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ACYLATIONS OF PENTAFLUOROSULFANYLAMINE, SF<sub>5</sub>NH<sub>2</sub>. PART II. REACTIONS OF N-PENTAFLUOROSULFANYLCARBAMYLFLUORIDE, SF<sub>5</sub>NHC(O)F, AND N-PENTAFLUOROSULFANYLPERFLUOROSUCCINIMIDE, SF<sub>5</sub>NC(O)CF<sub>2</sub>CF<sub>2</sub>C(O) [1]

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## SUMMARY

The carbamyl fluoride SF<sub>5</sub>NHC(O)F reacts with both H<sub>2</sub>O and H<sub>2</sub>S to give the urea (SF<sub>5</sub>NH)<sub>2</sub>CO. Evidence supports that this reaction proceeds through a mechanism involving dehydrofluorination; whereas, the reagents PhLi and PCl<sub>5</sub> serve only to dehydrofluorinate SF<sub>5</sub>NHC(O)F. The ring of the cyclic imide SF<sub>5</sub>NC(O)CF<sub>2</sub>CF<sub>2</sub>C(O) can be readily opened by nucleophiles to give products such as SF<sub>5</sub>NHC(O)CF<sub>2</sub>CF<sub>2</sub>C(O)OH, SF<sub>5</sub>NHC(O)CF<sub>2</sub>CF<sub>2</sub>C(O)NH<sub>2</sub>, and SF<sub>5</sub>NHC(O)CF<sub>2</sub>CF<sub>2</sub>C(O)OCH<sub>3</sub>. Attempts to prepare analogous six- and seven-membered cyclic imides failed; however, mono- (SF<sub>5</sub>NHC(O)(CF<sub>2</sub>)<sub>3,4</sub>C(O)F) and disubstituted products (SF<sub>5</sub>NHC(O)(CF<sub>2</sub>)<sub>3,4</sub>C(O)NHSF<sub>5</sub>) were formed. The amide-acid fluorides are easily hydrolyzed by atmospheric moisture to the amide-acids SF<sub>5</sub>NHC(O)(CF<sub>2</sub>)<sub>3,4</sub>C(O)OH.

## INTRODUCTION

We recently reported the synthesis of N-pentafluorosulfanyl amides from the reaction of SF<sub>5</sub>NH<sub>2</sub> with acyl halides [1]. Of particular interest was the reaction of SF<sub>5</sub>NH<sub>2</sub> with perfluorosuccinyl chloride which led not only to [SF<sub>5</sub>NHC(O)CF<sub>2</sub>]<sub>2</sub> but also to the cyclic imide SF<sub>5</sub>NC(O)CF<sub>2</sub>CF<sub>2</sub>C(O). We report herein our attempts at preparing the analogous six- and seven-membered cyclic imides as well as some reaction chemistry of SF<sub>5</sub>NC(O)CF<sub>2</sub>CF<sub>2</sub>C(O) and SF<sub>5</sub>NHC(O)F.

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## EXPERIMENTAL

Materials

The compounds  $\text{SF}_5\text{NH}_2$ ,  $\text{SF}_5\text{NHC(O)F}$ , and  $\text{SF}_5\overline{\text{NC(O)CF}_2\text{CF}_2}\text{C(O)}$  were synthesized as previously described [1]. Perfluoroglutaryl chloride and perfluoroadipoyl fluoride were obtained from PCR, Inc. and used as received. All other reagents were taken from laboratory stock and were suitably purified before use.

Spectra

Infrared spectra were obtained on a Beckman 20A-X infrared spectrophotometer, either on gases, pressure 1-100 torr, or on mulls in either halocarbon or mineral oil. Mass spectra were obtained on either a Hitachi Perkin-Elmer RMU-7 mass spectrometer, a Finnigan Model 3200 quadrupole mass spectrometer, or a Varian MAT 112 high-resolution mass spectrometer using either a solid inlet probe or a controlled gas flow inlet. The  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectra were taken on either a Varian EM-390 or a JEOL FX 60Q nuclear magnetic resonance spectrometer using  $\text{CCl}_3\text{F}$  and  $(\text{CH}_3)_4\text{Si}$ , respectively, as internal standards. The  $^{13}\text{C}$  NMR spectra were taken on a JEOL FX 60Q nuclear magnetic resonance spectrometer using  $\text{Me}_2\text{SO}-d_6$  as an internal standard. Elemental analyses were obtained from the Chemistry Department's Perkin-Elmer 240 elemental analyzer or from Galbraith Laboratories, Knoxville, TN.

Reaction of  $\text{SF}_5\text{NHC(O)F}$  with  $\text{H}_2\text{O}$ 

In a typical reaction  $\text{SF}_5\text{NHC(O)F}$  (1.86 g; 9.8 mmol) was condensed at  $-196^\circ\text{C}$  into a Kel-F reactor containing degassed water (0.5 ml). Approximately 1 h after this mixture had been allowed to warm to room temperature the volatile products, consisting primarily of  $\text{CO}_2$ , were removed. The remaining solid residue was then transferred to a Teflon watch glass and allowed to air dry overnight. This material was analyzed by infrared, NMR, and mass spectrometry and found to be the bis-urea  $(\text{SF}_5\text{NH})_2\text{CO}$  [2].

The hydrolysis reaction was found to be suppressed when  $\text{SF}_5\text{NHC(O)F}$  was reacted with aqueous 50% hydrofluoric acid. This was concluded from the appearance of appreciable quantities of both  $\text{SF}_5\text{NCO}$  and  $\text{CO}_2$  in the infrared spectrum of the volatile products taken after 1 h of reaction time.

### Reaction of SF<sub>5</sub>NHC(O)F with H<sub>2</sub>S

The carbamyl fluoride, SF<sub>5</sub>NHC(O)F, and H<sub>2</sub>S were reacted in a 2:1 molar ratio under conditions similar to those used in the preceding reaction. As before, the volatile products were examined after 1 h of reaction time but were found to consist primarily of SF<sub>5</sub>NCO along with a small quantity of COS. Little or no SiF<sub>4</sub> was observed thus indicating that the carbamyl fluoride had decomposed rapidly to the isocyanate. For if any SF<sub>5</sub>NHC(O)F had remained, SiF<sub>4</sub> would have also been present from the attack of HF on the glass vacuum system. After approximately 1 week, (SF<sub>5</sub>NH)<sub>2</sub>CO was again the product isolated following reaction workup.

### Reaction of SF<sub>5</sub>NHC(O)F with C<sub>6</sub>H<sub>5</sub>Li

A Kel-F reactor containing SF<sub>5</sub>NHC(O)F (1.32 g; 7.0 mmol) was chilled to -196°C prior to the addition of C<sub>6</sub>H<sub>5</sub>Li (4.4 ml of a 1.6 M solution in ether/benzene). After being degassed, the mixture was placed in a -120°C slush bath and allowed to warm slowly to room temperature overnight. The volatile products were then removed to the vacuum line where repeated distillations gave approximately 6 mmol of SF<sub>5</sub>NCO. The gelatinous precipitate remaining in the Kel-F reactor was thought to be LiF as it would not sublime under vacuum even at elevated temperatures. No evidence was obtained for the desired product SF<sub>5</sub>NHC(O)C<sub>6</sub>H<sub>5</sub>.

### Reaction of SF<sub>5</sub>NHC(O)F with PCl<sub>5</sub>

In a typical reaction, the carbamyl fluoride was prepared in situ prior to being placed on an excess of PCl<sub>5</sub>. In every case the volatile products isolated were SF<sub>5</sub>NCO, HCl, COF<sub>2</sub>, COClF, and COCl<sub>2</sub>. Analysis of the reaction mixture after heating at 60°C for 3 days gave no evidence for the imine SF<sub>5</sub>N=CCl<sub>2</sub>.

Preparation of SF<sub>5</sub>NHC(O)CF<sub>2</sub>CF<sub>2</sub>C(O)OH

The hydrolysis of the cyclic imide, SF<sub>5</sub> $\overline{\text{NC(O)CF}_2\text{CF}_2\text{C(O)}}$ , to SF<sub>5</sub>NHC(O)CF<sub>2</sub>CF<sub>2</sub>C(O)OH was followed by both NMR and mass spectrometry. In one experiment, a small aliquot of SF<sub>5</sub> $\overline{\text{NC(O)CF}_2\text{CF}_2\text{C(O)}}$  which had been opened to the air was examined by both electron impact and chemical ionization mass spectrometry and found to be SF<sub>5</sub>NHC(O)CF<sub>2</sub>CF<sub>2</sub>C(O)OH. In a second experiment, an unsealed sample of SF<sub>5</sub> $\overline{\text{NC(O)CF}_2\text{CF}_2\text{C(O)}}$  in deuterodimethyl sulfoxide was monitored by <sup>19</sup>F NMR spectrometry. Two sets of CF<sub>2</sub> resonances as well as two AB<sub>4</sub> splitting patterns were observed in the initial spectrum. With time the outer set of CF<sub>2</sub> resonances and the lower field AB<sub>4</sub> pattern diminished in intensity. The final product of the hydrolysis reaction was perfluorosuccinic acid.

<sup>19</sup>F<sup>A</sup>SF<sub>4</sub><sup>B</sup>NHC(O)CF<sub>2</sub><sup>C</sup>CF<sub>2</sub><sup>D</sup>C(O)OH: (nc) mass spectrum (70 eV) m/e (rel intensity): 316 [M+H]<sup>+</sup> (0.2), 298 [M-OH]<sup>+</sup> (0.4), 296 [M-F]<sup>+</sup> (0.1), 295 (0.2), 270 [M-COOH]<sup>+</sup> (0.7), 170 [SF<sub>5</sub>NHC(O)]<sup>+</sup> (20.6), 150 [SF<sub>4</sub>NCO]<sup>+</sup> (10.0), 146 (35.5), 128 (10.9), 127 (100.0), 126 (16.5), 124 (11.6), 117 (4.8), 109 (9.9), 106 (8.3), 105 (4.0), 104 (8.6), 100 (31.0), 97 (8.5), 89 (9.2), 69 (6.3), 51 (7.0), 50 (5.2); chemical ionization mass spectrum (isobutane) m/e (rel intensity): 316 [M+H]<sup>+</sup> (100.0), 298 (12.9), 296 (2.8), 170 (14.4), 146 (29.6), 128 (9.9), 127 (68.8), 126 (8.6), 124 (23.1), 112 (5.9), 109 (11.5), 107 (8.1), 106 (7.0), 105 (46.1); <sup>19</sup>F NMR (Me<sub>2</sub>SO-d<sub>6</sub>): δ<sub>A</sub> 91.1 (m), δ<sub>B</sub> 75.9 (m), δ<sub>C</sub> -116.7 (t), δ<sub>D</sub> -119.3 (t) [J<sub>AB</sub> = 158.3 Hz, J<sub>CD</sub> = 5.5 Hz (relative areas of A, B, C, and D were 1:4:2:2)].

Preparation of SF<sub>5</sub>NHC(O)CF<sub>2</sub>CF<sub>2</sub>C(O)NH<sub>2</sub>

Anhydrous ammonia (1 mmol) was condensed at -196°C into a 50 ml glass reaction cylinder containing SF<sub>5</sub> $\overline{\text{NC(O)CF}_2\text{CF}_2\text{C(O)}}$  (0.025 g; 0.084 mmol). Upon warming to room temperature, a viscous liquid formed in the reaction vessel. After several hours a white crystalline solid separated from this liquid. Approximately 36 h later the excess ammonia was removed under vacuum and the remaining solid residue was transferred to a vacuum sublimator. Sublimation at 60-70°C gave SF<sub>5</sub>NHC(O)CF<sub>2</sub>CF<sub>2</sub>C(O)NH<sub>2</sub> (0.0025 g) in 9.4% yield.

$F^A SF_4^B NHC(O)CF_2^D CF_2^E C(O)NH_2^F$ : (nc) IR (mul1): 3510 (mb), 3350 (mb), 3210 (mb), 2570 (w), 1737 (ssh), 1715 (s), 1655 (vs), 1470 (mb), 1340 (m), 1250 (w), 1195 (msh), 1175 (s), 1160 (s), 1137 (vs), 1068 (w), 1050 (w), 980 (ms), 887 (s), 850 (vs), 835 (vs), 808 (vs), 723 (m), 643 (m), 605 (m), 570 (m)  $cm^{-1}$ ; mass spectrum (70 eV) m/e (rel intensity): 315  $[M+H]^+$  (1.2), 298  $[M-NH_2]^+$  (0.1), 271 (25.7), 251 (1.7), 239 (5.2), 221 (1.0), 209 (2.6), 172  $[M-SF_5]^+$  (29.3), 170  $[SF_5NHC(O)]^+$  (14.0), 150  $[SF_4NCO]^+$  (10.7), 145 (93.3), 144 (13.3), 128 (27.7), 127 (80.0), 125 (16.7), 109 (20.7), 105 (14.7), 104 (4.9), 100 (40.0), 95 (32.7), 89 (18.0), 72 (30.0), 71 (15.3), 58 (86.7), 44 (100.0); chemical ionization mass spectrum (isobutane) m/e (rel intensity): 315  $[M+H]^+$  (26.0), 172  $[M-SF_5]^+$  (13.6), 74  $[NHC(O)CF]^+$  (100.0);  $^1H$  and  $^{19}F$  NMR ( $Me_2SO-d_6$ ;  $^{19}F$  spectrum-Fourier transform consisting of 3000 scans):  $\delta_A$  106.0 (m),  $\delta_B$  79.8 (m),  $\delta_C$  unresolved,  $\delta_D$  -113.8 (bs),  $\delta_E$  -117.4 (bs),  $\delta_F$  7.92 (bs) ( $J_{SF-SF_4} = 158.9$  Hz).

#### Attempted Preparation of $SF_5NHC(O)CF_2CF_2C(O)OCH_3$

Freshly distilled  $CH_3OH$  (0.15 ml; 3.75 mmol) was transferred by syringe to a glass reaction vessel containing  $SF_5NHC(O)CF_2CF_2C(O)$  (1.07 g; 3.6 mmol) which had been cooled to  $-196^\circ C$ . After being degassed, the reaction mixture was allowed to warm slowly to room temperature. Four hours later an infrared spectroscopic examination of the gases over the reaction mixture revealed that unreacted  $CH_3OH$  remained. Therefore, the mixture was heated at  $60-70^\circ C$  overnight. At this time the volatile products, which consisted primarily of  $SiF_4$ ,  $SO_2F_2$ , and  $HNS(O)F_2$  were removed under vacuum. The remaining less volatile liquid residue was then distilled into a detachable U-trap held at  $-196^\circ C$ . The distillate (0.175 g) was analyzed by IR, NMR, mass spectrometry, and elemental analysis but could not be identified. Several months later a crystalline solid had separated from the less volatile liquid product. This solid was purified by vacuum sublimation prior to being analyzed by mass spectrometry. An intense fragment (27.5%) at m/e 330 in the chemical ionization mass spectrum gave some evidence for the desired product  $SF_5NHC(O)CF_2CF_2C(O)OCH_3$ , but as shown below the compound was obviously contaminated with other by-products from the reaction.

C.I.	m/e	Relative Intensity	Ion
330		27.5	$[\text{SF}_5\text{NHC}(\text{O})\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_3+\text{H}]^+$
316		91.1	$[\text{SF}_5\text{NHC}(\text{O})\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{OH}+\text{H}]^+$
205		40.8	$[\text{CH}_3\text{OC}(\text{O})\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{OH}+\text{H}]^+$
204		100.0	$\text{CH}_3\text{OC}(\text{O})\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{OH}^+$
191		5.3	$[\text{HO}(\text{O})\text{CCF}_2\text{CF}_2\text{C}(\text{O})\text{OH}+\text{H}]^+$
190		79.2	$\text{HO}(\text{O})\text{CCF}_2\text{CF}_2\text{C}(\text{O})\text{OH}^+$

#### Reaction of $\text{SF}_5\text{NH}_2$ with $\text{ClC}(\text{O})(\text{CF}_2)_3\text{C}(\text{O})\text{Cl}$

Gaseous  $\text{NSF}_3$  (10.0 mmol) and HF (0.5 ml; 25 mmol) were condensed at  $-196^\circ\text{C}$  into a Kel-F reactor and allowed to react overnight at room temperature before refreezing to  $-196^\circ\text{C}$  and condensing in  $\text{ClC}(\text{O})(\text{CF}_2)_3\text{C}(\text{O})\text{Cl}$  (4.0 mmol). The reaction mixture was then allowed to warm slowly to room temperature. Thirteen days later the volatile products were moved onto a NaF scrubber. The reactor was then taken into an inert atmosphere box where the remaining solid material (1.06 g) was removed to a vacuum sublimator. A small quantity of material, subsequently identified as  $\text{SF}_5\text{NHC}(\text{O})(\text{CF}_2)_3\text{C}(\text{O})\text{F}$  (0.28 g; 19% yield), was found to sublime off the cold finger of the sublimator into the vacuum line. Further sublimation of the remaining product mixture gave  $\text{SF}_5\text{NHC}(\text{O})(\text{CF}_2)_3\text{C}(\text{O})\text{OH}$  (0.01 g) at  $60-70^\circ\text{C}$  and  $\text{SF}_5\text{NHC}(\text{O})(\text{CF}_2)_3\text{C}(\text{O})\text{NHSF}_5$  (0.44 g, 22% yield) at  $90-100^\circ\text{C}$ . Examination of the volatile products removed from the NaF scrubber gave no evidence for a cyclic imide product analogous to the one formed in the reaction of  $\text{SF}_5\text{NH}_2$  with  $\text{ClC}(\text{O})\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{Cl}$  [1].

$\text{F}^{\text{A}}\text{SF}_4^{\text{B}}\text{NH}^{\text{C}}\text{C}(\text{O})\text{CF}_2^{\text{D}}\text{CF}_2^{\text{E}}\text{CF}_2^{\text{D}}\text{C}(\text{O})\text{NH}^{\text{C}}\text{SF}_4^{\text{B}}\text{F}^{\text{A}}$ : (nc) mp  $173-175^\circ\text{C}$ ; IR (mull): 3235 (s), 2998 (m), 1738 (s), 1499 (s), 1255 (m), 1200 (s), 1170 (s), 1135 (s), 1072 (m), 950-852 (vs), 825 (s), 763 (m), 690 (w), 655 (w), 600 (s)  $\text{cm}^{-1}$ ; mass spectrum (70 eV) m/e (rel intensity): 491  $[\text{M}+\text{H}]^+$  (0.06), 451 (0.07), 348  $[\text{M}-\text{NHSF}_5]^+$  (5.5), 320  $[\text{M}-\text{C}(\text{O})\text{NHSF}_5]^+$  (5.1), 301 (6.8), 221 (3.3), 201 (2.0), 170  $[\text{SF}_5\text{NHC}(\text{O})]^+$  (32.3), 150  $[\text{SF}_4\text{NCO}]^+$  (14.7), 128 (14.0), 127 (100.0), 124 (3.0), 112 (3.0), 100 (8.7), 94 (2.4), 89 (7.3), 70 (1.0), 69 (2.5); chemical ionization mass spectrum (isobutane) m/e (rel intensity): 491  $[\text{M}+\text{H}]^+$  (61.9), 348 (35.0), 222 (12.0), 221 (11.1), 170 (40.8),

150 (33.1), 128 (15.3), 127 (100.0), 124 (18.8), 105 (26.3);  $^1\text{H}$  and  $^{19}\text{F}$  NMR ( $\text{Me}_2\text{SO}-d_6$ ):  $\delta_A$  93.1 (m),  $\delta_B$  76.6 (m),  $\delta_C$  8.91 (bs),  $\delta_D$  -114.6 (t),  $\delta_E$  -112.7 (qu) [ $J_{AB} = 158.6$  Hz,  $J_{DE} = 2.6$  Hz (relative areas of A, B, D, and E were 1:4:2:1)].  $^{13}\text{C}$  NMR ( $\text{Me}_2\text{SO}-d_6$ ):  $\delta_{C=O}$  156.2 (bm),  $\delta_{CF_2}$  111.3 (t of m) and 110.0 (t of m) ( $^1J_{C-F} = -268$  Hz).

Anal: Calcd. for  $\text{C}_5\text{H}_2\text{N}_2\text{S}_2\text{O}_2\text{F}_{16}$ : C, 12.24; H, 0.41; N, 5.71; S, 13.06. Found: C, 12.50; H, 0.34; N, 6.03; S, 12.64.

$\text{F}^{\text{A}}\text{SF}_4^{\text{B}}\text{NHC}^{\text{C}}(\text{O})\text{CF}_2^{\text{D}}\text{CF}_2^{\text{E}}\text{CF}_2^{\text{F}}\text{C}(\text{O})\text{F}^{\text{G}}$ : (nc) IR (neat): 3270 (w), 1875 (m), 1778 (vs), 1748 (vs), 1490 (w), 1355 (msh), 1330 (m), 1250 (sb), 1165 (vs), 1115 (vs), 1040 (vs), 955 (ms), 910 (m), 890 (m), 860 (m), 760 (w), 730 (w), 600 (m)  $\text{cm}^{-1}$ ; mass spectrum (70 eV) m/e (rel intensity): 368  $[\text{M}+\text{H}]^+$  (<0.1); 348  $[\text{M}-\text{F}]^+$  (<0.1), 347 (<0.1), 328 (<0.1), 320  $[\text{M}-\text{C}(\text{O})\text{F}]^+$  (<0.1), 221 (3.8), 201 (2.8), 197  $[\text{M}-\text{C}(\text{O})\text{NHSF}_5]^+$  (1.1), 193 (1.0), 178 (3.1), 173 (6.0), 170 (6.2), 169 (5.6), 150 (26.4), 131 (26.4), 127 (27.0), 109 (3.9), 100 (100.0), 93 (4.3), 89 (6.0), 81 (5.6), 70 (16.0), 69 (26.8), 64 (11.2), 50 (9.6), 48 (6.2), 47 (5.6), 43 (6.8), 31 (22.0);  $^1\text{H}$  and  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta_A$  67.8 (m),  $\delta_B$  72.5 (m),  $\delta_C$  8.68 (bs),  $\delta_D$  -118.5 (t),  $\delta_E$  -123.7 (d),  $\delta_F$  -117.8 (q),  $\delta_G$  24.6 (m) [ $J_{AB} = 158.2$  Hz,  $J_{DF} = 9.2$  Hz,  $J_{DG} = 9.2$  Hz,  $J_{EG} = 7.3$  Hz (relative areas of A, B, D, E, F, and G were 1:4:2:2:2:1)].

$\text{F}^{\text{A}}\text{SF}_4^{\text{B}}\text{NHC}^{\text{C}}(\text{O})\text{CF}_2^{\text{D}}\text{CF}_2^{\text{E}}\text{CF}_2^{\text{F}}\text{C}(\text{O})\text{OH}^{\text{G}}$ : (nc) IR (mu11): 3495 (w), 3275 (vsb), 3155 (mb), 1878 (w), 1744 (vsb), 1494 (s), 1442 (w), 1430 (w), 1375 (w), 1305 (w), 1247 (m), 1198 (vs), 1169 (vs), 1153 (s), 1140 (s), 1077 (ss), 933 (s), 878 (vs), 838 (s), 786 (w), 764 (w), 730 (w), 674 (w), 633 (msh), 598 (s)  $\text{cm}^{-1}$ ; mass spectrum (70 eV) m/e (rel intensity): 366  $[\text{M}+\text{H}]^+$  (0.1), 348  $[\text{M}-\text{OH}]^+$  (0.2), 320  $[\text{M}-\text{COOH}]^+$  (1.0), 301 (0.3), 221 (2.1), 201 (2.3), 176  $[\text{CF}_2\text{CF}_2\text{COOH}]^+$  (23.3), 170  $[\text{SF}_5\text{NHC}]^+$  (18.9), 150  $[\text{SF}_4\text{NCO}]^+$  (42.8), 131 (19.2), 127  $[\text{SF}_5]^+$  (100.0), 124 (7.9), 119 (22.1), 112 (9.8), 105 (6.9), 104 (8.7), 100 (43.5), 89 (9.1), 85 (6.5), 70 (3.2), 69 (6.6); chemical ionization (isobutane) m/e (rel intensity): 366  $[\text{M}+\text{H}]^+$  (100.0), 348  $[\text{M}-\text{OH}]^+$  (1.8), 346  $[\text{M}-\text{F}]^+$  (4.5), 222 (4.7), 221 (1.9), 124 (3.9), 105 (7.5), 104 (13.1), 100 (1.2), 89 (3.4), 85 (1.1), 70 (1.2), 69 (2.0);  $^1\text{H}$  and  $^{19}\text{F}$  NMR ( $\text{Me}_2\text{SO}-d_6$ ):  $\delta_A$  103.4 (m),  $\delta_B$  79.2 (m),  $\delta_C$  8.91 (bs),  $\delta_D$  -114.0 (bt),  $\delta_E$  -122.5 (bs),  $\delta_F$  -117.7 (bt),  $\delta_G$  unresolved [ $J_{AB} = 158.7$  Hz,  $J_{DF} = 10.0$  Hz (relative areas of A, B, D, E, and F were 1:4:2:2:2)].

Reaction of SF<sub>5</sub>NH<sub>2</sub> with FC(O)(CF<sub>2</sub>)<sub>4</sub>C(O)F

Reaction conditions were identical to those in the last experiment with the exception that a reaction time of one month was used. Fractional sublimation gave the following products: SF<sub>5</sub>NHC(O)(CF<sub>2</sub>)<sub>4</sub>C(O)F (0.167 g; 10.1% yield), SF<sub>5</sub>NHC(O)(CF<sub>2</sub>)<sub>4</sub>C(O)OH (0.07 g), SF<sub>5</sub>NHC(O)(CF<sub>2</sub>)<sub>4</sub>C(O)NHSF<sub>5</sub> (0.36 g; 16.7% yield). Again examination of the volatile products from the NaF scrubber gave no evidence for a cyclic imide product.

F<sup>A</sup>SF<sub>4</sub>B<sup>NH</sup>C(O)CF<sub>2</sub><sup>D</sup>CF<sub>2</sub><sup>E</sup>CF<sub>2</sub><sup>E</sup>CF<sub>2</sub><sup>D</sup>C(O)NHSF<sub>4</sub>B<sup>F</sup>A: (nc) mp 168-171°C; IR (mu11): 3275 (s), 2985 (m), 1740 (s), 1488 (s), 1260 (w), 1215 (w), 1193 (s), 1167 (m), 1150 (m), 1120 (m), 925 (s), 868 (s), 800 (w), 760 (w), 600 (s) cm<sup>-1</sup>; mass spectrum (70 eV) m/e (rel intensity): 541 [M+H]<sup>+</sup> (0.1), 502 (0.1), 501 (0.1), 398 [M-NHSF<sub>5</sub>]<sup>+</sup> (3.5), 370 [M-C(O)NHSF<sub>5</sub>]<sup>+</sup> (5.5), 351 (10.4), 170 [SF<sub>5</sub>NHCO]<sup>+</sup> (32.9), 150 (7.6), 131 (8.5), 128 (21.8), 127 [SF<sub>5</sub>]<sup>+</sup> (100.0), 104 (2.8), 100 (8.3), 89 (6.2), 85 (2.7), 69 (6.7); chemical ionization mass spectrum (isobutane) m/e (rel intensity): 541 [M+H]<sup>+</sup> (7.2), 398 (7.6), 378 (2.0), 371 (1.1), 370 (1.6), 351 (3.1), 170 (11.4), 150 (19.5), 131 (12.9), 128 (16.7), 127 (54.5), 105 (18.2), 104 (4.9), 100 (19.2), 89 (100.0), 70 (11.4), 69 (11.4); <sup>1</sup>H and <sup>19</sup>F NMR (Me<sub>2</sub>SO-d<sub>6</sub>): δ<sub>A</sub> 103.0 (m), δ<sub>B</sub> 79.0 (m), δ<sub>C</sub> 7.13 (bs), δ<sub>D</sub> -114.5 (bt), δ<sub>E</sub> -120.7 (bt) [J<sub>AB</sub> = 160 Hz, J<sub>DE</sub> = 12.5 Hz (relative areas of A, B, D, and E were 1:4:2:2)]; <sup>13</sup>C NMR (Me<sub>2</sub>SO-d<sub>6</sub>): δ<sub>C</sub>=0 153.7 (bm), δ<sub>CF<sub>2</sub></sub> 111.6 (t of m) and 109.6 (t of m) (<sup>1</sup>J<sub>C-F</sub> = -267 Hz).

Anal: Calcd. for C<sub>6</sub>H<sub>2</sub>N<sub>2</sub>S<sub>2</sub>O<sub>2</sub>F<sub>18</sub>: C, 13.33; H, 0.37; N, 5.19; S, 11.85. Found: C, 13.48; H, 0.42; N, 5.33; S, 11.30.

F<sup>A</sup>SF<sub>4</sub>B<sup>NH</sup>C(O)CF<sub>2</sub><sup>D</sup>CF<sub>2</sub><sup>E</sup>CF<sub>2</sub><sup>F</sup>CF<sub>2</sub><sup>G</sup>C(O)F<sup>H</sup>: (nc) IR (mu11): 3280 (s), 1860 (s), 1740 (vs), 1487 (s), 1367 (m), 1332 (m), 1260 (s), 1190 (vs), 1165 (vs), 1135 (vs), 1120 (vs), 1095 (s), 993 (m), 930 (vs), 905 (vs), 865 (vsb), 802 (ms), 758 (ss), 715 (ms), 635 (ssh), 590 (sb) cm<sup>-1</sup>; mass spectrum (70 eV) m/e (rel intensity): 418 [M+H]<sup>+</sup> (0.1), 398 [M-F]<sup>+</sup> (0.1), 370 [M-C(O)F]<sup>+</sup> (0.1), 350 (0.1), 320 (0.1), 247 [M-C(O)NHSF<sub>5</sub>]<sup>+</sup> (1.7), 219 (4.0), 197 (2.3), 170 (34.6), 169 (17.1), 150 (9.2), 131 (25.0), 128 (21.3), 127 (100.0), 119 (20.0), 104 (6.3),



100 (29.2), 89 (8.8), 85 (12.9), 70 (4.2), 69 (83.3), 47 (20.0), 43 (25.0), 31 (10.4).  $^1\text{H}$  and  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta_A$  68.1 (m),  $\delta_B$  72.4 (m),  $\delta_C$  8.55 (bs),  $\delta_D$  -119.1 (bt),  $\delta_E$  -112.5 (m),  $\delta_F$  -112.5 (m),  $\delta_G$  -118.6 (bq),  $\delta_H$  25.2 (m) [ $J_{AB} = 157.5$  Hz,  $J_{DF} = 9-10$  Hz,  $J_{EG} = 9-10$  Hz,  $J_{GH} = 9-10$  Hz (relative areas of A, B, D, E+F, G, and H were 1:4:2:4:2:1)].

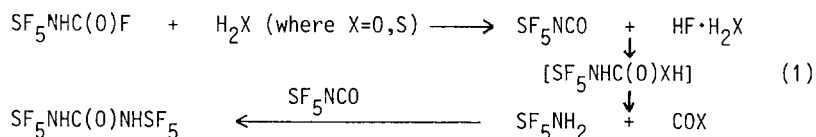
$\text{F}_4\text{S}_4\text{B}_4\text{NH}_4\text{C}(\text{O})\text{CF}_2\text{D}_2\text{CF}_2\text{E}_2\text{CF}_2\text{G}_2\text{C}(\text{O})\text{OH}_4\text{H}$ : (nc) mp 136-138°C; IR (mu11): 3545 (m), 3270 (s), 3150 (mb), 1748 (s), 1705 (s), 1490 (s), 1432 (w), 1330 (w), 1287 (w), 1244 (w), 1185 (s), 1155 (s), 1124 (s), 935 (s), 915 (s), 876 (s), 865 (s), 810 (w), 785 (w), 725 (w), 600 (s)  $\text{cm}^{-1}$ ; mass spectrum (70 eV) m/e (rel intensity): 416  $[\text{M}+\text{H}]^+$  (0.1), 398  $[\text{M}-\text{OH}]^+$  (0.3), 370  $[\text{M}-\text{COOH}]^+$  (0.9), 351 (0.9), 256 (0.4), 251 (0.7), 245  $[\text{M}-\text{C}(\text{O})\text{NHSF}_5]^+$  (2.6), 226 (20.3), 200 (0.4), 178 (4.9), 170 (22.8), 169 (5.8), 150 (8.7), 131 (29.2), 128 (26.9), 127 (100.0), 124 (3.6), 104 (9.6), 100 (15.7), 89 (4.1), 69 (11.0); chemical ionization mass spectrum (isobutane) m/e (rel intensity): 416  $[\text{M}+\text{H}]^+$  (100.0), 398 (7.2), 396 (2.2), 370 (4.4), 351 (3.1), 226 (10.9), 170 (12.1), 150 (27.9), 131 (40.5), 128 (20.2), 127 (71.1), 124 (8.9), 112 (6.3), 109 (4.8), 107 (10.7), 105 (76.8), 104 (25.7);  $^1\text{H}$  and  $^{19}\text{F}$  NMR ( $\text{Me}_2\text{SO}-d_6$ ):  $\delta_A$  104.2 (m),  $\delta_B$  78.9 (m),  $\delta_C$  7.87 (bs),  $\delta_D$  -114.3 (bt),  $\delta_E$  -121.1 (m),  $\delta_F$  -122.2 (m),  $\delta_G$  -118.1 (bt),  $\delta_H$  unresolved [ $J_{AB} = 159$  Hz,  $J_{DF} = 12.5$  Hz,  $J_{EG} = 12.5$  Hz (relative areas of A, B, D, E, F, and G were 1:4:2:2:2:2)].

Anal: Calcd. for  $\text{C}_6\text{H}_2\text{NSO}_3\text{F}_{13}$ : C, 17.35; H, 0.48; N, 3.37; S, 7.71. Found: C, 17.02; H, 0.79; N, 3.31; S, 8.08.

## RESULTS AND DISCUSSION

The isocyanate  $\text{SF}_5\text{NCO}$  has been shown to react readily with water upon warming from  $-78^\circ\text{C}$  to give  $\text{SF}_5\text{NH}_2$  and  $\text{CO}_2$  [3]. These products presumably result from the thermal decomposition of the carbamic acid  $\text{SF}_5\text{NHC}(\text{O})\text{OH}$ . On the other hand, the carbamyl fluoride  $\text{SF}_5\text{NHC}(\text{O})\text{F}$  reacts with both water and hydrogen sulfide to produce the bis-urea  $(\text{SF}_5\text{NH})_2\text{CO}$ . The observation of  $\text{SF}_5\text{NCO}$  as an early product in these reactions indicates that the mechanism is not a true hydrolysis of the carbamyl fluoride, but instead a dehydrofluorination.

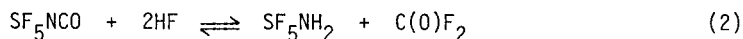
G. D. Buckley *et al.* has previously proposed this mechanism based on similar results for the hydrolysis of phenylcarbonyl fluoride [4]. The driving force for the dehydrofluorination is the ease of hydration of hydrogen fluoride. In fact Buckley found that the hydrolysis



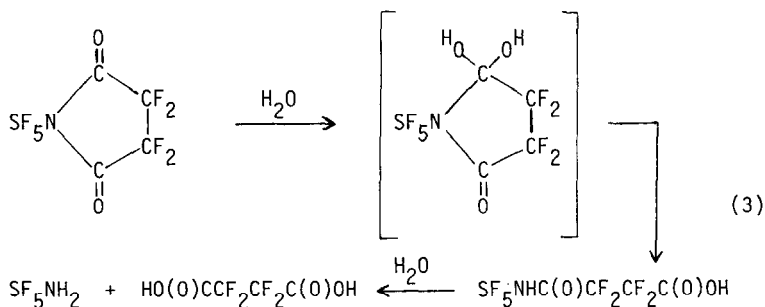
of phenylcarbonyl fluoride with aqueous 40% hydrofluoric acid was completely suppressed [4].

In this case, there is good evidence supporting the dehydrofluorination mechanism. The best evidence lies in the observation that a high percentage of  $\text{SF}_5\text{NCO}$  is formed when  $\text{H}_2\text{S}$  reacts with  $\text{SF}_5\text{NHC(O)F}$ . The  $\text{SF}_5\text{NCO}$  then reacts slowly with  $\text{H}_2\text{S}\cdot\text{HF}$  giving  $\text{SF}_5\text{NH}_2$  which produces  $(\text{SF}_5\text{NH})_2\text{CO}$  in the  $\text{SF}_5\text{NCO}$  rich environment. Additional evidence supporting the dehydrofluorination mechanism is found in the hydrolysis of  $\text{SF}_5\text{NHC(O)F}$  with aqueous 50% HF. Unlike the case with pure water where the reaction is complete within one hour, with aqueous 50% HF appreciable quantities of  $\text{SF}_5\text{NCO}$  are still present after one hour. Since hydrofluoric acid is present in both cases, it must influence the reaction at the rate determining step. This must be the formation of the carbamic acid. With this reaction step being rate determining, the formation of urea occurs since  $\text{SF}_5\text{NH}_2$  is formed in the presence of excess isocyanate. The reaction between water and pure  $\text{SF}_5\text{NCO}$  is fast and apparently no appreciable concentration of  $\text{SF}_5\text{NCO}$  is available to react with the amine being formed from the decomposing acid.

The reagents, phenyl lithium and phosphorus pentachloride, also act only to remove HF from the carbonyl fluoride. Phenyl lithium reacts as a strong base with  $\text{SF}_5\text{NHC(O)F}$  forming LiF and benzene. In the reaction with  $\text{PCl}_5$ , hydrogen chloride is formed either from the post dehydrofluorination exchange reaction between  $\text{PCl}_5$  and HF or through a halogen exchange on  $\text{SF}_5\text{NHC(O)F}$  and subsequent dehydrohalogenation. Carbonyl fluoride formed via isocyanate disproportionation in the presence of HF (eq. 2) has previously been observed in our laboratory [2].

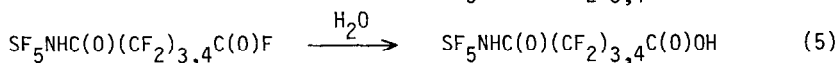
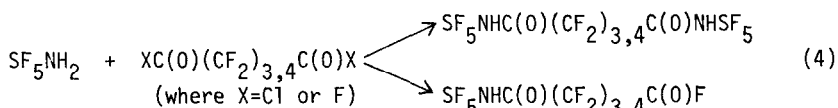


The ring of the cyclic imide  $\text{SF}_5\text{NC}(\text{O})\text{CF}_2\text{CF}_2\text{C}(\text{O})$  can be opened by reaction with various nucleophilic reagents. The results of the hydrolysis reaction can be explained by equation 3. This mechanism



is entirely consistent with the second order kinetics previously reported for the hydrolysis of imides [5]. Also, stable derivatives of cyclic imides that are similar to the proposed semi-hydrate intermediate have been isolated [6]. The amide  $\text{SF}_5\text{NHC}(\text{O})\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{NH}_2$  was isolated in 9.4% yield from the reaction of  $\text{SF}_5\text{NC}(\text{O})\text{CF}_2\text{CF}_2\text{C}(\text{O})$  with anhydrous ammonia, while only mass spectral evidence was obtained for  $\text{SF}_5\text{NHC}(\text{O})\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_3$  in the reaction of the imide with methanol.

In an attempt to prepare the analogous six- and seven-membered cyclic imides,  $\text{SF}_5\text{NH}_2$  was reacted with both perfluoroglutaryl chloride and perfluoroadipoyl fluoride. Neither reaction gave a cyclic imide product even when attempted under dilute solution conditions. However, both mono- and diacyl derivatives were isolated in each reaction (eq 4). The amide-acid fluoride products were found to be rapidly hydrolyzed by atmospheric moisture (eq 5).



The infrared, mass spectral, and nuclear magnetic resonance data are consistent with the proposed structures for the compounds reported. Each new compound gave a weak intensity  $[\text{M}+\text{H}]^+$  ion in the electron impact mass spectrum instead of a molecular ion. This is believed to be due to bimolecular collisions occurring in the ion chamber where a hydrogen atom is transferred from a neutral molecule to the molecular

ion. This phenomenon is generally observed only in molecules containing heteroatoms such as oxygen, sulfur, and nitrogen [7]. In all cases where the chemical ionization mass spectrum was also obtained, a stark  $[M+H]^+$  ion was observed.

The  $^{19}\text{F}$  NMR spectrum of each compound exhibited an  $\text{AB}_4$  splitting pattern characteristic of the  $\text{SF}_5$  group. The greater shielding of the axial fluorine in each of the two amide-acid fluorides, in comparison to the other derivatives, is most likely due to a solvent effect [1,8]. Beta couplings between organofluorines were also characteristically larger than alpha couplings [9].

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