Chem. Ber. **117**, 1707 – 1725 (1984)

Reactions of Pentafluorosulfanyl Isocyanate and Isothiocyanate

Joseph S. Thrasher *[1], *Jon L. Howell,* and *Alan F. Clifford*

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061 USA

Received July 22, 1983

The purification of pentafluorosulfanyl isocyanate (**1**) is rendered less difficult by isolation of the intermediate (pentafluorosulfanyl)carbamoyl fluoride, while pentafluorosulfanyl isothiocyanate (**2**) can easily be prepared by the reaction of dichloro(pentafluorosulfanylimino)methane with phosphorus pentasulfide in boiling toluene. Both **1** and **2** react readily with alcohols to give urethanes **3a – e** and thiourethane **4**, respectively, and with thiols to give thiolurethanes **5a, b** and dithiourethane **6**. With amines **1** and **2** form a variety of substituted ureas **7**, **8a – e**, **10a – c**, and thiourea **9**. Of particular interest is the reaction of **1** with tertiary amines which yields zwitterionic derivatives **11a, b**. *N*-(Pentafluorosulfanyl)imine derivatives **12a – e**, **13a, b**, **14** are prepared from the reactions of **1** or **2** with aldehydes and *N,N*-disubstituted amides. The reaction of **1** with acetylacetone gives the *N*-(pentafluorosulfanyl)amide of diacetoacetic acid (**16**), which in solution is observed in both the keto form and two distinct enol forms. With trimethyl orthoformate **1** gives not only the expected *N*-methyl-*N*-(pentafluorosulfanyl)urethane **18** but also the classical addition product 2,2,2-trimethoxy-*N*-(pentafluorosulfanyl)acetamide (**17**).

Reaktionen des (Pentafluorsulfanyl)isocyanats und -isothiocyanats

Die Reinigung des (Pentafluorsulfanyl)isocyanats (**1**) wird durch die Isolierung von (Pentafluorsulfanyl)carbamoylfluorid erleichtert. (Pentafluorsulfanyl)isothiocyanat (**2**) ist aus Dichlor-(pentafluorsulfanylimino)methan und Phosphorpentasulfid in siedendem Toluol leicht erhältlich. **1** und **2** reagieren mit Alkoholen zu den Urethanen **3a – e** bzw. Thiourethan **4** und mit Thiolen zu den Thiolurethanen **5a, b** bzw. Dithiourethan **6**. Mit Aminen reagieren **1** und **2** zu den verschiedenen substituierten Harnstoffen **7**, **8a – e**, **10a – c** bzw. Thioharnstoff **9**. Von besonderem Interesse ist die Reaktion von **1** mit tertiären Aminen zu den zwitterionischen Derivaten **11a, b**. *N*-(Pentafluorsulfanyl)imin-Derivate **12a – e**, **13a, b**, **14** werden aus **1** oder **2** mit Aldehyden und *N,N*-disubstituierten Amiden hergestellt. Die Reaktion von **1** mit Acetylaceton gibt das *N*-(Pentafluorsulfanyl)amid **16** der Diacetessigsäure, das in Lösung in der Ketoform und zwei Enolformen beobachtet wird. Mit Trimethyl-orthoformiat gibt **1** nicht nur das erwartete *N*-Methyl-*N*-(pentafluorsulfanyl)urethan **18**, sondern auch das klassische Additionsprodukt 2,2,2-Trimethoxy-*N*-(pentafluorsulfanyl)acetamid (**17**).

Reports on the reaction chemistry of isocyanates containing highly electron-withdrawing groups R continue to appear in the literature with great regularity[2-7]. However, to date very little has been reported on the reactivity of pentafluorosulfanyl isocyanate (**1**) and its thio analogue **2**. Both compounds were first reported in 1964 by *Tullock* et al.[8] from the reaction of (pentafluorosulfanyl)(trifluoromethyl)amine with benzoic and thiolbenzoic acid, respectively. At that time, both compounds were said to be rapidly decomposed by aqueous alkali and a urethane derivative of **1** was prepared

0009 – 2940/84/0505 – 1707 $ 02.50/0

by its reaction with benzyl alcohol. Approximately ten years later a new route to **1** was found in the reaction of thiazyl trifluoride, carbonyl fluoride, and anhydrous hydrogen fluoride[9]. Two urea derivatives, from (pentafluorosulfanyl)amine[9] and aniline[10], also resulted from this investigation. Other reactions of **1** include its reaction with phosphorus pentachloride forming the dichloroimine $SF_5N=CCl_2$ and its reaction with benzaldehyde and dimethyl sulfoxide yielding the carbimine and sulfilimine, respectively[11]. We recently reported the reaction of **1** with suitable carboxylic acids to give *N*-(pentafluorosulfanyl)amides[12].

$$SF_5NHCF_3 + C_6H_5C(O)XH \xrightarrow[-\ 2\ HF]{2\ NaF} SF_5N{=}C{=}X + C_6H_5C(O)F$$

1: X = O
2: X = S

The goal of the research reported herein was to characterize in a detailed and systematic fashion the reactions of **1**. This was carried out in three parts; the first included the reactions of **1** with alcohols, thiols, and amines, the second involved the reactions of **1** with aldehydes, formamides, and sulfoxides, and the third consisted of the addition reactions of **1** with certain compounds containing reactive CH bonds. At the same time several new synthetic routes to **2** have been found and its first derivatives prepared.

Results and Discussions

Although the reaction of (pentafluorosulfanyl)amine with carbonyl fluoride produces **1** in high yield[9], the analogous reactions of (pentafluorosulfanyl)amine with both thiocarbonyl chloride fluoride and thiocarbonyl chloride fail to produce more than a trace amount of **2**. Fortunately, a variety of other synthetic methods exist for the preparation of isothiocyanates. Two complementary methods which often produce isothiocyanates in high yield involve the reactions of iminodichloromethanes with either sodium sulfide or phosphorus pentasulfide[13]. The reaction with sodium sulfide requires an aqueous medium, and since only the base hydrolysis of **2** had been reported[8], the anhydrous method with phosphorus pentasulfide was used instead. This method converts dichloro(pentafluorosulfanylimino)methane into **2** in over 70% yield using refluxing toluene as the reaction medium. The physical properties observed for **2** are in agreement with those previously reported; however, a more complete characterization of **2** is given.

$$3\ SF_5N{=}CCl_2 + P_2S_5 \xrightarrow[C_6H_5CH_3]{120\,^\circ C} 3\ SF_5N{=}C{=}S + 2\ PSCl_3$$

2

Classical Addition Reactions

Isocyanates and isothiocyanates generally undergo addition reactions with substrate molecules containing easily replaceable hydrogen atoms, i.e., alcohols, thiols, amines, etc. **1** and **2** react with a variety of alcohols to give urethanes and thiourethanes, respectively. The urethanes **3** are indefinitely stable in aqueous solution, but are decomposed by aqueous sodium acetate or pyridine with cleavage of the NH – carbonyl bond as NSF_3 is observed in the ^{19}F NMR spectra of the solutions. With thiols, **1** and **2** give thiolurethanes and dithiourethanes respectively. In contrast to the stability of **5a, b**, even in aqueous dimethyl sulfoxide, compound **6** decomposes readily at room temperature. The white, crystalline solid had to be analyzed by infrared and mass spectrometry immediately following synthesis. The NMR spectra of **6** were obtained in a separate experiment carried out in a sealed NMR tube.

$$SF_5NCO + ROH \longrightarrow SF_5NHC(O)OR$$

1 → **3a – e**

3	R
a	CH_3
b	$-CH_2CH_2O(O)CNHSF_5$
c	C_6H_5
d	$4\text{-}C_6H_4O(O)CNHSF_5$
e	$C_6H_4OH\text{-}(4)$

$$SF_5NCS + CH_3OH \longrightarrow SF_5NHC(S)OCH_3$$

2 → **4**

$$\mathbf{1} + RSH \longrightarrow SF_5NHC(O)SR$$

5 — **5a**: R = CH_3; **b**: R = C_6H_5

$$\mathbf{2} + CH_3SH \longrightarrow SF_5NHC(S)SCH_3$$

6

The isocyanate **1** reacts rapidly with water upon warming from −78 °C to give SF_5NH_2 and CO_2. These products presumably result from the thermal decomposition of the carbamic acid $SF_5NHC(O)OH$. On the other hand, isothiocyanates are reported to be so stable toward hydrolysis that they can often be purified by steam distillation. In fact many have to be heated to 200 °C with water for complete hydrolysis[14]. **2** proves to be no exception, as temperatures in the vicinity of 150 – 175 °C are required in order to give evidence for hydrolysis.

$$\mathbf{1} + H_2O \longrightarrow [SF_5NHC(O)OH] \xrightarrow[-CO_2]{} SF_5NH_2 \xleftarrow[-COS]{} [SF_5NHC(S)OH] \longleftarrow \mathbf{2} + H_2O$$

Ammonia, primary, secondary, and tertiary amines all react with **1** to form a variety of substituted ureas. Aniline and **2** give the thiourea $SF_5NHC(S)NHC_6H_5$ (**9**); whereas (pentafluorosulfanyl)amine and **2** fail to give the bis(pentafluorosulfanyl)thiourea $SF_5NHC(S)NHSF_5$. Unlike the urethanes which can be readily purified by vacuum sublimation, attempts to sublime the urea derivatives result only in thermal decomposition. Thus, many of these products had to be purified by washing or recrystallization. The trisubstituted ureas **10a – c** are extremely susceptible to degradation by atmospheric moisture; in fact, compound **10a** had to be prepared several times before sufficient characterization could be obtained.

Of particular importance in the mass spectra of the ureas is the ion corresponding to the loss of hydrogen fluoride. For example, the heaviest ion observed for the two bis-substituted ureas **8d** and **e** corresponds to the $[M - 4\,HF]^+$ ion. The fragmentation pattern of **9** compares favorably with those reported for other substituted thioureas

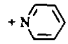
1 —(RNH_2)→ $SF_5NHC(O)NHR$

2 —($H_2NC_6H_5$)→ $SF_5NHC(S)NHC_6H_5$ **9**

1 —($RR'NH$)→ $SF_5NHC(O)NRR'$ **10**; **1** —(R_3N)→ $SF_5\bar{N}C(O)\overset{+}{N}R_3$ **11**

	R
7	H
8a	CH_3
b	$CH_2CH_2NHC(O)NHSF_5$
c	C_6H_5
d	$4\text{-}C_6H_4NHC(O)NHSF_5$
e	$4\text{-}C_6H_4CH_2C_6H_4\text{-}NHC(O)NHSF_5\text{-}(4)$

10	R	R'
a	C_2H_5	C_2H_5
b	-$[CH_2]_5$-	
c	C_6H_5	C_6H_5

11	$\overset{+}{N}R_3$
a	
b	$\overset{+}{N}Et_3$

with the $[M - H_2S]^+$ ion being prominent[15,16]. The zwitterionic derivatives **11a,b** are far less thermally stable than the analogous fluorosulfonyl derivatives recently reported by *Appel* and *Montenarh*[17]. The reaction of SF_5NCO with triphenylphosphane gives some evidence for the zwitterionic compound, but the product could not be isolated even when SF_5NCO was used in excess. On the other hand, fluorosulfonyl isocyanate has been shown to react with a variety of tertiary phosphanes producing the corresponding adducts in high yield[18]. But it is interesting to note, that melting points which differ by 40°C have been reported for the compound $FSO_2\bar{N}C(O)\overset{+}{P}(C_6H_5)_3$[17,18].

Elimination Reactions

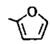
Certain electron-deficient isocyanates react with organic carbonyls and sulfoxides producing the corresponding imines and carbon dioxide[2,19]; however, these reactions are generally limited to aldehydes, ketones, formamides, and dimethyl sulfoxide. Although we reported the reactions of **1** with benzaldehyde and dimethyl sulfoxide in 1976[11], this investigation reconfirms those results and further broadens the scope of these reactions. Other aromatic aldehydes also react with **1** to give imine derivatives (**12a – d**). *N*-(Pentafluorosulfanyl)amidines **13**, **14** are formed from the reaction of **1** or **2** with *N,N*-disubstituted amides.

Compound **14** is one of the few solid *N*-(pentafluorosulfanyl)imine derivatives[20]. Most of the other are liquids presumably due to the apparent lack of hydrogen bonding. In contrast to **14**, the ^1H and ^{13}C NMR spectra of **13a** give separate resonances for the methyl groups attached to the amino nitrogen. We had previously observed this phenomenon only in the case where R = C_6H_5 in the series of compounds $SF_5N=C(R)N(C_2H_5)_2$ were R = Cl, $N(C_2H_5)_2$, OCH_3, C_6H_5, CH_3, and CF_3[20]. Preliminary temperature-dependent NMR studies indicate hindered rotation about the C – N(amino) bond in both cases. The imine carbon resonance in the ^{13}C NMR spectrum of each imine appears as a quintet due to coupling with the four equatorial fluorines of the SF_5 group. This coupling which ranges from 5 to 11 Hz has also been reported in other (pentafluorosulfanyl)imine derivatives[20].

The isocyanate **1** reacts slowly with acetone, but the expected product $SF_5N=C(CH_3)_2$ could not be isolated and characterized due to its instability. No reaction was observed between **1** and hexafluoroacetone, phenyl methyl sulfoxide, or carbon disulfide.

$\mathbf{1} + RC(O)H \longrightarrow SF_5N{=}C(H)R + CO_2$

12a-d

12	R
a	C_6H_5
b	$C_6H_4CH_3$-(4)
c	$C_6H_4OCH_3$-(4)
d	

$\mathbf{1} + RR'NC(O)H \longrightarrow SF_5N{=}C(H)NRR' + CO_2$

13a, b

13	R	R'
a	CH_3	CH_3
b	CH_3	C_6H_5

$\mathbf{2} + (CH_3)_2NC(O)H \longrightarrow \mathbf{13a} + COS$

$\mathbf{1} + (CH_3)_2NC(O)CH_3 \longrightarrow SF_5N{=}C(CH_3)N(CH_3)_2 + CO_2$

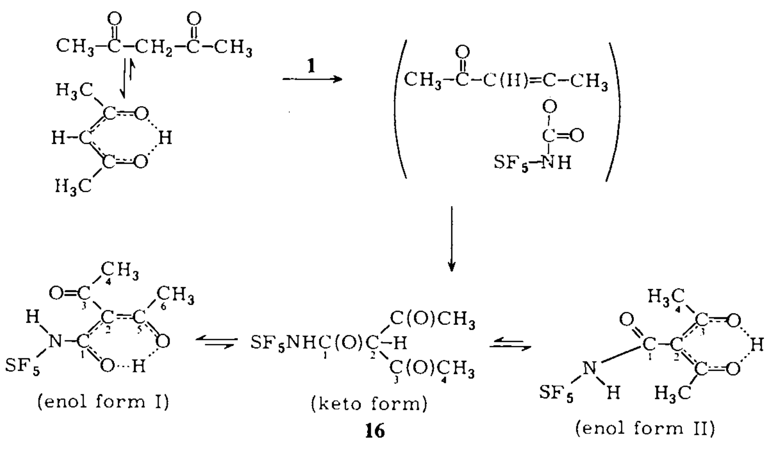
14

$\mathbf{1} + (CH_3)_2SO \longrightarrow SF_5N{=}S(CH_3)_2$

15

Reactions with Reactive C – H Bonds

The reaction of **1** with acetylacetone gives the *N*-(pentafluorosulfanyl)amide of diacetoacetic acid (**16**). When dissolved in deuteriochloroform, **16** is completely enolized to two distinct enol forms (I and II, 7:3 ratio); however, in $(CD_3)_2SO$ one observes only enol form II and the keto form, the former being predominate (4:1 ratio). The structures of these tautomers, which are given as resonances forms, are conclusively shown by ^1H, ^{19}F, and ^{13}C NMR spectroscopy; the ^{13}C NMR spectra are given in Figures 1 and 2.



The above reaction is not surprising as *Clauß* et al. have reported the analogous reaction with both chloro- and fluorosulfonyl isocyanate[21]. The surprising difference is that in $CDCl_3$ they found only the form analogous to enol form I. More recently *Arbuzov* and co-workers have reported the addition of aliphatic and aromatic acyl isocyanates to a variety of β-dicarbonyl compounds[5]. They observed both enol forms for the *N*-(trichloroacetyl)amide of diacetoacetic acid in polar proton-donor solvents[5]. Although both of these research groups have isolated the intermediate carbamate in some cases[5,21], we made no attempt to do so.

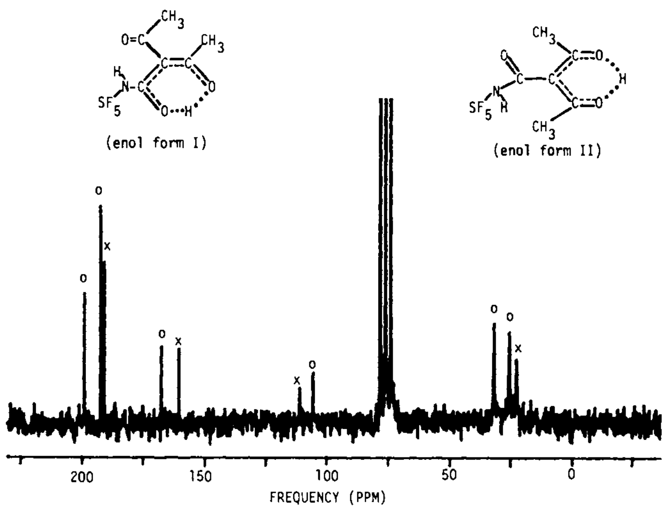


Figure 1. ^{13}C NMR Spectrum of $SF_5NHC(O)CH[C(O)CH_3]_2$ (**16**) (15 MHz, $CDCl_3$): enol form I (○) and enol form II (×)

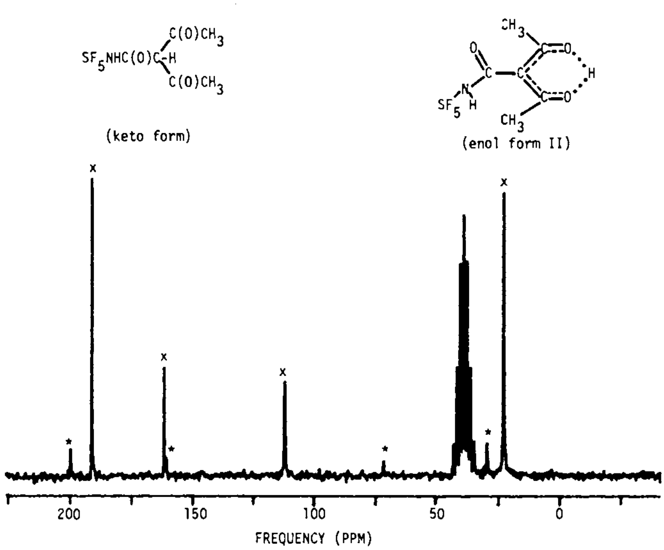
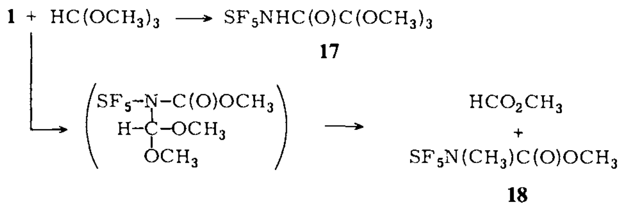


Figure 2. ^{13}C NMR Spectrum of $SF_5NHC(O)CH[C(O)CH_3]_2$ (**16**) (15 MHz, $[D_6]DMSO$): keto form (*) and enol form II (×)

The chemical shift of C-3 (199.6) in enol form I indicates that there is little or no hydrogen bonding between the NH proton and the carbonyl oxygen as previously suggested[5,21]. Carbon 2 in both the keto form and the enol form II is coupled to the four basal fluorines of the SF_5 group, thus providing another example of a $^4J_{F\text{-}C}$ coupling as previously seen in $SF_5NHC(O)C(O)NHSF_5$[12]. The appearance of the keto form in $(CD_3)_2SO$ is consistent with the fact that acetylacetone is far less enolized in $(CD_3)_2SO$ than in $CDCl_3$.

The reaction of **1** with trimethyl orthoformate unexpectedly follows two reaction pathways. The formation of **17** from a classical addition reaction is unique in that this pathway is generally not observed in the reactions of isocyanates with orthoformates or acetals[2,22-24].



The expected product **18** most likely results by the mechanism previously proposed by *Biener* in the reaction with chlorosulfonyl isocyanate[23]. Supporting evidence for this mechanism has been given by both *Graf*[24] and *v. Brachel* and *Merten*[22]. They have reported analogous reactions where the final product corresponds directly to the above intermediate.

The trimethoxyacetamide **17** has characteristics similar to those of the urethanes and ureas, while the *N*-methyl substituted urethane **18** is a liquid. The ^{13}C NMR data given for **17** are incomplete as the sample quantity was too small to obtain a signal for all carbons even after many repetitive scans. Compound **18** is only the second example of an *N,N*-disubstituted urethane containing an SF_5 – nitrogen bond[8].

NMR Parameters

All of the new *N*-pentafluorosulfanyl derivatives exhibit a characteristic AB_4-splitting pattern in the ^{19}F NMR spectrum. The chemical shift of the axial fluorine is downfield from that of the equatorial fluorines in every case. The reverse is true in the two starting materials **1** and **2**. It should also be pointed out that the chemical shift difference (δ_{AB}) is larger in the imine derivatives. The ^1H NMR spectrum of each compound is consistent with its hydrocarbon portion.

The assignment of the resonances in the ^{13}C NMR spectra of many of these derivatives was aided by the use of an empirical additivity rule for substituted benzenes[25] shown in the equation

$$\delta C = 128.5 + \sum_i A_i(R) .$$

$A_i(R)$ represents the chemical shift increment for a substituent R in the i^{th} position (C-1, *ortho, meta,* or *para*). By using known empirical parameters for H, OH, CH_3, and

OCH_3[25], it was possible to calculate additivity parameters for R = $-OC(O)NHSF_5$ and $-C(H)=NSF_5$. Comparisons of the experimental ^{13}C NMR values and those

R	A_i C-1	*ortho*	*meta*	*para*
$-O(X)S=NSF_5$[26]	+21.8	−7.1	+2.3	−2.0
$-C(H)=NSF_5$	+4.0	+3.5	+1.6	+7.6
$-OC(O)NHSF_5$	+22.1	−6.3	+1.4	−0.8

calculated using the empirical additivity rule are given in Tables 1, 2. A discussion of the imine carbon resonances in the series of *N*-(pentafluorosulfanyl)imine derivatives has previously been given[20]. The carbonyl carbon chemical shifts in various *N*-pentafluorosulfanyl compounds are given in Table 3 for sake of comparison. The variation observed in these chemical shifts can be explained by mesomeric effects[25].

Table 1. Carbon-13 NMR Data (δ in ppm) of the $SF_5NHC(O)OC_6H_4R$ Derivatives (Values in Parentheses were Obtained Using the Empirical Additivity Rule)

Compound	R	1	2	3	4
$SF_5NHC(O)OC_6H_5$ (**3c**)	H	151.2 (150.6)	122.4 (122.2)	130.4 (129.9)	127.1 (127.7)
1,4-$SF_5NHC(O)OC_6H_4OH$ (**3e**)		143.8 (143.3)	123.3 (123.6)	116.6 (117.2)	156.3 (154.6)
1,4-$[SF_5NHC(O)O]_2C_6H_4$ (**3d**)	$OC(O)NHSF_5$	148.6 (149.8)	123.6 (123.6)	123.6 (123.6)	148.6 (149.8)

Table 2. Carbon-13 NMR Data (δ in ppm) of the $SF_5N=C(H)C_6H_4R$ Derivatives (Values in Parentheses were Obtained Using the Empirical Additivity Rule)

Compound	R	1	2	3	4
$SF_5N=C(H)C_6H_5$ (**12a**)	H	132.5 (132.5)	131.6 (132.0)	130.2 (130.1)	135.7 (136.1)
$SF_5N=C(H)C_6H_4CH_3$-(4) (**12b**)	CH_3	129.8 (129.6)	131.6 (132.0)	130.9 (130.9)	147.1 (145.4)
$SF_5N=C(H)C_6H_4OCH_3$-(4) (**12c**)	OCH_3	124.7 (124.8)	133.8 (133.0)	115.7 (115.7)	166.2 (167.5)

Table 3. Carbonyl Chemical Shifts (ppm) in Various *N*-Pentafluorosulfanyl Compounds

	δC=O		δC=O
$SF_5NHC(O)F$[12]	141.6	$SF_5NHC(O)NHC_6H_5$ (**8c**)	148.6
$SF_5NHC(O)CF_3$[12]	152.8	$SF_5NHC(O)OCH_3$ (**3a**)	151.1
$SF_5NHC(O)(CF_2)_3C(O)NHSF_5$[27]	156.2	$[SF_5NHC(O)OCH_2]_2$ (**3b**)	150.5
$SF_5NHC(O)(CF_2)_4C(O)NHSF_5$[27]	153.7	$SF_5NHC(O)OC_6H_5$ (**3c**)	149.0
$SF_5NHC(O)CH_3$[12]	164.8	1,4-$SF_5NHC(O)OC_6H_4OH$ (**3e**)	149.4
$SF_5NHC(O)CH=CH_2$[12]	159.6	1,4-$[SF_5NHC(O)O]_2C_6H_4$ (**3d**)	149.0
$SF_5NHC(O)C(O)NHSF_5$[12]	156.1	$SF_5NHC(O)SCH_3$ (**5a**)	164.2
$SF_5NHC(O)NHSF_5$[12]	161.2	$SF_5NHC(O)SC_6H_5$ (**5b**)	161.8

This investigation demonstrates synthetic methods which allow the preparation of a large variety of *N*-pentafluorosulfanyl compounds. These methods clearly indicate a very high degree of reactivity for **1** and **2** due to the strong electron-withdrawing effect of the SF_5 group. The spectroscopic data are in agreement with the proposed formulae. Complete infrared and mass spectral data can be requested from the authors.

Experimental Part

An all pyrex high-vacuum system was employed for handling the reactants and products. Infrared spectra: Beckman 20A-X, either gases, pressure 1 to 100 Torr, mulls in either halocarbon or mineral oil, or neat films. – Mass spectra (70 eV): Hitachi Perkin-Elmer RMU-7, Finnigan Model 3200 quadrupole mass spectrometer, or Varian MAT 112, using either a solid inlet probe or a controlled gas flow inlet. – ^{19}F and ^{1}H NMR spectra: JEOL PS-100, JEOL FX-60Q, or Varian EM-390, CCl_3F and $(CH_3)_4Si$, respectively, as internal standards. The method of *Harris* and *Packer*[28] was used to calculate the chemical shifts and coupling constants of the AB_4 portion of the ^{19}F NMR spectra. – ^{13}C NMR spectra: JEOL FX-60Q, $[D_6]$acetone internal standard. – Elemental analyses: Chemistry Department's Perkin-Elmer 240 elemental analyzer. – Melting points: Mel-Temp apparatus, uncorrected.

Pentafluorosulfanyl Isocyanate (**1**): For years we have prepared **1** by the reaction of NSF_3, COF_2, and anhydrous HF and have always passed the reaction contents over NaF prior to distillation[9]. We have now found, however, that if an equimolar reaction mixture of NSF_3, COF_2, and HF is examined without being placed over NaF, the product $SF_5NHC(O)F$ is obtained in high yield[12]. This product is a colorless liquid which spontaneously loses HF when in contact with NaF. The preparation and purification of **1** was therefore greatly simplified by first preparing $SF_5NHC(O)F$ and then removing any excess reactants to the NaF scrubber, while the product was retained in the reaction cylinder kept at -50 to $-10\,^{\circ}C$. The remaining $SF_5NHC(O)F$ was then transferred to a second NaF scrubber from which **1** could be removed essentially pure without further fractionation. Other properties of **1** not previously reported were: ^{13}C NMR: $\delta NCO = 130.7$ (bm).

Pentafluorosulfanyl Isothiocyanate (**2**)

a) *Reaction of SF_5NH_2 with CSClF:* Anhydrous hydrogen fluoride (0.25 ml, 12.5 mmol) and NSF_3 (12.5 mmol) were condensed at $-196\,^{\circ}C$ into a stainless steel reaction cylinder. This mixture was allowed to react at room temperature overnight[12] before condensing in CSClF (9.3 mmol). The reaction mixture was then placed in a $-78\,^{\circ}C$ dry ice slush and allowed to warm slowly to room temperature. After 24 h the reaction mixture was heated to $60-70\,^{\circ}C$ and maintained at that temperature for an additional 60 h. At this time the volatile products were moved to the vacuum line for trap-to-trap distillation. The infrared spectrum of the contents of the trap held at $-105\,^{\circ}C$ displayed a strong NCS stretching frequency at 1950 cm^{-1} compared to the previously reported value of 1955 cm^{-1} for **2**[8]. However, the contents of the $-105\,^{\circ}C$ trap were primarily other by-products from the reaction which could not be separated from **2**. Examination of this mixture by fluorine-19 NMR spectroscopy revealed that the overall yield of **2** was less than one percent.

b) *Reaction of SF_5NH_2 with $CSCl_2$:* The compounds NSF_3 (25 mmol) and HF (1 ml, 50 mmol) were condensed into a stainless steel cylinder and allowed to react at room temperature for 1 h[12] prior to the addition of $CSCl_2$ (25 mmol). The volatile materials were monitored regularly by infrared spectroscopy and after only one day the NCS stretching frequency of **2** at 1950 cm^{-1} had begun to appear. This stretching frequency continued to increase in intensity up to 7 days of reaction time. The reaction mixture was then heated to 60°C overnight with no noticeable increase in the intensity of the NCS stretching frequency. The volatile products were moved to the vacuum line, but again the small quantity of **2** produced could not be completely purified by trap-to-trap distillation. However, mass spectral analysis of a fraction containing **2** gave the following ions: *m/e* = 185 M^+, 166 $[M - F]^+$, and 127 $[SF_5]^+$.

c) *Reaction of $SF_5N=CCl_2$ with P_2S_5:* Phosphorus pentasulfide (2.22 g, 10 mmol) was loaded into a 100 ml glass reaction cylinder in an Ar atmosphere box. After degassing under dynamic vacuum for several days, the P_2S_5 was frozen to −196°C and $SF_5N=CCl_2$ (3.97 g, 17.7 mmol) was condensed into the reaction vessel. Several ml of dry toluene was then syringed into the vessel. After degassing, the mixture was warmed slowly to room temperature and then heated at 120°C for 8 days. At this time the volatile products were moved to the vacuum line for separation by trap-to-trap distillation. After repeated distillation through a −70°C trap to remove the toluene, the product **2** (12.7 mmol) was isolated in 72% yield.

The vapor pressure was determined by using an isoteniscope, and the data [T (°C), p (mm)] were: −44.0, 9.0; −21.5, 37.0; −13.5, 46.0; −7.5, 76.5; 2.0, 129.0. The vapor pressure data treated by least-squares method gave the equation $\ln P$ (mm) = 17.77 − 3574 T^{-1}. The extrapolated boiling point was found to be 48°C compared to the literature value of 47−48°C[8]. The heat of vaporization was calculated to be 7.10 kcal/mol, and the Trouton constant to be 22.1 cal/K-mol. − IR (gas): 2045 (msh), 1950 (vs), 1865 (wsh), 1015 (m), 910 (vs), 840 (vs), 638 (wsh), 600 (vs) cm^{-1}. − Mass spectrum: *m/e* (rel. intensity) = 185 M^+ (21.0), 166 $[M - F]^+$ (10.5), 127 $[SF_5]^+$ (53.8), 108 (4.2), 89 $[SF_3]^+$ (100.0), 82 (7.6), 77 (7.1), 72 (2.1), 70 (37.8), 63 (7.6), 60 (3.4), 58 $[NCS]^+$ (77.1), 51 (12.6). − ^{19}F NMR (toluene): δ_A 69.3 (m), δ_B 83.1 (d of m) (J_{AB} = 158.1 Hz). − ^{13}C NMR: NCSδ 155.6 (bm).

Methyl (Pentafluorosulfanyl)carbamate (**3a**): 3 ml of freshly distilled methanol was transferred by syringe into a glass reaction vessel and frozen to −196°C. After the cylinder was degassed, 5 mmol of **1** was condensed onto the methanol and the mixture was allowed to warm to room temperature in 15 min. After 15 min more, an IR spectrum of the volatile gases showed no **1** to be present. Aspiration of the excess methanol gave **3a** (1.00 g, ≈100%) as water white, sublimable crystals, m.p. 64−65°C. − IR (mull): 3200 (sb), 1770 (s), 970 (s), 895 (s), 600 (m) cm^{-1}. − Mass spectrum: *m/e* (rel. intensity) = 201 M^+ (7.2), 127 $[SF_5]^+$ (92.5), 59 $[C(O)OCH_3]^+$ (100.0). − ^{19}F NMR ([D$_6$]acetone): δ_A 79.4 (m), δ_B 72.0 (d of m) (J_{AB} = 158.7 Hz). − ^1H NMR ($CDCl_3$): NHδ 9.25 (bs), CH_3 4.34 (s). − ^{13}C NMR: C=Oδ 151.1 (s), OCH_3 53.6 (q) ($^1J_{CH}$ = 148.1 Hz).

$C_2H_4F_5NO_2S$ (201.1) Calcd. C 11.95 H 2.00 N 6.97 Found C 12.07 H 1.65 N 6.92

1,2-Ethanediyl Bis[(pentafluorosulfanyl)carbamate] (**3b**): Freshly distilled ethylene glycol (0.19 g, 3.0 mmol) was reacted with 6.0 mmol of **1** in dichloromethane as before, producing the expected diurethane **3b**; white crystalline, sublimable solid, 0.43 g (36%), m.p. 150−151°C. − IR (mull): 3250 (vsb), 1750 (vsb), 930 (vsb), 900 (vsb), 850 (vsb), 600 (ms) cm^{-1}. − Mass spectrum: *m/e* (rel. intensity) = 213 $[SF_5NHC(O)OCHCH_2]^+$ (6.8), 150 $[SF_4NCO]^+$ (100.0), 127 $[SF_5]^+$ (59.7). − ^{19}F NMR ([D$_6$]acetone): δ_A 78.9 (m), δ_B 72.1 (d of m) (J_{AB} = 157.1 Hz). − ^1H NMR (1,4-dioxane): NHδ 10.41 (bs), CH_2 4.32 (s). − ^{13}C NMR: C=Oδ 150.5 (s), OCH_2 64.9 (t) ($^1J_{CH}$ = 150.4 Hz).

$C_4H_6F_{10}N_2O_4S_2$ (400.2) Calcd. C 12.00 H 1.51 N 7.00 Found C 11.93 H 1.75 N 7.20

Phenyl (Pentafluorosulfanyl)carbamate (**3c**): In a typical experiment freshly distilled phenol (0.47 g, 5.0 mmol) was dissolved in 2 ml of dry dichloromethane and transferred by syringe into a glass reaction vessel. The solution was frozen to −196°C and outgassed in vacuo. 5.0 mmol of **1** was then condensed onto the phenol/dichloromethane mixture and the vessel allowed to warm to room temperature. After 30 min the white crystals of **3c** (1.31 g, ≈100%) were precipitated by removing the solvent. The product was then purified by vacuum sublimation at 90°C; m.p. 134–135°C. – IR (mull): 3220 (vsb), 1775 (vsb), 950 (vsb), 885 (vsb), 790 (vsb), 590 (s) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 263 M^+ (4.0), 127 $[SF_5]^+$ (32.0), 94 $[C_6H_5OH]^+$ (100.0). – ^{19}F NMR ([D$_6$]acetone): δ_A 78.2 (m), δ_B 72.0 (d of m) (J_{AB} = 158.7 Hz). – ^1H NMR (1,4-dioxane): NH δ 11.46 (bs), C_6H_5 7.32 (bm). – ^{13}C NMR: C=O δ 149.9 (s), C-1 151.2 (m), C-2 122.4 (d of m) ($^1J_{CH}$ = 164.1 Hz), C-3 130.4 (d of m) ($^1J_{CH}$ = 162.1 Hz), C-4 127.1 (d of m) ($^1J_{CH}$ = 163 Hz).

$C_7H_6F_5NO_2S$ (263.2) Calcd. C 31.95 H 2.30 N 5.32 Found C 31.72 H 1.97 N 5.32

1,4-Phenylene Bis[(pentafluorosulfanyl)carbamate] (**3d**) *and 4-Hydroxyphenyl (Pentafluorosulfanyl)carbamate* (**3e**): Hydroquinone (0.33 g, 3.0 mmol) was allowed to react with 6.0 mmol of **1** in 3 ml acetone in the same fashion as in the previous reactions yielding, after solvent removal, white crystalline material (**3d**) (1.34 g, ≈100%). A small quantity of the monosubstituted derivative **3e** was also isolated by fractional sublimation from a separate reaction carried out in diethyl ether.

3d: m.p. 190–191°C. – IR (mull): 3220 (sb), 1740 (vsb), 970 (vsb), 810 (vsb), 800 (vsb), 600 (s) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 448 M^+ (0.1), 127 $[SF_5]^+$ (69.3), 110 $[HOC_6H_4OH]^+$ (100.0). – ^{19}F NMR ([D$_6$]acetone): δ_A 78.0 (m), δ_B 71.9 (d of m) (J_{AB} = 152.8 Hz). – ^1H NMR (1,4-dioxane): NH δ 10.73 (bs), C_6H_4 7.12 (s). – ^{13}C NMR: C=O δ 149.0 (s), C-1 and -4 148.6 (m), C-2 and -3 123.6 (d of m) ($^1J_{CH}$ = 167 Hz).

$C_8H_6F_{10}N_2O_4S_2$ (448.3) Calcd. C 21.44 H 1.35 N 6.25 Found C 21.53 H 1.05 N 6.14

3e: IR (mull): 3260 (sb), 3160 (sb), 1748 (s), 900 (s), 885 (vs), 835 (vs), 805 (s), 600 (m) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 279 M^+ (1.2), 259 $[M - HF]^+$ (0.7), 127 $[SF_5]^+$ (14.4), 110 (100.0). – ^{19}F NMR ([D$_6$]acetone): δ_A 78.6 (m), δ_B 72.1 (d of m) (J_{AB} = 152.0 Hz). – ^1H NMR (1,4-dioxane): NH δ 8.41 (bs), OH 7.58 (bs), C_6H_4 6.82 (bm). – ^{13}C NMR: C=O δ 149.4 (s), C-1 143.8 (m), C-2 123.3 (d of m) ($^1J_{CH}$ = 163 Hz), C-3 116.6 (d of m) ($^1J_{CH}$ = 160 Hz), C-4 156.3 (m).

$C_7H_6F_5NO_3S$ (279.2) Calcd. C 30.12 H 2.17 N 5.02 Found C 30.52 H 1.95 N 5.02

O-Methyl (Pentafluorosulfanyl)thiocarbamate (**4**): Freshly distilled methanol (0.8 ml) was transferred by syringe into a glass reaction cylinder and frozen to −196°C. After degassing, 0.9 mmol of **2** was condensed onto the methanol and the mixture was allowed to warm to room temperature. The volatile gases were examined by IR spectroscopy after 1 h of reaction time at room temperature and **2** was found not to be present. Removal of the excess methanol gave a white solid product which was purified by vacuum sublimation and analyzed to be **4** (0.17 g, 87%). M.p. 72–73°C. – IR (mull): 3150 (w), 1220 (m), 895 (s), 885 (s), 845 (m), 600 (m) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 217 M^+ (5.3), 185 $[SF_5NCS]^+$ (16.5), 127 $[SF_5]^+$ (28.5), 73 (100.0). – ^{19}F NMR ($CDCl_3$): δ_A 72.8 (m), δ_B 70.8 (d of m) (J_{AB} = 158 Hz). – ^1H NMR ($CDCl_3$): NH δ 8.91 (bs), CH_3 4.20 (s). – ^{13}C NMR: C=S δ 188.3 (s), OCH_3 60.1 (q) ($^1J_{CH}$ = 149.4 Hz).

$C_2H_4F_5NOS_2$ (217.2) Calcd. C 11.06 H 1.86 N 6.45 Found C 10.87 H 1.50 N 6.24

S-Methyl (Pentafluorosulfanyl)thiocarbamate (**5a**): Methanethiol (5.0 mmol) was condensed onto several ml of previously outgassed dry dichloromethane and the solution warmed, shaken to insure uniformity of solution, and refrozen. At this time 5.0 mmol of **1** was condensed onto the thiol solution and the reaction mixture warmed to room temperature within 15 min. Removal of the solvent followed by vacuum sublimation gave **5a** (1.05 g, 97%) as a white, highly crystalline material, m.p. 120–121°C. – IR (mull): 3260 (sb), 1775 (sb), 920 (vsb), 880 (vsb), 850 (vsb), 600 (ms) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 217 M^+ (5.7), 197 (4.7), 127 (54.0), 47

$[CH_3S]^+$ (100.0). – ^{19}F NMR ([D$_6$]acetone): δ_A 78.1 (m), δ_B 73.0 (d of m) (J_{AB} = 158.7 Hz). – ^{1}H NMR ($CDCl_3$): NH δ 9.30 (bs), CH_3 2.75 (s). – ^{13}C NMR: C=O δ 164.2 (s), SCH_3 12.4 (q) ($^1J_{CH}$ = 142.6 Hz).

$C_2H_4F_5NOS_2$ (217.2) Calcd. C 11.06 H 1.86 N 6.45 Found C 11.28 H 1.01 N 6.54

S-Phenyl (Pentafluorosulfanyl)thiocarbamate (**5b**): Freshly distilled thiophenol (5.0 mmol) was added to 2 ml of carbon tetrachloride in a glass reaction cylinder and the cylinder was outgassed. 6.0 mmol of **1** was condensed onto the thiophenol and the cylinder was warmed as before. Removal of the solvent and vacuum sublimation yielded white crystals (1.00 g, 60%), m.p. 130–131 °C. – IR (mull): 3240 (sb), 1700 (sb), 920 (sb), 860 (sb), 600 (m) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 279 M$^+$ (<2.4), 127 (22.6), 110 $[C_6H_5SH]^+$ (100.0). – ^{19}F NMR (1,4-dioxane): δ_A 84.0 (m), δ_B 78.9 (d of m) (J_{AB} = 159.8 Hz). – ^{1}H NMR (1,4-dioxane): NH δ 12.64 (bs), C_6H_5 8.56 (bm). – ^{13}C NMR: C=O δ 161.8 (s), C-1 127.2 (m), C-2 130.0 (d of m) ($^1J_{CH}$ = 159.0 Hz), C-3 136.4 (d of m) ($^1J_{CH}$ = 163.1 Hz), C-4 130.7 (d of m) ($^1J_{CH}$ = 160 Hz).

$C_7H_6F_5NOS_2$ (279.3) Calcd. C 30.11 H 2.17 N 5.02 Found C 30.40 H 1.89 N 5.31

Methyl (Pentafluorosulfanyl)dithiocarbamate (**6**): 1.0 mmol each of **2** and CH_3SH was condensed into a glass reaction vessel at –196 °C. The mixture was then warmed to room temperature. After 1 h the volatile materials were removed under vacuum, and the remaining white, crystalline solid was immediately examined by infrared and mass spectroscopy. The product **6** was found to decompose readily at room temperature; and thus, elemental analysis was not obtained. The NMR data were obtained in a separate experiment where the progress of the reaction was monitored in a sealed tube. In this experiment, 1/2 mmol of each reactant was condensed into an NMR tube. The reaction mixture was then warmed to –50 °C and was placed in the probe of the NMR spectrometer (34 °C) after 15 min of reaction time. The ^{1}H and ^{19}F NMR spectra of **6**, along with unreacted **2** and CH_3SH, were obtained within 30 min. **6**: IR (mull): 3120 (mb), 1215 (mb), 880 (vs), 860 (vs), 838 (vs), 580 (s) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 233 M$^+$ (1.0), 200 $[M - SH]^+$ (83.2), 195 $[SF_5NCS]^+$ (23.0), 127 $[SF_5]^+$ (100.0), 79 $[SSCH_3]^+$ (21.7), 58 $[NCS]^+$ (21.1). – ^{19}F NMR: δ_A 73.5 (m), δ_B 70.7 (d of m) (J_{AB} = 158.1 Hz). – ^{1}H NMR: NH δ 9.50 (bs), CH_3 2.70 (s).

Reaction of **1** *with Water:* 900 mg of water was added to a Kel-F reaction vessel containing 5 ml of dry isopentane. The reactor was sealed and outgassed in the usual fashion and 5.0 mmol of **1** was condensed onto the mixture. The mixture was warmed to –78 °C for 12 h and the volatile gases were removed. Afterwards the Kel-F reactor was opened and several droplets of water were observed. Again the reactor was charged with 900 mg of water and the **1**-isopentane solution condensed onto the frozen outgassed water. The infrared spectrum of the volatile mixture after 12 h at room temperature showed only SF_5NH_2, NSF_3, CO_2, and isopentane to be present. The Kel-F tube did not contain SF_5NHCO_2H and the gases identified above could result only from the thermal decomposition of the (pentafluorosulfanyl)carbamic acid.

Reaction of **2** *with Water:* 1.0 mmol of **2** was condensed at –196 °C into a glass reaction cylinder containing 0.1 ml of water (5.6 mmol). This mixture was then heated in 25 °C increments from 25 to 175 °C while the hydrolysis was monitored by IR spectroscopy at each increment. Only after the mixture has been heated for ≈24 h at 150 °C was hydrolysis observed in the appearance of COS and NSF_3 in the IR spectrum. Even after the mixture had been heated at 175 °C for 4 days some **2** remained unreacted.

N-(Pentafluorosulfanyl)urea (**7**): 3.0 mmol of gaseous ammonia was condensed into an evacuated cylinder containing isopentane (3.0 mmol) and onto this mixture was condensed 3.0 mmol of **1**. The cylinder was placed into a –78 °C slush bath for 12 h and at the end of this time the solvent was removed. The tube was broken open and 7 (0.19 g, 34%) was recovered as a white powder, m.p. 116 – 118 °C. – IR (mull): 3440 (ms), 3240 (sb), 3110 (sb), 1690 (s), 905 (sb), 875 (sb), 600 (mb) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 186 M^+ (8.3), 143 (16.7), 127 (25.0), 44 (100.0). – ^{19}F NMR ([D_6]DMSO): δ_A 81.6 (m), δ_B 72.4 (d of m). – ^1H NMR ([D_6]DMSO/CCl_4): NH δ 8.71 (bs), NH_2 4.60 (bs).

$CH_3F_5N_2OS$ (186.1) Calcd. C 6.45 H 1.62 N 15.05 Found C 6.51 H 1.76 N 15.59

N-Methyl-N'-(pentafluorosulfanyl)urea (**8a**): Methylamine (10.0 mmol) was condensed into a reaction vessel containing 10 mmol of **1** in 5 ml of ether and the solution allowed to warm to room temperature over 12 h. When the solvent was removed, a tan solid remained, which, when washed with dichloromethane, gave a white solid which proved to be **8a** (1.95 g, 98%), m.p. 124 – 126 °C. – IR (mull): 3350 (s), 3180 (s), 1665 (vs), 920 (vsb), 860 (vsb), 600 (s) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 200 M^+ (1.0), 180 (1.0), 127 $[SF_5]^+$ (21.0), 58 (97.0), 28 (100.0). – ^{19}F NMR (1,4-dioxane): δ_A 93.8 (m), δ_B 82.1 (d of m). – ^1H NMR (1,4-dioxane): SF_5NH δ 10.79 (bs), CH_3NH 6.70 (bs); CH_3 3.16 (s) and 3.10 (s).

$C_2H_5F_5N_2OS$ (200.1) Calcd. C 12.00 H 2.52 N 14.00 Found C 11.08 H 2.33 N 14.33

1,1'-(1,2-Ethanediyl)bis[3-(pentafluorosulfanyl)urea] (**8b**): A solution of ethylenediamine (1.0 mmol) in 3.0 mmol of chloroform was introduced into a reaction cylinder and the contents were frozen to – 196 °C and outgassed. 2.0 mmol of **1** was then condensed into the cylinder and the contents were warmed to room temperature over a 12 h period. At this time the solvent was removed and **8b** was collected as a tan solid (0.40 g, 100%), m.p. 193 – 194 °C. – IR (mull): 3360 (s), 3200 (s), 1685 (s), 870 (vsb), 600 (s) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 228 $[SF_5NHC(O)NHCH_2CH_2NH]^+$ (6.0), 199 $[SF_5NHC(O)NHCH_2]^+$ (6.5), 159 $[SF_3NC(O)NCH_2]^+$ (100.0), 128 $[NHC(O)NCH_2CH_2NHCO]^+$ (45.2), 127 (48.3). – ^{19}F NMR ([D_6]DMSO): δ_A 81.7 (m), δ_B 71.9 (d of m). – ^1H NMR ([D_6]DMSO): SF_5NH δ 10.35 (bs), CH_2NH 3.48 (bs); CH_2 3.08 (bs).

$C_4H_8F_{10}N_4O_2S_2$ (398.2) Calcd. C 12.07 H 2.03 N 14.07 Found C 12.36 H 2.31 N 14.79

N-(Pentafluorosulfanyl)-N'-phenylurea (**8c**)[10]: Freshly distilled aniline (5.0 mmol) was added to 3 ml of carbon tetrachloride in a glass reaction cylinder. After the mixture was chilled to – 196 °C and outgassed, 5.0 mmol of **1** was condensed onto the aniline solution. As the mixture was warmed to room temperature, a white solid formed in the cylinder, 1.31 g of **8c** (100%), m.p. 125 – 166 °C (decomposition). – IR (mull): 3300 (s), 3230 (s), 1670 (sb), 940 (vsb), 900 (vsb), 865 (vsb), 800 (m), 590 (s) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 262 M^+ (20.7), 242 (1.4), 222 (3.4), 127 (9.8), 93 $[C_6H_5NH_2]^+$ (100.0). – ^{19}F NMR ([D_6]acetone): δ_A 81.5 (m), δ_B 74.6 (d of m) (J_{AB} = 159.5 Hz). – ^1H NMR (1,4-dioxane): SF_5NH δ 8.77 (b), C_6H_5 and C_6H_5NH 8.02 to 8.60 (bm). – ^{13}C NMR: C=O δ 148.6 (s), C-1 139.2, C-2 120.5, C-3 129.8, C-4 124.5.

$C_7H_7F_5N_2OS$ (262.2) Calcd. C 32.07 H 2.69 N 10.68 Found C 32.03 H 2.44 N 10.92

1,1'-(1,4-Phenylene)bis[3-(pentafluorosulfanyl)urea] (**8d**): 2.0 mmol of **1** was condensed onto a frozen, degassed solution containing recrystallized *p*-phenylenediamine (1.0 mmol) and chloroform (5 ml). The resulting mixture was held at – 78 °C for 12 h. A pale greenish yellow solid was observed in the liquid at this time. The solid turned into a dark brown powder as the solvent was removed, yield 0.39 g. Since the parent diamine is very susceptible to oxidative degradation the brown coloration of this compound is thought to be due to a slight amount of a decomposition product. **8d**: the brown compound shrank 10% in volume during heating but did not melt below 260 °C. – IR (mull): 3340 (sb), 1680 (vsb), 950 (vsb), 885 (vsb), 865 (vsb), 600 (vsb) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 366 [M – 4 HF]$^+$, 149 (58.8), 127 $[SF_5]^+$

(82.3), 104 (100.0), 85 (100.0). – ^{19}F NMR (1,4-dioxane): δ_A 74.6 (m), δ_B 67.2 (d of m) (J_{AB} = 153 Hz). – ^{1}H NMR (1,4-dioxane): C_6H_4 δ 7.92 (d), SF_5NH 5.64 (bs), C_6H_4NH 4.16 (bs).

$C_8H_8F_{10}N_4O_2S_2$ (446.3) Calcd. C 21.53 H 1.81 N 12.55 Found C 25.00 H 1.73 N 12.55

1,1'-(Methylenedi-4,1-phenylene)bis[3-(pentafluorosulfanyl)urea] (**8e**) was prepared by the condensation of 2.0 mmol of **1** onto a solution of 4,4'-methylenedianiline (1.0 mmol) dissolved in chloroform (5 ml) at –196°C. The mixture was warmed to room temperature slowly over a period of 4 h. Removal of the solvent left a pale tannish powder, yield 0.54 g (≈100%), m.p. 165–166°C. – IR (mull): 3311 (sb), 1680 (s), 905 (sh), 875 (sb), 810 (w), 600 (s) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 456 [M – 4 HF]$^+$ (20.0), 223 (21.0), 150 (42.1), 149 (100.0), 127 $[SF_5]^+$ (23.1). – ^{19}F NMR ([D$_6$]DMSO): δ_A 79.7 (m), δ_B 71.3 (d of m). – ^{1}H NMR ([D$_6$]DMSO): SF_5NH δ 10.60 (bs), C_6H_4 7.14 (vb), C_6H_4NH 4.10 (bs) or 3.84 (bs), CH_2 3.84 (bs) or 4.10 (bs).

$C_{15}H_{14}F_{10}N_4O_2S_2$ (536.4) Calcd. C 33.59 H 2.63 N 10.44 Found C 30.73 H 2.79 N 9.71

N-(Pentafluorosulfanyl)-N'-phenylthiourea (**9**): Diethyl ether (5 ml) and 1.67 mmol **2** were condensed at –196°C into a 75 ml glass reaction cylinder containing freshly distilled aniline (0.15 ml, 1.67 mmol). The mixture was warmed to room temperature and allowed to stand for 48 h. The volatile products were removed under vacuum leaving a pale tan solid. The vessel was then connected to a detachable U-trap held at –196°C and was heated to 80°C in order to sublime the product. The initial fraction, a white, crystalline solid, was found to be **9** (0.025 g, 5.4%). Further attempts at isolating more of the product resulted in thermal decomposition which produced elemental sulfur. IR (mull): 3340 (w), 3220 (m), 1690 (m), 870 (s), 835 (m), 580 (m) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 278 M$^+$ (<0.1), 245 [M – HS]$^+$ (5.7), 244 $[M - H_2S]^+$ (47.5), 127 $[SF_5]^+$ (15.7), 117 (100.0). – ^{19}F NMR ([D$_6$]DMSO): δ_A 103.8 (m), δ_B 81.1 (d of m) (J_{AB} = 161 Hz). – ^{1}H NMR ([D$_6$]DMSO): SF_5NH δ 8.30 (b), C_6H_5 7.3 (bm), C_6H_5NH 7.2 (b).

N,N-Diethyl-N'-(pentafluorosulfanyl)urea (**10a**): This reaction had to be repeated several times before sufficient product could be obtained for characterization. The first attempt was carried out in the normal fashion by putting freshly distilled diethylamine (5.0 mmol) into a glass reaction vessel along with dry isopentane (3 ml). The mixture was frozen, outgassed, and 5.0 mmol of **1** was condensed onto the solution which was then held at –78°C for several hours before being allowed to warm slowly to room temperature. A tan powder left after removal of the solvent was hydrolyzed immediately upon being removed from the reaction vessel. The urea **10a** was prepared successfully by allowing the reaction of 1.0 mmol of the amine, 1.0 mmol of **1**, in 0.25 ml of [D$_6$]DMSO (containing 0.01 ml of TMS and Freon 11) to proceed in a sealed NMR tube. The NMR spectra were taken on the sealed tube. The tube was then broken, evacuated, and a small aliquot removed and stored in an air tight sample vial until the mass spectrum was taken. This was accomplished within 12 h of sample preparation. All attempts to get a distinct infrared spectrum of this urea failed. Mass spectrum: *m/e* (rel. intensity) = 222 [M – HF]$^+$ (3.8), 150 $[SF_4NCO]^+$ (70.8), 127 $[SF_5]^+$ (9.2), 100 $[C(O)N(C_2H_5)_2]^+$ (38.5), 72 $[N(C_2H_5)_2]^+$ (46.1), 30 $[HNCH_3]^+$ (100.0). – ^{19}F NMR ([D$_6$]DMSO): δ_A 79.3 (m), δ_B 69.9 (d of m) (J_{AB} = 153 Hz). – ^{1}H NMR ([D$_6$]DMSO): SF_5NH δ 8.36 (bs), CH_2 3.28 (q), CH_3 1.18 (t).

N-(Pentafluorosulfanyl)-1-piperidinecarboxamide (**10b**) was prepared by condensing 2.0 mmol of **1** into a glass reaction vessel containing piperidine (2.0 mmol) and isopentane (3 ml) and the reaction vessel allowed to warm slowly to room temperature. The highly moisture-sensitive urea was isolated as a tan solid. Mass spectrum: *m/e* (rel. intensity) = 211 (40.0), 210 (25.0), 127 $[SF_5]^+$ (26.5), 125 $[NHC(O)NC_5H_{10}]^+$ (65.0), 83 $[NC_5H_9]^+$ (100.0). – ^{19}F NMR ([D$_6$]DMSO):

δ_A 80.8 (m), δ_B 70.7 (d of m) (J_{AB} = 153.2 Hz). – ^1H NMR ([D$_6$]DMSO): $SF_5NH\delta$ 8.16 (b), (CH_2-2,6) 3.24 – 3.52 (bm), (CH_2-3,4,5) 1.40 – 1.68 (bm).

$C_6H_{11}F_5N_2OS$ (254.2) Calcd. C 28.35 H 4.36 N 11.02 Found C 26.99 H 4.58 N 10.80

N'-(Pentafluorosulfanyl)-N,N-diphenylurea (**10c**): 3.0 mmol of **1** was condensed into an outgassed cylinder containing diphenylamine (3.0 mmol) and chloroform (3 ml). When the reaction mixture was warmed slowly to room temperature, a white solid appeared almost immediately upon its reaching room temperature, yield 1.01 g (≈100%), m.p. 93 – 94°C (decomposition). – IR (mull): 3230 (mb), 1690 (s), 910 (vsb), 880 (vsb), 825 (vsb), 590 (s) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 338 M^+ (20.0), 318 $[M - HF]^+$ (10.1), 169 $[(C_6H_5)_2NH]^+$ (100.0), 127 (2.6). – ^{19}F NMR ([D$_6$]DMSO): δ_A 78.1 (m), δ_B 70.6 (d of m) (J_{AB} = 152.0 Hz). – ^1H NMR ([D$_6$]DMSO): $SF_5NH\delta$ 8.20 (bs), C_6H_5 7.31 (bm).

$C_{13}H_{11}F_5N_2OS$ (338.3) Calcd. C 46.16 H 3.28 N 8.28 Found C 46.33 H 3.45 N 8.46

N-(Pyridiniocarbonyl)-N-(pentafluorosulfanyl)amide (**11a**): Dry ether and 2.0 mmol of **1** were condensed at – 196°C into a glass reaction cylinder containing freshly distilled, degassed pyridine (0.16 ml; 2.0 mmol). The reaction mixture was allowed to warm slowly to room temperature by which time a solid precipitate had formed. The volatile products were then removed under vacuum and the remaining solid was transferred to a vacuum sublimator. Sublimation at room temperature gave a white solid identified as **11a** (0.33 g, 67%). The zwitterion was found to be somewhat unstable with respect to decomposition back to the starting materials. It was found to be most stable when stored sealed under its own pressure. Mass spectral analysis gave peaks corresponding only to the two starting materials. M.p. 76 – 78°C. – IR (mull): 3140 (m), 1770 (sb), 895 (sb), 835 (vsb), 585 (w) cm^{-1}. – ^{19}F NMR ([D$_6$]DMSO): δ_A 99.4 (m), δ_B 77.3 (d of m) (J_{AB} = 158.7 Hz). – ^1H NMR ([D$_6$]DMSO): 2,6-Hδ 9.21 (bd), 4-H 8.46 (bt), 3,5-H 7.91 (bt).

$C_6H_5F_5N_2OS$ (248.2) Calcd. C 29.04 H 2.03 N 11.29 Found C 28.73 H 2.01 N 11.46

N-(Triethylammoniocarbonyl)-N-(pentafluorosulfanyl)amide (**11b**): In a typical reaction freshly distilled triethylamine (0.28 ml; 2.00 mmol) was syringed into a 75 ml glass reaction cylinder, frozen to – 196°C and degassed. While the vessel was maintained at – 196°C, dry ether (5 ml) and 2.0 mmol of **1** were condensed in. This mixture was allowed to warm slowly to room temperature, by which time a white precipitate had formed. The volatile products were then removed under vacuum and the crude solid product (0.45 g) was transferred to a vacuum sublimator. This zwitterion was found to decompose readily at room temperature to the starting materials; therefore, analyses had to be completed immediately after synthesis and sublimation. Mass spectral analysis again gave peaks corresponding only to the two starting materials. IR (mull): 2995 (m), 1770 (s), 887 (sb), 833 (vsb), 588 (m) cm^{-1}. – ^{19}F NMR ($CDCl_3$): δ_A 95.0 (m), δ_B 74.4 (d of m) (J_{AB} = 157 Hz). – ^1H NMR ($CDCl_3$): $CH_2\delta$ 3.08 (q), CH_3 1.14 (t) (J_{HH} = 7.5 Hz).

$C_7H_{15}F_5N_2OS$ (270.3) Calcd. C 31.11 H 5.59 N 10.37 Found C 30.36 H 6.11 N 9.17

N-(Pentafluorosulfanyl)-1-phenylmethanimine (**12a**)[11]: The first attempt to prepare this imine was carried out by condensing 5.0 mmol of **1** onto freshly distilled benzaldehyde (5.0 mmol) dissolved in several ml of ether. The mixture was warmed to room temperature and allowed to stand for 2 days. Examination of the gases over the reaction mixture by IR spectroscopy revealed that no reaction had occurred. The experiment was repeated under the same conditions except that no solvent was present, and again no reaction occurred. At this point the reaction mixture was heated to 60°C for 36 h, and the imine **12a** (0.80 g, 69%) was isolated following vacuum distillation as a clear liquid of low volatility (v.p. <1 Torr at 25°C). IR (film): 1630 (vs), 900 – 825 (vsb), 595 (vs) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 231 M^+ (20.2), 212

$[M - F]^+$ (1.2), 127 $[SF_5]^+$ (12.2), 77 $[C_6H_5]^+$ (100.0). – ^{19}F NMR ([D$_6$]acetone): δ_A 80.9 (m), δ_B 59.2 (d of m) (J_{AB} = 154 Hz). – ^1H NMR (CCl_4): N=CH δ 8.70 (s), C_6H_5 7.80 (bm). – ^{13}C NMR: N=C δ 171.3 (d of qu) ($^1J_{CH}$ = 166, J_{SF_4C} = 9.8 Hz), C-1 132.5 (m), C-2 131.6 (d of m) ($^1J_{CH}$ = 163.1 Hz), C-3 130.2 (d of m) ($^1J_{CH}$ = 163.1 Hz), C-4 135.7 (d of m) ($^1J_{CH}$ = 163.1 Hz).

$C_7H_6F_5NS$ (231.2) Calcd. C 36.37 H 2.62 N 6.06 Found C 36.64 H 2.38 N 6.05

1-(4-Methylphenyl)-N-(pentafluorosulfanyl)methanimine (**12b**) was prepared in the same way as the previous one, by condensing 5.0 mmol of **1** onto 4-methylbenzaldehyde (5.0 mmol) and allowing the contents to warm to room temperature. In this case the reaction proceeded very slowly at room temperature. Therefore, the reaction mixture was heated at 60°C for 36 h in order to complete the reaction. Removal of the CO_2 followed by vacuum distillation left the imine (1.18 g, 96%) as a clear liquid of low vapor pressure (v.p. <1 Torr at 25°C). IR (film): 1605 (vs), 900–825 (vsb), 595 (vs) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 245 M^+ (43.3), 226 $[M - F]^+$ (1.9), 127 (9.4), 118 $[M - SF_5]^+$ (43.4), 91 $[C_7H_7]^+$ (100.0). – ^{19}F NMR ([D$_6$]acetone): δ_A 81.5 (m), δ_B 59.4 (d of m) (J_{AB} = 152.7 Hz). – ^1H NMR (CH_2Cl_2): N=CH δ 8.75 (s), C_6H_4 7.61 and 7.17 (d of d), CH_3 2.34 (s). – ^{13}C NMR: N=C δ 171.0 (d of qu) ($^1J_{CH}$ = 166, J_{SF_4C} = 9.8 Hz), C-1 129.8 (m), C-2 131.6 (d of m) ($^1J_{CH}$ = 167 Hz), C-3 130.9 (d of m) ($^1J_{CH}$ = 167 Hz), C-4 147.1 (m), CH_3 21.9 (q) ($^1J_{CH}$ = 127 Hz).

$C_8H_8F_5NS$ (245.2) Calcd. C 39.19 H 3.29 N 5.71 Found C 39.82 H 3.19 N 5.27

1-(4-Methoxyphenyl)-N-(pentafluorosulfanyl)methanimine (**12c**): As with the first two imines, a mixture of 4-methoxybenzaldehyde and **1** (5.0 mmol each) was allowed to warm to room temperature. After heating at 60°C for 36 h, the volatile materials were removed and the residue (v.p. <1 Torr at 25°C) was distilled into a detachable U-trap held at –196°C and identified as **12c** (0.93 g, 3.56 mmol, 71%). – IR (film): 1605 (vs), 890–830 (vsb), 595 (vs) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 261 M^+ (75.0), 242 $[M - F]^+$ (2.5), 134 $[M - SF_5]^+$ (100.0), 127 (20.0), 107 $[C_6H_4OCH_3]^+$ (63.8). – ^{19}F NMR ([D$_6$]acetone): δ_A 82.8 (m), δ_B 60.0 (d of m) (J_{AB} = 155.2 Hz). – ^1H NMR (isopentane): N=CH δ 8.77 (s), C_6H_4 7.73 and 6.87 (d of d), CH_3 3.76 (s). – ^{13}C NMR: N=C δ 170.2 (d of qu) ($^1J_{CH}$ = 167, J_{SF_4C} = 9.8 Hz), C-1 124.7 (m), C-2 133.8 (d of m) ($^1J_{CH}$ = 163 Hz), C-3 115.8 (d of m) ($^1J_{CH}$ = 168 Hz), C-4 166.2 (m), OCH_3 56.1 (q) ($^1J_{CH}$ = 145 Hz).

. $C_8H_8F_5NS$ (261.2) Calcd. C 36.79 H 3.09 N 5.36 Found C 37.68 H 2.91 N 5.09

N-(Pentafluorosulfanyl)-2-furanmethanimine (**12d**): The reaction of 5.0 mmol of **1** with 2-furancarbaldehyde (5.0 mmol) was carried out at room temperature for 36 h, at which time the volatile materials consisting primarily of CO_2 were removed under vacuum. The resulting liquid residue (v.p. <1 Torr at 25°C) was distilled into a detachable U-trap held at –196°C to give **12d** (0.81 g; 73%) as a pale yellow liquid, v.p. <1 Torr at 25°C. – IR (film): 1620 (vsb), 900–825 (vsb), 595 (vs) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 221 M^+ (14.3), 202 $[M - F]^+$ (2.8), 127 (25.7), 94 $[M - SF_5]^+$ (54.3), 39 $[C_3H_3]^+$ (100.0). – ^{19}F NMR ([D$_6$]acetone): δ_A 81.8 (m), δ_B 60.1 (d of m) (J_{AB} = 156.4 Hz). – ^1H NMR ($CDCl_3$): N=CH δ 9.62 (s), 5-H 7.80 (m), 3-H 7.28 (m), 4-H 6.62 (m). – ^{13}C NMR: N=C δ 157.6 (d of qu) ($^1J_{CH}$ = 174, J_{SF_4C} = 10.5 Hz), C-2 148.0 (m), C-3 127.1 (d of m) ($^1J_{CH}$ = 182 Hz), C-4 114.6 (d of m) ($^1J_{CH}$ = 180 Hz), C-5 151.2 (d of m) ($^1J_{CH}$ = 207 Hz).

$C_5H_4F_5NOS$ (221.1) Calcd. C 27.16 H 1.82 N 6.33 Found C 28.80 H 1.73 N 6.04

N,N-Dimethyl-N'-(pentafluorosulfanyl)formamidine (**13a**)

a) *Reaction of* **1** *with N,N-Dimethylformamide:* 3.0 mmol of **1** was condensed onto freshly distilled *N,N*-dimethylformamide (0.21 g; 2.9 mmol) and the resulting mixture allowed to react at room temperature for 36 h. The volatile materials consisting primarily of CO_2 and unreacted **1** were removed under vacuum. The resulting liquid of very low volatility was then distilled into a detachable U-trap held at –196°C to give **13a** (0.475 g, 83%).

b) *Reaction of* **2** *with N,N-Dimethylformamide:* Freshly distilled *N,N*-dimethylformamide (2.9 mmol) was transferred to a 75 ml glass reaction cylinder, frozen to –196°C, and degassed prior to addition of 2.9 mmol of **2**. The resulting mixture was warmed to room temperature and allowed to react for 36 h. Examination of the gases by IR spectroscopy showed that COS had been produced and no **2** remained in the cylinder. The gases were removed under vacuum and the remaining liquid of low volatility was distilled into a detachable U-trap held at –196°C: **13a** (0.45 g, 78%), v.p. <1 Torr at 25°C. – IR (film): 1638 (vsb), 903 (vs), 835 (vsb), 580 (s) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 198 M^+ (14.3), 179 $[M - F]^+$ (11.4), 127 (16.4), 71 $[M - SF_5]^+$ (33.6), 44 $[N(CH_3)_2]^+$ (100.0). – ^{19}F NMR ($CDCl_3$): δ_A 93.1 (m), δ_B 70.6 (d of m) (J_{AB} = 156.5 Hz). – ^1H NMR ($CDCl_3$): N=CH δ 8.02 (s), NCH_3 3.17 (s) and 2.92 (s). – ^{13}C NMR (neat): N=C δ 158.3 (d of qu) ($^1J_{CH}$ = 188.5, J_{SF_4C} = 9.8 Hz), CH_3 40.3 (q) and 33.6 (q) ($^1J_{CH}$ = 139 Hz).

$C_3H_7F_5N_2S$ (198.2) Calcd. C 18.18 H 3.56 N 14.14 Found C 18.38 H 3.27 N 14.18

N-Methyl-N'-(pentafluorosulfanyl)-N-phenylformamidine (**13b**): 5.0 mmol each of **1** and *N*-methylformanilide was allowed to react at 60°C for 36 h. The product was isolated in 90% yield as a clear, viscous liquid following vacuum distillation, v.p. <1 Torr at 25°C. – IR (film): 1620 (vs), 890 (vs), 870–825 (vsb), 585 (vs) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 260 M^+ (9.7), 241 $[M - F]^+$ (7.7), 133 $[M - SF_5]^+$ (100.0), 127 (20.5), 106 $[N(CH_3)C_6H_5]^+$ (67.9). – ^{19}F NMR ([D_6]acetone): δ_A 91.7 (m), δ_B 70.5 (d of m) (J_{AB} = 153.7 Hz). – ^1H NMR (hexane): N=CH δ 8.20 (s), C_6H_5 7.16 (bm), CH_3 3.24 (s). – ^{13}C NMR: N=C δ 158.7 (d of qu) ($^1J_{CH}$ = 183.6, J_{SF_4C} = 10.7 Hz), C-1 144.6 (m), C-2 123.2 (d of m) ($^1J_{CH}$ = 160.2 Hz), C-3 130.7 (d of m) ($^1J_{CH}$ = 162.1), C-4 127.9 (d of m) ($^1J_{CH}$ = 161.1 Hz), CH_3 35.6 (q) ($^1J_{CH}$ = 141 Hz).

$C_8H_9F_5N_2S$ (260.2) Calcd. C 36.92 H 3.49 N 10.76 Found C 36.68 H 2.96 N 10.78

N,N-Dimethyl-N'-(pentafluorosulfanyl)acetamidine (**14**): Freshly distilled *N,N*-dimethylacetamide (0.50 g; 5.75 mmol) was transferred to a glass reaction cylinder, frozen to –196°C, and degassed prior to the addition of 5.8 mmol of **1**. After a 36 h reaction period the volatile materials, consisting primarily of CO_2, were removed under vacuum. The remaining solid residue was sublimated into a detachable U-trap held at –196°C to give **14** (0.94 g, 77%), m.p. 29–30°C. – IR (film): 1565 (vs), 860–820 (vs), 598 (m) cm^{-1}. – Mass spectrum (50 eV): *m/e* (rel. intensity) = 212 M^+ (2.5), 193 $[M - F]^+$ (5.6), 127 (21.2), 44 $[N(CH_3)_2]^+$ (100.0). – ^{19}F NMR (Freon 113): δ_A 97.9 (m), δ_B 76.5 (d of m) (J_{AB} = 155.6 Hz). – ^1H NMR (Freon 113): $N(CH_3)_2$ δ 3.06 (s), CH_3 2.30 (s). – ^{13}C NMR: N=C δ 165.3 (qu) (J_{SF_4C} = 4.9 Hz), $N(CH_3)_2$ 39.4 (q) ($^1J_{CH}$ = 138 Hz), CH_3 18.8 (q) ($^1J_{CH}$ = 131 Hz).

$C_4H_9F_5N_2S$ (212.2) Calcd. C 22.64 H 4.25 N 13.21 S 15.09
Found C 22.33 H 3.82 N 12.40 S 15.19

S,S-Dimethyl-N-(pentafluorosulfanyl)sulfilimine (**15**)[11]: In several different experiments freshly distilled dimethyl sulfoxide was put into a glass reaction cylinder and outgassed and then appropriate amounts of **1** were condensed onto the sulfoxide. In each experiment, run at room temperature, a white solid formed after several hours. The only absorptions observed in the IR spectra of the gases were due to CO_2. However, every attempt to characterize this solid met with failure. Identification of the product was finally obtained by allowing the reaction of dimethyl sulfoxide (1.0 mmol) and **1** (1.0 mmol) in ether (2.0 mmol) to occur in a sealed NMR tube. After the NMR spectra of $SF_5N=S(CH_3)_2$ were obtained, the NMR tube was broken in a special tube breaker on the vacuum line allowing the volatile materials to be removed. Attempts to characterize the remaining white paste failed, indicating that the product was thermally unstable. In another NMR tube experiment where [D$_6$]DMSO was used as a solvent, the mass spectrum of the reaction mixture taken within an hour of product formation showed four peaks attributable to $SF_5N=S(CD_3)_2$: *m/e* = 209 $[SF_5N=S(CD_3)_2]^+$, 207 $[SF_5N=S(CD_3)CD_2]^+$, 191 $[SF_5N=SCD_3]^+$, 190 $[SF_4N=S(CD_3)_2]^+$. – **15**: ^{19}F NMR (ether): δ_A 95.3 (m), δ_B 79.6 (d of m) (J_{AB} = 150 Hz). – ^{1}H NMR (ether): CH_3 δ 2.70 (s).

2-Acetyl-3-oxo-N-(pentafluorosulfanyl)butanamide (**16**): 5.0 mmol of freshly distilled acetylacetone was transferred by syringe into a glass reaction vessel containing 20 mmol of dichloromethane and the contents were frozen and outgassed. 5.0 mmol of **1** was condensed onto the mixture and the mixture allowed to warm to room temperature. After 5 min a white crystalline material formed in the cylinder. After standing for an hour removal of the solvent afforded 5.0 mmol of **16** as a white crystalline, sublimable compound, m.p. 112 – 113 °C. – IR (mull): 3160 (sb), 1690 (vsb), 952 – 860 (vsb), 590 (ms), 575 (m)$^{-1}$. – Mass spectrum: *m/e* (rel. intensity)

Table 4. NMR Spectra of the Keto and Enol Forms of **16** (δ in ppm, *J* in Hz)

^{19}F	CDCl$_3$		[D$_6$]DMSO
enol form I	δ_A = 74.7 (m) δ_B = 73.3 (d of m) J_{AB} = 159.2	keto form	δ_A = 81.5 (m) δ_B = 72.6 (d of m) J_{AB} = 160.5
enol form II	δ_A = 73.9 δ_B = 70.7 (d of m) J_{AB} = 158.9	enol form II	δ_A = 80.6 (m) δ_B = 71.6 (d of m) J_{AB} = 159.0
^{1}H	**CDCl$_3$**		**[D$_6$]DMSO**
enol form I	CH_{3a} 2.52 (s) CH_{3b} 2.56 (s) NH 13.56 (bs) OH 17.08 (s)	keto form	CH_3 2.17 (s) CH 5.03 (s) NH unresolved
enol form II	CH_3 2.05 (s) NH 8.60 (bs) OH 16.40 (bs)	enol form II	CH_3 2.17 (s) NH 12.60 (bs) OH 16.10 (bs)
^{13}C	**CDCl$_3$**		**[D$_6$]DMSO**
enol form I	C-6 26.5 C-4 32.6 C-2 106.4 C-1 168.2 C-5 193.1 C-3 199.6	keto form	C-4 30.0 C-2 72.1 (qu) (J_{SF_4C} = 2.9) C-1 160.4 C-3 199.5
enol form II	C-4 23.6 C-2 111.8 (J_{SF_4C} unresolved) C-1 161.3 C-3 191.5	enol form II	C-4 23.3 C-2 112.2 (qu) (J_{SF_4C} = 2.9) C-1 161.3 C-3 190.8

= 269 M^+ (0.7), 142 $[NHC(O)CH(COCH_3)_2]^+$ (2.4), 127 (9.3), 98 $[C(COCH_3)_2]^+$ (15.0), 43 (100.0); NMR spectra s. Table 4.

$C_6H_8F_5NO_3S$ (269.2) Calcd. C 26.77 H 3.00 N 5.20 Found C 26.79 H 3.00 N 5.38

2,2,2-Trimethoxy-N-(pentafluorosulfanyl)acetamide (**17**) *and Methyl Methyl(pentafluorosulfanyl)carbamate* (**18**): 10.0 mmol of freshly distilled trimethyl orthoformate was put into a glass reaction vessel, frozen with liquid nitrogen and outgassed. Isopentane (10 mmol) and 10 mmol of **1** were condensed into the vessel and the contents were held at −78 °C for 12 h. The vessel was then brought to room temperature for 4 h. The IR spectrum of the gases from the reaction showed isopentane and methyl formate. Removal of the solvent left a crystalline material and a liquid (v.p. <1 Torr at 25 °C) which were identified as **17** and **18**, respectively.

17: m.p. 68–69 °C. – IR (mull): 3200 (vsb), 1750 (vsb), 920 (vsb), 820 (vsb), 595 (s) cm^{-1}. – Mass spectrum: *m/e* (rel. intensity) = 275 M^+ (8.7), 244 $[M - OCH_3]^+$ (4.5), 224 $[M - OCH_3, - HF]^+$ (3.1), 127 $[SF_5]^+$ (100.0), 105 $[C(OCH_3)_3]^+$ (30.0). – ^{19}F NMR ($CDCl_3$): δ_A 71.6 (m), δ_B 67.3 (d of m) (J_{AB} = 147.5 Hz). – ^1H NMR ($CDCl_3$): NH δ 8.22 (bs), OCH_3 3.80 (s). – ^{13}C NMR: OCH_3 δ 53.6.

18: v.p. <1 Torr at 25 °C. – Mass spectrum: *m/e* (rel. intensity) = 215 M^+ (1.4), 184 $[M - OCH_3]^+$ (14.3), 170 $[SF_5N(CH_3)CH_2]^+$ (30.7), 127 $[SF_5]^+$ (64.3), 59 $[C(O)OCH_3]^+$ (100.0). – ^{19}F NMR (neat): δ_A 73.0 (m), δ_B 61.2 (d of m) (J_{AB} = 147.5 Hz). – ^1H NMR (neat): OCH_3 δ 3.82 (s), NCH_3 3.47 (s).

1) Current Address: Department of Chemistry, Clemson University, Clemson, South Carolina 29631, U.S.A.
2) *S. Patai,* The Chemistry of Cyanates and Their Thio Derivatives, Part 1/2, John Wiley and Sons, New York 1977.
3) *R. J. Delasquale,* J. Fluorine Chem. **8**, 311 (1976).
4) *L. Willms, D. Günther,* and *T. Hüttelmaier,* Chem. Ber. **115**, 2943 (1982).
5) *B. A. Arbuzov* and *N. N. Zobova,* Synthesis **1982**, 433, and references within.
6) *W. Lutz* and *W. Sundermeyer,* Chem. Ber. **112**, 2158 (1979).
7) *W. Kiemstedt* and *W. Sundermeyer,* Chem. Ber. **115**, 919 (1982).
8) *C. W. Tullock, D. D. Coffman,* and *E. L. Muetterties,* J. Am. Chem. Soc. **86**, 357 (1964).
9) *L. C. Duncan, T. C. Rhyne, A. F. Clifford, R. E. Shaddix,* and *J. W. Thompson,* J. Inorg. Nucl. Chem. Supplement **1976**, 33.
10) *R. E. Shaddix,* Masters Thesis, Virginia Polytechnic Institute and State University 1974.
11) *A. F. Clifford* and *A. Shanzer,* J. Fluorine Chem. **7**, 65 (1976).
12) *J. S. Thrasher, J. L. Howell,* and *A. F. Clifford,* Inorg. Chem. **21**, 1616 (1982).
13) *E. Kuhle, B. Anders, E. Klauke, H. Tarnow,* and *G. Zumach,* Angew. Chem. **81**, 18 (1969); Angew. Chem., Int. Ed. Engl. **8**, 20 (1969).
14) *P. Raizman* and *Q. E. Thompson* in the Analytical Chemistry of Sulfur and Its Compounds (*J. Karchmer*), Part II, Chapter 10, Wiley-Interscience, New York 1972.
15) *M. A. Baldwin, A. M. Kirkier, A. G. London,* and *A. Maccoll,* Org. Mass Spectrum. **4**, 81 (1970).
16) *R. H. Shapiro, J. W. Serum,* and *A. M. Duffield,* J. Org. Chem. **33**, 243 (1968).
17) *R. Appel* and *M. Montenarh,* Chem. Ber. **110**, 2368 (1977).
18) *H. W. Roesky* and *G. Sidiropoulos,* Chem. Ber. **110**, 3730 (1977).
19) *C. King,* J. Org. Chem. **25**, 352 (1960).
20) *J. S. Thrasher* and *A. F. Clifford,* J. Fluorine Chem. **19**, 411 (1982).
21) *K. Clauß, H.-J. Friedrich,* and *H. Jensen,* Liebigs Ann. Chem. **1974**, 561.
22) *H. v. Brachel* and *R. Merten,* Angew. Chem. **74**, 872 (1962); Angew. Chem., Int. Ed. Engl. **1**, 592 (1962).
23) *H. Biener,* Liebigs Ann. Chem. **686**, 102 (1965).
24) *R. Graf,* Angew. Chem. **80**, 179 (1968); Angew. Chem., Int. Ed. Engl. **7**, 172 (1968).
25) *F. W. Wehrl* and *T. Wirthlin,* Interpretation of Carbon-13 NMR Spectra, Chapter 2, Heyden & Son, London 1978.
26) *J. S. Thrasher, G. A. Iannaccone, N. S. Hosmane, D. E. Maurer,* and *A. F. Clifford,* J. Fluorine Chem. **18**, 537 (1981).
27) *J. S. Thrasher, J. L. Howell,* and *A. F. Clifford,* J. Fluorine Chem., in press.
28) *R. K. Harris* and *K. J. Packer,* J. Chem. Soc. **1961**, 4736.

[250/83]