *J* = 7 Hz, CH<sub>3</sub>CH), *c.* 10% of total sample).

<sup>l</sup>In entry 7, molar ratio of 1:1,6-heptadiene = 1:2; in entry 8, molar ratio = 1:1, heated for 1 h (see Table 6 for GC results).

<sup>m</sup>The sealed ampoule was heated at 70.0 °C for 15 h.

<sup>n</sup>GC analysis, 97.6% of 12 and 2.4% of 13; NMR analysis, δ 0.9 and 1.0 ppm (0.2 H, d, *J* = 7 Hz, CH<sub>3</sub>CH) of presumably *cis*-(13), *trans*-(13), 6% of total area.

<sup>p</sup>From integrated CH<sub>2</sub>=CH resonances, 14 contained *c.* 30% of 12; thus, 75.3% of 12 and 16.4% of 14 in product. Sample showed broad resonances at δ 0.7–1.1 ppm and a doublet at δ 0.9 ppm (total, 0.7 H), expected for CH<sub>3</sub>CH. This indicates the presence of 13 and/or regio isomers similar to 4.

TABLE 2  
Reaction of compound **1** with cycloalkenes at 70 °C<sup>a</sup>

Cycloalkene	Adduct					
	Entry No.	Compound No.				
Name	Weight g	mmol				
Boiling point (°C/mmHg)	$n_D^{25}$	Yield (%)				
cyclopentene <sup>b</sup>	1.70	25.0	114/12	1.3765	8.012	84.4 <sup>c</sup>
			[2-( <i>F</i> -hexyl)ethanethio]cyclopentane ( <b>15</b> )			
cyclohexene <sup>b</sup>	2.05	25.0	126/12	1.3830	10.89	94.3
			[2-( <i>F</i> -hexyl)ethanethio]cyclohexane ( <b>16</b> )			
cycloheptene <sup>b</sup>	2.40	25.0	143/12 <sup>d</sup>	1.3908	11.42	95.9
			[2-( <i>F</i> -hexyl)ethanethio]cycloheptane ( <b>17</b> )			
cyclooctene <sup>e</sup>	2.54	23.0	156/13	1.3968	3.26	53.2
			[2-( <i>F</i> -hexyl)ethanethio]cyclooctane ( <b>18</b> )			
norbornene <sup>f</sup>	0.9414	10.0	90/1.2	—	3.75	79.1
			<i>exo</i> -2-[2-( <i>F</i> -hexyl)ethanethio]norbornane ( <b>19</b> )			
norbornadiene	1.388	15.0	52/0.10	—	3.61	76.4
			<i>exo</i> -2-[2-( <i>F</i> -hexyl)ethanethio]nortricyclene ( <b>20</b> )			

<sup>a</sup>Procedure A was employed unless stated otherwise: compound **1** (3.80 g, 9.448 mmol), alkene (15.0 mmol), AIBN (0.0131 g, 0.080 mmol) in *n*-heptane (10 ml).

<sup>b</sup>Procedure B was used: compound **1** (11.41 g; 28.5 mmol), alkene (25.0 mmol) and AIBN (0.60 mmol) was heated at 70 °C for 3–5 h. No *n*-heptane solvent.

<sup>c</sup>Compound **15**, 99% purity established by GC methods. A residue (2.13 g) was not distilled.

<sup>d</sup>A sample was also distilled at 125 °C/7.0 mmHg.

<sup>e</sup>Treatment of cyclooctene (23.0 mmol) at 70 °C for 17 h with compound **1** (5.00 g, 12.5 mmol) and AIBN (0.30 mmol) gave unreacted cyclooctene (1.18 g, 46.6%) and low conversion to an adduct.

<sup>f</sup>Heated at 70 °C for 21 h.

TABLE 3  
Reaction of compound **1** with alkynes and vinyl monomers at 70 °C<sup>a</sup>

Entry No.	Alkyne/vinyl monomer Name	Weight		Adduct Compound No.	Boiling point (°C/mmHg)	$n_D^{25}$	Weight (g)	Yield (%)
		g	mmol					
16	styrene	1.56	15.0	<b>21</b>	77/0.10	—	3.00	65.6 <sup>b</sup>
17	phenyl acetylene <sup>c</sup>	2.04	20.0	<i>cis</i> -( <b>22</b> )	45/0.03	—	3.81	8.40
18	phenyl acetylene <sup>c</sup>	0.5105	5.00	<i>trans</i> -( <b>22</b> )	60/0.06	—	2.10	87.3
19	vinyl acetate <sup>d</sup>	7.14	82.5	<b>23</b>	108/3.6	1.3692	30.70	94.0
20	allyl acetate <sup>d,e</sup>	5.506	55.0	<b>24</b>	136/0.03	1.3674	27.6	95.0 <sup>f</sup>
21	propargyl acetate <sup>g</sup>	5.89	60.0	<b>25</b>	88/0.15	—	6.93	55.8 <sup>h</sup>

*cis*- and *trans*-3-[2-(*F*-hexyl)ethanethio]-2-propenyl acetate (**25**)

22	ethyl 3-butenate	1.141	10.0	<b>26</b>	90/0.55 ethyl 4-[2-( <i>F</i> -hexyl)ethanethio]butanoate ( <b>26</b> )	4.05	86.7
23	ethyl propynoate	0.9810	10.0	<b>27</b>	88/0.30 ethyl <i>trans</i> -3-[2-( <i>F</i> -hexyl)ethanethio]-2-propenoate ( <b>27</b> )	3.52	77.9 <sup>i</sup>

<sup>a</sup>Procedure A was employed unless stated otherwise: compound **1** (3.80 g, 9.448 mmol), alkene (20.0 mmol), AIBN (0.0131 g, 0.080 mmol) in *n*-heptane (10 ml).

<sup>b</sup>Residue (0.75 g, *c.* 19% calcd. as adduct) also obtained.

<sup>c</sup>Heated at 70 °C for 18 h; see Experimental section for details.

<sup>d</sup>See Typical Procedure C.

<sup>e</sup>2-(*F*-Octyl)ethanethiol (24.0 g, 50.0 mmol) and AIBN (0.090 g, 0.55 mmol) were heated at 60–70 °C while allyl acetate was added (0.5 h); then heated at 70 °C for 5 h.

<sup>f</sup>See Experimental section. GC and NMR methods showed that the reaction product was **24** (95.1%) and the regio isomer 2-[2-(*F*-hexyl)ethanethio]propyl acetate (4.9%). These were not capable of separation by distillation. Unreacted compound **1** and allyl acetate were also recovered.

<sup>g</sup>Typical Procedure B was used; heated at 70 °C for 16 h.

<sup>h</sup>Distillation gave unreacted compound **1** (2.43 g, 6.39 mmol, 21.5% based on amount of **1** charged) and adduct mixture **25**; 98% pure by GC. However, NMR spectroscopy showed a *cis/trans* mixture and elemental analysis indicated that impurities were present. A large amount of a viscous, liquid residue (5.80 g) remained which appeared to be a mixture of telomers.

<sup>i</sup>The <sup>1</sup>H NMR spectrum of **27** showed *tt*o doublets for *trans*-CH=CH (*J* = 16 Hz). Compare with the NMR spectrum of the *trans*-(**22**) adduct. A liquid residue (0.75 g, 19% when calcd. as adduct **27**) was also obtained.

TABLE 4

Elemental analysis and NMR spectroscopic parameters for adducts of compound **1** with alkenes and alkynes as listed in Tables 1, 2 and 3<sup>a</sup>

Adduct Entry No.	Compound No.	Formula	Analysis (%) <sup>b</sup>			<sup>1</sup> H NMR chemical shifts and multiplicity				Group assignment
			C	H	F	$\delta$ (ppm)	m	J (Hz)		
1	2	C <sub>14</sub> H <sub>17</sub> F <sub>13</sub> S	36.2 36.1	3.69 3.67	53.2 53.6	0.9	m	-	CH <sub>3</sub> CH <sub>2</sub>	
2	3 <sup>c</sup>	C <sub>15</sub> H <sub>19</sub> F <sub>13</sub> S	37.7 37.6	4.00 3.91	51.6 51.4	0.9	(t)	-	CH <sub>3</sub> CH <sub>2</sub>	
3	4, 5	C <sub>15</sub> H <sub>19</sub> F <sub>13</sub> S	37.7 37.7	4.00 3.97	51.6 50.6	0.9, 1.2	d t	- -	CH <sub>3</sub> CH of <b>4</b> CH <sub>3</sub> CH <sub>2</sub> of <b>5</b>	
4	6	C <sub>16</sub> H <sub>21</sub> F <sub>13</sub> S	39.0 39.0	4.30 4.25	50.2 50.7	0.9	(t)	-	CH <sub>3</sub> CH <sub>2</sub>	
5	7	C <sub>14</sub> H <sub>15</sub> F <sub>13</sub> S	36.4 36.8	3.27 3.10	53.4 53.2	4.75-5.45	m m	- -	CH <sub>2</sub> =CH CH=CH <sub>2</sub>	
6	8	C <sub>22</sub> H <sub>20</sub> F <sub>13</sub> S	31.4 32.9	2.39 2.85	58.6 56.3	1.5	m	-	(CH <sub>2</sub> ) <sub>4</sub> -CH <sub>2</sub> S	
7	9, 10 <sup>c</sup>	C <sub>15</sub> H <sub>17</sub> F <sub>13</sub> S	37.8 37.9	3.60 3.57	51.9 51.9	5.0, 5.8	m m	- -	CH <sub>2</sub> =CH of <b>9</b> CH=CH <sub>2</sub> of <b>9</b>	
7	<i>cis</i> -( <b>10</b> ) <sup>c</sup> <i>trans</i> -( <b>10</b> )					0.85, 1.1	d d	7 6	CH <sub>3</sub> CH of <i>cis</i> -( <b>10</b> ) CH <sub>3</sub> CH of <i>trans</i> -( <b>10</b> )	
8	11 <sup>c</sup>	C <sub>23</sub> H <sub>22</sub> F <sub>26</sub> S <sub>2</sub>	32.3 33.3	2.59 2.77	57.7 57.9	1.2-1.8; 2.0-2.9	m m	- -	(CH <sub>2</sub> ) <sub>5</sub> R <sub>F</sub> CH <sub>2</sub> CH <sub>2</sub> SCH <sub>2</sub>	
9	12 <sup>d</sup>	C <sub>16</sub> H <sub>19</sub> F <sub>13</sub> S	39.2 39.5	3.90 3.89	50.4 50.4	2.05, 4.98, 5.75	m m m	- - -	CH <sub>2</sub> CH=CH <sub>2</sub> CH=CH <sub>2</sub> CH <sub>2</sub> =CH	
9	<i>cis</i> -( <b>13</b> ) <sup>d</sup> <i>trans</i> -( <b>13</b> )					0.9, 1.0	d d	7 7	CH <sub>3</sub> CH of <i>cis</i> -( <b>13</b> ) CH <sub>3</sub> CH of <i>trans</i> -( <b>13</b> )	



9	14 <sup>d</sup>	C <sub>24</sub> H <sub>24</sub> F <sub>20</sub> S	33.1 <b>35.4</b>	2.78 <b>3.19</b>	56.8 <b>53.3</b>	0.9, 1.2-1.7, 1.8-3.0	d m m	7 - -	CH <sub>3</sub> CH-S (CH <sub>2</sub> ) <sub>6</sub> R <sub>F</sub> CH <sub>2</sub> CH <sub>2</sub> SCH <sub>2</sub>
10	15 <sup>c</sup>	C <sub>13</sub> H <sub>13</sub> F <sub>13</sub> S	34.8 <b>34.8</b>	2.92 <b>2.99</b>	55.1 -	1.0-2.1, 2.1-3.5	m m	- -	(CH <sub>2</sub> ) <sub>4</sub> ring R <sub>F</sub> CH <sub>2</sub> CH <sub>2</sub> SCH-
11	16 <sup>c</sup>	C <sub>14</sub> H <sub>15</sub> F <sub>13</sub> S	36.4 <b>36.5</b>	3.27 <b>3.35</b>	53.4 -	1.0-2.2, 2.1-3.1	m m	- -	(CH <sub>2</sub> ) <sub>6</sub> ring R <sub>F</sub> CH <sub>2</sub> CH <sub>2</sub> SCH-
12	17 <sup>c</sup>	C <sub>15</sub> H <sub>17</sub> F <sub>13</sub> S	37.8 <b>37.8</b>	3.60 <b>3.77</b>	51.8 -	1.0-2.0, 2.0-3.1	m m	- -	(CH <sub>2</sub> ) <sub>6</sub> ring R <sub>F</sub> CH <sub>2</sub> CH <sub>2</sub> SCH-
13	18 <sup>c</sup>	C <sub>16</sub> H <sub>19</sub> F <sub>13</sub> S	39.2 <b>38.8</b>	3.90 <b>3.84</b>	50.4 -	1.2-2.1, 2.1-3.2	m m	- -	(CH <sub>2</sub> ) <sub>7</sub> ring R <sub>F</sub> CH <sub>2</sub> CH <sub>2</sub> SCH-
14	19	C <sub>15</sub> H <sub>15</sub> F <sub>13</sub> S	38.0 <b>37.9</b>	3.19 <b>3.21</b>	52.1 <b>51.2</b>	1.0-2.0, 2.0-3.0	m m	- -	H-1, H-3 <sub>endo</sub> , H-7 <sub>anti</sub> , H-2 <sub>endo</sub> , H-3 <sub>exo</sub> , H-7 <sub>syn</sub>
15	20	C <sub>16</sub> H <sub>13</sub> F <sub>13</sub> S	38.1 <b>38.3</b>	2.77 <b>2.81</b>	52.3 <b>51.6</b>	1.2-2.1, 2.1-3.0	m m	- -	H-1, H-3 to H-7 R <sub>F</sub> CH <sub>2</sub> CH <sub>2</sub> SCH <sub>2</sub> <sub>endo</sub>
16	21	C <sub>16</sub> H <sub>13</sub> F <sub>13</sub> S	39.7 <b>40.4</b>	2.70 <b>2.68</b>	51.0 <b>49.7</b>	1.8-3.15, 7.25	m m	- -	R <sub>F</sub> CH <sub>2</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>2</sub> aromatic ring
17	22 <sup>f</sup>	C <sub>16</sub> H <sub>11</sub> F <sub>13</sub> S	39.8 <b>39.3</b>	2.30 <b>2.35</b>	51.2 <b>50.6</b>	6.1, 6.5, 6.6, 7.3	2d s m	11 - -	CH=CH ( <i>cis</i> ) CH=CH ( <i>trans</i> ) aromatic ring
18	<i>trans</i> -(22) <sup>g</sup>	C <sub>16</sub> H <sub>11</sub> F <sub>13</sub> S	39.8 <b>38.6</b>	2.30 <b>2.43</b>	51.2 <b>51.1</b>	6.61	(s)	-	CH=CH ( <i>trans</i> )
19	23	C <sub>12</sub> H <sub>11</sub> F <sub>13</sub> O <sub>2</sub> S	30.9 <b>32.4</b>	2.38 <b>2.57</b>	53.0 <b>52.1</b>	2.0, 2.1-3.0, 4.22	s m t	- - 7	CH <sub>3</sub> CO <sub>2</sub> R <sub>F</sub> CH <sub>2</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>3</sub> CH <sub>2</sub> O <sub>2</sub> CCH <sub>3</sub>
20	24 <sup>c,e</sup>	C <sub>16</sub> H <sub>13</sub> F <sub>17</sub> O <sub>2</sub> S	31.0 <b>31.0</b>	2.26 <b>2.18</b>	55.7 -				
21	25 <sup>b</sup>	C <sub>13</sub> H <sub>11</sub> F <sub>13</sub> O <sub>2</sub> S	35.5 <b>32.5</b>	2.52 <b>2.0</b>	47.5 <b>49.5</b>	2.07, 5.75, 6.2	s m m	- - -	COOCH <sub>3</sub> -SC=CHCH <sub>2</sub> -SCH=CHCH <sub>2</sub>

(continued)

TABLE 4 (continued)

Adduct	Analysis (%) <sup>b</sup>			<sup>1</sup> H NMR chemical shifts and multiplicity					
	Compound No.	Formula	C	H	F	$\delta$ (ppm)	m	J (Hz)	Group assignment
22	<b>26</b>	C <sub>14</sub> H <sub>16</sub> F <sub>13</sub> O <sub>2</sub> S	34.0 <b>34.0</b>	3.06 <b>3.01</b>	50.0 <b>49.8</b>	1.0, 1.7, 2.0-2.8	t 5 m	7 7 -	CH <sub>3</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>2</sub>
23	<b>27</b>	C <sub>13</sub> H <sub>11</sub> F <sub>13</sub> O <sub>2</sub> S	32.6 <b>33.1</b>	2.32 <b>2.32</b>	51.6 <b>50.1</b>	2.5, 3.0, 5.7b, 7.58	m m d d	- - 16 16	R <sub>F</sub> CH <sub>2</sub> R <sub>F</sub> CH <sub>2</sub> CH <sub>2</sub> SCH=CH CH=CHCO <sub>2</sub> Et

<sup>a</sup>See Tables 1, 2 and 3 for preparation, structures and entry numbers for each substance. <sup>1</sup>H NMR spectra were recorded in DCCl<sub>3</sub> with Me<sub>4</sub>Si as an internal reference at ambient temperature and 100 MHz, except where noted.

<sup>b</sup>The upper figures refer to Calculated values and the lower figures (bold) to Found values.

<sup>c</sup>See Experimental section for details.

<sup>d</sup>NMR spectrum of the mono adduct showed resonances for CH<sub>2</sub>CH (0.9 and 1.0 ppm, 0.2 H, d, J = 7 Hz) of presumably *cis*- and *trans*-1-[2-(*F*-hexyl)ethanethio]-2-methylcyclohexane [*cis*-(**13**), *trans*-(**13**)], *c*. 6% of total. Similarly, the NMR spectrum of **14** (in addition to *c*. 30% of the mono adduct **12**, CH<sub>2</sub>=CH resonances) showed broad resonances at  $\delta$  0.7-1.1 ppm (0.7 H) and a doublet at  $\delta$  0.9 ppm, expected for CH<sub>2</sub>CH. This may be attributed to branched-chain regio isomers of the type found in 1-heptene and 1-octene adduct mixtures.

<sup>e</sup>NMR spectrum at 60 MHz in CCl<sub>4</sub> solution.

<sup>f</sup>The product was a mixture of *cis* and *trans* isomers, principally *c*. 70% the *cis* isomer as established by NMR spectroscopy.

<sup>g</sup>The product was principally (95%) the *trans* isomer as established by NMR spectroscopy with about 5% of the *cis* isomer.

<sup>h</sup>A mixture of *cis* and *trans* isomers, see Table 3.

GC) together with three unknown substances. The first is believed to be the regio isomer 2-[2-(*F*-hexyl)ethanethio]hexane (2.29%) by analogy to 1-heptene (and other alkenes) and the known chemistry of thiol addition reactions [19–21]. An unknown (0.503%) and the homolog 1-[2-(*F*-octyl)ethanethio]hexane (2.13%) were also observed, and are probably derived from the small amount of 2-(*F*-octyl)ethanethiol known to be present in compound **1**. Sulfide **2** has been prepared in 90% yield [22] by phase-transfer-catalyzed reaction of compound **1** with an (unspecified) hexyl halide. This displacement method afforded the thioether **2** without regio isomers and is therefore to be recommended for synthesis. Regrettably, the physical constants and the usual analytical data for **2** did not appear in this report.

Free-radical addition of compound **1** to 1-heptene gave 1-[2-(*F*-hexyl)ethanethio]heptane (**3**) in 96% yield (GC methods) and the regio isomers 2-[2-(*F*-hexyl)ethanethio]heptane (**4**) (0.61% yield) and 3-[2-(*F*-hexyl)ethanethio]heptane (**5**) (3.0% yield) (see Table 1, entry 2 and Table 5). The identities of **4** and **5** were established by time coincidence in capillary GC with regio isomers from *cis*-2-heptene (see Table 1, entry 4 and Table 5). An experiment in which a mixture of compound **1** and 1-heptene was exposed to air and heated without initiator (Table 1, entry 3) gave **3** in 69% yield. Surprisingly, the product mixture was similar to that of entry 2, with only an insignificant amount of the disulfide( $[\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{S}]_2$ ) or other higher boiling (possibly oxygenated) product being formed. Conversion to adducts was lower than when AIBN was used, as expected, and the starting materials were recovered.

The disubstituted alkene *cis*-2-heptene (Table 1, entry 4) gave the regio isomer **4** (GC, 55% yield), 3-[2-(*F*-hexyl)ethanethio]heptane (**5**) (GC, 43% yield) and 4-[2-(*F*-hexyl)ethanethio]heptane (GC, 2.17% yield). This last substance and **5** are the expected products from the addition of compound **1** to 3-heptene. NMR spectroscopy and MS/GC methods confirmed the identities of **4** and **5** via the unique fragmentation products for each isomer. Additional experiments showed that 3-heptene gave the predicted addition products; these results will be reported later [18]. When samples of the reaction products from either 1-heptene or *cis*-2-heptene were mixed, the resolved peaks of **4** and **5** were coincident on three capillary GC columns (Table 5). The mechanism by which 4-[2-(*F*-hexyl)ethanethio]heptane is derived from *cis*-2-heptene is currently being investigated [18].

Terminal alkadienes differed widely in their radical chemistry during the addition of compound **1**. 1,5-Hexadiene (Table 1, entry 6) gave a linear mono adduct (60.5% of **7**) and a bis adduct (26.3% of **8**). There was no evidence for cyclic products. However, the bis adduct **8** contained a small amount (*c.* 10% from the integrated area in the NMR spectrum) of regio isomers similar to **4** ( $\delta$  0.90 ppm, d,  $J=7.0$  Hz,  $\text{CH}_3\text{CH}$ ).

1,6-Heptadiene (Table 1, entries 7 and 8) gave both linear and cyclic mono adducts and a bis adduct as depicted in Scheme 1. The thiol radical **1'** and 1,6-heptadiene form an intermediate radical (**9'**) which cyclizes in part to the 2-[(*F*-hexyl)ethanethio]methylcyclopentanemeth-1-yl radical (**10'**)

TABLE 5

Capillary GC analyses of adducts **3**, **4** and **5** from *cis*-2-heptene or 1-heptene and mixtures of samples of the same for proof of identity<sup>a</sup>

Compound No.	GC sample from reaction mixture by entry No. in Table 1									
	Entry No. 4 <sup>b</sup>		Entry No. 2 <sup>c</sup>		Entry No. 3 <sup>e</sup>		Mixture of No. 4/No. 2		Mixture of No. 4/No. 3	
	Retention time (min)	Area (%)	Retention time (min)	Area (%)	Retention time (min)	Area (%)	Retention time (min)	Area (%)	Retention time (min)	Area (%)
- <sup>d</sup>	16.96	2.20	17.04	0.554	-	-	16.92	0.799	16.91	1.438
<b>5</b>	17.24	43.08	17.30	3.601	17.37	2.22	17.13	13.39	17.11	27.65
<b>4</b>	17.54	53.98	-	-	17.45	0.613	17.41	18.45	17.38	34.94
<b>3</b>	18.21	0.115	18.28	95.85	18.34	96.74	18.35	66.95	18.22	35.97

<sup>a</sup>GC analyses using a Varian 3400 instrument. Conditions: sample held at 50 °C for 5 min, then temperature programmed at 10 °C min<sup>-1</sup> from 50 °C to 250 °C; helium flow, 4 ml min<sup>-1</sup>; DB-5 column, 30 m length. Similar results were obtained using DB-1 and DB-5 columns of 15 m length.

<sup>b</sup>The sample comprised the adduct mixture obtained from reacting compound **1** with *cis*-2-heptene.

<sup>c</sup>The sample comprised the adduct mixture obtained from reacting compound **1** with 1-heptene.

<sup>d</sup>Further work to be published [18] shows that this substance is 4-[2-(*F*-hexyl)ethanethio]heptane.

<sup>e</sup>The sample was taken from fraction II of the distillate obtained from the reaction mixture of compound **1** and 1-heptene in the absence of initiator.



TABLE 6

Capillary GC analyses of products from the reaction of compound **1** and 1,6-heptadiene<sup>a</sup>

Substance	On DB-1 column, 15 m in length		On DB-5 column, 15 m in length		On DB-5 column, 30 m in length	
	Retention time (min)	Area (%)	Retention time (min)	Area (%)	Retention time (min)	Area <sup>b</sup> (%)
<i>Entry No. 7, Table 1: fraction I, distilled mono-adduct mixture</i>						
Regio of <b>9</b> <sup>c</sup>	14.85	1.65	15.80	1.63	17.24	1.70
<b>9</b>	15.82	73.9	16.78	74.4	18.27	74.8
<i>cis</i> -( <b>10</b> ), <i>trans</i> -( <b>10</b> )	16.07	20.9	17.06	21.2	18.59	20.7
Regio of <b>10</b> <sup>d</sup>	16.29	0.579	—	—	18.83	0.573
Homolog <sup>e</sup>	16.83	1.52	17.79	1.56	19.30	1.47
<i>Entry No. 8, Table 1: GC sample only</i>						
Regio of <b>9</b> <sup>c</sup>	—	—	—	—	17.21	1.13 <sup>f</sup>
Disulfide <sup>g</sup>	14.78	1.503	—	—	17.30	3.17 <sup>f</sup>
<b>9</b>	15.67	61.63	—	—	18.11	50.9 <sup>f</sup>
<i>cis</i> -( <b>10</b> ), <i>trans</i> -( <b>10</b> )	15.94	8.85	—	—	18.53	7.48 <sup>f</sup>
Regio of <b>11</b> <sup>c</sup>	21.54	1.21	—	—	24.11	1.42 <sup>f</sup>
<b>11</b>	22.30	26.80	—	—	24.95	31.3 <sup>f</sup>

<sup>a</sup>GC analyses using a Varian 3400 instrument. Conditions: sample held at 50 °C for 5 min, then temperature programmed at 10 °C min<sup>-1</sup> from 50 °C to 250 °C; helium flow, 4 ml min<sup>-1</sup>; DB-5 column, 30 m length. Similar results were obtained using DB-1 and DB-5 columns of 15 m length.

<sup>b</sup>Duplicate analysis.

<sup>c</sup>Probably regio isomer of substance indicated.

<sup>d</sup>Regio isomer of C<sub>8</sub>F<sub>17</sub> homolog of **9** or **10**.

<sup>e</sup>C<sub>8</sub>F<sub>17</sub> homolog of **9** or **10**.

<sup>f</sup>Mol% amounts calculated using FID response factors of known mixtures. Amounts were based on compound **1** charged to reaction mixture.

<sup>g</sup>Disulfide [C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>S]<sub>2</sub>. Identity and FID response factor obtained with known mixtures and by injection with sample mixture to hand.

and 1.0 ppm, 0.18 H,  $J = 7$  Hz). The former is assigned to the *cis* isomer and the latter to the *trans* isomer, as found previously for related cyclopentane substances [23]. The amounts calculated by NMR methods agree with the relative areas of the resolved peaks for cyclic (20.9%) and linear (74.4%) adducts, using three capillary GC columns. Unfortunately, the conditions used were insufficient to separate the *cis*- and *trans*-cyclopentane products by GC methods. Small amounts of isomeric substances were detected by GC, as listed in Table 6.

<sup>1</sup>H NMR spectroscopy at 300 MHz of the bis-thioether **11** gave interesting and valuable results. The CH<sub>2</sub> units of the heptamethylene chain between the sulfur atoms were separated into three unique groups while the two CH<sub>2</sub> units between the sulfur and the R<sub>F</sub> group on each end of the molecule were also uniquely isolated. This gave resonances for five cleanly separated sets of protons, as listed in Table 7. Three CH<sub>2</sub> groups in the center of the molecule appeared at  $\delta$  1.50 ppm, followed by the adjacent pair at  $\delta$  1.70

TABLE 7

<sup>1</sup>H NMR spectrum of the bis-thioether **11** at 300 MHz C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub><sup>1</sup>CH<sub>2</sub><sup>2</sup>SCH<sub>2</sub><sup>3</sup>CH<sub>2</sub><sup>4</sup>-  
<sup>5</sup>CH<sub>2</sub><sup>6</sup>CH<sub>2</sub><sup>7</sup>CH<sub>2</sub><sup>8</sup>CH<sub>2</sub><sup>9</sup>SCH<sub>2</sub><sup>10</sup>CH<sub>2</sub><sup>11</sup>F<sub>13</sub>C<sub>6</sub>

Carbon atom No.	δ (ppm)	No. of protons	Multiplicity	J (Hz)	Type of proton
5, 6, 7	1.50	6	m	—	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub>
4, 8	1.70	4	m	—	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub>
1, 11	2.45	4	m	—	CF <sub>2</sub> CH <sub>2</sub> S × 2
3, 9	2.68	4	t	7	CH <sub>2</sub> SCH <sub>2</sub> × 2
2, 10	2.85	4	m	—	CH <sub>2</sub> SCH <sub>2</sub> × 2

ppm. The two CH<sub>2</sub> units of R<sub>F</sub>CH<sub>2</sub>CH<sub>2</sub>S at each end of the molecule appeared at δ 2.45 ppm and showed the complex splitting of fluorines in the adjacent R<sub>F</sub> group. The inner pairs of CH<sub>2</sub> units in CH<sub>2</sub>SCH<sub>2</sub> at δ 2.68 ppm were coupled to adjacent methylene protons to give a triplet. This is the only set of CH<sub>2</sub> units that is so isolated and shifted downfield by proximity to the sulfur atom. Finally, the pairs of CH<sub>2</sub> units found on the outer side of sulfur were coupled to the adjacent R<sub>F</sub>CH<sub>2</sub> moiety; this accounts for the greater complexity of the resonance at δ 2.85 ppm. These assignments are tentative and need to be confirmed by further study. A less pure solid sample of **11** gave the expected resonances in the NMR spectrum (Table 4, entry 8) and indicated the presence of a small amount of **10** and/or regio isomers similar to **4**.

1,7-Octadiene (Table 1, entry 9) gave a linear mono adduct **12** (c. 75% yield) and a bis adduct **14** (c. 16% yield). These amounts are corrected for the amount of **12** remaining in undistilled **14**. However, the NMR spectrum showed resonances at δ 0.9 ppm and δ 1.0 ppm in distilled **12**, attributable to the cyclic isomers *cis*-(**13**) and *trans*-(**13**) by analogy with *cis*-(**10**) and *trans*-(**10**). From the NMR spectrum, compound **14** also contained some regio isomers in small amount.

Cyclic alkenes (Table 2) reacted readily with compound **1**, though not so rapidly as terminal alkenes. A small excess of **1** was used for C<sub>5</sub>, C<sub>6</sub> and C<sub>7</sub> cycloalkenes and the distilled, pure adduct ranged from 85 to 96 mol% in yield. With cyclooctene an excess of alkene was employed, and a lower conversion to adduct **18** resulted. However, further work [18] has shown that the rate of addition of compound **1** to cyclooctene is much smaller than for other cycloalkenes. Hence, these are the results expected. The yield of distilled product from norbornene and norbornadiene (Table 2, entries 14 and 15) was 76–79%; however, there was no residual undistilled material in either case and thus the actual yield of adduct approached the theoretical value.

The composition and structure of the adducts was readily ascertained by combustion and NMR spectral analysis, as listed in Table 4. It should be noted that, in a comparison of the IR spectra, compound **15** gave a doublet

in the  $\text{CH}_2$  deformation band region at 1440 and  $1450\text{ cm}^{-1}$ , compound **16** exhibited only the  $1445\text{ cm}^{-1}$  band, compound **17** showed bands at 1445 and  $1455\text{ cm}^{-1}$  while compound **18** gave absorption bands at 1445 and  $1465\text{ cm}^{-1}$ . The  $\text{CH}_2$  stretching band region also showed a consistent trend: **15**, 2950; **16**, 2930; **17**, 2925; **18**,  $2915\text{ cm}^{-1}$ .

The  $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{S}$  group of the norbornene adduct **19** is assigned to the *exo* position, by analogy with the structure of closely similar norbornene products [13]. This assignment will be rigorously demonstrated in a subsequent paper [18]. The NMR spectrum of adduct **20** from norbornadiene ([2.2.1]-bicyclo-2,5-heptadiene) was that of substituted tricyclene in which the  $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{S}$  group occupies an *exo* position [18].

Some reactive monomers and alkynes were allowed to react with compound **1** in *n*-heptane solution (Table 3). Surprisingly, styrene (entry 1) provided a distillable adduct in reasonable yield (65.6%). GC analysis indicated a purity of 97.6% and the NMR spectrum was consistent with that for **21**. A telomeric product of unknown composition was also obtained; in general, its NMR and IR spectra resemble that of compound **21**.

Phenylacetylene (20 mmol), compound **1** (10 mmol) and AIBN in *n*-heptane solution gave a mixture of *cis*- and *trans*-(**22**) in 84% yield as a distillable product (Table 3, entry 2). The NMR spectrum indicated two sets of vinyl proton resonances: at  $\delta$  6.1 and 6.52 ppm for the *cis* isomer (64% relative area) and at  $\delta$  6.6 ppm for *trans*-(**22**) (36% relative area). The same reaction conditions and a molar reactant ratio of phenylacetylene to compound **1** of 1:2 led to nearly pure *trans*-(**22**) (5% of the *cis* isomer by NMR methods) in 87.3% yield after distillation. This effect of the reactant ratio on the stereochemistry has been reported previously [20–22]; with an excess of thiol the product composition approaches that of the equilibrium mixture [21]. Hydrogen abstraction from **1** by the intermediate *trans*-adduct vinyl radical occurs faster than abstraction by the *cis*-adduct vinyl radical [21].

Vinyl acetate, allyl acetate and propargyl acetate (Table 3, entries 4, 5 and 6, respectively) added compound **1** with varying degrees of efficiency. These substances will be described in more detail in a subsequent paper [18].

Ethyl 3-butenolate and compound **1** (entry 7) gave adduct **26** in 86.7% yield (recovered by distillation; essentially quantitative in reaction) as a single substance. There was no evidence for the regio isomer in the distilled product and there was no distillation residue. Thus, this could be an attractive method for the synthesis of the homologous series of  $\text{R}_f$ -terminated linear thioalkanoic acids and derivatives  $\text{R}_f(\text{CH}_2)_m\text{S}(\text{CH}_2)_m\text{COOR}$ .

Ethyl propynoate and compound **1** (entry 8) in an equimolar reactant ratio gave both the desired adduct **27** in 77.9% yield (distilled) and a higher boiling liquid mixture (19% yield, calculated as **27**) which may have consisted of the bis adduct and possibly telomeric products. The distilled product was chiefly the *trans* adduct from NMR spectroscopic evidence. The two vinyl protons were shifted chemically to  $\delta$  5.75 ppm and  $\delta$  7.58 ppm, and appeared as two clean doublets ( $J = 16\text{ Hz}$ ). A small amount of *cis*-(**27**) may have



been present. These substances will be described in more detail in a subsequent paper [18].

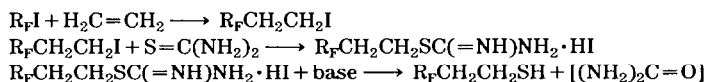
## Experimental

### *Sources of materials and physical methods*

The reagents used were the best commercial materials available; liquids were redistilled and analyzed by GC methods. Other substances were synthesized as described below. Capillary GC analysis was undertaken using a Varian 3400 gas chromatograph. The conditions used were: helium flow rate, 4 ml min<sup>-1</sup>; sample held at 50 °C for 5 min then temperature-programmed from 50 °C to 250 °C at 10 °C min<sup>-1</sup>. A DB-1 column 15 m in length, a DB-5 column 15 m in length and a DB-5 column 30 m in length were employed. These columns, having a film thickness of 1.5 μm and a diameter of 0.539 mm or 0.538 mm (30 m in length), gave a base-line separation of most substances, except for *cis*- and *trans*-(10). <sup>1</sup>H NMR spectra at 100 MHz or 300 MHz were obtained with an Me<sub>4</sub>Si reference in DCCl<sub>3</sub> solution. The distillation columns used were: Column A, 24-in. Nester–Faust platinum spinning band; and Column B, fitted with a 16-in. stainless-steel band. Combustion analyses were obtained from Analytical Services of the Ciba-Geigy Corporation at Ardsley, NY.

### *Preparation of 2-(F-alkyl)ethanethiols*

The thiols needed for this investigation were synthesized from (*F*-alkyl) iodides in a two (or three) step sequence, as elaborated in Scheme 2. The intermediate 2-(*F*-alkyl)-1-iodoethanes, prepared in high yield by a convenient laboratory method at atmospheric pressure [4, 24], were converted to the isothiuronium salts (90% yield, C<sub>6</sub>F<sub>13</sub>, isolated) by reaction with thiourea [12, 16, 22, 25]. Hydrolysis with aqueous alkali gave the desired thiols in good yield. The special handling required for these sensitive compounds is described below. The <sup>13</sup>C chemical shifts and coupling constants of compound 1 have been reported [26].



Scheme 2. Preparation of 2-(*F*-alkyl)ethanethiols.

### *1-Iodo-2-(F-hexyl)ethane*

**CAUTION! C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>I is a highly toxic substance and any contact must be carefully avoided. Use of protective covering is recommended. All transfers and reactions must be carried out in a well-ventilated space.** 1-Iodoperfluorohexane (b.p. 62 °C/12 mmHg; 195 g, 0.438 mol) and benzoyl peroxide (0.726 g, 3.00 mmol, in three portions) were heated to 92 °C (bath temp. 116 °C), and ethene (Matheson, from a cylinder) was admitted via a sparging tube and the heating continued for 3 h at 98–102

°C. Benzoyl peroxide was added initially, and after 1 h and 2.5 h. The mixture was sparged with nitrogen for 1 h and the colorless liquid obtained cooled and weighed (205.1 g including 2.6 g collected in the Dry Ice-cooled trap). The increase in weight (10.1 g) represents 0.361 mol of ethene. Distillation (Column A) gave three fractions of  $C_6F_{13}I$  and  $C_6F_{13}CH_2CH_2I$ : fraction I, b.p. 50–78 °C/65 mmHg, 7.6 g; fraction II, b.p. 78–99 °C/63 mmHg, 6.4 g; and fraction III, b.p. 99 °C/63 mmHg to 93 °C/48 mmHg, 8.20 g.  $C_6F_{13}CH_2CH_2I$  distilled at 93 °C/46 mmHg,  $n_D^{25} = 1.3586$ , 175.3 g (0.369 mol); 84.5% yield, 100% GC purity. Analysis: Calcd. for  $C_8F_{13}H_4I$ : C, 20.3; F, 52.1; H, 0.85; I, 26.8%. Found: C, 20.4; F, 52.2; H, 0.84; I, 25.8%.

### *2-(F-Hexyl)ethanylisothiourea hydroiodide*

Thiourea (29.0 g, 0.382 mol) and ethanol (anhydrous, 300 ml) was stirred under a nitrogen atmosphere in a four-necked flask at 75 °C (steam bath) while compound **1** (170 g, 0.359 mol) was added over 5 min. Initially the temperature fell to 70 °C and was then maintained at 76–80 °C (reflux) for 4 h followed by cooling to 25 °C. Ligroine (200 ml) was added and the ethanol mixture distilled (c. 400 ml). After cooling to 30 °C, 200 ml of ligroine was again added when the crystalline isothiuronium salt separated (150 g, m.p. 146–154 °C). The filtrate, diluted with ligroine (100 ml) and cooled to 0 °C, gave 9.0 g of the salt and a further 8.0 g (m.p. 145 °C) was obtained by evaporation and cooling. The total yield of pure product was 178.5 g (90.5% of theory). A residue (11.5 g), mostly 2-(*F*-hexyl)ethanyl disulfide, was recovered when the solvent was removed. Analysis: Calcd. for  $C_9F_{13}H_8IN_2S$ : C, 19.65; F, 44.90; H, 1.47; I, 23.07; N, 5.09; S, 5.83%. Found: C, 19.55; F, 44.69; H, 1.61; I, 22.05; N, 6.42; S, 8.24%.

### *2-(F-Hexyl)ethanethiol (1)*

2-(*F*-Hexyl)ethanylisothiourea hydroiodide (177.5 g, 0.322 mol) was charged into the flask used above, and stirred under nitrogen as NaOH (16.0 g, 0.400 mol, dissolved in 160 ml water) was added. Two liquid layers separated immediately and remained after 1 h heating at 88–92 °C (steam bath, at reflux). When cool, the lower layer was separated into a flask protected by nitrogen and the aqueous layer extracted twice with diethyl ether. The aqueous layer was returned to the stirred flask and heated for 3 h at reflux when a small oil layer formed. The combined ether extracts were dried ( $MgSO_4$ ) and filtered under nitrogen into a flask and distilled (Column A or Column B). Compound **1**, b.p. 73 °C/30 mmHg, 91.8 g (75% yield); lit. value [16], b.p. 110–113 °C/65 mmHg, 65% yield. A semi-solid residue, primarily the disulfide, was recovered. The column was flushed with nitrogen during removal of the distilled fraction and a sample was immediately sealed in an ampoule for analysis. GC gave 98.4% area under one peak. Analysis: Calcd. for  $C_8F_{13}H_5S$ : C, 25.27; F, 64.97; H, 1.33; S, 8.44%. Found: C, 25.49; F, 64.17; H, 1.40; S, 9.39%.  $^1H$  NMR  $\delta$ : 1.09 ppm (1 H, t, SH) exchanges slowly with  $D_2O$ ; 1.85–3.06 ppm (4 H, complex m,  $CH_2CH_2$ ); lit. value [26], see  $^{13}C$  NMR chemical shifts and coupling constants.

*2-(F-Octyl)ethanethiol*

1-Iodo(*F*-octane) (54.6 g, 0.100 mol) and benzoyl peroxide (0.242 g, 1.00 mmol) as above were sparged with ethene at 92–101 °C whilst cooling as necessary for 2 h. The product, 2(*F*-octyl)-1-iodoethane, melted at 54–55 °C. The experiment was repeated with double the amount of reactants and the products were combined for distillation. A heat gun was used to melt the distillate as necessary. The following fractions were collected: fraction I, b.p. 88–91 °C/9 mmHg, m.p. 55.5–56.5 °C, 60.3 g; fraction II, b.p. 94–97 °C/9 mmHg, m.p. 55.3–56.3 °C, 92.4 g; and fraction III, b.p. 109.5 °C/9 mmHg, m.p. 51.5–53 °C, 3.7 g. A hold-up in the head (4.5 g) and a pot residue (2.5 g) were also obtained. The combined yield was 92% of 2(*F*-octyl)-1-iodoethane.

As above, 2(*F*-octyl)-1-iodoethane (144 g, 0.250 mol), thiourea (22.0 g, 0.290 mol) and ethanol (500 ml) were heated at reflux (79 °C) under a nitrogen atmosphere for 20 h and hydrolyzed without isolating the isothio-uronium salt. Whilst stirring vigorously at 34 °C, NaOH (11.2 g, 0.280 mol, dissolved in 40 ml water) was added and the stirring continued for 1 h at 78–80 °C. The mixture was cooled to 28 °C and sulfuric acid (13.85 g, 0.140 mol) in 50 ml of water was added. A white precipitate formed, and the slurry was poured into 500 ml of water and extracted twice with CCl<sub>4</sub> under nitrogen. The orange colored solution was washed with NaHSO<sub>3</sub> solution (25 ml) and dried (MgSO<sub>4</sub>) before distillation (Column A). The column was kept under positive nitrogen pressure, through a Dry Ice-cooled trap, by means of a bubbler system. After the CCl<sub>4</sub> had been removed, distillation was continued at the water pump. A small forerun (b.p. 65 °C/9.0 mmHg, 1.8 g) of a dark colored liquid was taken at a high reflux ratio. Then colorless C<sub>8</sub>F<sub>17</sub>CH<sub>2</sub>CH<sub>2</sub>SH, b.p. 80 °C/9.0 mmHg, was collected at a 10:1 reflux ratio, 75.0 g (pot temperature, 88–93 °C), yield, 62%; lit. value [16], m.p. 63–64 °C, 48% yield. A cloudy, orange-brown liquid residue (13.3 g) remained. Samples were sealed under nitrogen for analysis, and the remaining material transferred under nitrogen to tightly closed bottles that were stored in a cold, dark place. Under these conditions the purity of the product was not seriously affected. <sup>1</sup>H NMR δ: 1.09 ppm (1 H, t, SH) exchanges slowly with D<sub>2</sub>O; 1.85–3.06 ppm (4 H, m, CH<sub>2</sub>CH<sub>2</sub>SH). Analysis: Calcd. for C<sub>10</sub>H<sub>5</sub>F<sub>17</sub>S: C, 25.01; H, 1.05; F, 67.26; S, 6.67%. Found: C, 24.92; H, 1.13; F, 66.14; S, 6.09%.

*Ethyl 3-butenolate*

A mixture of 3-butenic acid, ethanol and benzene was heated under reflux and the azeotrope removed until the solution was clear. The product was worked-up and distilled twice (packed column), b.p. 124 °C; lit. value [30], b.p. 124.2–124.4 °C.

*Ethyl 2-propynoate*

A mixture of propiolic acid, ethanol and sulfuric acid (catalyst) was kept at 30–37 °C for 24 h, then worked-up and distilled (packed column), b.p. 118–119 °C; lit. value [31], b.p. 119 °C/745 mmHg.

*Preparation of adducts from C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>SH (1) and alkenes or alkynes*

*Procedure A: reaction of compound 1 with substrate molecule in n-heptane solution*

A stock solution of **1** (47.52 g; 118.1 mmol; the sample contained 94.5% of C<sub>6</sub>F<sub>13</sub> and 5.5% of C<sub>8</sub>F<sub>17</sub> homologs of R<sub>F</sub>CH<sub>2</sub>CH<sub>2</sub>SH) and azo-bis-isobutyronitrile (AIBN, 0.1640 g; 1.00 mmol) in n-heptane (Merck Spectro grade) was made up to a total volume of 100 ml in a volumetric flask. The clear solution was covered with nitrogen and kept at 0 °C before use. A quantity of this solution, usually 8.00 ml, was removed by pipet under nitrogen and placed in a 10 ml volumetric flask; the *total* quantity of compound **1** was thus 9.448 mmol, and of AIBN, 0.080 mmol. An amount of each alkene or alkyne equal to or greater in moles than that of compound **1** was weighed in as listed in Tables 1–3. The flask was made up to the mark with n-heptane. The concentration of **1** was 1 M, of AIBN was 0.008 M and of the alkene 1–2 M. This reaction mixture was transferred by pipet to an ampoule that was cooled to –78 °C under nitrogen, filled with nitrogen three times, and finally evacuated down to 0.1 mmHg pressure. The sealed ampoule was heated in a stirred oil bath at 70 °C for 5 h. A portion of the reaction product mixture was sealed in an ampoule for GC analysis. The remainder was distilled in a short-path distillation apparatus to recover the reaction products for elemental analysis and spectroscopic examination. Volatile solvent and any unreacted alkene or thiol were collected in the cold trap. The yields reported in Tables 1–3 do not include the material removed for analysis, nor any recovered starting material. If no residue was found on distillation, the actual product yield may have approached the theoretical value.

*Procedure A: Table 1, entry 7: compound 1 with 1,6-heptadiene; 7-[2-(F-hexyl)ethanethio]-1-heptene (9); cis- and trans-1-methyl-2-[2-(F-hexyl)ethanethio]methylcyclopentane [cis-(10), trans-(10)] and 1,7-bis-[2-(F-hexyl)-ethanethio]heptane (11)*

1,6-Heptadiene (1.925 g, 20.0 mmol) was added by pipet under a nitrogen atmosphere to 2-(F-hexyl)ethanethiol (**1**) (3.80 g, 9.448 mmol) and AIBN (0.0131 g, 0.080 mmol) in n-heptane solution (8.00 ml), and made up to 10.0 ml with n-heptane. The mixture was sealed and heated for 5 h at 70 °C, sampled for GC and elemental analysis and distilled. Fraction I, b.p. 42 °C/0.05 mmHg, 2.68 g; adduct mixture **9** and *cis*-(**10**), *trans*-(**10**). Fraction II, solid residue of **11**, 1.60 g. The yield of **9** and **10** was 5.63 mmol, 59.5% based on **1**; that of **11** was 1.87 mmol, 39.7% based on **1**. GC results are given in Table 6 and elemental analyses in Table 4. Fraction I: <sup>1</sup>H NMR (CDCl<sub>3</sub>; 100 MHz and 300 MHz) δ: 0.85 (0.56 H, d, *J* = 7 Hz, CH<sub>3</sub>, *cis*-(**10**); 1.00 (0.18 H, d, *J* = 6.5 Hz, CH<sub>3</sub>, *trans*-(**10**); 1.1–3.3 (14.3 H, complex multiplets, CH<sub>2</sub> and CH of **7**, *cis*-(**10**) and *trans*-(**10**)); 5.0 (1.43 H, approximate triplet (300 MHz), complex multiplet (100 MHz), CH<sub>2</sub> = of **9**); and 5.8 (0.72 H, complex multiplet, CH = of **9**) ppm. The ratio of the areas corresponding to *cis*- and *trans*-(**10**) was 3.1:1. The combined areas of methyl CH<sub>3</sub>CH in

the isomers of **10** totalled 0.64 H or 21.3% of fraction I, distilled mono-adduct mixture. The vinyl  $\text{CH}_2=$  area was 71.7% of the theoretical area for **9**. Thus, linear adducts (**9** and **11**) totalled 7.93 mmol of thiol **1** utilized (83.9%), and cyclic mono adducts 1.22 mmol, or 13.3%, of the total. Side-products indicated in GC analyses (Table 6) comprised approximately 4.5% of the mixture.

*Procedure A: Table 3, entry 2: compound 1 with phenyl acetylene; cis- and trans-1-phenyl-2-[2-(F-hexyl)ethanethio]ethene [cis-(21) and trans-(21)]*

Phenyl acetylene (2.04 g, 20.0 mmol), compound **1** (3.80 g, 9.448 mmol) and AIBN were heated for 18 h at 70 °C. Subsequent distillation gave *cis*-(**21**) and *trans*-(**21**), b.p. 45 °C/0.03 mmHg, 3.81 g, 84.0% yield, and a few drops of residue. Elemental analysis (Table 4) conformed to the mono adduct.  $^1\text{H}$  NMR spectroscopy ( $\text{CDCl}_3$ , 100 MHz) gave resonances at 6.1 and 6.52 ppm, 63.7% of the area corresponding to two vinyl protons. The 6.1 ppm resonance was a clean doublet ( $J=11$  Hz) and the 6.52 ppm resonance appeared to be a singlet. A second singlet appeared at 6.61 ppm, 36.3% of the area for two vinyl protons. This was assigned to *trans*-(**21**). The expected proton resonances for the phenyl ring and of the  $\text{CH}_2$  groups were present.

*Procedure A: Table 3, entry 3*

A second experiment employed compound **1** (3.80 g, 9.448 mmol) and phenyl acetylene (0.5105 g, 5.00 mmol) in a 2:1 molar ratio. Distillation gave solid *trans*-(**21**), b.p. 55–60 °C/0.06 mmHg, 2.10 g, 87.3% yield. Only a trace of liquid residue remained, i.e. a very small amount of bis adduct could have been present. Elemental analysis, particularly fluorine analysis (Table 4), again conformed to the mono adduct.  $^1\text{H}$  NMR spectroscopy gave a resonance at 6.61 ppm (singlet), with 94% of the area for two vinyl protons assigned to *trans*-(**21**). There was a small doublet at 6.1 ppm and a singlet at 6.52 ppm corresponding to *cis*-(**21**), *c.* 6% relative area.

*Procedure B: Reaction of compound 1 with substrate molecules without solvent*

A heavy-wall glass tube was fitted with a Teflon<sup>®</sup> pressure valve, threaded to the glass to provide a sealed tube when closed. A small magnet bar was enclosed to provide stirring during reaction in a magnetically stirred, heated oil bath, maintained at a constant temperature. The tube was cooled to –78 °C (if needed), charged with materials as listed (optionally purged with nitrogen), evacuated and filled with nitrogen three times. The mixture was heated as required, and optionally fractionally distilled under reduced pressure by means of Column B. A constant boiling fraction was used for analysis and spectroscopic evaluation.

*Procedure B: Table 1, entry 2: 1-heptene with compound 1;  
1-[2-(F-hexyl)ethanethio]heptane and isomers*

1-Heptene (2.45 g, 25.0 mmol, single peak GC) compound **1** (11.45 g, 30.0 mmol) and AIBN (0.164 g, 0.600 mmol) were heated for 16 h at 70 °C giving 13.7 g of filtered liquid (GC sample removed). The remainder distilled to give: fraction I, b.p. 94 °C/1.5 mmHg, 0.55 g; fraction II, b.p. 94–96 °C/1.05 mmHg,  $n_D^{25} = 1.3745$ , 7.45 g; fraction III, b.p. 93–71 °C/1.05–0.25 mmHg,  $n_D^{25} = 1.3745$ , 2.87 g; liquid hold-up and residue, 0.75 g; trap liquid, 0.26 g. GC analysis of the reaction sample gave: 1-heptene, 0.44%; **1**, 2.08%; adduct (**1**), 3.42%; adduct (**2**), 93.07%; and adduct (**3**), 0.98%. See Table 5 for capillary GC analyses of distilled fractions and Table 4 for NMR and elemental analyses.

*Procedure B: Table 1, entry 3: free-radical addition of compound 1 to 1-heptene without initiator added*

2-(F-Hexyl)ethanethiol (3.80 g, 10.0 mmol), 1-heptene (0.52 g, 5.00 mmol, redistilled, b.p. 91 °C) and dichloromethane (5.0 ml) were heated for 2 h in a constant temperature bath at 70 °C. The vacuum in the tube was retained during heating. GC samples were taken after standing for 4 h at 25 °C (No. 1); after 2 h at 70 °C; and after distillation (fraction I and fraction II). Transfer to Column B and distillation gave: fraction I, b.p. 51–53 °C/10 mmHg, 1.90 g; GC analysis on column DB-1, 15m in length gave: **1**, 1.78 g, 93.8% recovery; **5**, 3.20%; unknown, 0.77%; and **3**, 0.843%; fraction II, b.p. 82–91 °C/1.05–0.75 mmHg (bath temperature 123 °C) without careful fractionation, 1.60 g; GC analysis on column DB-5, 30 m in length gave: **1**, none; **5**, 2.22%; **4**, 0.613%; and adduct **3**, 96.74%. (See Table 5 where the identities of the adducts are demonstrated via the retention times with known substances.) The total yield of **3** was 64.4%. Including isomers, the yield was 69%. The oil residue amounted to 0.07 g and thus no significant amount of disulfide or oxygenated compounds was formed. Any unreacted 1-heptene was collected with dichloromethane in the cold trap. See Table 4 for NMR and elemental analyses.

*Procedure B: Table 1, entry 4: cis-2-heptene with compound 1;  
2-[2-(F-hexyl)ethanethio]heptane (**4**) and 3-[2-(F-hexyl)ethanethio]-  
heptane (**5**)*

*cis*-2-Heptene (2.45 g, 25.0 mmol, single peak GC), compound **1** (11.41 g, 30.00 mmol) and AIBN (0.100 g, 0.600 mmol) were charged into a heavy-wall glass tube fitted with Teflon<sup>®</sup> valve and a magnetic stirring bar. The tube was heated for 16 h at 70 °C in a stirred, constant-temperature oil bath. The resulting cloudy suspension was filtered under nitrogen (sintered glass funnel) and the liquid (13.4 g, loss of 0.4 g) was samples for GC analysis and distilled (Column B). Fraction I, b.p. 54–66 °C/0.12 mmHg, 0.44 g; fraction II, b.p. 68–69 °C/0.10 mmHg,  $n_D^{25} = 1.3740$ , 8.80 g; residual oil (heated to 118 °C), 1.9 g. Cold trap liquid, 1.54 g. GC analysis (Table 5) was performed on three capillary columns. The identities of the isomers

were determined by time coincidence in GC with known substances. A new compound was identified as 4-[(2-*F*-hexyl)ethanethio]heptane; this substance was obtained from the addition of **1** to 3-heptene [18].

*Procedure B: Table 1, entry 8: compound 1 with 1,6-heptadiene*

A cold pressure tube was charged by means of a pipet with a mixture of 1,6-heptadiene (0.9761 g, 10.15 mmol) and compound **1** (3.7211 g, 9.788 mmol). AIBN (0.0181 g, 0.110 mmol) was added directly, and the funnel and the weighing vial rinsed with benzene (0.50 ml, added in portions). After 1 h at 70 °C, the stirred mixture was cooled and sampled for GC analysis. (See Table 6, cf. entry 7, Table 1.) From the GC results and making use of FID factors of known mixtures with the internal standard 1,2-dichlorobenzene, **9** and a regio isomer amounted to 5.091 mmol (52.0% yield); the cyclic adducts *cis*-(**10**) and *trans*-(**10**) comprised 0.732 mmol (7.48%); i.e. 59.5% of combined mono adducts based on **1**. The bis adduct **11** (3.202 mmol) amounted to 32.8% based on the amount of **1** charged. In addition, [C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>S]<sub>2</sub> was formed (0.155 mmol, 3.17% yield based on **1**). Thus, the combined yield of products was 95.0%. The oil residue amounted to 0.07 g. Distillation of the remaining product mixture without a column but with a total reflux, partial take-off head gave: fraction I, b.p. 88–92 °C/0.75–0.38 mmHg, 2.23 g; 97.5% of mono adducts and 0.618% of bis adduct (by area). After heating to 125 °C (bath temperature) for 15 min, the liquid residue (fraction II) weighed 2.00 g; GC analysis, 20.3% of linear and 2.98% of cyclic mono adducts, and 76.6% of **11** and regio isomers. See Table 4 for NMR and elemental analyses; see also Table 7.

*Isolation of the solid bis adduct 11* – The liquid residue from the above distillation crystallized on standing at 21 °C and a sample (0.7469 g) was collected on a Hirsch funnel. A GC sample with 1,2-dichlorobenzene as the reference gave an FID of 0.4019; the sample contained 6.01% of **9** and the isomers of **10**, and 1.19% and 92.8% of two bis adducts, including **11**. <sup>1</sup>H NMR spectroscopy at 300 MHz gave five separate sets of proton resonances as listed in Table 7.

*Procedure C: Reaction of compound 1 with alkenes in a stirred flask: Table 3, entry 20: addition of 2-(F-octyl)ethanethiol to allyl acetate*

A 100 ml, round-bottom flask was fitted with a thermometer, a two-necked adapter, dropping funnel, reflux condenser and nitrogen inlet tube, and stirred via a magnet bar. The flask was charged with 2-(*F*-octyl)ethanethiol (24.0 g, 50.0 mmol) and AIBN (0.090 g, 0.55 mmol) whilst under nitrogen purge. Allyl acetate (5.506 g, 55.0 mmol) was added dropwise during 0.5 h at 67–73 °C by means of a pressure-equalized 'Varibor' dropping funnel, under a positive nitrogen pressure. The flask was heated by a stirred, constant-temperature oil bath controlled by a sensor. Stirring was continued for 4 h at 72 °C and a sample removed for analysis by GC (6 ft. × 1.4 in. column

filled with 10% QF-1 silicone oil on Chromosorb WA and heated at 185 °C/20 psi helium). Distillation in Column B gave the following: fraction I, b.p. 98 °C/0.06 mmHg, 1.50 g (23.3% of regio isomer and 55.8% of **24**); fraction II, b.p. 100 °C/0.06 mmHg,  $n_D^{25} = 1.3674$ , 21.51 g (4.58% of regio isomer and 95.42% of **24**); fraction III, b.p. 98 °C/0.10 mmHg,  $n_D^{25} = 1.3676$ , 4.54 g (0.41% of regio isomer and 99.6% of **24**). The liquid residue amounted to 0.32 g. The cold trap contained 0.42 g of material; GC analysis: allyl acetate (36.6%) and thiol (40.0%). The yield of distilled product was 95%. IR ( $\text{cm}^{-1}$ ): 1705 (C=O).  $^1\text{H}$  NMR (60 MHz)  $\delta$  1.6–2.2 (5 H,  $\text{CH}_3\text{CO}$  and  $\text{CF}_2\text{CH}_2$ ); 2.2–2.9 (6 H,  $\text{CH}_2\text{SCH}_2\text{CH}_2$ ); 4.15 (2 H, t,  $J = 7$  Hz,  $\text{CH}_2\text{OAc}$ ) ppm. Elemental analyses are listed in Table 4.

### Summary and perspective

The radical addition of thiols to unsaturated compounds has been thoroughly studied and reviewed [19, 20, 21, 27–29]. However, little work has been published on fluorine-substituted thiols. Stacey and Harris [29] examined  $\text{CF}_3\text{SH}$  and  $\text{CF}_3\text{CH}_2\text{SH}$  and their addition to fluorinated alkenes.  $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{SH}$  (**1**) has been used in radical addition to allyl- and vinylsilanes with excellent results [17]. This present work covers a wider range of substrates with the readily accessible **1** and prepares the way for a quantitative study of reaction parameters and relative rates, as well as important synthetic applications [18]. Interesting facets of the radical addition reactions of compound **1** have been observed. Regio- and stereo-chemistry as well as radical rearrangement reactions have been uncovered. GC analyses of the regio isomers from 1-heptene and *cis*-2-heptene revealed the possibility of double-bond isomerization of the alkene or of the substitution position of the adducts, in addition to the known [20, 21, 27] *cis/trans* isomerization of the alkene substrate. Addition of compound **1** to 1,6-heptadiene gave both linear (**9**) and the cyclic mono adducts [*cis*- and *trans*-(**10**)]. However, capillary GC analysis again indicated that isomers, possibly a regio isomer of **9** and/or of **10**, were present in the product mixture in small amounts (Table 6).

The relative rates for the addition of 2-(*F*-alkyl)ethanethiols to unsaturated compounds examined in this paper will be reported in a subsequent paper [18]. The question of the acceleration of the radical addition rate, as influenced by the strong electron-withdrawing  $\text{R}_F$  group [29], will be taken up therein.

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