# **Preliminary Note**

On the reaction of 1,1-dichloropolyfluoroalkylsulfenyl chlorides with lithium hexamethyldisilylamide

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## Abstract

1,1-Dichloropolyfluoropentylsulfenyl chlorides react with lithium hexamethyldisilylamide with the formation of *N*,*N*-bis-(trimethylsilyl)-1-chloro-polyfluoropentyl-1-en-sulfenamide.

We have found that the reaction of 1,1-dichloro-2,2,3,3,4,4,5,5-octafluoropentylsulfenyl chloride (Ia) and 1,1,2-trichloro-2,3,3,4,4,5,5-heptafluoropentylsulfenyl chloride (Ib) [1] with lithium hexamethyldisilylamide, irrespective of the reagent ratio, leads not only to the substitution of a bis(trimethylsilyl)amino group for the chlorine atom at sulfur, but also to dehalogenation with the formation of N,N-bis(trimethylsilyl)-1-chloro-2,3,3,4,4,5,5-heptafluoropentyl-1-en-sulfenamide (II). The highest yield of compound II is attained when sulfenyl chloride and lithium hexamethyldisilylamide are present in a 1:2 ratio.

$$H(CF_{2})_{3}CFXCCl_{2}SCl + LiN[Si(CH_{3})_{3}]_{2} \longrightarrow$$
(Ia, b)  

$$HC^{5}F_{2}C^{4}F_{2}C^{3}F_{2}C^{2}F = C^{1}CISN[Si(CH_{3})_{3}]_{2}$$
(II)

**a**, X = Cl; **b**, X = F

It should be noted that the formation of the polyfluorovinyl moiety is typical only of sulfenyl chlorides I, while sulfides III [2] and sulfenamides IV, which also contain the  $H(CF_2)_3CF_2CCl_2$  substituent, undergo no reaction with LiN[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub> under similar conditions.  $H(CF_2)_3CF_2CCl_2SR$ 

III, R = Alk; IV,  $R = NAlk_2$ 

Compound II is a colorless, vacuum-distillable liquid, which is stable to water and methanol and does not change upon heating at 140 °C for 1 h. The composition of compound II has been confirmed by elementary analysis and mass spectrometry, and its structure demonstrated by NMR spectroscopy.

The <sup>1</sup>H NMR spectrum of the compound obtained contains two sets of signals for the trimethylsilyl protons and for the proton of the  $HCF_2$  moiety with an intensity ratio of 1:1.9 in the case of sulfenyl chloride **Ia** and with a ratio of 1:5.7 in the case of sulfenyl chloride **Ib**. Two sets of signals with similar intensity ratios were also recorded in the <sup>19</sup>F and <sup>13</sup>C NMR spectra. Thus, the reaction seems to result in a mixture of *cis* and *trans* isomers.

The <sup>13</sup>C NMR spectrum of the most abundant isomer showed signals for the carbon atoms of the trimethylsilyl groups (SiCH<sub>3</sub>), a group of multiplets corresponding to the carbon atoms of the HCF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub> moiety, as well as doublets for vinyl carbons of the  $-C^2F=C^1Cl-S-$  moiety. The values obtained were in good accord with the data for the <sup>13</sup>C NMR spectrum of the model compound V [1]. The parameters of the carbon spectrum obtained for the isomer present in the smaller amount were not very different from those for the predominant isomer, except that the <sup>2</sup>J<sub>C<sup>1</sup>F</sub> and <sup>3</sup>J<sub>C<sup>1</sup>F</sub> coupling constants were appreciably smaller in the case of the low yield isomer, and the <sup>1</sup>J<sub>C<sup>2</sup>F</sub> coupling constant was, in contrast, considerably larger.

 $\frac{HC^{5}F_{2}C^{4}F_{2}C^{3}F_{2}}{F}C = C \xrightarrow{SCH_{2}Ph}{SCH_{2}Ph}$ (V)

#### Experimental

In a typical experiment, to a solution of sulfenyl chloride I (0.01 mol) in ether (30 ml) was added with stirring over 20 min at room temperature a solution of Li silazane (0.02 mol) in ether (75 ml). The resulting mixture was stirred for 4 h, the precipitated solid filtered off and the residue fractionated *in vacuo*. The yield of compound II obtained was 75–81%, b.p. 69–70 °C/ 0.05 mmHg. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, TMS)  $\delta$ : 0.13 (\*) (s, 18H,

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 $SiCH_3$ ; 0.15 (s, 18H, SiCH<sub>3</sub>); 5.17 (tt, 1H, J=51.9, 5.1 Hz, CHF<sub>2</sub>); 5.22 (\*) (tt, 1H, J = 51.6, 5.1 Hz) ppm. <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>, CFCl<sub>3</sub>)  $\delta$ : -137.0 (\*) (dm, 2F, J=51 Hz,  $CHF_2$ ; -137.0 (dm, J = 51 Hz,  $CHF_2$ ); -129.3 (\*) (m,  $2F, CF_2$ ; -129.0 (m, 2F, CF<sub>2</sub>); -121.7 (\*) (m, 1F, C=CF; -115.8 (m, 1F, C=CF); -113.2 (m, 2F, CF<sub>2</sub>); -113.0 (\*) (m, 2F, CF<sub>2</sub>) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, TMS) δ: 1.31 (\*) (s, SiCH<sub>3</sub>); 1.43 (s, SiCH<sub>3</sub>); 108.75 (tt, J = 251.0, 31.4 Hz, C<sup>5</sup>); 108.76 (\*) (tt, J =251.0, 31.4 Hz, C<sup>5</sup>); ~111.2 (m, C<sup>4</sup>); ~111.3 (\*) (m, C<sup>3</sup>); ~111.4 (m, C<sup>3</sup>); 134.96 (\*) (dt, J = 36.2, 2.5 Hz, C<sup>1</sup>); 135.48 (dt, J = 13.5, <1Hz, C<sup>1</sup>); 137.09 (\*) (dt, J = 248.5, 28.7 Hz, C<sup>2</sup>); 137.17 (dt, J = 260.9, 31.5 Hz, C<sup>2</sup>) ppm. Analysis: Found: C, 31.25; H, 4.42; Cl, 8.46; F, 30.64; N, 3.75; S, 7.60%; M<sup>+</sup>, 421. C<sub>11</sub>H<sub>19</sub>ClF<sub>7</sub>NSSi<sub>2</sub> requires: C, 31.31; H, 4.54; Cl, 8.40; F, 31.52; N, 3.32; S, 7.60%; M<sup>+</sup>, 421.

1,1-bis(benzylthio)-2,3,4,4,5,5-heptafluoro-1-pentene (V) [1]: <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, TMS)  $\delta$ : 37.95 (d, J = 4.5 Hz, SCH<sub>2</sub>); 39.21 (d, J = 1.2 Hz, SCH<sub>2</sub>); 108.97 (tt, 250.9, 30.8 Hz, C<sup>5</sup>); ~111.2 (m, C<sup>4</sup>); ~111.3 (m, C<sup>3</sup>); 127.56

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(dt, J = 20.3, 1.8 Hz, C<sup>1</sup>); 146.54 (dt, J = 263.4, 26.4 Hz, C<sup>2</sup>); 128.32; 128.33; 129.35; 129.38; 129.80; 129.88; 137.27; 137.79 (s, C<sub>arom</sub>) ppm.

NMR spectra were measured using a Varian VXR-300 spectrometer, frequency 299.96 MHz (for <sup>1</sup>H), 282.14 MHz (for <sup>19</sup>F) and 75.43 MHz (for <sup>13</sup>C), the chemical shifts quoted being from internal TMS and  $CCl_3F$ .

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### References

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<sup>\*</sup>Isomer formed in greater amount.