different from $FN{=}SF_4$ and $CH_2{=}SF_4$ in this regard.

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Registry No. SF_5NClF, 74542-21-5; SF_5NHF, 74542-22-6; $FN{=}SF_4$, 74542-20-4; $SF_3{\equiv}N$, 15930-75-3; ClF, 7790-89-8; F_2, 7782-41-4; TFA, 76-05-1.

Contribution from the Department of Chemistry,
Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Acylations of Pentafluorosulfanylamine, SF_5NH_2

JOSEPH S. THRASHER, JON L. HOWELL, and ALAN F. CLIFFORD*

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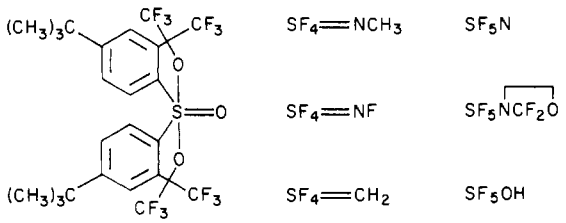
Acylation of SF_5NH_2 with select acyl halides has produced the corresponding *N*-pentafluorosulfanyl amides. The best yields were obtained in the reactions of acyl halides containing electron-deficient carbonyls. The first liquid pentafluorosulfanylcarbamyl derivative $SF_5NHC(O)F$ was prepared by the reaction of equimolar quantities of NSF_3, COF_2, and anhydrous HF. The reaction of SF_5NH_2 with $ClC(O)CF_2CF_2C(O)Cl$ produced not only the expected diamide $[SF_5NHC(O)CF_2]_2$ but also the novel cyclic imide $SF_5NC(O)CF_2CF_2C(O)$. Other *N*-pentafluorosulfanyl amides were prepared from the reaction of SF_5NCO with suitable carboxylic acids. Several of the *N*-pentafluorosulfanyl amides synthesized were allowed to react with PCl_5 to produce the corresponding chloro imines. The compound $SF_5NHC(O)NHSF_5$ was also found to react with PCl_5 to produce the carbodiimide $SF_5N{=}C{=}NSF_5$. The products isolated were characterized by infrared and NMR spectroscopy, mass spectrometry, and elemental analysis.

Introduction

In recent years there has been considerable interest in the synthesis and characterization of compounds containing five- and six-coordinate sulfur(VI).[1-11] This interest includes compounds containing sulfur as the central atom surrounded by five or six ligands as well as those employing six-coordinate sulfur as a functional group (e.g., the pentafluorosulfanyl group, SF_5).



Compounds containing the pentafluorosulfanyl group are of particular interest since they often possess the advantageous properties of the parent compound sulfur hexafluoride. These properties include a high group electronegativity, a large steric bulk (greater than than of F or CF_3), a nonfluctional hexacoordinate stereochemistry, and high thermal and hydrolytic stability.

While investigations of carbon- and oxygen-substituted SF_6 derivatives have been carried out in other laboratories, we have for sometime been investigating those compounds containing the *N*-pentafluorosulfanyl linkage. Along these lines we wish to report our results in the synthesis and characterization of several new $SF_5N<$ compounds as well as an alternate synthesis of several previously reported $SF_5N<$ compounds. Three types of reactions have been investigated: the acylation of SF_5NH_2, the reaction of SF_5NCO with carboxylic acids, and the conversion of NSF_5 amides to chloro imines by reaction with PCl_5.

Prior to this investigation two methods for the synthesis of compounds containing pentafluorosulfanyl-nitrogen-carbon linkages had been reported. The first, reported by Tullock et al., involves the photolytically induced free radical reaction between SF_5Cl and selected nitriles.[12] This reaction is limited in scope and provides only low yields of these materials. The chloro pentafluorosulfanylimines produced can further react to give secondary amines or alternate imines as shown by the two examples in Scheme I.[12,13]

Scheme I

$$SF_5Cl + R_fCN \xrightarrow{h\nu} SF_5N{=}C(Cl)R_f \quad (1)$$

$$SF_5N{=}C(Cl)R_f + HF \xrightarrow{NaF} SF_5NHCF_2R_f \quad (2)$$

$$SF_5N{=}C(Cl)R_f + NaN_3 \rightarrow SF_5N{=}C(N_3)R_f \quad (3)$$

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The other method, reported by Shreeve and co-workers,[14,15] employs nucleophilic displacement of fluorine from a hexacoordinate sulfur(VI) species. They have found that the choice of nucleophiles is extremely limited. Only $(CH_3)_3SiN(CH_3)_2$ or $LiN{=}C(CF_3)_2$ has been found to react with hexacoordinate sulfur(VI) compounds in such a way as to preserve the high coordination number and oxidation state—all others either fail to react or cause reduction of the sulfur. Also, these reactions proceed only under controlled low-temperature reaction conditions. Scheme II gives examples of reactions involving both nucleophiles.[14] The example described in eq 4 has been reported only for the reaction of the silane with SF_5Cl or SF_5Br. The product shown in eq 5 contains a pentacoordinate sulfur(VI) and is probably formed from an intramolecular 1,3-fluoride shift since the stereochemistry is fixed and the molecule nonfluctional. This product could probably be coordinately saturated by the addition of hydrogen fluoride as in the reported reaction of HF and $CF_3SF_3{=}NCF_3$.[16]

Scheme II

$$SF_5Cl + (CH_3)_2NSi(CH_3)_3 \rightarrow \textit{trans}\text{-}ClSF_4N(CH_3)_2 + FSi(CH_3)_3 \quad (4)$$

$$SF_5Br + LiN{=}C(CF_3)_2 \rightarrow BrSF_3{=}NCF(CF_3)_2 + LiF \quad (5)$$

We have investigated methods which have a broader scope than either of the two aforementioned methods. These methods, which are not limited to one or several specific reagents, have allowed us to prepare several new compounds and to provide an alternate synthesis for several previously reported compounds. The scope of our investigation, as well as a discussion of the characteristics of the new compounds, is included.

Results and Discussion

Acylations of SF_5NH_2. The present investigation shows that SF_5NH_2 reacts readily at room temperature with various acid chlorides and fluorides containing electron-deficient carbonyl groups to produce the novel *N*-pentafluorosulfanyl amides, $SF_5NHC(O)R$. Since the reaction of NSF_3 and HF to produce SF_5NH_2 has been shown to be an equilibrium reaction,[17] the SF_5NH_2 used in these reactions was generated in situ. We have also found by monitoring the reaction of NSF_3 and HF at −25 °C that within approximately 40 min the pressure of the reaction mixture has returned to the vapor pressure of HF at that temperature.[18] Therefore, the NSF_3 and HF were allowed to react for a minimum of 35 min, and usually longer, prior to the addition of the acid chloride or fluoride. In several of the reactions with acid fluorides only 1 equiv of HF/1 equiv of NSF_3 was used since an additional equiv of HF would be produced as a byproduct in the reaction.

Remarkably enough, the analogous acylation reactions of fluorosulfonamide, FSO_2NH_2, have not been reported; however, (trifluoroacetyl)fluorosulfonylimide, $FSO_2NHC(O)CF_3$, has been prepared via an alternate route[19,20] as shown in eq 6. Thus, SF_5NH_2 was first allowed to react with $CF_3C(O)F$

$$CF_3COOH + FSO_2N{=}PCl_3 \rightarrow FSO_2NHC(O)CF_3 + O{=}PCl_3 \quad (6)$$

in order to produce the corresponding *N*-pentafluorosulfanyl derivative. This amide $SF_5NHC(O)CF_3$, a white solid with approximately 10 torr vapor pressure at 25 °C, was produced in 79% yield and was identified by its NMR, IR, and mass spectral analyses.

$$CF_3C(O)F + SF_5NH_2 \rightarrow SF_5NHC(O)CF_3 + HF \quad (7)$$

The isolation of $SF_5NHC(O)CF_3$ from the above reaction led us to speculate that $SF_5NHC(O)F$ could be made from the reaction of SF_5NH_2 and COF_2. Previously the only product isolated from this reaction was SF_5NCO (eq 8);[21]

$$COF_2 + SF_5NH_2 \rightarrow SF_5NCO + 2HF \quad (8)$$

however, the reaction mixture was always placed on sodium fluoride to remove the excess HF. We have found that if an equimolar reaction mixture of NSF_3, COF_2, and AHF is examined without being placed on NaF, the product $SF_5NHC(O)F$ is obtained in high yield. This product is a colorless liquid, whereas all previously reported pentafluorosulfanylcarbamyl derivatives have been white crystalline solids.[12,21-23] The compound $SF_5NHC(O)F$ has a vapor pressure of approximately 50 torr at 25 °C and spontaneously loses HF when in contact with glass or NaF.

The acylation of SF_5NH_2 by oxalyl chloride produced the corresponding diamide $SF_5NHC(O)C(O)NHSF_5$ in 78% yield, while acylation by perfluorosuccinyl chloride yielded not only the expected diamide $[SF_5NHC(O)CF_2]_2$ but also the novel cyclic succinimide $SF_5NC(O)CF_2CF_2C(O)$. The succinimide, obtained in 43% yield, is a white, extremely air-sensitive solid with a vapor pressure of approximately 1 torr at 25 °C. Its identity was confirmed by exact mass spectrometry along with IR and NMR spectroscopy and EI mass spectrometry.

The acylation of SF_5NH_2 can even be accomplished by acetyl chloride and acrylyl chloride, but these seem to be the extreme limits of the synthetic method since low yields are obtained in both reactions. The acrylamide $SF_5NHC(O)CH{=}CH_2$ is not the isolated product in the reaction with acrylyl chloride, as the HCl generated readily saturated the double bond to give $SF_5NHC(O)CH_2CH_2Cl$ (eq 9). The reaction

$$CH_2{=}CHC(O)Cl + SF_5NH_2 \rightarrow SF_5NHC(O)CH{=}CH_2 + HCl \rightarrow SF_5NHC(O)CH_2CH_2Cl \quad (9)$$

of SF_5NH_2 with malonyl chloride did not yield a product containing the pentafluorosulfanyl moiety,[22,24] and no reaction occurred between the amine and benzoyl chloride.

Reactions of SF_5NCO with Carboxylic Acids. The reaction of SF_5NCO with certain carboxylic acids provides an alternate synthetic method to the previously unknown $SF_5NHC(O)R$ compounds. The reaction is believed to pass through a mixed-acid anhydride intermediate which readily loses CO_2 to give the corresponding *N*-pentafluorosulfanyl amide (eq 10); however, no attempts were made to isolate such intermediates in the reactions being discussed.

$$SF_5NCO + RCOOH \rightarrow [SF_5NHC(O)O(O)CR] \rightarrow SF_5NHC(O)R + CO_2 \quad (10)$$

Both CH_3COOH and $CH_2{=}CHCOOH$ were found to react readily with SF_5NCO at 25 °C. The yields of 98 and 35% for $SF_5NHC(O)CH_3$ and $SF_5NHC(O)CH{=}CH_2$, respec-

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Table I. NMR Data

^{19}F	$\delta(SF_A)$	$\delta(SF_B)$	$\delta(CF)$	J_{AB}/Hz	solvent
		Pentafluorosulfanyl Amides and Imides			
$SF_5NHC(O)F$	68.7	68.7	−8.3		Freon 11
$SF_5NHC(O)CF_3$	87.4	73.5	−59.6	156.7	Me_2SO-d_6
$SF_5NHC(O)CH_3$	77.1	67.8		157.3	Me_2SO-d_6
$SF_5NHC(O)CH{=}CH_2$	81.5	73.7		157.9	Me_2SO-d_6
$SF_5NHC(O)CH_2CH_2Cl$	82.3	72.9		153.7	Me_2SO-d_6
$[SF_5NHC(O)-]_2$	76.2	69.1		158.2	Me_2SO-d_6
$[SF_5NHC(O)-]_2$	69.3	67.7		158.9	acetone
$[SF_5NHC(O)]_2CH_2$	81.0	72.8		158.9	Me_2SO-d_6
$SF_5NHC(O)CH_2C(O)OH$	81.5	72.6		159.7	Me_2SO-d_6
$[SF_5NHC(O)CF_2-]_2$	89.8	75.6	−114.4	159.6	Me_2SO-d_6
$SF_5NC(O)CF_2CF_2C(O)$	59.6	73.2	−126.7	156.5	$CDCl_3$
		Chloro Pentafluorosulfanylimines and -carbodiimides			
$SF_5N{=}C(Cl)CF_3$	64.0	59.2	−66.7	155.4	CCl_4
$SF_5N{=}C(Cl)CH_3$	69.8	58.3		156.0	CCl_4
$[SF_5N{=}C(Cl)-]_2$	65.1	59.5		153.2	CCl_4
$SF_5N{=}C{=}NSF_5$	65.6	82.1		157.6	CCl_4

tively, make this a better synthetic method for preparing these amides than the corresponding acylations of SF_5NH_2. Unlike the room-temperature reaction of CH_3COOH or $CH_2{=}CH$-COOH with SF_5NCO, a temperature of 60 °C was required before malonic acid would react with SF_5NCO. In this case both the amide–acid $SF_5NHC(O)CH_2COOH$ and the diamide $SF_5NHC(O)CH_2C(O)NHSF_5$ were obtained from the product mixture. We had previously synthesized this diamide from the reaction of SF_5NH_2 with carbon suboxide[22] as shown in eq 11.

$$2SF_5NH_2 + C_3O_2 \rightarrow SF_5NHC(O)CH_2C(O)NHSF_5 \quad (11)$$

$$2SF_5NCO + CH_2(COOH)_2 \rightarrow SF_5NHC(O)CH_2C(O)NHSF_5 + 2CO_2 \quad (12)$$

Pentafluorosulfanyl isocyanate failed to react with carboxylic acids in which the carboxylate group is electron deficient, including CCl_3COOH and CF_3OOH. It also failed to react with PhCOOH presumably due to steric hindrance as well as the weakly nucleophilic nature of the carboxylate group. The sulfonyl analogue, fluorosulfonyl isocyanate (FSO_2NCO), has been reported to react with CCl_3COOH[25] but not with CF_3-COOH,[20] thus indicating that this isocyanate is slightly more reactive than SF_5NCO. The compound $ClSO_2NCO$ has also been reported to react with PhCOOH[26] to yield $ClSO_2NHC$-(O)Ph. Only the *N*-(pentafluorosulfanyl)benzamides could not be prepared by either synthetic method, but work is continuing in our laboratory on synthesizing this other class of compounds.

Chloro Imines. Pentafluorosulfanylimines were prepared from PCl_5 and the appropriate amide (eq 13). This reaction

$$SF_5NHC(O)R + PCl_5 \xrightarrow[60\text{–}100\ °C]{CCl_4} SF_5N{=}C(Cl)R + POCl_3 + HCl \quad (13)$$

has also been successfully employed by Roesky[20,25,27] in the synthesis of *N*-fluorosulfonylimines and is a general method for the synthesis of chloroimines from amides.[28] This synthetic procedure provides an alternate method for the preparation of chloro pentafluorosulfanylimines previously unavailable except through the photolytic method of Tullock et al.[12] Of

Table II. ^{19}F Chemical Shifts of the Sulfonyl Fluorine in $FSO_2NHC(O)CX_3$ and $FSO_2N{=}C(Cl)CX_3$ Compounds[20,25]

compd	SF shift	compd	SF shift
$FSO_2NHC(O)CH_3$	51.4	$FSO_2N{=}C(Cl)CH_3$	53.8
$FSO_2NHC(O)CH_2Cl$	52.4	$FSO_2N{=}C(Cl)CH_2Cl$	54.9
$FSO_2NHC(O)CHCl_2$	54.9	$FSO_2N{=}C(Cl)CHCl_2$	56.0
$FSO_2NHC(O)CCl_3$	53.3	$FSO_2N{=}C(Cl)CCl_3$	57.3
$FSO_2NHC(O)CH_2F$		$FSO_2N{=}C(Cl)CH_2F$	54.5
$FSO_2NHC(O)CF_3$	53.8	$FSO_2N{=}C(Cl)CF_3$	55.2

the several representative amides treated with PCl_5, only the product $SF_5N{=}C(Cl)CH_3$ had not been previously synthesized. The chloro imines are liquids at room temperature and are surprisingly stable toward hydrolysis.[20,28]

One amide not prepared by the previously described procedures, of long term interest to us, is $SF_5NHC(O)NHSF_5$.[21] This amide also reacts with PCl_5 producing the carbodiimide $SF_5N{=}C{=}NSF_5$. Equation 15 shows a method previously

$$SF_5NHC(O)NHSF_5 + PCl_5 \xrightarrow[60\ °C]{CCl_4} SF_5N{=}C{=}NSF_5 + POCl_3 + 2HCl \quad (14)$$

$$SF_5NH_2 + SF_5N{=}CCl_2 \rightarrow SF_5N{=}C{=}NSF_5 + 2HCl \quad (15)$$

reported by us[29] for the synthesis of this carbodiimide. The new procedure has allowed a more complete analysis of this compound. The physical characteristics for the carbodiimide are included with those of the chloro imines.

NMR Parameters. The fluorine-19 NMR spectrum of a pentafluorosulfanyl group is a powerful diagnostic proof for the positive identification of compounds containing this moiety. This is due to its distinctive AB_4 splitting pattern. All of the compounds described in this paper exhibit this distinctive splitting pattern, and some interesting observations have emerged from the study of the ^{19}F NMR spectral parameters.

The ^{19}F NMR spectrum of $SF_5NHC(O)F$ exhibits an atypical AB_4X pattern seen before only in SF_5OF.[30] The spectrum is very similar to that of SF_5OF initially described by Cady et al.[30a] as a doublet and an asymmetrical sextet. Cady[30b] as well as Harris and Packer[30c] have since shown that the spectrum of SF_5OF consists of many more lines and that the overall appearance is merely a consequence of the AB_4X

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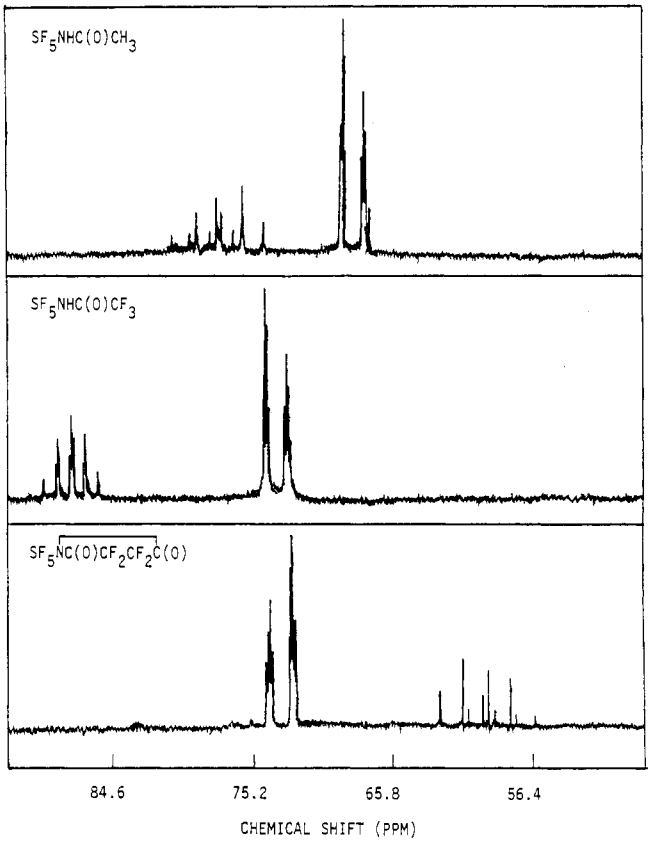

Figure 1. ^{19}F NMR spectra comparison of the sulfur(VI)–fluorine region in $SF_5NHC(O)CH_3$, $SF_5NHC(O)CF_3$, and $SF_5\overline{NC(O)C}\overline{F_2CF_2C}(O)$ (relative to CCl_3F).

spin system. Several other pentafluorosulfanyl compounds, including SF_5OOSF_5, SF_5OOCF_3, and SF_5SF_5, have also been shown to exhibit atypical AB_4 patterns due to the small chemical shift difference between the A and B nuclei.[31,32]

It is widely known that ^{19}F NMR chemical shift values vary significantly even in compounds containing slightly different substituents. This effect can be seen in the case of the fluorosulfonyl amides and imines[18,23] as shown in Table II. The sulfonyl fluorine is deshielded, sometimes nonuniformly, by the introduction of chlorine and fluorine substituents as much as five bonds away. A similar effect is observed on the chemical shifts of the axial and equatorial fluorines of the pentafluorosulfanyl amides and imines shown in Table I; however, the axial fluorine is often more influenced by a change of substituents. This is especially clear when one examines the S(VI) region of the ^{19}F NMR spectrum of both $SF_5NHC(O)CH_3$ and $SF_5NHC(O)CF_3$ as shown in Figure 1. Since the downfield shifts of the axial and equatorial fluorine resonances in $SF_5NHC(O)CF_3$ are not relative, the overall appearance of the splitting pattern changes remarkably as the SF_5 group moves toward an AX_4 spin system. The fact that the axial fluorine is often more influenced by substitution in SF_5R compounds has been observed by others[33,34] and explained as a trans effect.[34]

Several reports have appeared in the literature concerning significant solvent effects on ^{19}F NMR chemical shifts.[35] Another example of this with a unique difference is reported here. Analysis of the ^{19}F NMR of $[SF_5NHC(O)]_2$ taken in acetone and Me_2SO-d_6 shows that not only are the chemical shifts different but that the axial fluorine is substantially more affected by the change of solvents than are the equatorial fluorines. This solvent effect is most likely due to an interaction which disrupts hydrogen bonding in the compound. As shown in Table I, this solvent-induced magnetic disruption is of sufficient strength that the chemical shift of the equatorial fluorines changes by 1.4 ppm, while the chemical shift of the fluorine trans to the amide nitrogen changes by 6.9 ppm. This effect has been observed previously by us[36] and is the only report of the nonrelative shifting of the axial and equatorial fluorine resonances of a pentafluorosulfanyl group as an effect of solvent.

The ^{13}C NMR spectrum of $[SF_5NHC(O)]_2$ also proves to be interesting, especially when compared to that of $(SF_5NH)_2CO$. In $[SF_5NHC(O)]_2$ the carbon resonance centered at 156.1 ppm is a quintet (J_{SF_4-C} = 3.4 Hz) due to coupling with four equatorial fluorines of an SF_5 group, while in $(SF_5NH)_2CO$ the carbon resonance at 161.i ppm is a sharp singlet. These observations may be best explained by considering "through-space" coupling with the fact that in SF_5X compounds, where X contains fluorine, $|J_{BX}|$ is always much larger than $|J_{AX}|$.[32,37]

Another important, and as yet unexplained, feature of compounds containing the pentafluorosulfanyl moiety involves the relative chemical shifts of the axial and equatorial fluorines with respect to each other. As shown in Figure 1, the resonance of the axial fluorine in both amides appears downfield from the resonance of the equatorial fluorines, while the opposite is true for the succinimide. This is also the case when comparing the chloro imines to the carbodiimide as shown in Table I. Generally the resonance of the axial fluorine in an SF_5–nitrogen compound appears farthest downfield; however, there is a reasonable number of exceptions, including $SF_5N{=}C{=}O$,[21] $SF_5N{=}C{=}S$,[23] $SF_5N{=}SF_2$,[38] $SF_5N{=}S(O)F_2$,[39] and $SF_5N(CF_3)_2$.[40] No unified theory has yet been proposed or reported to explain these observations.

Infrared Spectra. All of the amides exhibit the N–H stretching frequency in the 3430–3180-cm^{-1} region, as well as the carbonyl amide I stretch in the 1830–1690-cm^{-1} region with the expected higher energy shift with increasing electronegativity of the substituent. For example, the amide I stretch of $SF_5NHC(O)F$ has the highest frequency at 1830 cm^{-1} followed by the amide I stretch of $SF_5NHC(O)CF_3$ at 1800 cm^{-1}. The amides also show the characteristic S–F stretching and wagging frequencies of the SF_5 group. These appear at 950–830 and 600 ± 12 cm^{-1}, respectively.

The pentafluorosulfanylimines show a strong N=C stretching frequency in the high 1600-cm^{-1} region which is typical of this type of compound. They also show the characteristic S–F stretching and wagging frequencies of the SF_5 group. The compound $SF_5N{=}C{=}NSF_5$ also has the characteristic SF_5 bands as well as the band normally associated with the N=C=N group[41] (2154 cm^{-1}).

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This investigation has demonstrated synthetic methods which allow the preparation of a variety of *N*-pentafluorosulfanyl compounds. These methods allow the synthesis of alkyl, perfluoroalkyl, cyclic and *F*-formyl amides as well as providing an alternate, more versatile synthesis of $N-SF_5$ imines. Each compound has been identified through its infrared, mass spectroscopic and NMR spectra.

Several new, exciting, and heretofore unreported observations about the NMR spectra of these compounds have been made.

Experimental Section

The compounds synthesized were analyzed by infrared and nuclear magnetic resonance spectroscopy and mass spectrometry and where possible by C, H, N, and S analysis.

An all-Pyrex glass high-vacuum system was employed for handling the reactants and products except for anhydrous HF (AHF) which was handled on a metal vacuum system. Infrared spectra were obtained on a Beckman 20A-X infrared spectrophotometer, either on gases, pressure 1–100 torr, or on mulls in either halocarbon or mineral oil. Mass spectra were obtained on either a Hitachi Perkin-Elmer RMU-7 mass spectrometer, a Finnigan Model 3200 quadrupole mass spectrometer, or a Varian MAT 112 high-resolution mass spectrometer using either a solid inlet probe or a controlled-gas-flow inlet. The ^{19}F and ^1H NMR spectra were taken on either a JEOL PS-100 or a Varian EM-390 nuclear magnetic resonance spectrometer using CCl_3F and $(CH_3)_4Si$, respectively, as internal standards. The ^{13}C NMR spectra were taken on a JEOL FX 60Q nuclear magnetic resonance spectrometer using Me_2SO-d_6 as an internal standard. Elemental analyses were obtained from the Chemistry Department's Perkin-Elmer 240 elemental analyzer or from Galbraith Laboratories, Knoxville, TN. Melting points were taken on a Mel-Temp apparatus and are uncorrected.

All solvents and reagents were distilled or sublimed prior to use. Phosphorus pentachloride was used only in an inert (Ar) atmosphere box and was not purified prior to use. The compounds COF_2,[42] $CF_3C(O)F$,[43] SF_5NCO,[21] and $SF_5NHC(O)NHSF_5$[21] were synthesized and purified by known literature methods. The compound SF_5NH_2[17] was produced in situ from the reaction of NSF_3 and HF.

Preparation of $SF_5NHC(O)F$. In a typical reaction, 150 mmol each of NSF_3, COF_2, and HF were condensed into a 75-mL stainless-steel cylinder at −196 °C. After the mixture was allowed to react for 5 days at room temperature, the volatile components were transferred onto a NaF scrubber while the reaction cylinder was held at −50 °C. The product could then be removed from the cylinder as a colorless liquid. The $SF_5NHC(O)F$ has a vapor pressure of ~50 torr at 25 °C and spontaneously loses HF when in contact with glass or NaF. The yield (~50%) was determined by removing the product to a NaF scrubber for several hours and then measuring the quantity of SF_5NCO recovered. IR (capillary film): 3260 (vs), 2980 (m), 2720 (w), 1830 (vs), 1500 (vs), 1350 (w), 1215 (vs), 875 (vs), 790 (m), 750 (m), 705 (m), 655 (m), 605–575 (s) cm^{-1}. Mass spectrum (70 eV) *m/e* (relative intensity): 170 $[M - F]^+$ (0.7), 169 $[M - HF]^+$ (15.3), 150 $[SF_4NCO]^+$ (34.4), 127 $[SF_5]^+$ (100.0), 108 (7.4), 104 (9.3), 103 (3.2), 89 (50.0), 70 (16.0), 51 (7.8), 47 $[COF]^+$ (84.4), 44 (31.3), 43 (3.4), 42 (7.4). ^1H NMR: δ 9.28 (s, NH).

Anal. Calcd for $CHNSF_6O$: C, 6.35; H, 0.53; N, 7.54; S, 16.93. Found: C, 6.41; H, 0.48, N, 7.54; S, 17.58.

Preparation of $SF_5NHC(O)CF_3$. Gaseous NSF_3 (10.0 mmol) and HF (0.25 mL, 12.5 mmol) were condensed into a Kel-F reactor at −196 °C and were allowed to react at room temperature. After 12 h, $CF_3C(O)F$ (10.0 mmol) was condensed into the reaction vessel and the solution was warmed slowly to ambient temperature. Within the period of 1 week a product had precipitated from the reaction mixture. The volatile products were then removed to a NaF scrubber while the temperature of the reaction vessel was maintained between −60 and −15 °C. The product remaining in the reaction vessel was then further purified by trap-to-trap distillation, the −30 °C trap retaining the $SF_5NHC(O)CF_3$ (7.9 mmol); 79.0% yield. The compound is an easily sublimable white solid with a vapor pressure of ~10 torr at room temperature; mp 49–51 °C. IR (gas): 34.30 (s), 1800 (s), 1485 (s), 1310 (m), 1230 (s), 1185 (s), 1130 (s), 950-875 (s), 780 (w), 730 (w), 665 (m), 612 (m), 590 (w), 560 (w) cm^{-1}. Mass spectrum (70 eV) *m/e* (relative intensity): 239 M^+ (<0.1), 220 $[M - F]^+$ (<0.1), 170 $[SF_5NHCO]^+$ (33.5), 150 $[SF_4NCO]^+$ (4.1), 127 $[SF_5]^+$ (100.0), 104 (29.4), 97 (5.3), 89 (18.8), 70 (7.7), 69 $[CF_3]^+$ (79.4), 51 (8.2), 50 (7.1), 47 (7.7), 43 (12.9) 31 (4.1). ^1H NMR: δ 12.38 (s, NH). ^{13}C NMR: δ(CO) 152.8 (q) ($^2J_{C-F}$ = 40 Hz); δ(CF_3) 116.3 (q) ($^1J_{C-F}$ = −289 Hz).[44]

Attempted Preparation of $SF_5NHC(O)CF_3$. SF_5NCO (2 mmol) and CF_3COOH (2 mmol) were condensed at −196 °C into a 75-mL glass reaction cylinder containing dry $(C_2H_5)_2O$ (12.0 mmol). The reaction mixture was allowed to warm slowly to room temperature, and after several hours the volatile components were checked by infrared spectroscopy. There was no evidence for reaction; therefore, the reaction mixture was heated at 70 °C for 48 h. Again the IR spectrum of the volatile components showed only unreacted SF_5NCO and CF_3COOH along with the solvent $(C_2H_5)_2O$.

Attempted Preparation of $SF_5NHC(O)CCl_3$. A 5-mmol sample of SF_5NCO was condensed onto freshly sublimed CCl_3COOH (0.60 g, 3.67 mmol) in a 75-mL glass reaction cylinder at −196 °C. The reaction mixture was warmed to room temperature, and after 12 h the volatile components were examined by infrared spectroscopy. Since no reaction had occurred, several milliliters of dry THF was condensed into the reaction flask at −196 °C and the reaction mixture was heated at 70 °C for ~36 h. Even after the reaction mixture was heated at 100 °C for an additional 6 h the IR spectrum showed no evidence for reaction.

Preparation of $SF_5NHC(O)CH_3$. Method A. Thiazyl trifluoride, NSF_3, (5 mmol) and HF (0.17 mL, 8 mmol) were condensed into a Kel-F reactor at −196 °C and allowed to react overnight prior to the addition of freshly distilled $CH_3C(O)Cl$ (5 mmol). After 9 days the volatile products of the reaction were moved onto a NaF scrubber and 0.165 g of a crude solid product was collected. Vacuum sublimation yielded 0.105 g of a white compound analyzed to be $SF_5NHC(O)CH_3$ (14.19% yield; mp 88–90 °C).

Method B. The isocyanate, SF_5NCO (5 mmol), was condensed onto freshly distilled CH_3COOH (5 mmol) in a 75-mL glass reaction vessel at −196 °C. The mixture was warmed to room temperature and allowed to stand for 48 h at that temperature. At this time a quantity of gas in the cylinder was removed for analysis. Infrared spectroscopy showed that the gas recovered was essentially CO_2. After removal of the volatile products, the resulting solid residue was sublimed in vacuo in yield reasonably pure $SF_5NHC(O)CH_3$ (0.915 g, 98.9% yield).

$SF_5NHC(O)CH_3$: IR (mull) 3180 (vs), 2960 (s), 1720 (vs), 1680 (vs), 1510 (vs), 1250 (m), 1015 (w), 880 (vs), 765 (m), 685 (m), 600 (m), 565 (s) cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 185 M^+ (3.4), 170 $[SF_5NHCO]^+$ (2.7), 150 $[SF_4NCO]^+$ (1.0), 127 $[SF_5]^+$ (39.2), 104 (8.1), 89 (18.9), 70 (5.4), 51 (1.0), 47 (1.0), 46 $[NS]^+$ (100.0), 43 (14.9), 31 (2.2), 29 (2.4); ^1H NMR δ 11.93 (s), NH), 1.97 (s, CH_3); ^{13}C NMR: δ 164.8 (s, CO), 23.4 (q, CH_3, $^1J_{C-H}$ = 101.6 Hz).

Anal. Calcd for $C_2H_4NSF_5O$: C, 12.97; H, 2.16; N, 7.57; S, 17.30. Found: C, 12.97; H, 1.95; N, 7.59; S, 17.41.

Attempted Preparation of $SF_5NHC(O)Ph$. Method A. Hydrogen fluoride (0.4 mL, 20.0 mmol) was condensed with NSF_3 (10.0 mmol) in a Kel-F reactor at −196 °C. The mixture was allowed to warm to room temperature over 20 min and remained at that temperature for 15 min. The mixture was then refrozen, and PhC(O)Cl (10.0 mmol) was added. After a period of 2 weeks, no precipitate had yet formed in the Kel-F reactor and the volatile materials were removed to a NaF scrubber. No evidence for the production of $SF_5NHC(O)Ph$ was found upon examination of either the volatile materials or contents of the Kel-F reactor.

Method B. The isocyanate SF_5NCO (3 mmol) and $(C_2H_5)_2O$ (7.4 mmol) were condensed onto PhCOOH (0.366 g, 3.0 mmol) in a 75-mL glass reaction cylinder at −196 °C. The reaction mixture was warmed slowly to room temperature and heated at 60 °C overnight. Examination of the IR spectrum of the reaction volatiles revealed that no CO_2 had been formed. The reaction mixture was then heated at 95–100 °C for 1 week, and infrared analysis showed the absence of SF_5NCO and CO_2 but the presence of SO_2F_2.

Preparation of $SF_5NHC(O)CH{=}CH_2$. The isocyanate, SF_5NCO, (12.0 mmol) and dried $CH_2{=}CHCOOH$ (11.25 mmol) were con-

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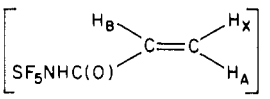
densed together at −196 °C into a 500-mL round-bottomed flask, and the mixture was allowed to warm to room temperature. After 4 days, 18.0 mmol of volatile materials containing CO_2, NSF_3, SiF_4, and some unreacted SF_5NCO were removed. Several vacuum sublimations gave $SF_5NHC(O)CH{=}CH_2$ (0.79 g, 4.0 mmol, 35.6% yield) in reasonable purity: mp 94–96 °C.

$SF_5NHC(O)CH{=}CH_2$: IR (mull) 3315 (m), 3010 (w), 2995 (w), 1705 (s), 1680 (m), 1630 (w), 1510 (s), 1415 (w), 1205 (m), 930–860 (vs), 720 (s), 590 (vs) cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 197 M^+ (2.2), 170 $[SF_5NHCO]^+$ (0.6), 127 $[SF_5]^+$ (17.7), 104 (2.0), 89 (10.1), 70 (2.9), 56 (4.3), 55 $[CH_2{=}CHCO]^+$ (100.0), 44 (4.9), 43 (12.5), 27 (65.2), 25 (11.6), 19 (50.0); ^1H NMR δ 12.65 (s, NH), 6.35 (m, CH_A), δ 6.28 (m, CH_B), 5.87 (m, CH_X, J_{AX} = 2.3 Hz, J_{BX} = 9.6 Hz, J_{AB} = 16.9 Hz);



^{13}C NMR δ 159.6 (m, CO), 130.7 (t of m, CH_2, $^1J_{C-H}$ = 161.1 Hz), 128.9 (d of m, CH, $^1J_{C-H}$ = 167.0 Hz).

Anal. Calcd for $C_3H_4NSF_5O$: C, 18.27; H, 2.03; N, 7.11; S, 16.24. Found: C, 17.91; H, 1.93; N, 7.32; S, 16.80.

Preparation of $SF_5NHC(O)CH_2CH_2Cl$. Thiazyl trifluoride, NSF_3 (6.0 mmol), and HF (0.25 mL, 12.5 mmol) were condensed into a Kel-F reactor at −196 °C and allowed to react at room temperature for 5–6 h before refreezing to −196 °C and condensing in $CH_2{=}C$-HC(O)Cl (5.0 mmol). After this mixture was allowed to react for 11 days at room temperature, the volatile materials were transferred to a NaF scrubber. The syrupy residue and white solid remaining in the Kel-F reactor were dissolved in acetone and transferred to a sublimator. From this product mixture, a white solid, SF_5NHC-$(O)CH_2CH_2Cl$ (0.035 g, 3.0% yield), was sublimed at about 40 °C. The ^1H and ^{19}F NMR spectra run on the crude product mixture showed the presence of small quantities of $SF_5NHC(O)CH{=}CH_2$ as well as $SF_5NHC(O)NHSF_5$.

$SF_5NHC(O)CH_2CH_2Cl$: mp 100–102 °C; IR (mull), 3200 (s), 2970 (s), 2740 (m), 1710 (s), 1500 (s), 1420 (s), 1370 (m), 1290 (m), 1230 (m), 1200 (m), 1140 (m), 1030 (m), 980–800 (vs), 755 (m), 718 (w), 680 (w), 650 (m), 600–555 (vs) cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 235, 233, M^+ (0.6, 1.7), 198 $[M - Cl]^+$ (4.7), 170 $[SF_5NHCO]^+$ (3.3), 150 $[SF_4NCO]^+$ (3.3), 127 $[SF_5]^+$ (19.5), 104 (1.6), 102 (3.1), 102 (4.7), 101 (5.7), 93, 91 $[ClCH_2CH_2CO]^+$ (25.0, 75.0), 89 (17.2), 87 (4.2), 85 (12.5), 70 (5.2), 65, 63 $[ClCH_2CH_2]^+$ (21.9, 65.5), 55 (18.2), 49 (6.8), 47 (13.5), 44 (13.0), 43 (8.3), 42 (10.4), 36 (6.3), 27 (100.0), 26 (15.6); ^1H NMR δ 12.26 (s, NH), 3.77 (t, CH_2Cl), 2.76 (t, $C(O)CH_2$, $J_{CH_2-CH_2}$ = 7.0 Hz).

Anal. Calcd for $C_3H_5NSF_5ClO$: C, 15.45; H, 2.15; N, 6.01; S, 13.73. Found: C, 15.70, H, 1.99; N, 5.98; S, 13.90.

Preparation of $SF_5NHC(O)C(O)NHSF_5$. A 10-mmol sample of NSF_3 and HF (0.25 mL, 12.5 mmol) were condensed into a Kel-F reactor at −196 °C and allowed to react overnight at room temperature before being refrozen to −196 °C and ClC(O)C(O)Cl (4.0 mmol) being condensed in. The reaction mixture was then allowed to warm slowly to room temperature. After 12 days the volatile reaction products were removed to a NaF scrubber. Vacuum sublimation of the remaining product mixture at 60–70 °C yielded the white solid $SF_5NHC(O)C(O)NHSF_3$ (0.83 g, 78.1% yield; mp 220 °C); IR (mull) 3260 (s), 1725 (vs), 1450 (s), 1302 (m), 1170 (m), 935–835 (vs), 826 (m), 667 (m), 595–585 (s) cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 340 M^+ (0.1), 321 $[M - F]^+$ (0.1), 297 (0.1), 170 $[SF_5NHCO]^+$ (35.7), 150 $[SF_4NCO]^+$ (2.2), 127 $[SF_5]^+$ (100.0), 124 (15.1), 112 (0.7), 108 (1.0), 104 (9.9), 89 (10.4), 70 (3.0), 67 (1.0) 58 (1.1); chemical ionization mass spectrum (isobutane) *m/e* (relative intensity) 341 $[M + H]^+$ (0.1), 340 M^+ (0.1); ^1H NMR (Me_2SO-d_6) δ 11.96 (br s, NH), ^1H NMR (acetone) δ 11.78 (br s, NH); ^{13}C NMR δ 156.1 (q, CO, J_{SF_4-C} = 3.4 Hz).

Anal. Calcd for $C_2H_2N_2S_2F_{10}O_2$: C, 7.06; H, 0.59; N, 8.24; S, 18.82. Found: C, 7.13; H, 0.53; N, 8.41; S, 19.02.

Preparation of $SF_5NHC(O)CH_2C(O)NHSF_5$ and $SF_5NHC(O)C$-$H_2C(O)OH$. The isocyanate, SF_5NCO, (10.0 mmol) was condensed into a 75-mL glass reaction cylinder containing sublimed $CH_2(CO$-$OH)_2$ (4.0 mmol) dissolved in several milliliters of dry THF. The reaction mixture was then heated at 60 °C for 48 h, at which time the volatile materials, consisting of CO_2, THF, and unreacted SF_5-NCO, were removed. The remaining solid residue was removed to a vacuum sublimator, and after several fractional sublimations unreacted $CH_2(COOH)_2$, $SF_5NHC(O)CH_2C(O)OH$, and SF_5NHC-$(O)CH_2C(O)NHSF_5$ were separated in reasonable purity. Not enough $SF_5NHC(O)CH_2C(O)OH$ was isolated for elemental analysis, and thus this compound has been identified only by IR, NMR, and mass spectral analyses. The yield of $SF_5NHC(O)CH_2C(O)NHSF_5$ was far lower than the 80% yield previously reported in the reaction of SF_5NH_2 and C_3O_2.[22]

$SF_5NHC(O)CH_2C(O)NHSF_5$: mp 170 °C dec; IR (mull) 3280 (m), 2980 (w), 1735 (m), 1700 (s), 1508 (m), 1405 (m), 1335 (m), 1272 (m), 1220 (m), 1170 (s), 940–850 (s), 770 (m), 600 (s) cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 354 M^+ (2.0), 335 $[M - F]^+$ (0.2), 294 (1.2), 212 $[SF_5NHC(O)CH_2C(O)]^+$ (29.6), 194 (1.5), 193 (1.0), 185 $[SF_5NHC(O)CH_3]^+$ (38.0), 170 $[SF_5NHCO]^+$ (13.6), 169 (0.8), 150 $[SF_4NCO]^+$ (11.2), 143 (1.2), 139 (2.1), 127 $[SF_5]^+$ (100.0), 124 (6.2), 117 (1.1), 112 (1.6), 105 (3.1) 104 (9.7), 102 (13.3), 101 (5.5), 100 (4.1), 89 (37.4), 70 (8.2), 69 (21.1), 67 (10.0), 65 (3.7); chemical ionization mass spectrum (isobutane) *m/e* (relative intensity): 355 $[M + H]^+$ (28.1); ^1H NMR δ 12.30 (s, NH), 3.34 (s, CH_2).

Anal. Calcd for $C_3H_4N_2S_2F_{10}O_2$: C, 10.17; H, 1.13; N, 7.91; S, 18.08. Found: C, 10.37; H, 1.18; N, 7.81; S, 17.96.

$SF_5NHC(O)CH_2C(O)OH$: mp 117–119 °C; IR (mull) 3280 (s), 3150–3020 (m), 2990 (w), 2675 (w), 1725 (s), 1690 (s), 1500 (s), 1429 (m), 1391 (m), 1328 (m), 1277 (m), 1165 (s), 945–860 (vs), 769 (m), 695 (m), 600 (vs) cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 229 M^+ (6.6), 212 $[M - OH]^+$ (4.1), 185 $[SF_5NHC(O)$-$CH_3]^+$ (6.8), 170 $[SF_5NHCO]^+$ (5.6), 169 (5.4), 150 $[SF_4NCO]^+$ (4.6), 128 (43.8), 127 $[SF_5]^+$ (63.7), 124 (3.6), 105 (2.1), 104 (9.6), 102 (3.7), 101 (4.2), 89 (31.4), 87 $[(HOOCCH_2CO]^+$ (100.0), 76 (9.6), 70 (7.7), 69 (26.8), 67 (9.6), 61 (6.8), 60 (44.2); chemical ionization mass spectrum (isobutane) *m/e* (relative intensity) 230 $[M + H]^+$ (100.0 for $m/e > 200$); ^1H NMR δ 11.33 (br s, NH), 7.85 (br s, OH), 3.30 (s, CH_2).

Preparation of $SF_5NHC(O)CF_2CF_2C(O)NHSF_5$ and $SF_5\overline{NC(O)CF_2CF_2C(O)}$. Thiazyl trifluoride, NSF_3 (10.0 mmol), and HF (0.5 mL, 25 mmol) were condensed into a Kel-F reactor and allowed to react overnight at room temperature before refreezing to −196 °C and condensing in $ClC(O)CF_2CF_2C(O)Cl$ (4.0 mmol). The reaction mixture was then allowed to warm slowly to room temperature. After 4 days the reaction volatiles were stripped onto a NaF scrubber and the remaining solid material (0.44 g) was removed to a vacuum sublimator. The white solid $SF_5NHC(O)CF_2CF_2C(O)NHSF_5$ (0.053 g, 3.0% yield) was obtained after repreated sublimations at 55–60 °C. The volatile materials placed on the NaF scrubber were vacuum disilled with a −30 °C trap stopping $SF_5\overline{NC(O)CF_2CF_2C(O)}$ (0.51 g, 43% yield). This cyclic compound is a white solid with ~1 torr vapor pressure at room temperature and is extremely air sensitive. Exact mass spectrometry was used along with IR and NMR spectroscopy and EI mass spectrometry to confirm the identity of this cyclic imide.

$SF_5NHC(O)CF_2CF_2C(O)NHSF_5$: mp 180 °C dec; IR (mull) 3265 (s), 2990 (w), 1752 (s), 1494 (s), 1410 (w), 1251 (m), 1185 (s), 1145 (s), 990 (w), 950–850 (vs), 837 (s), 759 (m), 688 (w), 605 (s), 540 (w) cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 440 M^+ (0.3), 297 $[SF_5NC(O)CF_2CF_2C(O)]^+$ (16.8), 270 $[SF_5NHC(O)$-$CF_2CF_2]^+$ (37.2), 269 (11.2), 170 $[SF_5NHCO]^+$ (59.2), 150 $[SF_4NCO]^+$ (20.6), 127 $[SF_5]^+$ (100.0), 124 (6.6), 109 (20.0), 108 (1.4), 105 (2.4), 104 (4.4), 103 (2.3), 100 (26.6), 89 (13.4), 70 (2.6), 69 (2.2); chemical ionization mass spectrum (isobutane) *m/e* (relative intensity) 442 $[M + 2H]^+$ (9.5), 441 $[M + H]^+$ (6.6), 440 M^+ (100.0); ^1H NMR δ 11.67 (s), NH).

Anal. Calcd. for $C_4H_2N_2S_2F_{14}O_2$: C, 10.94; H, 0.45; N, 6.36; S, 14.54. Found: C, 11.71; H, 0.65; N, 6.72; S, 14.50.

$SF_5\overline{NC(O)CF_2CF_2C(O)}$: mp 95 °C; IR (gas) 1805 (vs), 1368 (m), 1255 (s), 1182 (s), 1115 (s), 1070 (s), 1033 (m), 932 (vs), 885 (vs), 832 (w), 788 (w), 595 (s), 480 (m) cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 297 M^+ (0.2), 278 $[M - F]^+$ (0.1), 269 $[M - CO]^+$ (0.5), 250 $[M - CO - F]^+$ (0.7), 222 $[M - 2CO - F]^+$ (0.5), 150 $[SF_4NCO]$ (2.4), 127 $[SF_5]^+$ (7.3), 119 (2.4), 109 (3.5), 100 $[CF_2CF_2]^+$ (100.0), 89 (2.2), 81 (1.8), 70 (6.2), 69 (1.6), 50 (1.4), 47 (1.8), 31 (2.9).

Exact mass for $C_4F_9NO_2S$: calcd, 296.9506; found, 296.9465 ± 0.0075.

Preparation of $SF_5N{=}C(Cl)CF_3$. The compound $SF_5NHC(O)CF_3$ (1.89 g, 7.9 mmol) was sublimed onto PCl_5 (2.08 g, 10.0 mmol) in a 100-mL glass reaction cylinder. Several milliliters of CCl_4 was added, and the reaction vessel was frozen and degassed. After warming slowly to room temperature, the mixture was heated at 60–70 °C for 48 h. Infrared analysis of the reaction volatiles revealed that CCl_4, HCl, $POCl_3$, and a compound believed to be the expected reaction product[12] were present. There was no evidence for unreacted $SF_5NHC(O)CF_3$. Repeated trap-to-trap distillations and placement on $AlCl_3$ to remove any remaining $POCl_3$[45] yielded $SF_5N{=}C(Cl)CF_3$ (3.8 mmol, 47.8% yield): IR (gas) 1745 (w), 1690 (m), 1285 (m), 1245 (s), 1200 (vs), 973 (s), 910 (vs), 885 (s), 850 (w), 675 (w), 630 (w), 605 (m) cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 240, 238 $[M - F]^+$ (1.0, 4.8), 222 $[M - Cl]^+$ (2.5), 190, 188 $[M - CF_3]^+$ (2.5, 6.3), 137, 135 (5.0, 15.6), 127 $[SF_5]^+$ (100.0), 102 (12.5), 101 (13.8), 89 (32.5), 69 (41.3).

Preparation of $SF_5N{=}C(Cl)CH_3$. The amide $SF_5NHC(O)CH_3$ (0.20 g, 1.1 mmol) and PCl_5 (0.42 g, 2.0 mmol) were placed into a 75-mL glass reaction cylinder in an inert-atmosphere box. Carbon tetrachloride ($\sim^1/_2$ mL) was added to the reaction cylinder which was then chilled to −196 °C and degassed. The reaction mixture was then warmed to room temperature and heated at 60–70 °C for 48 h. The product was purified by repeated trap-to-trap distillations and by placement on $AlCl_3$ to remove any excess $POCl_3$.[45] $SF_5N{=}C(Cl)CH_3$ (0.2 mmol, 18.2% yield): a colorless liquid with 50 torr vapor pressure at room temperature; IR (gas) 1677 (s), 1421 (m), 1330 (m), 1225 (vs), 1133 (m), 998 (s), 904 (vs), 870 (vs), 689 (m), 679 (m), 631 (m), 622 (m), 598 (s) cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 203 M^+ (0.2), 202 (0.7), 190, 188 $[M - CH_3]^+$ (0.6, 1.5), 184 $[M - F]^+$ (0.5), 168 $[M - Cl]^+$ (38.4), 127 $[SF_5]^+$ (100.0), 89 (22.7), 76 (4.7); ^1H NMR δ 2.60 (s, CH_3).

Preparation of $SF_5N{=}C(Cl)C(Cl){=}NSF_5$. The compound $SF_5NHC(O)C(O)NHSF_5$ (1.70 g, 5 mmol) and PCl_5 (2.08 g, 10.0 mmol) were put into a 75-mL glass reaction cylinder in an inert-atmosphere box. The cylinder was degassed and frozen to − 196 °C, and 1–2 mL of CCl_4 were added. After warming to room temperature the mixture was allowed to stand for 24 h before being heated at 90–100 °C for 24 h. At this time the volatile gasses were removed to the vacuum line for separtion by trap-to-trap distillation. The product $SF_5N{=}C(Cl)C(Cl){=}NSF_5$ (<25% yield) was collected primarily in a −8 °C trap. IR (gas): 1670 (s), 1140 (m), 99 (m), 915 (vs), 875 (vs), 825 (m), 735 (m), 600 (s) cm^{-1}. Mass spectrum (70 eV) *m/e* (relative intensity): 343, 341 $[M - Cl]^+$ (0.3, 0.7), 272, 270, 268 $[M - SF_4]^+$ (0.9, 2.3, 1.4), 233 (1.4), 197, 195 (0.7, 1.72), 190, 188 $[SF_5N{=}C(Cl)]^+$ (5.7, 15.0), 131 (14.5), 127 $[SF_5]^+$ (100.0), 108 (1.5), 89 (25.0).

Preparation of $SF_5N{=}C{=}NSF_5$. The urea $SF_5NHC(O)NHSF_5$ (3.12 g, 10.0 mmol) and PCl_5 (3.12 g, 15 mmol) were put into a 100-mL glass reaction vessel in an inert-atmosphere box. The cylinder was degassed and frozen to −196 °C and 2 mL of CCl_4 was added. The reaction vessel was warmed slowly to room temperature and heated at 60 °C for ~16 h. At this time the volatile reaction products were removed to the vacuum line for trap-to-trap disillation. Even after repeated distillations the product could not be totally separated from the solvent CCl_4. The resulting solution was light orange in color. IR (gas): 2154 (s), 1839 (m), 1417 (m), 1355 (m), 1300 (w), 1167 (w), 1029 (m), 993 (m), 918 (vs), 883 (s), 805 (vs), 662 (m), 585 (s) cm^{-1}. Mass spectrum (70 eV) *m/e* (relative intensity): 294 M^+ (2.9), 275 $[M - F]^+$ (5.8), 230 (1.4), 172 (4.3), 155 (2.2), 153 (2.2), 127 $[SF_5^+]$ (100.0), 108 (2.2), 89 (21.7), 64 (8.7), 51 (1.5), 44 (2.9).

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Registry No. $SF_5NHC(O)F$, 80409-40-1; $SF_5NHC(O)CF_3$, 80409-41-2; $SF_5NHC(O)CH_3$, 80409-42-3; $SF_5NHC(O)CH{=}CH_2$, 80409-43-4; $SF_5NHC(O)CH_2CH_2Cl$, 80409-44-5; $SF_5NHC(O)C(O)NHSF_5$, 80409-45-6; $[SF_5NHC(O)]_2CH_2$, 80409-46-7; $SF_2NHC(O)CH_2C(O)OH$, 80409-47-8; $[SF_2NHC(O)CF_2]_2$, 80409-48-9; $SF_5NC(O)CF_2CF_2C(O)$, 80409-49-0; $SF_5N{=}C(Cl)CF_3$, 2375-40-8; $SF_5N{=}C(Cl)CH_3$, 80409-50-3; $[SF_5N{=}C(Cl)]_2$, 2375-46-4; $SF_5N{=}C{=}NSF_5$, 58776-14-0; NSF_3, 15930-75-3; COF_2, 353-50-4; HF, 7664-39-3; $CF_3C(O)F$, 354-34-7; $CH_3C(O)Cl$, 75-36-5; SF_5NCO, 2375-30-6; CH_3COOH, 64-19-7; $CH_2{=}CHCOOH$, 79-10-7; $CH_2{=}CHC(O)Cl$, 814-68-6; $ClC(O)C(O)Cl$, 79-37-8; $CH_2(COOH)_2$, 141-82-2; $ClC(O)CF_2CF_2C(O)Cl$, 356-15-0; PCl_5, 10026-13-8.

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Contribution from the Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

Hypochlorite Oxidation of Morpholine–Borane

IAN WILSON and HENRY C. KELLY*

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Morpholine–borane reacts with sodium hypochlorite in a 1:4 mole ratio wherein three OCl^- species are utilized for hydride oxidation and a fourth is consumed in the chlorination of morpholine. The determination of kinetic parameters, based upon the stopped-flow spectrophotometric measurement of the rate of disappearance of OCl^- at 290 nm (pH 9–11), is complicated by these consecutive competitive reactions of hypochlorite. At a given pH, the second-order rate constant for the reaction of OCl^- with morpholine is about 10^3 times greater than that for attack of hypochlorite on amine–borane; thus, a reliable determination of the latter constant was based upon "initial rate" studies under pseudo-first-order conditions involving a large stoichiometric excess of morpholine–borane. The rate of reaction of hypochlorite with amine–borane is also first order in hydrogen ion and is subject to a normal substrate isotope effect with $O(CH_2)_4NH{\cdot}BH_3$ reacting about 1.6 times more rapidly than $O(CH_2)_4NH{\cdot}BD_3$. At a given lyonium ion concentration, the reaction is enhanced by a factor of about 3.5 in D_2O. It is proposed that the rate-limiting step involves oxidative attack of hypochlorous acid at a boron–hydrogen bond in the amine–borane and that subsequent oxidation of the two remaining hydridic hydrogen atoms is rapid relative to the chlorination of morpholine. The inverse solvent isotope effect is attributed to a higher concentration of DOCl in D_2O relative to that of HOCl in normal water at a given pD (pH), but is is likely that this influence is partially offset by a normal secondary isotope effect associated with attack of HOCl (DOCl) at the B–H bond. A four-center activated complex involving the elements O, Cl, B, and H that is formally similar to other transition-state configurations proposed for selected reactions of amine–boranes is considered.

The relatively high solubility of morpholine–borane in water[1] and the high level of kinetic stability displayed by its solutions[2] have made this reagent an attractive source of hydridic hydrogen for reactions in aqueous media. Studies of the

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