

PREPARATION AND PROPERTIES OF
N-PENTAFLUOROSULFANYLAMIDO DERIVATIVES

by

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Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE
in
Chemistry

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August, 1974
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ACKNOWLEDGEMENTS

I wish to thank Dr. Alan F. Clifford for his advice during the project.

I wish to thank Mr. Tom Glass for the many NMR spectra obtained.

To my wife, I express my appreciation for her continual support.

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CHAPTER I

THE ATTEMPTED PREPARATION OF N,N'-BIS(PENTAFLUOROSULFANYL)- PYRIMIDINE DERIVATIVES

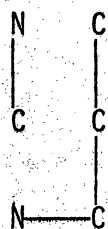
INTRODUCTION

The chemistry of pyrimidines has become very important over the years as a result of the relationship between pyrimidines and nucleic acids having been established (1) (2) (3). The di- and trioxypyrimidines, uracils and barbiturates, are used extensively as synthetic drugs. The most biologically active barbiturates, 5,5-diakylbarbiturates, have proven to be very versatile depressants, producing effects from mild sedation to deep anesthesia. Most N-substituted derivatives have proven to have much less activity, but none have ever been studied with a group of such high electronegativity or large size as the SF₅ on the nitrogen. One obvious effect would be a decrease in the basicity of the nitrogen. Another possible effect would be a decrease in the solubility in lipids. This decreased solubility could be advantageous or disadvantageous depending on the biological effect shown. Once the biological properties exhibited by the SF₅ group are determined, it could find extensive use, just as the CF₃ group has, in fluorinated drugs (2). The CF₃ group has proven to be very stable in vivo (3) and the SF₅ stability closely parallels that of the CF₃ group.

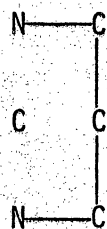
The three basic types of synthesis of pyrimidine derivatives are illustrated below (4).



Type I



Type II



Type III

Type I, the most common method of obtaining a pyrimidine, was employed in the earliest recorded synthesis of barbituric acid in the preparation of Grimeaux (5) in 1879 using malonic acid and urea in the presence of phosphoryl chloride. Malonamide and its derivatives, Type III, are used less frequently to obtain pyrimidine derivatives while Type II is seldom used because of a lesser availability of starting materials as compared to Types I and III.

This part of the research describes attempts to prepare a barbiturate or uracil derivative containing N,N'-bis(pentafluorosulfanyl) groups. From a study of synthetic methods used to prepare barbiturates and uracils from urea, it was our belief that N,N'-bis(pentafluorosulfanyl)urea (6), $(\text{SF}_5\text{NH})_2\text{CO}$, would be an excellent starting material. Also included in this first part is a further study into the preparation and characterization of N,N'-bis(pentafluorosulfanyl)urea and a new compound N,N'-bis(pentafluorosulfanyl)malonamide. Further characterization of the urea was needed due to inconsistencies in IR and NMR spectra. It was hoped the substituted

malonamide could be used in an alternate route to synthesize the barbiturate.

EXPERIMENTAL

Equipment.

Reactors.

The preparation of some of the starting materials was carried out in stainless steel or Monel cylinders (Hoke, Inc., Cresskill, N. J.) of either 35 ml or 75 ml capacity for the stainless steel or 90 ml for the Monel. These were equipped with Whitey DK series valves (Crawford Fitting Co.). Teflon tape (Crawford Fitting Co., Cleveland, Ohio) was applied to the threads on the fittings to provide leak-tight seals. Brass Swagelok unions (Crawford Fitting Co.) fitted with brass Swagelok ferrules were used for vacuum tight connections when connected to 1/4 inch O. D. Kovar-Pyrex tubing.

Pyrex reaction vessels equipped with Teflon high vacuum stop-cocks (Kontes, Vineland, N. J.) were used for many of the reactions where either pressure or hydrofluoric acid was not a problem. Kel-F reaction tubes, (Argonne National Laboratory) were fitted with a brass female flare nut and a Kel-F tapered plug drilled and threaded to provide a vacuum tight seal when the Kel-F plug was screwed into the brass nut. Materials of high volatility were stored in the metal cylinders, while those of low volatility were stored in glass vessels

equipped with high vacuum Teflon stopcocks. Standard ground glass equipment was used for reactions done outside the vacuum line.

Vacuum System.

An all Pyrex glass vacuum system equipped with Teflon high vacuum stopcocks was used for measurements, handling and purification of volatile reactants and products. High vacuum measurements were made using a Hastings VT-6S gauge and gauge tube (Hastings-Raydist, Hampton, Va.). All vacuum stopcocks and ground glass joints were lubricated with Halocarbon wax or grease (Halocarbon Products Corp., Hackensack, N. J.).

Infrared Spectra.

Infrared spectra in the 4000 cm^{-1} to 250 cm^{-1} region were recorded using a Beckman IR-20AX Infrared Spectrometer. The spectra were used routinely to determine the purity of materials and the efficiency of separations.

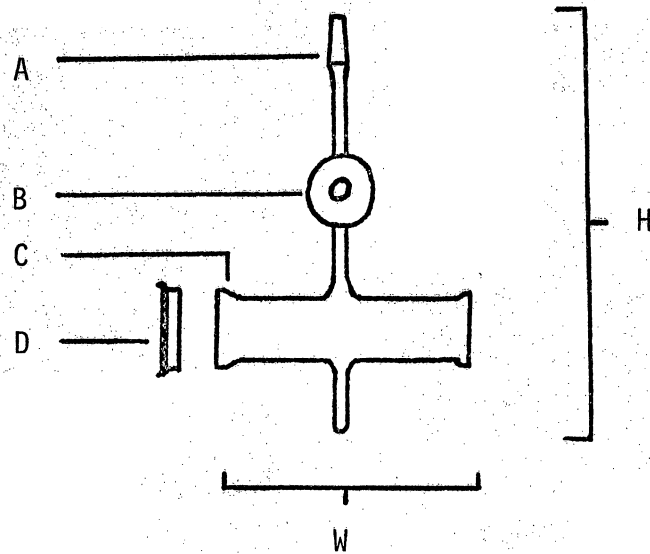
Spectra of the gas samples were taken using a 10-cm gas cell, shown in Photograph 1, designed by Dr. A. F. Clifford's research group consisting of myself, Dave Wooten, Jon Howell, and Avi Shanzer. (See Figure 1 for specifications.) The cell was fitted with either KCl or KBr windows (Harshaw Chemical Co.)

Reagents.

Thiazyl Trifluoride, $\text{N}=\text{SF}_3$ (8) was prepared by silver difluoride



Photograph 1. Infrared Gas Cell



H - Height: 17.2 cm

W - Pathlength: 10 cm

A - $\frac{12}{30}$ Standard Taper ground glass joint

B - 4mm Kontes high vacuum Teflon stopcock

C - 15mm I.D. connector, with Type-M "O" Ring

D - Coverplate, for 25 x 5mm cell windows, equipped with 4 inch stainless steel spring (not shown above)

Figure 1. Infrared Cell Specifications

(Ozark-Mahoning) fluorination of N-fluoroformyliminosulfur difluoride (9), FC(O)N=SF_2 , at room temperature. The by-product of the fluorination, carbonyl fluoride, was also used.

Pentafluorosulfanylamine, SF_5NH_2 , was prepared from the addition of HF to thiazyl trifluoride as described by Clifford and Duncan (7).

Anhydrous Hydrogen Chloride (Matheson Company) was used after distillation through a -78° trap to remove water.

Anhydrous Hydrogen Fluoride, furnished by Blockson Chemical Division of Olin Mathieson Corp., was used without further treatment.

Sodium Fluoride pellets (Harshaw) were heated to 200° to dry them before use.

Malonyl Chloride, $\text{CH}_2(\text{COCl})_2$, purchased from Aldrich Chemical was transferred to a glass storage vessel and opened to the vacuum line, while keeping the vessel at 0° , to remove any dissolved HCl.

Pyridine (Eastman) was stored over and distilled from sodium hydroxide pellets.

N,N-Dimethylaniline (Fisher) was stored and distilled from sodium hydroxide pellets.

Cesium Fluoride (Ozark-Mahoning) was dried at 200° in a vacuum for 24 hours.

Carbonyl Chloride, purchased from Air Products, was condensed into a -196 trap open to the vacuum pump to remove carbon monoxide impurities.

Carbonyl Sulfide (Matheson) was used without further purification.

Ethanol (100%) (Baker) was stored over molecular sieves.

Diethyl Ether (anhydrous) (Fisher) was used without further.

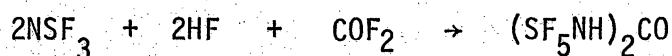
treatment.

Tetrahydrofuran (Fisher) was stored and distilled from sodium.

Preparation of N,N'-Bis(pentafluorosulfanyl)urea.

The Synthesis Catalyzed by Anhydrous Hydrogen Fluoride.

$(\text{SF}_5\text{NH})_2\text{CO}$ was prepared using an exact ratio reaction from the equation:



Quantities of 50 mmol of NSF_3 , 25 mmol of COF_2 and 50 mmol of HF were condensed into a Kel-F reactor. The vessel was then allowed to warm to room temperature and remain for seven days. Crystals were observed to form after only a few hours, but substantial liquid remained for several days. After seven days the reactor was checked for nonvolatiles and then the volatiles were transferred to a metal cylinder containing NaF pellets to absorb the HF. After most of the volatiles were condensed into the NaF trap, the Kel-F reactor was warmed to 35° to help remove any residual HF or SF_5NH_2 from the urea. This was necessary because of the tendency of SF_5NH_2 to coprecipitate with the urea. After the NaF trap containing the volatiles had been allowed to warm to room temperature, the volatiles were transferred to the vacuum line and separated by trap-to-trap distillation. The -78° trap (dry ice slush) contained SF_5NH_2 while the -131° trap (n-pentane slush) contained NSF_3 and SF_5NCO . No unreacted COF_2 was found. The Kel-F reactor was opened and found

to contain 6.5g (83% Yield) of white crystals of urea. Changing the ratios of reactants only decreased the yield. Any impurities in the urea were removed by sublimation at 90° under high vacuum.

The Synthesis Catalyzed by Anhydrous Hydrogen Chloride.

Thiazyl trifluoride, 8 mmol, carbonyl fluoride, 8 mmol, and anhydrous hydrogen chloride, 16 mmol, were condensed into a Monel cylinder equipped with a Monel valve and allowed to warm to room temperature. After seven days the volatiles were removed from the cylinder and distilled in the vacuum line. The -196° trap contained HCl, COF_2 and some COFCl , the -131° trap contained SF_5NCO , NSF_3 and an unidentified compound. The infrared spectrum of the unidentified compound showed peaks in the carbonyl and nitrogen-sulfur double bond region. Remaining in the cylinder was 0.8g of the $(\text{SF}_5\text{NH})_2\text{CO}$. Increasing the amount of HCl decreased the amount of the urea and increased the amount of SF_5NCO .

Physical Properties of $(\text{SF}_5\text{NH})_2\text{CO}$.

Infrared Spectrum. The results are listed in Table I for both the original precipitate and one recrystallized out of CCl_4 with both spectra taken in KBr pellets. The spectral assignments are in agreement with those of related compounds (10) (11) (12) (13) (14) (15) (16).

NMR Spectrum. The proton and fluorine NMR spectra for the reactants, SF_5NH_2 and SF_5NCO , and product, $(\text{SF}_5\text{NH})_2\text{CO}$, were obtained on a JEOL PS-100 FT at 100 MHz and 94 MHz, respectively. While the spectrum for SF_5NCO has been previously reported (17), those of

SF_5NH_2 and $(\text{SF}_5\text{NH})_2\text{CO}$ have not been published. Acetonitrile was used as a solvent for all three compounds, but in addition $(\text{SF}_5\text{NH})_2\text{CO}$ was also run in dry diethyl ether. In addition a carbon-13 spectrum was obtained for $(\text{SF}_5\text{NH})_2\text{CO}$ in diethyl ether at 25 MHz. All fluorine spectra are referenced to external Freon-11 except for $(\text{SF}_5\text{NH})_2\text{CO}$ in diethyl ether which is referenced to internal Freon-11. The SF_5NH_2 (Figure 2) and SF_5NCO gave appropriate AB_4 spectra with apical resonances at -89.4 ppm and -72.4 ppm, respectively, and basal resonances at -77.8 ppm and -88.6 ppm, respectively. (Note the reversal of positions.) Coupling constants J_{AB} , were 145 cps and 148 cps, respectively. In $(\text{SF}_5\text{NH})_2\text{CO}$ (Figure 3) the peaks due to the apical and basal fluorines lie very close to each other giving a triangular shaped spectrum with the apical and basal centers at -76.8 and -73.0 ppm, respectively, in acetonitrile and -72.7 and -69.2 ppm, respectively, in diethyl ether. The coupling constant was determined to be 149 cps. These values are in the range previously reported for the SF_5 group (18) (19) (20) (21). Proton spectra of SF_5NH_2 and $(\text{SF}_5\text{NH})_2\text{CO}$ in acetonitrile gave broad peaks at 5.6 and 8.5, respectively, with no resolvable structure. In diethyl ether the $(\text{SF}_5\text{NH})_2\text{CO}$ gave a sharper peak at 8.9. No observable hydrogen-fluorine coupling could be observed for SF_5NH_2 or $(\text{SF}_5\text{NH})_2\text{CO}$. The carbon-13 spectra gave a peak at -145.22 ppm from TMS. This value is slightly upfield from the previously reported value of ≈ -160 for ureas (22).

Solubility. $(\text{SF}_5\text{NH})_2\text{CO}$ was found to be moderately soluble in dry diethyl ether, acetonitrile, 1,4-dioxane, methanol, ethanol, and

Table I

Infrared Spectrum of N,N'-Bis(pentafluorosulfonyl)urea

<u>Crystals</u>		<u>CCl₄Solvate</u>		Assignment
cm ⁻¹	Intensity*	cm ⁻¹	Intensity*	
3310	s.	----		N-H stretch (cis rotamer)
3240	m.	3170	s.	N-H stretch (trans rotamer)
3000	m.	2960	m.	fermi resonance
2720	w.	2710	w.	overtone
1715	v.s.	1725	v.s.	C=O stretch
1685	m.	1690	m.	C=O stretch
1535	s.	1490	s.	N-H bend
1515	s.	1470	m.	N-H bend
1210	m.	1245	s.	C-N stretch
1105	w.	1095	w.	C-N bend
920	v.s.	935	s.	SF ₄ square stretch
875	v.s.			S-F stretch
855	v.s.	860	v.s.-b	S-F stretch
825	v.s.			S-N stretch
740	w.	745	w.	C=O bend
700	m.	660	m.	N-H bend
590	v.s.	590	m.	SF ₄ wag
		775 and 765		CCl ₄

*v.s., very strong; s., strong; m., medium; w., weak; b., broad

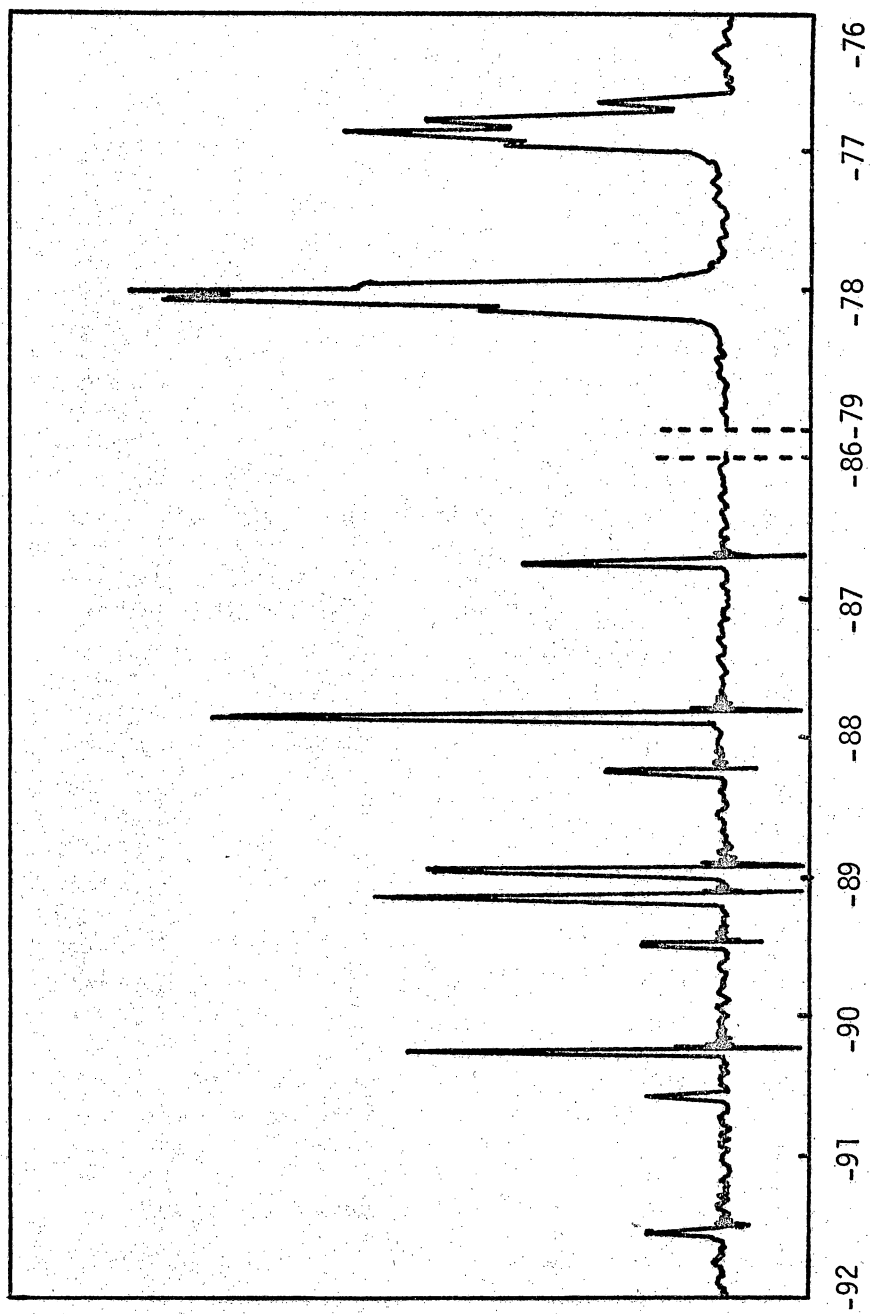


Figure 2. Fluorine NMR of SF_5NH_2

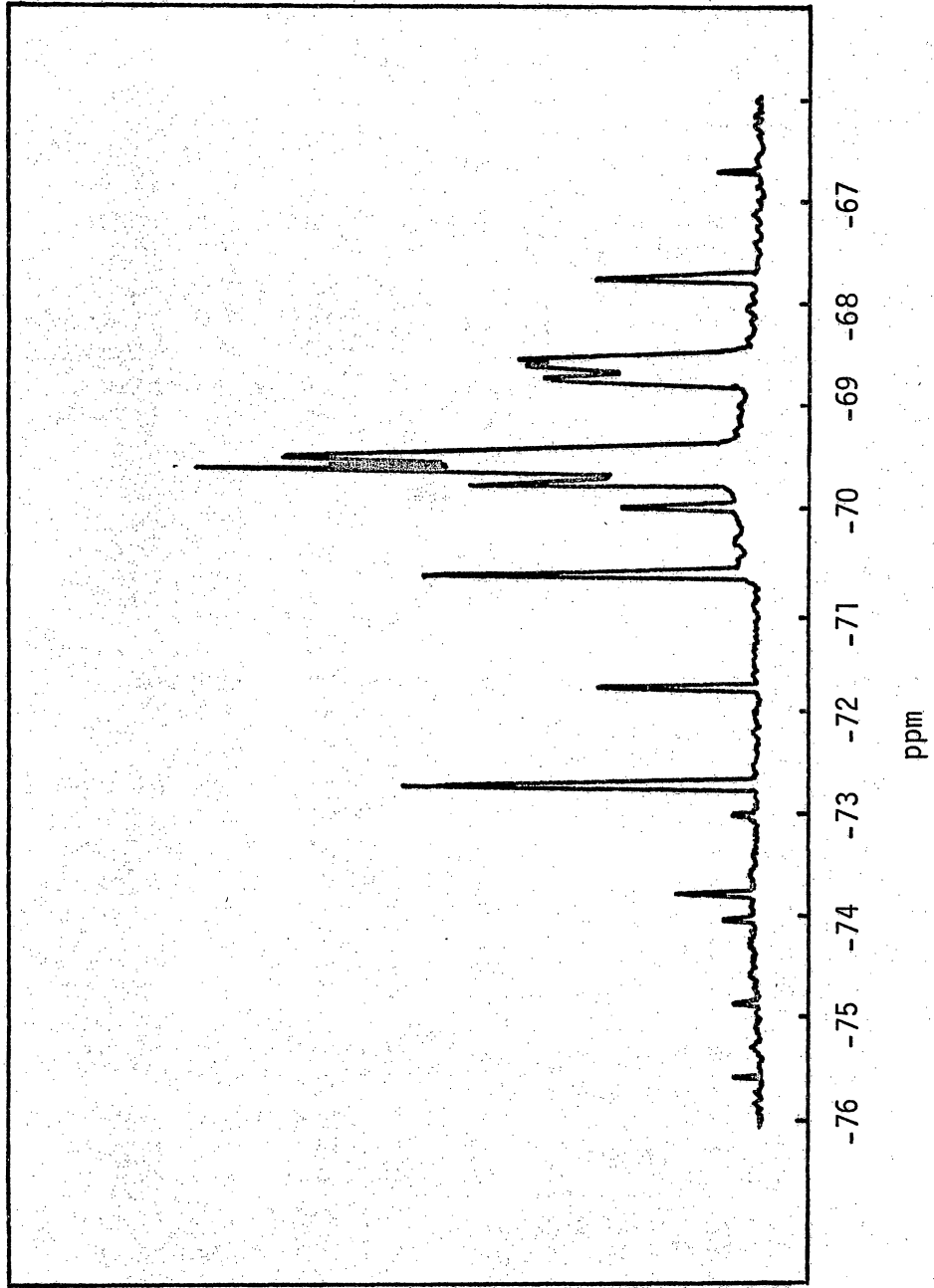
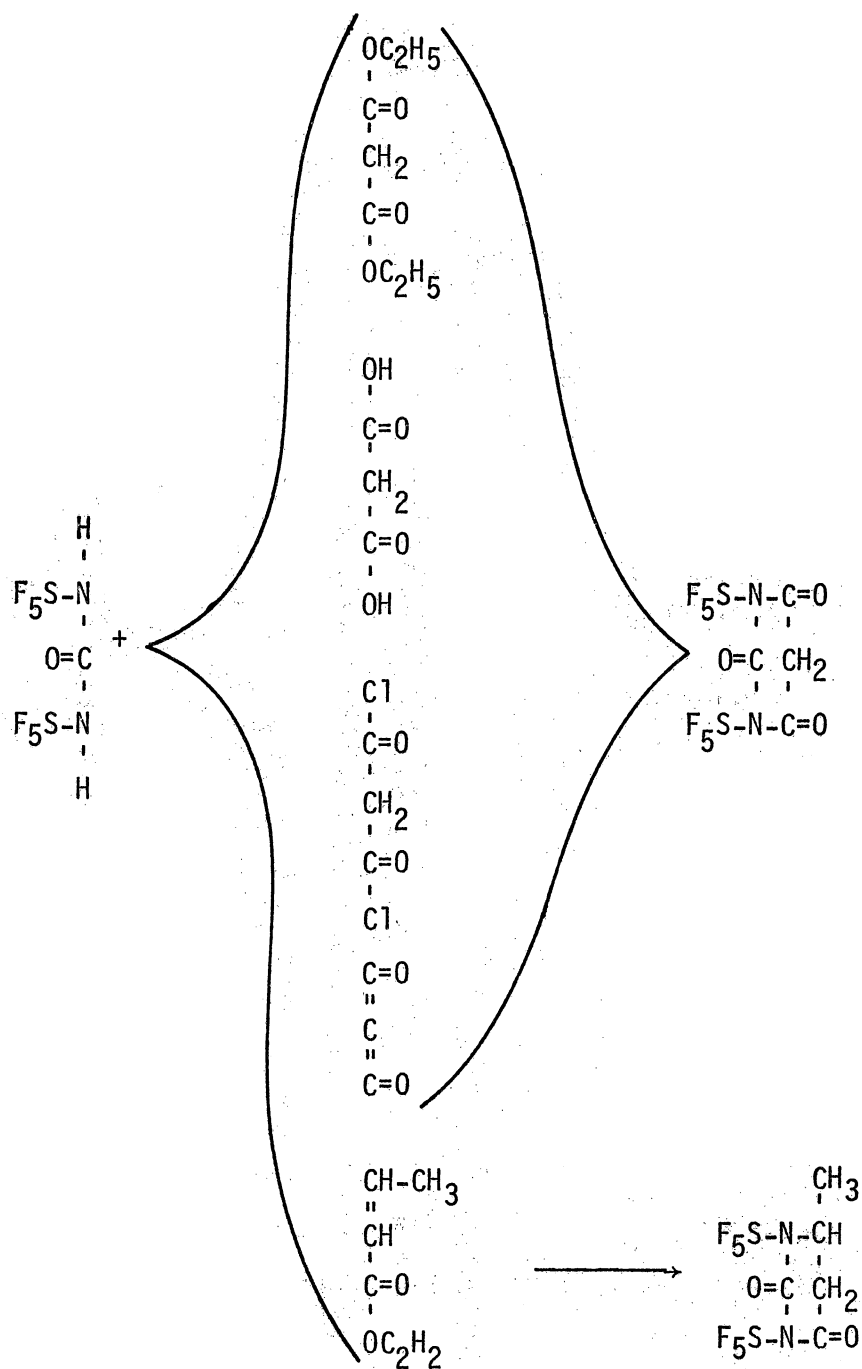


Figure 3. Fluorine NMR of $(\text{SF}_5\text{NH})_2\text{CO}$

acetone but when exposed to wet solvents it decomposed. It was also decomposed by pyridine, N,N-dimethylaniline, triethylamine, N,N-dimethylformamide, acetic acid, and trifluoroacetic acid. It is apparently insoluble or only slightly soluble in chloroform, carbon tetrachloride and other non-polar solvents. Its slight solubility in CCl_4 enables a CCl_4 solvate to be formed which analyzes to have C 5.55% and N 6.27% implying a 1 to 1 ratio of CCl_4 to urea.

Reactions of $(\text{SF}_5\text{NH})_2\text{CO}$ (See Figure 4).

With Ethyl Malonate. Using the known literature reaction (23) for producing barbiturates from ethyl malonate and urea as a basis, 0.23 g (10 mmol) of sodium (Fisher) was dissolved in 10 ml of absolute ethanol followed by 1.56 g (5 mmol) of ethyl malonate (Fisher). After complete mixing by stirring, 1.56 g (5 mmol) of $(\text{SF}_5\text{NH})_2\text{CO}$ was added. The mixture was refluxed and stirred for 8 hours. A white precipitate formed very quickly upon addition of the urea. After continued reacting for 3 days, 5 ml of water was added. There was no apparent reaction or dissolution of the white precipitate. The pH of the solution was found to be 2. Considerable etching of the flask used was noted. The white compound showed broad peaks in the infrared spectrum from $1200\text{-}1100\text{ cm}^{-1}$ and $850\text{-}700\text{ cm}^{-1}$. It proved to be insoluble in all organic solvents tried. The sodium ethoxide appeared to have destroyed the urea to give HF which attacked the glass to give an insoluble silicon-oxygen compound.

Figure 4. Reactions of $(\text{SF}_5\text{NH})_2\text{CO}$

With Malonic Acid Using HF as Solvent. The urea $(\text{SF}_5\text{NH})_2\text{CO}$, 0.626 g (2 mmol) and 0.220 g (2.1 mmol) of malonic acid (Fisher) were placed in a Kel-F reactor and 1.2 ml of anhydrous HF added. After allowing the mixture to react for 2 days, the volatiles were condensed in a NaF trap with slight warming. A white solid remained which became yellow on standing. The volatiles were shown to contain SF_5NH_2 , SF_5NCO , and SOF_2 . The solid began turning red overnight. Comparing an infrared spectrum of the solid with one taken of malonic acid showed the solid to be mostly malonic acid with some carbon suboxide polymer. An NMR spectrum of the solid in acetonitrile showed a peak at 3.65, corresponding to the value for malonic acid, in the proton spectrum but no peaks in the fluorine spectrum.

With Malonic Acid Using Acetic Acid as Solvent. Since the second most common method of preparing barbiturates is through the use of malonic acid in acetic acid and acetic anhydride (24), a similar reaction was tried by dissolving 0.628 g (2 mmol) of $(\text{SF}_5\text{NH})_2\text{CO}$ and 0.208 g (2 mmol) malonic acid (Fisher) separately in 10 ml each of a mixture of acetic acid (Fisher) and acetic anhydride (Mallinckrodt). The two solutions were then mixed and the mixture refluxed for 1 hour. After removing all volatiles, a brown solid remained which showed no evidence for fluorine in the NMR spectrum. No further work was done on this solid.

With Malonyl Chloride. Following the work of Biltz and Hamburger (25), 0.628 g (2 mmol) of $(\text{SF}_5\text{NH})_2\text{CO}$ was dissolved in anhydrous diethyl ether followed by addition of 0.302 g (2.1 mmol) of malonyl chloride. After refluxing for 2 hours, the volatiles were removed by

vacuum. A light yellow solid was left which gave an infrared spectrum identical to that of the original urea.

Repeating the reaction using pyridine as a base produced a reaction. After dissolving 1.25 g (4 mmol) of the urea in 40 ml of anhydrous diethyl ether, 0.645 g (8 mmol) of pyridine was added. The mixture thoroughly stirred before the addition of 0.580 g (4.1 mmol) malonyl chloride. A white precipitate, which was unstable in air, was formed upon addition of the pyridine, but was replaced with a red precipitate upon addition of the malonyl chloride. After separating the ether from the solid, more ether was added to insure that all soluble products were removed. Removing the ether under vacuum left a light yellow solid.

The product, which was soluble in ether, partially dissolved in carbon tetrachloride to leave an insoluble dark yellow product. This insoluble product gave the infrared spectrum of an ammonium salt and showed no SF_5 group in either the infrared or the fluorine NMR spectrum. The infrared spectrum of the soluble compound still appeared to have a small impurity, but was almost identical to that of N,N' -bis(pentafluorosulfanyl)malonamide. Proton and fluorine NMR spectra, which were obtained in diethyl ether, showed peaks at 3.6 and -76.3 ppm, respectively. These also correspond to those values for the substituted malonamide. The mass spectrum of this compound gave a weak peak at 314 which corresponds to loss of two HF molecules from the malonamide, which is similar to the loss of two HF molecules observed in $(\text{SF}_5\text{NH})_2\text{CO}$ (6). The mass spectrum for the product which was insoluble in CCl_4 gave a parent peak of 229. NMR spectra of the

red precipitate showed a peak at 123 ppm from Freon-11 and gave an ammonium ion peak at 7.3 ppm as well as peaks for pyridine. Changing the order of adding the reactants produced similar results.

An attempt using a more sterically hindered base, N,N-dimethylaniline, produced a purple solid which gave an infrared spectrum similar to that of an ammonium salt. A fluorine NMR spectrum showed peaks for the starting $(\text{SF}_5\text{NH})_2\text{CO}$, SF_5NH_2 , and a carbon-fluorine compound. Using malonyl chloride produced in situ from malonic acid and phosphorus oxychloride (Baker) (5), gave the malonamide as product, while cesium fluoride used as a catalyst with malonyl chloride produced no reaction.

With Carbon Suboxide. Carbon suboxide, C_3O_2 , prepared according to the method of Brauer (26), was used in a reaction (27) with the urea. Two mmol C_3O_2 was condensed into a solution of 0.626 g (2 mmol) $(\text{SF}_5\text{NH})_2\text{CO}$ dissolved in 5 ml anhydrous diethyl ether. The reaction vessel was allowed to warm to room temperature with stirring of the reaction mixture. After about 30 minutes an orange solid began forming which became red within a day. Three days later the volatiles which contained only ether and some SF_5NCO were removed from the solid. The red solid, which was insoluble in ether, gave an IR spectrum identical to carbon suboxide polymer. The product which was soluble in ether gave an IR spectrum identical to that of the original urea.

Using approximately 2 ml each of tetrahydrofuran and N,N-dimethylformamide as solvent, a mixture of 2 mmol of $(\text{SF}_5\text{NH})_2\text{CO}$ and 2 mmol of C_3O_2 was let stand at -20° for an hour and then at 0° for

another hour. After another hour at room temperature, the reaction was stopped and the volatiles removed. A red product remained in the reaction vessel. The volatiles contained tetrahydrofuran, N,N-dimethylformamide, and some SF₅NCO. Besides the red carbon suboxide polymer, an ether-soluble white compound was obtained which gave an IR spectrum containing peaks for N,N'-(pentafluorosulfanyl)malonamide plus some small impurity.

With Ethyl Crotonate. Hoping to produce a uracil by the procedure of Fischer and Roeder (28), (SF₅NH)₂CO, 0.320 g (1 mmol) was placed in a glass reaction vessel and 0.344 g (3 mmol) of ethyl crotonate, obtained from Mr. Darko Butina, was condensed into the vessel. The reaction mixture was heated at 80° for 3 days. The volatiles were removed leaving a solid which gave no peaks for sulfur-fluorine in the infrared. The volatiles were checked and found to contain HNSOF₂, SiF₄, and ethyl crotonate.

Preparation of N,N'-Bis(pentafluorosulfanyl)malonamide.

N,N'-Bis(pentafluorosulfanyl)malonamide, CH₂(CONHSF₅)₂, was prepared by a gas phase reaction between C₃O₂ (26) and SF₅NH₂ (7). Using a reaction vessel consisting of a 1000 ml and 500 ml Pyrex vessels connected by a vacuum stopcock. Pentafluorosulfanylamine, 4 mmol, was condensed into the smaller vessel and the valve between the two vessels closed. The carbon suboxide, 1 mmol, was then condensed into the larger vessel. After both vessels had been allowed to warm to room temperature and the contents vaporized, the connecting valve was opened to allow the gases to mix. After reacting overnight,

the gases were condensed into a separate 250 ml reaction vessel and allowed to react overnight. Both reaction vessels contained a white compound on the walls, which was removed by dissolving it in diethyl ether. This proved to be N,N'-bis(pentafluorosulfonyl)-malonamide. The remaining volatiles were SF₅NH₂, SiF₄, and SOF₄.

The amide was also produced using acetonitrile as solvent, but was slightly impure. The amine, SF₅NH₂, 10 mmol, and C₃O₂, 5 mmol, were condensed into a glass reaction vessel containing 4 ml of acetonitrile. The reaction vessel was allowed to warm to 0° and was kept at that temperature overnight. The reaction mixture was then allowed to warm to room temperature and remain for 3 days. A light orange precipitate began forming during the first day and continued to increase. Removing the volatiles, C₃O₂, NSF₃, SiF₄ and CH₃CN left a light orange solid 1.4 g (80% yield). Purification of the solid was accomplished using acetonitrile and carbon tetrachloride as solvents, the orange solid being more soluble in the CCl₄. The advantage of this method is that larger quantities of the amide can be made; the disadvantage is the necessity of removing the orange impurity.

Attempted Preparation of N,N'-Bis(pentafluorosulfonyl)malonamide Using CH₂(COCl)₂.

Hoping to find an easier path to the amide, malonyl chloride (2 mmol) and 4 mmol of SF₅NH₂ were condensed into a glass reaction vessel containing dried NaF pellets. After 1 hour the volatiles were checked using infrared spectra and found to contain SF₅NH₂, NSF₃, and

SiF₄. Anhydrous diethyl ether, 2 ml, and 2 mmol more of the malonyl chloride were added to the vessel along with the original volatiles. There was immediate formation of a white product on warming to room temperature. After reacting overnight, the volatiles were removed and found to contain NSF₃, CH₂(COCl)₂, and SiF₄. There was etching observed on the walls and an infrared spectrum of the white solid showed it to be an ammonium salt with strong peaks in the carbon-fluorine region. Attempts using a pyridine as the base also gave decomposition products, while an attempt using no base produced no reaction.

Physical Properties of CH₂(CONHSF₅)₂.

Infrared Spectrum. The results, taken in a KBr pellet, are listed in Table II and shown in Figure 5. The spectral assignments are in agreement with those of related compounds (10) (11) (12) (13) (14) (15) (16).

NMR Spectrum. The NMR spectra were run on the JEOL-PS-100 FT at 100 MHz for the proton, 94 MHz for the fluorine-19, and 25 MHz for the carbon-13. The proton resonance spectrum using acetonitrile as solvent consisted of a sharp peak at 3.50 ppm and a very broad peak of low resolution at 10.4 ppm from TMS for the CH₂ and NH protons, respectively. The fluorine-19 spectrum (Figure 6) displayed a normal SF₅ spectrum with the center of the peaks for the apical fluorine at -74.0 ppm and the basal fluorines at -68.8 ppm from internal Freon-11. The coupling constant was determined to be 149 cps. Integration of the proton and fluorine spectra gave one to one and one

to four ratios respectively. The carbon-13 spectrum displayed singlets at -44.53 ppm and -161.39 ppm from TMS for the methylene and carbonyl carbons, respectively. The proton, fluorine, and carbon peaks were in the range of similar compounds (10) (20) (22).

Mass Spectrum. Peaks of less than 3% relative intensity are not listed in Table III unless they have some special significance.

Decomposition Point. At 182° the malonamide began turning brown and by 186° had become a dark brown solid which showed no further signs of decomposition.

Elemental Analysis. The carbon, hydrogen, and nitrogen analysis was done by the Departmental analysts on a Perkin-Elmer 240 Elemental Analyzer. Calculated for $S_2F_{10}N_2H_4C_3O_2$: C 10.17, H 1.13, N 7.91. Found C 9.95, H 1.16, N 7.59.

Solubility. The malonamide was found to be very soluble in diethyl ether, acetone, and acetonitrile, moderately soluble in chloroform and dichloromethane, and apparently insoluble in benzene. Wet solvents and tertiary amines such as pyridine and triethylamine decomposed the amide.

Some Reactions of N,N'-Bis(pentafluorosulfonyl)malonamide.

Reaction With Carbonyl Chloride. The amide, 0.175 g (0.5 mmol), was placed in a glass reaction vessel. Following evacuation of the vessel, 4 ml of diethyl ether and 2 mmol of $COCl_2$ were condensed into the vessel. The mixture was allowed to warm to room temperature and remain for 5 days. The volatiles remaining proved to be ether and $COCl_2$. An infrared spectrum of the remaining solid showed only the

Table II

Infrared Spectrum of N,N'-Bis(pentafluorosulfanyl)malonamide

cm ⁻¹	Intensity*	Assignment
3280	s.	N-H stretch
2980	m.	C-H stretch
1735	s.	C=O stretch
1705	v.s.	C=O stretch
1510	s.	N-H bend
1410	s. ^b	CH ₂ bend
1335	m. ^b	CH ₂ bend
1275	w. ^b	C-N stretch
1185	m. ^b	C-C stretch
1160	m.	C-C stretch
1005	m. ^b	C-N bend
930	s.	SF ₄ square stretch
865	v.s.	S-F stretch
830	s. ^b	S-N stretch
795	s. ^b	CH ₂ rock
760	m. ^b	N-H out of plane bend
710	w. ^b	CH ₂ rock
680	w. ^b	C-C stretch
635	v.w.	N-C=O deformation
600	s.	SF ₄ wag

Table II
(Cont.)

cm ⁻¹	Intensity*	Assignment
565	m.	C=O bend
550	m.	

* v.s., very strong; s., strong; m., intensity; w., weak;

v.w. very weak

^a, shoulder; ^b, sharp

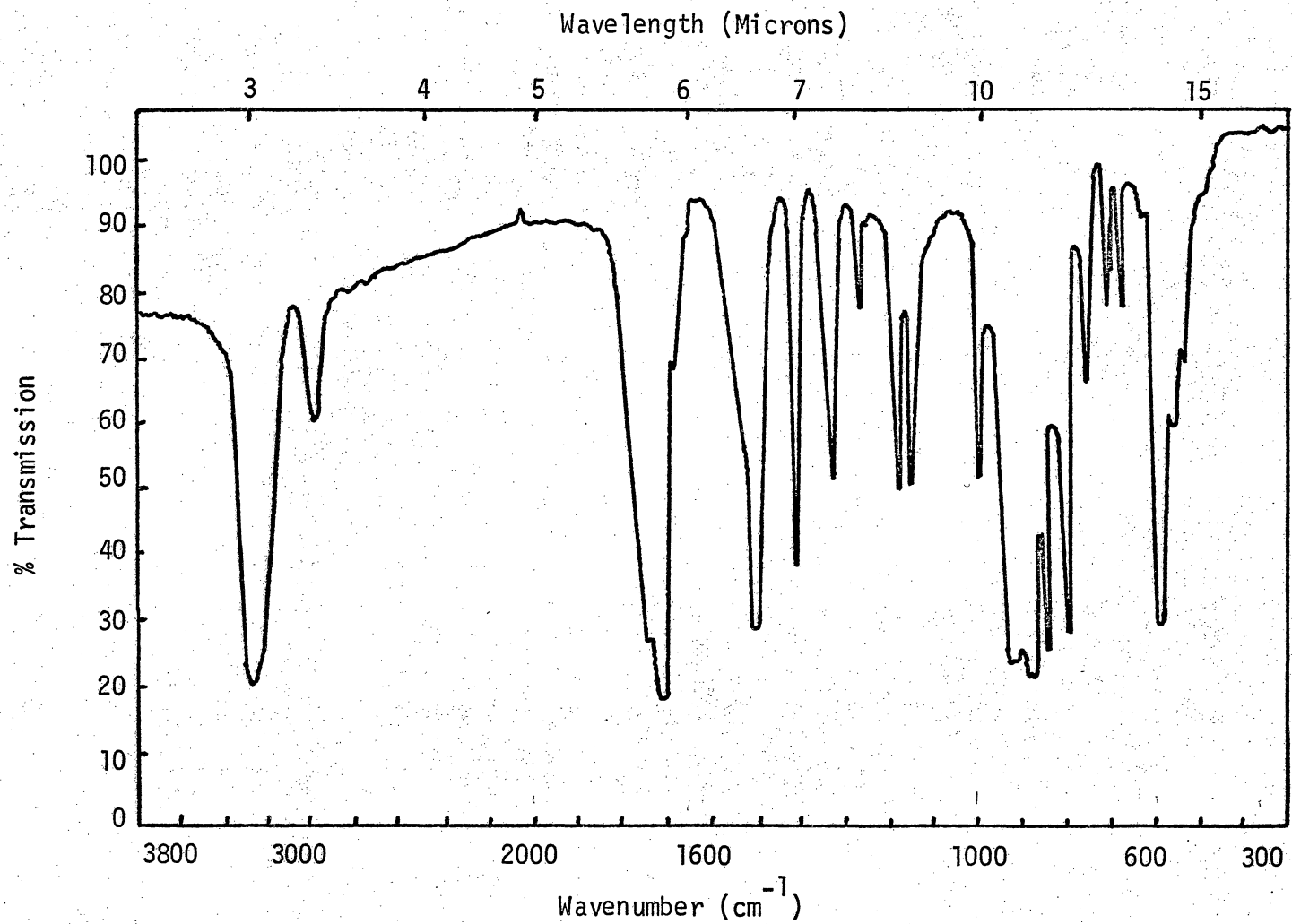


Figure 5. Infrared Spectrum of $(\text{SF}_5\text{NHC(O)}_2)\text{CH}_2$

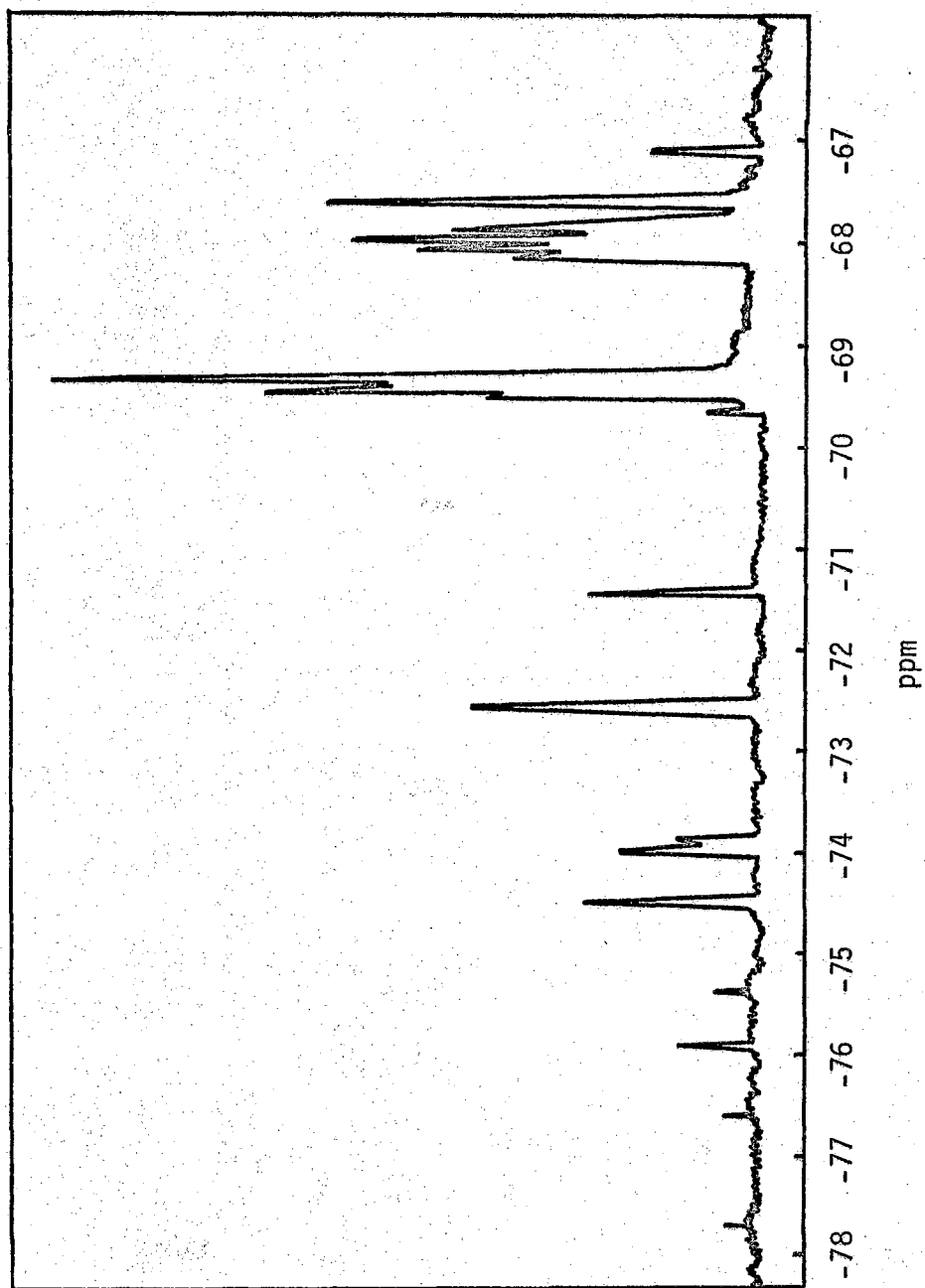


Figure 6. Fluorine NMR of $(\text{SF}_5\text{NHC(O)}_2)_2\text{CH}_2$

Table III

Mass Spectrum of N,N'-Bis(pentafluorosulfonyl)malonamide

50 ev Inlet Temperature 120°

Intensity Relative to SF₅⁺

m/e	Relative Intensity	Ion
356	0.1	S ³⁴ F ₅ N(H)C(O)C(H ₂)C(O)N(H)SF ₅ ⁺
355	0.1	S ³³ F ₅ N(H)C(O)C(H ₂)C(O)N(H)SF ₅ ⁺
354	1.1	S ³² F ₅ N(H)C(O)C(H ₂)C(O)N(H)SF ₅ ⁺ (parent)
314	0.5	(SF ₄ NCO) ₂ CH ₂ ⁺
294	10.3	SF ₄ NC(O)C(H)C(O)NSF ₃ ⁺
212	14.8	SF ₅ N(H)C(O)C(H ₂)C(O) ⁺
194	6.3	SF ₄ NC(O)C(H ₂)C(O) ⁺
185	17.5	SF ₅ N(H)C(O)CH ₃ ⁺
170	6.4	SF ₅ N(H)CO ⁺
169	7.5	SF ₅ NCO ⁺
150	5.5	SF ₄ NCO ⁺
139	7.5	SF ₂ NC(O)C(H)C(H) ⁺
127	100.0	SF ₅ ⁺
124	3.6	N(H ₂)C(H ₂)C(O)N(H)SF ⁺
105	5.2	SF ₅ NH ₂ ⁺
104	5.3	SF ₃ NH ⁺
103	6.7	NSF ₃ ⁺
101	12.8	CH ₃ C(H)(OH)N(H)SF ⁺
100	10.3	CH ₂ C(H)(OH)N(H)SF ⁺

Table III
(Cont.)

m/e	Relative Intensity	Ion
89	35.5	$\text{CH}_2\text{C}(\text{O})\text{NS}^+$
88	3.1	$\text{C}(\text{H})(\text{OH})\text{N}(\text{H}_2)\text{SF}^+$
87	13.3	$\text{C}(\text{H})(\text{OH})\text{N}(\text{H})\text{SF}^+$
86	5.9	$\text{C}(\text{H})(\text{OH})\text{NSF}^+$
82	4.8	$\text{NCCH}_2\text{C}(\text{O})\text{N}^+$
79	9.9	CH_2NSF^+
70	9.9	$\text{C}(\text{H})(\text{O})\text{C}(\text{H})\text{CO}^+$
69	29.1	$\text{C}(\text{O})\text{C}(\text{H})\text{CO}^+$
68	3.2	$\text{C}(\text{O})\text{C}(\text{H}_2)\text{CN}^+$
67	17.8	$\text{C}(\text{O})\text{C}(\text{H})\text{CN}^+$
65	3.3	NSF^+
61	14.3	$\text{CH}_3\text{C}(\text{O})\text{OH}^+$
60	7.0	$\text{CH}_3\text{C}(\text{O})\text{O}^+$
59	4.5	$\text{C}(\text{H})\text{NS}^+$
53	14.3	$\text{C}(\text{H})(\text{O})\text{CCH}^+$
52	7.0	$\text{C}(\text{O})\text{CCH}^+$
51	4.5	SF^+
47	5.1	HNS^+
46	3.2	NS^+
45	14.3	$\text{C}(\text{H})(\text{O})\text{NH}_2^+$
44	26.6	$\text{C}(\text{O})\text{NH}_2^+$
43	41.0	$\text{C}(\text{O})\text{NH}^+$
42	45.0	OCN^+

Table III
(Cont.)

m/e	Relative Intensity	Ion
41	9.4	CH_3CN^+
40	11.3	CH_2CN^+
39	7.5	CH_3CC^+
38	6.4	F_2^+
36	14.3	C_3^+
32	36.4	O_2^+
31	4.9	CH_2OH^+
29	12.3	CHO^+
28	100.0	N_2^+
27	4.8	HCN^+
20	27.6	HF^+
18	40.0	H_2O^+

original amide and an infrared spectrum taken after heating the reaction mixture overnight at 100° showed only the original amide and a large peak from $1200\text{-}1100\text{ cm}^{-1}$ which indicated a C-F stretching.

Reaction With Carbonyl Fluoride. A small amount of dry cesium fluoride and the amide, 0.125 g (0.5 mmol), were placed in a Kel-F reaction vessel. After the vessel was evacuated, 2 ml of diethyl ether and 1 mmol of COF_2 were condensed into the reaction vessel. After reacting for 2 days at room temperature, the volatiles were found to contain ether and a small amount of COF_2 . The solid remaining was $\text{Cs}^+\text{OCF}_3^-$ and all of the original amide.

Reaction With Carbonyl Sulfide. The amide, 0.175 g (0.5 mmol), was placed in a glass reaction vessel. After evacuation of the vessel, 5 ml of diethyl ether and 0.5 mmol of COS were condensed into the vessel. The mixture was allowed to warm with stirring, to room temperature and remain for two days. The volatiles were then checked and found to contain ether and COS. An infrared spectrum of the solid was identical to that of the amide. The vessel containing the amide was placed back on the vacuum line and evacuated. The volatiles were then condensed back into the vessel and heated to 100° for 1 day. Infrared spectra of the volatiles showed COS, diethyl ether, and a very small amount of SiF_4 , while one of the solid showed only the original amide with a small amount of an impurity containing carbon-fluorine bonds. No peaks due to H_2S , the expected gaseous product, were observed in the infrared.

DISCUSSION

Thiazyl trifluoride reacts with carbonyl fluoride in the presence of an appropriate amount of hydrogen fluoride or hydrogen chloride to produce $(\text{SF}_5\text{NH})_2\text{CO}$. While the reaction employing hydrogen fluoride is not nearly so critical as that of hydrogen chloride in its reaction. The urea is much more easily destroyed by the more strongly acidic hydrogen chloride.

Attempted reactions of the urea with carbon suboxide and its derivatives either gave no reaction or gave N,N'-bis(pentafluoro-sulfanyl)malonamide. Since all reactions of the urea occurred in the presence of a base, pyridine or N,N-dimethylformamide, it must be an intermediate decomposition product of the urea which is reacting. This is supported by the fact that the urea reacts initially with pyridine to give a white product and that all attempts to react malonyl chloride directly with the SF_5NH_2 failed to give the malonamide. The instability of any intermediate can be related to the apparent stability of SF_5NCO as compared to that of SF_5NH_2 or the urea. The isocyanate appears to have greater thermal stability, as well as a greater stability toward bases. This apparent stability of SF_5NCO could result in easy elimination from any intermediate.

The inability of the urea and the malonamide to react could be due to the large size and high electronegativity of the SF_5 group. Since the first step in the reaction would probably be a nucleophilic attack of the lone pair of electrons of the nitrogen on the carbonyl

carbon, the reaction is prevented if the attacking lone pair is sterically hindered or insufficiently basic. The SF₅ group can conceivably accomplish both tasks. If this is the case, then attempts of similar nucleophilic reactions will be unlikely to succeed.

SUMMARY

N,N'-Bis(pentafluorosulfanyl)urea was synthesized from thiazyl trifluoride, carbonyl fluoride, and either anhydrous hydrogen fluoride or anhydrous hydrogen chloride. Attempts at reacting the urea with specific compounds to give barbiturates and uracils all failed. The urea was found to decompose in the presence of pyridine and N,N-dimethylaniline.

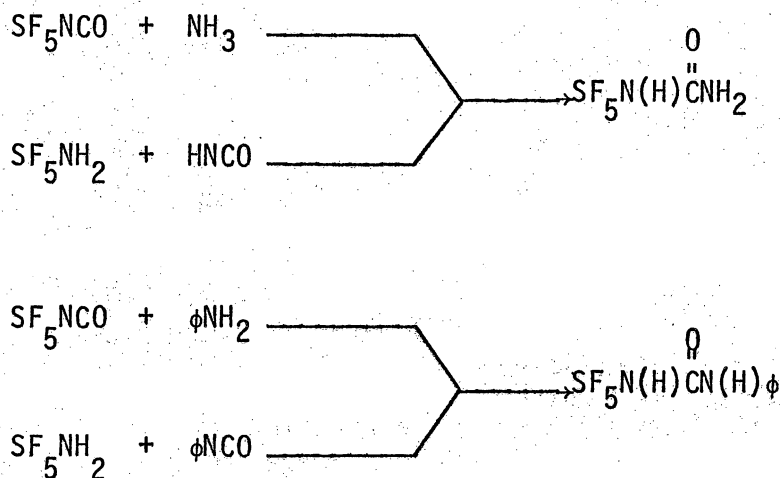
N,N'-Bis(pentafluorosulfanyl)malonamide was prepared from pentafluorosulfanylamine and carbon suboxide by mixing them either as gases or in a solvent. The malonamide was also found to be decomposed by tertiary amines such as pyridine. Attempts to react the malonamide with carbonyl chloride, fluoride, or sulfide to form the barbiturate failed.

CHAPTER II

THE PREPARATION OF MONOSUBSTITUTED N-PENTAFLUOROSULFANYLUREAS

INTRODUCTION

Because of the difficulty encountered in trying to synthesize N,N'-bis(pentafluorosulfanyl)barbiturates, it was hoped that with only a single pentafluorosulfanyl group in the urea chances for synthesis would be improved. Attempts were made to synthesize both N-pentafluorosulfanylurea and N-phenyl-N'-pentafluorosulfanylurea by reacting either pentafluorosulfanylamine (7), SF_5NH_2 , or pentafluorosulfanyl isocyanate (17), SF_5NCO , with an appropriate compound, such as isocyanic acid, $HNCO$, as shown in the following equations:



EXPERIMENTAL

Equipment.

The vacuum line and related equipment were described in Chapter I.

Reagents.

Pentafluorosulfanylamine (7) was prepared by the method described in Chapter I.

Pentafluorosulfanyl isocyanate (17) was prepared from the addition of SF_5NH_2 and COF_2 (6).

Aniline (Fisher) was stored and distilled from sodium hydroxide pellets.

Phenyl isocyanate (Aldrich) was used without further purification.

Ammonia (Matheson) was used without further purification.

Isocyanic acid, $HNCO$, was prepared from the decomposition of cyanuric acid (29).

Attempted Preparation of N-Pentafluorosulfanylurea.

Reaction of SF_5NCO and NH_3 .

A mixture (1 mmol) of SF_5NCO and diethyl ether was condensed into a Kel-F reactor containing 2 ml more of diethyl ether. This was followed by the addition of ammonia (1.1 mmol). Upon warming to room temperature, there was immediate formation of a white solid. This reaction was allowed to continue for 2 days with a small amount of yellow appearing on the second day. The volatiles were removed from the reaction vessel and found to contain only ether. The

infrared spectrum of the white solid was similar to that for an ammonium salt, while the proton NMR spectrum showed a characteristic ammonium salt triplet at 6.9 and the fluorine spectrum showed no peaks for sulfur-fluorine.

Reaction of SF_5NH_2 and HNCO .

After condensing SF_5NH_2 (4 mmol) into a glass reaction vessel containing diethyl ether, isocyanic acid (4 mmol) was condensed into the vessel. This was allowed to warm to room temperature. A small amount of white precipitate was formed after only a day. The volatiles were removed after 5 days and found to contain most of the isocyanic acid, some NSF_3 and SiF_4 , and ether. The solid proved to be insoluble in all solvents tried and gave an infrared spectrum almost identical to that of cyanuric acid.

In a second attempt at this reaction, the SF_5NH_2 (4 mmol) was condensed into 1 ml of CH_3CN and kept at 0° . The isocyanic acid (4 mmol) was also condensed into 1 ml of CH_3CN and allowed to warm to room temperature. The isocyanic acid solution was then slowly dripped into a second reaction vessel and allowed to stand at room temperature for a week. A white precipitate, which later was shown to have an infrared spectrum identical to that of cyanuric acid, was slowly formed during this time period. The volatiles contained acetonitrile, some NSF_3 and SiF_4 .

Preparation of N-Phenyl-N'-Pentafluorosulfanylurea.

Reaction of SF₅NCO and Aniline.

Aniline (10 mmol) and ether (1 ml) were condensed into a glass reaction vessel and allowed to warm to insure a uniform mixture. The SF₅NCO (4 mmol) was then condensed into the vessel in 1 mmol quantities. After each addition the vessel was allowed to warm to room temperature. The first addition produced immediately a light yellow product which seemed to increase only slightly after the last 3 additions. The reaction mixture was allowed to sit for several hours before the volatiles, ether and aniline, were removed. No SF₅NCO was observed in the volatiles. The solid from the reaction was separated into two fractions using CCl₄. An infrared spectrum of the CCl₄-soluble product contained no peak at 600 cm⁻¹ for an SF₅ group, while in the fluorine NMR spectrum there was a singlet at -53 ppm. These results indicated a reaction of the aniline with some impurity in the SF₅NCO, possibly NSF₃. The CCl₄-soluble product contained the N-phenyl-N'-pentafluorosulfanylurea plus a small impurity, possibly $\phi\text{N}=\text{S}(\text{F}_2) = \text{NH}$ or $\phi\text{NHS}(\text{F}_2) \equiv \text{N}$. Because of the small amount of material obtained, it was impossible to purify the mixture any further.

Attempted Preparation of N-Phenyl-N'-Pentafluorosulfanylurea Using SF₅NH₂ and Phenyl Isocyanate.

The SF₅NH₂ (4 mmol) was dissolved in 1 ml of acetonitrile (Fisher) kept at 0°. The phenyl isocyanate (4.1 mmol) was also

dissolved in 1 ml of acetonitrile and this solution slowly dripped into the SF_5NH_2 solution over a period of an hour. After a few days, large crystals were observed to form. They continued to grow for a week. The volatiles CH_3CN and NSF_3 , were then removed from the crystals. These large crystals (0.8 g) were determined to be N,N'-diphenylurea from its melting point and infrared and NMR spectra. Phenyl isocyanate in HF was found to produce $(\phi\text{NH})_2\text{CO}$ and a small amount of impurity, possibly phenylcarbonyl fluoride, which showed a peak at 8.0 ppm in the fluorine NMR. Attempts at mixing NSF_3 and ϕNCO in HF produced only the diphenylurea.

Physical Properties of the Impure N-Phenyl-N'-Pentafluorosulfanylurea.

Infrared Spectrum. The infrared spectrum taken in a KBr pellet is shown in Figure 7 and partial assignments made in Table IV. In addition to the mixed urea, there appears to be a primary ammonium salt as an impurity.

NMR. The NMR spectra were obtained on a JEOL PS-100 FT for proton and fluorine at 100 MHz and 94 MHz respectively. Dimethyl sulfoxide was used as the solvent. The proton spectrum consisted of a very broad peak at 8.8 ppm, a sharp peak at 8.5 ppm, a multiplet centered at 7.3 ppm, a small peak at 5.7 ppm, and a broad peak at 4.5 ppm. The broad peak at 8.8 ppm is probably due to the two different NH protons. The peak at 8.5 and the multiplet at 7.3 are due to the phenyl protons. The small peak at 5.7 could be an NH proton in the impurity, while the broad peak at 4.5 ppm could be due to water. The fluorine spectrum (Figure 8) consisted of a typical

AB_4 spectrum with the center of the apical and basal peaks at -91.79 ppm and -76.08 ppm referenced to internal Freon-11. The coupling constant was determined to be 146 cps. The values for the proton and fluorine peaks are within the range of those for similar compounds (10) (20).

Mass Spectrum. Because of the presence of an unknown impurity, only the six peaks for the heaviest fragments are listed in Table V. In addition a few lower peaks are listed which corresponds to other important fragments. The fragmentation is similar to that observed for the symmetrically substituted urea (6) and malonamide (See Table III) in loss of two molecules of HF.

Melting Point. The impure sample had a melting point starting at 132° and continuing up to 140° .

Elemental Analysis. The carbon, hydrogen, and nitrogen analysis was done by the Departmental analyst on a Perkin-Elmer 240 Elemental Analyzer. Calculated for $C_7H_7N_2OSF_5$: C 32.06, H 2.67, N 10.69. Found C 34.00, H 3.20, N 9.51.

Solubility. The urea was found to be soluble in dimethyl sulfoxide and slightly soluble in chloroform. It was insoluble in carbon tetrachloride.

DISCUSSION

Pentafluorosulfonyl isocyanate reacts with aniline to produce N-phenyl-N'-pentafluorosulfonylurea. This reaction is a classical organic synthesis and illustrates the ability of the isocyanate to react with compounds containing acidic protons. The only drawback in

Table IV

Infrared Spectrum of Impure
N-Phenyl-N'-Pentafluorosulfonylurea

cm ⁻¹	Intensity*	Assignment
3310	s.	N-H stretch
3240	s.	N-H stretch
3000	s. (broad)	NH ₃ ⁺
2600	m.	NH ₃ ⁺
1665	v.s.	C=O stretch
1600	s.	C=C (aromatic)
1550	v.s.	N-H bend
1510	s.	NH ₃ ⁺
1495	s.	C=C (aromatic)
1450	m.	C=C (aromatic)
1320	m.	
1295	m.	
1250	m.	
1210	s.	C-N
1190	s.	
1160	m.	
1105	m.	
1080	s.	
1060	s.	
1025	m.	

Table IV
(Cont.)

cm ⁻¹	Intensity	Assignment
940	s.	
900	v.s.	SF ₄ square stretch
865	v.s.	SF stretch
850	v.s.	
835	s.	S-N stretch
795	s.	
755	m.	C-H bend (aromatic)
735	s.	
690	m.	C-H bend (aromatic)
675	s.	
630	m.	
590	s.	SF ₄ wag
550	m.	
480	m.	

*v.s., very strong; s., strong; m., medium

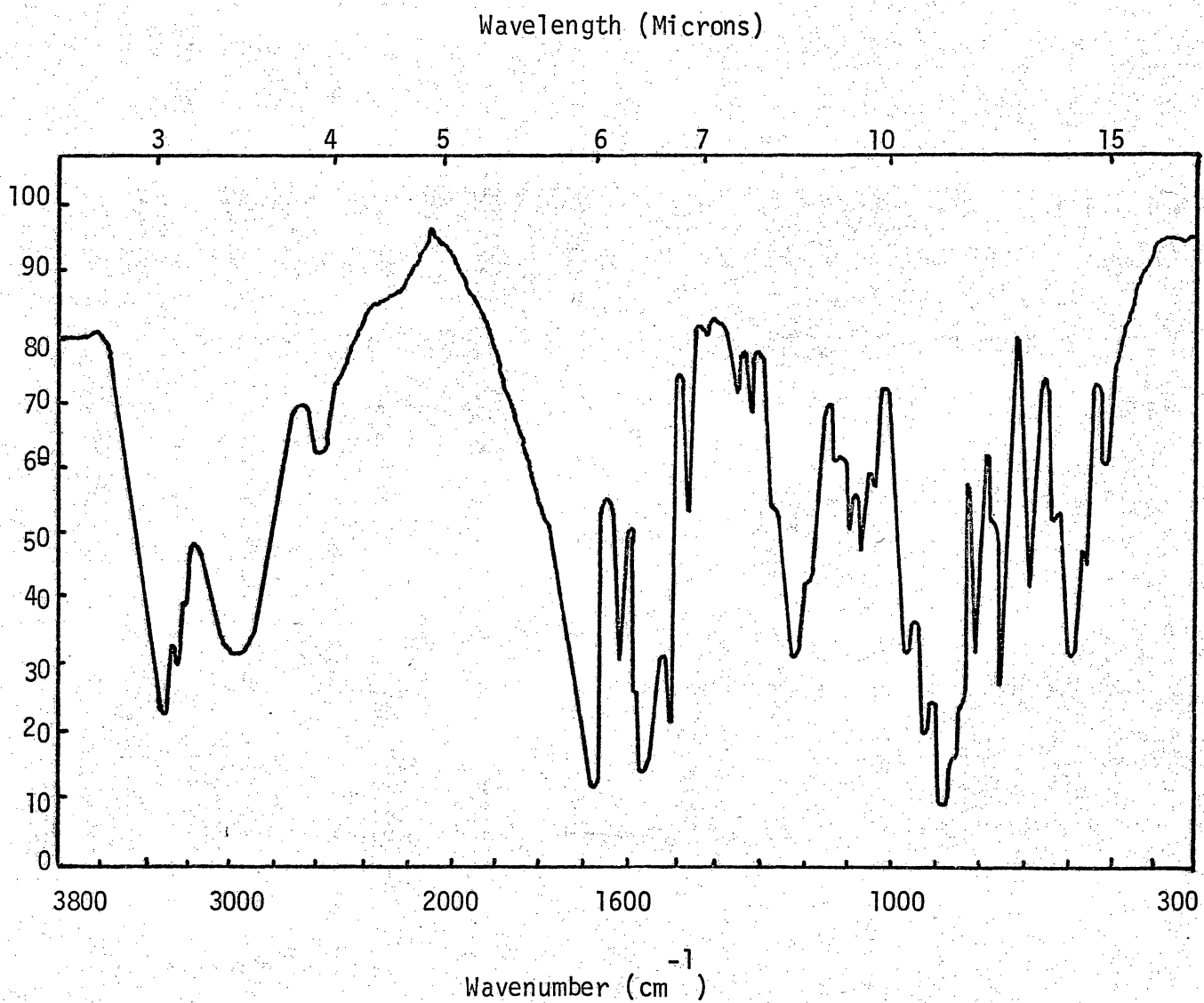


Figure 7. Infrared Spectrum of Impure N-Phenyl-N'-Pentafluorosulfanylurea

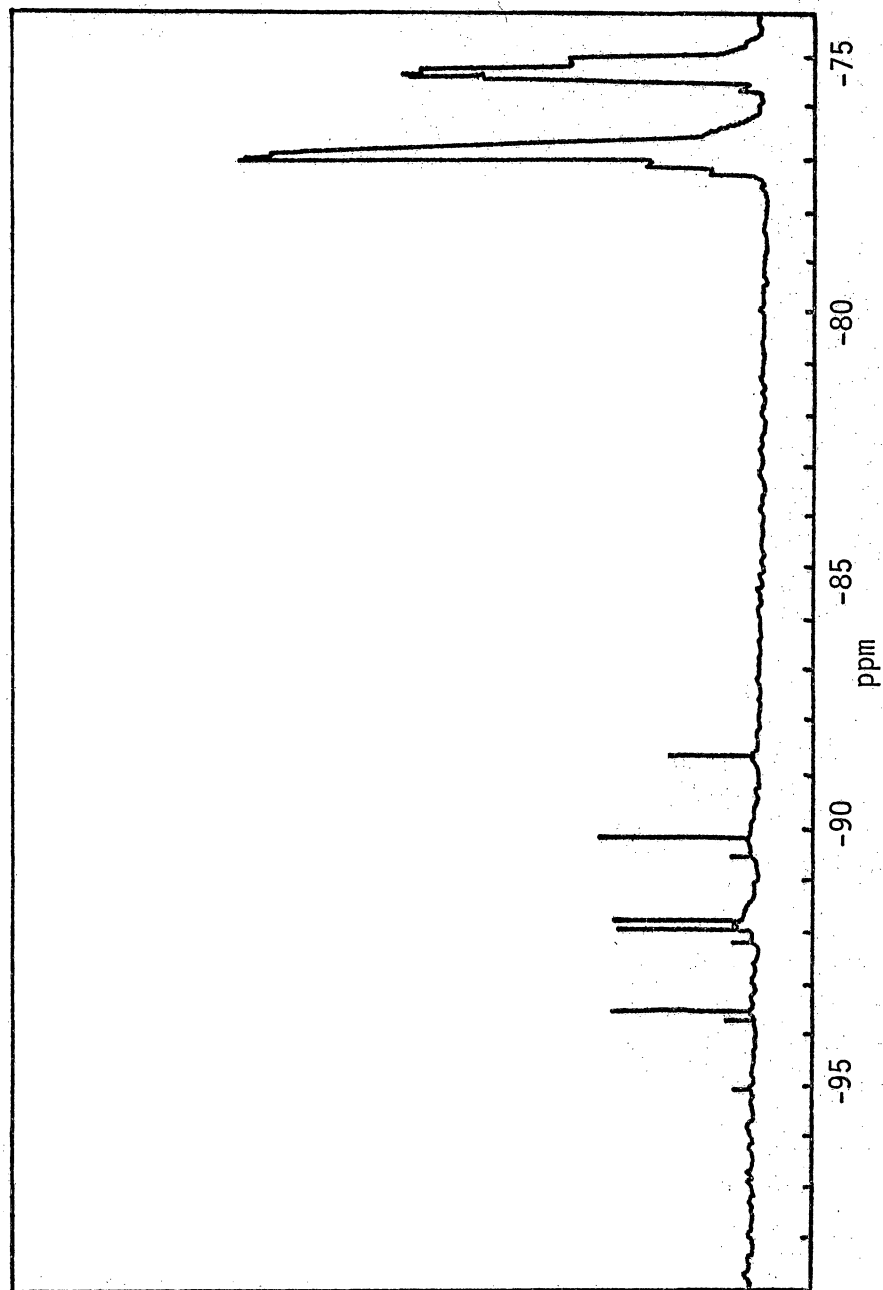


Figure 8. Fluorine NMR of $\text{SF}_5\text{N}(\text{H})\text{C}(\text{O})\text{N}(\text{H})\phi$

Table V

Partial Mass Spectrum of N-Phenyl-N'-Pentafluorosulfanylurea

	70 ev	110°
	Intensity Relative to SF ₃ ⁺	
m/e	Relative Intensity	Ion
262	2.2	C ₆ H ₅ N(H)C(O)N(H)SF ₅ ⁺
242	1.1	C ₆ H ₅ N(H)C(O)NSF ₄ ⁺
222	18.9	C ₆ H ₅ NC(O)NSF ₃ ⁺
169	3.9	SF ₅ NCO ⁺
157	27.8	C ₆ H ₅ NS(F)NH ⁺
150	27.8	SF ₄ NCO ⁺
136	55.5	C ₆ H ₄ NSN ⁺
127	73.5	SF ₅ ⁺
119	95.5	C ₆ H ₅ NCO ⁺
109	93.2	C ₅ H ₃ NS ⁺
93	93.2	C ₆ H ₅ NH ₂ ⁺
89	100.0	SF ₃ ⁺
77	83.3	C ₆ H ₅ ⁺

further reactions using SF_5NCO appears to be the basicity of the other reactant, as shown by the decomposition of SF_5NCO by ammonia. The SF_5NCO appears to an ideal compound for producing compounds containing a pentafluorosulfanyl-amido group. The use of SF_5NCO is hindered due to problems inherent in its preparation. Impurities, such as NSF_3 , are almost always present and are difficult to remove. Preparation of SF_5NCO using NSF_3 , COF_2 , and HCl appears to offer the best route due to the inability of a stable intermediate such as SF_5NH_2 to be formed which can further react with the isocyanate to give $(\text{SF}_5\text{NH})_2\text{CO}$. The peak in the mass spectrum at 157 and the singlet in the fluorine NMR at -53 ppm suggests the the impurity is a new compound $\phi\text{N}=\text{S}(\text{F}_2) = \text{NH}$ or $\phi\text{NHS}(\text{F}_2) \equiv \text{N}$. This could occur from a reaction of NSF_3 and ϕNH_2 followed by addition of HF .

Attempts to prepare the mixed urea from SF_5NH_2 and phenyl isocyanate failed, but did produce diphenylurea. This was probably due to the SF_5NH_2 decomposing to NSF_3 and HF to form the carbamyl fluoride. Two molecules of carbamyl fluoride could then react and eliminate COF_2 to give diphenylurea.

SUMMARY

N-Phenyl-N'-pentafluorosulfanylurea was produced from the reaction of SF_5NCO and aniline. Attempts to prepare the urea from SF_5NH_2 and phenyl isocyanate failed to produce N-phenyl-N'-pentafluorosulfanylurea, but produced a nearly quantitative yield of diphenylurea. There is also evidence for the formation of a new compound $\phi\text{N}=\text{S}(\text{F}_2) = \text{NH}$ or $\phi\text{NHS}(\text{F}_2) \equiv \text{N}$. Attempts to prepare

N-pentafluorosulfanylurea from the reaction of SF_5NH_2 and HNCO or SF_5NCO and NH_3 failed.

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PREPARATION AND PROPERTIES OF
N-PENTAFLUOROSULFANYLAMIDO DERIVATIVES

by

Robert Edwin Shaddix

(Abstract)

N,N'-Bis(pentafluorosulfanyl)urea was synthesized from thiazyl trifluoride, carbonyl fluoride, and either anhydrous hydrogen fluoride or anhydrous hydrogen chloride. Attempts at reacting the urea with ethyl malonate, malonic acid, malonyl chloride, carbon suboxide, and ethyl crotonate all failed. The urea was found to be unstable in both acidic and basic media.

N,N'-Bis(pentafluorosulfanyl)malonamide was prepared from pentafluorosulfanylamine and carbon suboxide by mixing them either as gases or in a solvent. The malonamide was found to decompose with tertiary amines such as pyridine. Attempts to react the malonamide with carbonyl chloride, fluoride, and sulfide to form a barbiturate were unsuccessful.

N-Phenyl-N'-pentafluorosulfanyl was prepared from pentafluorosulfanyl isocyanate and aniline. Attempts to prepare the mixed urea from pentafluorosulfanylamine and phenyl isocyanate failed. A possible product from a reaction of thiazyl trifluoride and aniline was either $\phi N=S(F_2) = NH$ or $\phi NHS(F_2) \equiv N$. Attempts to prepare N-pentafluorosulfanylurea from the reaction of SF_5NCO and NH_3 or SF_5NH_2 and $HNCO$ failed.