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PREPARATION AND CHARACTERIZATION OF N-PENTAFLUOROSULFANYLIMINE DERIVATIVES

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SUMMARY

Reactions of $SF_5N{=}CCl_2$ with sodium methoxide and phenoxide have produced both the mono- and disubstituted derivatives $SF_5N{=}C(Cl)OR$ and $SF_5N{=}C(OR)_2$. The monosubstituted derivative $SF_5N{=}C(Cl)N(C_2H_5)_2$ was the sole product produced in a 2:1 molar reaction of diethylamine with $SF_5N{=}CCl_2$. Further reaction of this chloroimine with diethylamine gave the disubstituted derivative $SF_5N{=}C[N(C_2H_5)_2]_2$. Other mixed disubstituted compounds $SF_5N{=}C(R)N(C_2H_5)_2$, where $R{=}CH_3$, CF_3, C_6H_5, and OCH_3, were also prepared. Each of the new N-pentafluorosulfanyl derivatives was characterized by IR, ^1H, ^{19}F and ^{13}C NMR, mass spectrometry and elemental analysis where possible.

INTRODUCTION

The first N-pentafluorosulfanylimine derivatives were synthesized by Tullock et al. from the photolytically induced free radical reaction of SF_5Cl and selected nitriles [1]. Since then, many of these derivatives have been prepared by an alternate method in our laboratory as shown in equations 2 and 3 [2,3]. Some of these chloroimines have

$$SF_5Cl + RCN \xrightarrow{h\nu} SF_5N{=}C(Cl)R \qquad (1)$$

$$SF_5N{=}C{=}O + PCl_5 \longrightarrow SF_5N{=}CCl_2 + POCl_3 \qquad (2)$$

$$SF_5NHC(O)R + PCl_5 \longrightarrow SF_5N{=}C(Cl)R + HCl + POCl_3 \qquad (3)$$

$$SF_5N{=}C(Cl)R + NaF \longrightarrow SF_5N{=}C(F)R + NaCl \qquad (4)$$

been converted to fluoroimines as in the case with sodium fluoride [1]. Also treatment of $SF_5N{=}C(Cl)CF_3$ with sodium azide has yielded $SF_5N{=}C(N_3)CF_3$ [4].

Other N-pentafluorosulfanylimines have been prepared from classical elimination reactions of SF_5NCO. Aromatic aldehydes have been found to react readily with SF_5NCO with the elimination of carbon dioxide [2,5]. The isocyanate has also been shown to react with formamides and tertiary amides to produce the corresponding imines [5]. Similar

$$SF_5N{=}C{=}O + ArC(O)H \longrightarrow SF_5N{=}C(H)Ar + CO_2 \qquad (5)$$

$$SF_5N{=}C{=}O + R_2NC(O)H \longrightarrow SF_5N{=}C(H)NR_2 + CO_2 \qquad (6)$$

$$SF_5N{=}C{=}O + R_2NC(O)R \longrightarrow SF_5N{=}C(R)NR_2 + CO_2 \qquad (7)$$

reactions have been observed for the isothiocyanate SF_5NCS [5].

We wish to report here the results of our study of the reactions of $SF_5N{=}CCl_2$ and $SF_5N{=}C(Cl)R$ compounds with various nucleophilic reagents. Also included is a comparison of the hydrolytic stability of the N-pentafluorosulfanylchloroimines to other N-substituted chloroimines.

RESULTS AND DISCUSSION

Both carbon-chlorine bonds in $SF_5N{=}CCl_2$ are readily cleaved when allowed to react with excess sodium methoxide as shown in equation 8.

$$SF_5N{=}CCl_2 + 2NaOCH_3 \longrightarrow SF_5N{=}C(OCH_3)_2 \quad 88\% \qquad (8)$$

When $SF_5N{=}CCl_2$ and $NaOCH_3$ react in a 1:1 molar ratio, a mixture of $SF_5N{=}C(Cl)OCH_3$ and $SF_5N{=}C(OCH_3)_2$ is obtained. These two compounds are easily separated by vacuum distillation. The reaction of $SF_5N{=}CCl_2$ with $NaOC_6H_5$ was carried out in a 1:2.24 molar ratio and was allowed to proceed for 48 hours. Purification by trap-to-trap distillation and recrystallization afforded $SF_5N{=}C(Cl)OC_6H_5$ in 17% yield and $SF_5N{=}C(OC_6H_5)_2$ in 31% yield. These reactions represent a general method for the synthesis of imidates [6,7]. The results from the above reactions parallel those of our recent study of the reactions of $SF_5N{=}SF_2$ with sodium alkoxides and phenoxides [8].

An analogous N-fluorosulfonyl derivative $FSO_2N{=}C(Cl)OCH_3$ has been prepared by the reaction of the urethane $FSO_2NHC(O)OCH_3$ with PCl_5 [9]. However, Werner had previously shown that only phenyl isocyanate is isolated in the reaction between N-phenylurethane and PCl_5 [10]. Thus, the reaction of $SF_5NHC(O)OCH_3$ [5] with PCl_5 was carried out to determine whether $SF_5N{=}C(Cl)OCH_3$ could be produced by this alternate method. The isolation of SF_5NCO along with HCl, CH_3Cl, and $POCl_3$ from this reaction supports the conclusion that the reaction pathway between urethanes and PCl_5 is not governed by the electronegativity of the nitrogen substituent of the urethane.

When $SF_5N{=}CCl_2$ was treated with two molar equivalents of diethylamine (the second molar equivalent being used as an HCl scrubber), the monosubstituted derivative $SF_5N{=}C(Cl)N(C_2H_5)_2$ was obtained in 88% yield. This chloroformamidine was found to react rather sluggishly with further diethylamine or other nucleophilic reagents. The compounds $SF_5N{=}C(CF_3)N(C_2H_5)_2$ and $SF_5N{=}C(CH_3)N(C_2H_5)_2$ were also synthesized

$$SF_5N{=}C(Cl)N(C_2H_5)_2 + 2HN(C_2H_5)_2 \xrightarrow{\text{11 days}} SF_5N{=}C[N(C_2H_5)_2]_2 \quad 12\% \qquad (9)$$

$$SF_5N{=}C(Cl)N(C_2H_5)_2 + NaOCH_3 \xrightarrow{\text{3 days}} SF_5N{=}C(OCH_3)N(C_2H_5)_2 \quad 19\% \qquad (10)$$

$$SF_5N{=}C(Cl)N(C_2H_5)_2 + C_6H_5Li \xrightarrow{\text{12 days}} SF_5N{=}C(C_6H_5)N(C_2H_5)_2 \quad 41\% \qquad (11)$$

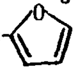
by allowing excess diethylamine to react with the corresponding chloroimines. Many analogous N-fluorosulfonyl derivatives have been prepared by Roesky and co-workers [11-14]. Our attempts to prepare $SF_5N{=}C(C_6H_5)_2$ and $SF_5N{=}C(NCO)_2$ from the reactions of $SF_5N{=}CCl_2$ with C_6H_5Li and AgNCO, respectively, were unsuccessful.

All of the new N-pentafluorosulfanyl derivatives described exhibit a characteristic AB_4 splitting pattern in the ^{19}F NMR spectrum. As shown in Table 1, the resonance of the axial fluorine is downfield from that of the equatorial fluorines in every case. The resonance of the CF_3 group in $SF_5N{=}C(CF_3)N(C_2H_5)_2$ appears as a quintet with only the J_{BX} coupling (16.9 Hz) readily resolvable. This is consistent with the fact that in SF_5X compounds, where X contains fluorine, $|J_{BX}|$ is always much larger than $|J_{AX}|$ [15].

TABLE 1

IR and NMR Data of the N-Pentafluorosulfanylimine Derivatives

Compound	Infrared	^{19}F NMR			^{13}C NMR	
	$\nu(N{=}C)/cm^{-1}$	δ_{SF_A}/ppm	δ_{SF_B}/ppm	J_{AB}/Hz	$\delta N{=}C/ppm$	J_{SF_4-C}/Hz
$SF_5N{=}CCl_2$ [1]	1653	66.3	59.7	157.5	140.2	7.8
$SF_5N{=}C(Cl)CF_3$ [1,3]	1690	64.0	59.2	155.4		
$SF_5N{=}C(Cl)CH_3$ [1,3]	1677	69.8	58.3	156.0		
$[SF_5N{=}C(Cl)]_2$ [1,3]	1670	65.1	59.5	153.2		
$SF_5N{=}C(Cl)OCH_3$	1665	77.3	67.0	155.6	149.3	7.3
$SF_5N{=}C(OCH_3)_2$	1665	89.2	74.7	158.5	156.1	5.9
$SF_5N{=}C(Cl)OC_6H_5$	1650	78.7	68.5	158.5		
$SF_5N{=}C(OC_6H_5)_2$	1670	86.5	73.9	156.7		
$SF_5N{=}C(Cl)N(C_2H_5)_2$	1600	90.5	74.2	158.0	141.7	7.8
$SF_5N{=}C[N(C_2H_5)_2]_2$	1510	106.3	81.8	155.5	160.0	unresolved
$SF_5N{=}C(OCH_3)N(C_2H_5)_2$		97.1	79.4	156.1		
$SF_5N{=}C(C_6H_5)N(C_2H_5)_2$	1550	98.1	80.3	158.3	163.5	unresolved

$SF_5N=C(CF_3)N(C_2H_5)_2$	1600	90.4	79.9	153-159	146.3	unresolved
$SF_5N=C(CH_3)N(C_2H_5)_2$		97.4	76.2	155.4		
$SF_5N=C(H)N(CH_3)_2$ [5]	1638	93.1	70.6	156.5	158.3	9.8
$SF_5N=C(CH_3)N(CH_3)_2$ [5]	1565	97.9	76.5	155.6	165.3	4.9
$SF_5N=C(H)C_6H_5$ [2,5]	1630	80.9	59.2	154.0	171.5	9.8
$SF_5N=C(H)p\text{-}C_6H_4CH_3$ [5]	1605	81.5	59.4	152.7	171.0	9.8
$SF_5N=C(H)p\text{-}C_6H_4OCH_3$ [5]	1600	82.8	60.0	155.2	170.2	9.8
$SF_5N=CH-$  [5]	1620	81.8	60.1	156.4	157.6	10.5

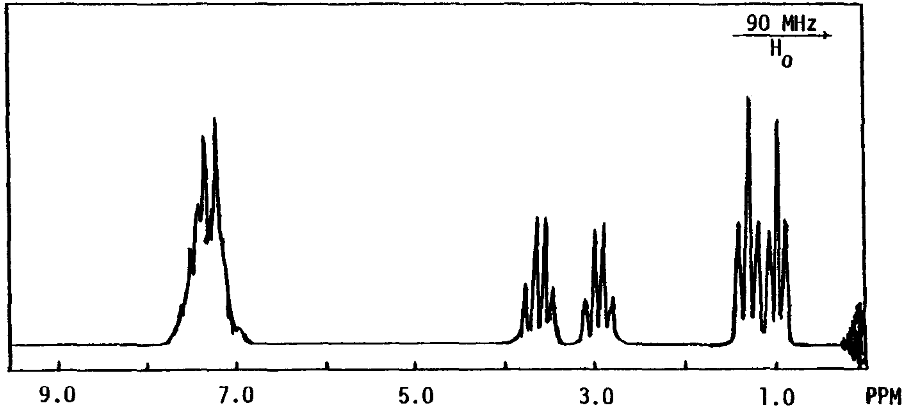


Fig. 1. ^1H NMR Spectrum of $SF_5N=C(C_6H_5)N(C_2H_5)_2$.

The proton spectra of the imine derivatives offer few surprises with the exception of that recorded for $SF_5N=C(C_6H_5)N(C_2H_5)_2$. As shown in Figure 1, two distinct ethyl proton resonances are observed for this compound. This observation is further verified by the appearance of two distinct sets of ethyl carbon resonances in the ^{13}C NMR spectrum of the compound. Previously, we had observed this phenomenon only in $SF_5N=C(H)N(CH_3)_2$ [5]. We believe that these observations are due to hindered rotation about the C-N(substituent) bond and not isomerization about the imino nitrogen. Preliminary temperature-dependent NMR studies support this belief.

The ^{13}C NMR spectra of the imines described also prove to be of interest. For each compound the imine carbon resonance appears as a quintet due to coupling with the four equatorial fluorines of the SF_5 group. In several instances the signal to noise ratio was not sufficient for this coupling to be resolved. Such coupling has also been observed in the compound $SF_5NHC(O)C(O)NHSF_5$ [3] and in other N-pentafluorosulfanylimine derivatives [5] shown in Table 1. The variation in the chemical shifts of the imine carbons is best explained by the same mesomeric effects used to explain the great variation in the chemical shifts of carbonyl carbons [16].

The N-pentafluorosulfanylimine derivatives all show characteristic S-F stretching and wagging frequencies, and the N=C stretch of each appears in the 1700 to 1500 cm^{-1} region. Mass spectral analyses are consistent with the proposed structures.

A kinetic study of the hydrolysis of a series of chloroimines has shown that electron-withdrawing groups at carbon or nitrogen generally cause a pronounced decrease in reactivity [6,17]. The chloroimines produced from the photolytic reactions of SF_5Cl with nitriles have been described as having moderate resistant to hydrolysis at 25°C [1]. In fact a sample of $[SF_5N=C(Cl)]_2$ in carbon tetrachloride was found by ^{19}F NMR spectroscopy to be intact even almost one month after the addition of several drops of water [5]. The compound $SF_5N=C(Cl)N(C_2H_5)_2$ was found to be surprisingly stable towards hydrolysis as it was not attacked by dilute acid or base even after two months. A hydrolysis reaction of $SF_5N=C(Cl)OCH_3$ being monitored by infrared spectroscopy gave no evidence for hydrolysis after 12 hours; however, reaction work-up after 35 days gave 33% yield of $SF_5NHC(O)OCH_3$. The urethane $SF_5NHC(O)OC_6H_5$ was not isolated from the hydrolysis of $SF_5N=C(Cl)OC_6H_5$

as further hydrolysis gave NSF_3, HF and CO_2. **The** results of these hydrolysis reactions are indeed surprising when compared to those reported for analogous N-fluorosulfonyl compounds. Air hydrolysis of $FSO_2N=C(Cl)CF_3$ for 1 day gave 57% yield of $FSO_2NHC(O)CF_3$ [13] and hydrolysis of $FSO_2N=C(Cl)OCH_3$ with a 5% aqueous solution of tetraphenylphosphonium chloride gave 85% yield of the salt after only 2 hours [12].

EXPERIMENTAL

An all Pyrex-glass high-vacuum system was employed for handling the reactants and products. Infrared spectra were obtained with a Beckman 20A-X infrared spectrophotometer either on gases, pressure 1 to 10 torr, on mulls in either halocarbon or mineral oil, or on neat films. Mass spectra were obtained with either a Hitachi Perkin-Elmer RMU-7 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 ^{1}H NMR spectra were taken on a Varian EM-390 nuclear magnetic resonance spectrometer using CCl_3F and $(CH_3)_4Si$, respectively, as standards. The method of Harris and Packer [18] was used to calculate the chemical shifts and coupling constants of the AB_4 portion of the ^{19}F NMR spectra. The ^{13}C NMR spectra were taken on a Jeol FX 60Q nuclear magnetic resonance spectrometer. 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.

The compound $SF_5N=CCl_2$ was prepared by the photolytic reaction of SF_5Cl and ClCN [1]. The reaction of PCl_5 with the respective N-pentafluorosulfanylamide was used to prepare $SF_5N=C(Cl)CF_3$ and $SF_5N=C(Cl)CH_3$ [3]. All other solvents or reagents were distilled prior to use.

Preparation of $SF_5N=C(Cl)N(C_2H_5)_2$

The preparation of $SF_5N=C(Cl)N(C_2H_5)_2$ given below represents a general method to the compounds described in this work and thereafter only specific variations will be noted.

The compound $SF_5N=CCl_2$ (2.24 g 10.0 mmol) and ∿75 ml of dry $(C_2H_5)_2O$ were condensed into a 250 ml flask held at -196°C. While the mixture was maintained at -196°C, $HN(C_2H_5)_2$ (2.06 ml, 20.0 mmol) was syringed into the reaction vessel, which was then degassed. The reaction mixture was allowed to warm slowly to room temperature by which time a white precipitate had formed.

After approximately 18 h the precipitate ($(C_2H_5)_2NH{\cdot}HCl$) was removed by vacuum filtration and the ether was stripped from the product mixture giving a nonvolatile (v.p. < 1 torr) liquid residue. Vacuum distillation of this liquid into a detachable U-trap held at -196°C gave $SF_5N{=}C(Cl)N(C_2H_5)_2$ (nc) (2.3 g, 8.83 mmol). The properties of $SF_5N{=}C(Cl)N(C_2H_5)_2$ observed were: v.p. < 1 torr @ 25°C; IR (capillary film): 2980 (w), 2940 (w), 2880 (w), 2820 (w), 1600 (vs), 1464 (m), 1423 (m), 1362 (m), 1209 (m), 956 (m), 889 (s), 852 (vsb), 831 (vs), 782 (s), 734 (s), 662 (m), 584 (s) cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 260 M^+ (5.2), 245 $[M-CH_3]^+$ (9.8), 243, 241 $[M-F]^+$ (7.8, 20.4), 225 $[M-Cl]^+$ (46.8), 197 (24.7), 190, 188 $[SF_5NCCl]^+$ (7.8, 21.7), 177 (8.3), 169 (32.6), 149 (12.4), 137 (5.3), 136 (6.7), 135, 133 $[NC(Cl)N(C_2H_5)_2]^+$ (31.7, 94.8), 127 $[SF_5]^+$ (96.3), 122 (7.0), 105 (6.8), 104 (10.6), 98 (20.4), 97 (12.2), 94 (8.3), 92, 90 (38.2, 100.0), 89 (25.5), 85 (5.4), 84 (41.5), 75 (6.9), 73 (29.2), 71 (5.9), 70 (22.3); ^1H NMR (neat); $\delta(CH_3)$ 0.95 (t), $\delta(CH_2)$ 3.27 (q) (J_{H-H} = 7.0 Hz); ^{13}C NMR (neat): δN=C 141.7 (qu) (J_{SF_4-C}= 7.8 Hz), δCH_2 46.2(t) ($^1J_{C-H}$ = 136 Hz), δCH_3 11.4 (q) ($^1J_{C-H}$ = 128 Hz).

Anal: Calcd for $C_5H_{10}N_2SClF$: C, 23.03; H, 3.84; N, 10.75; S, 12.28. Found: C, 23.32; H, 3.71; N, 10.80; S, 11.76.

Hydrolysis of $SF_5N{=}C(Cl)N(C_2H_5)_2$

The hydrolysis experiment was conducted on several unsealed NMR tube samples of $SF_5N{=}C(Cl)N(C_2H_5)_2$. Both deuterodimethyl sulfoxide and 1,4-dioxane were used as solvents in separate experiments. The imine was found to be surprisingly stable towards hydrolysis as it was not attacked by 10% NaOH or 6M HCl even after two months.

Preparation of $SF_5N{=}C[N(C_2H_5)_2]_2$

The chloroimine $SF_5N{=}C(Cl)N(C_2H_5)_2$ (1.40 g, 5.36 mmol) was allowed to react with $HN(C_2H_5)_2$ (1.14 ml, 11.0 mmol) as before at room temperature for 11 days. The resulting crude product mixture was examined by ^{19}F NMR and was found to be a 7:1 mixture of $SF_5N{=}C(Cl)N(C_2H_5)_2$ and a product later identified as $SF_5N{=}C[N(C_2H_5)_2]_2$. Since $SF_5N{=}C(Cl)N(C_2H_5)_2$ was found to be more volatile than $SF_5N{=}C[N(C_2H_5)_2]_2$, the unreacted starting material was readily removed by distillation into a detachable U-trap held at -196°C. The clear liquid product $SF_5N{=}C[N(C_2H_5)_2]$ (nc) (0.20 g, 0.7 mmol) was then distilled with the aid of a heat gun into another detachable U-trap. The properties of

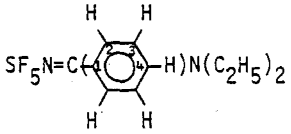
$SF_5N{=}C[N(C_2H_5)_2]$ observed were: v.p. < 1 torr @ 25°C; IR (capillary film): 2980 (m), 2940 (m), 2882 (w), 1510 (vsb), 1455 (s), 1428 (s), 1379 (m), 1335 (m), 1277 (s), 1195 (m), 1140 (m), 1115 (w), 1100 (w), 1070 (m), 1004 (w), 980 (m), 935 (w), 850 (vs), 830 (vsb), 800 (vsb), 720 (vs), 654 (m), 628 (m), 600 (m) cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 298 $[M+1]^+$ (0.6), 278 $[M-F]^+$ (2.4), 225 $[M-N(C_2H_5)_2]^+$ (60.0), 197 (16.4), 177 (10.1), 170 $[NC[N(C_2H_5)_2]_2]^+$ (26.3), 169 (22.5), 149 (9.5), 127 (12.1), 122 (16.1), 99 (57.5), 98 (12.9), 97 (10.6), 89 (6.0), 85 (11.8), 83 (15.2), 73 (12.9), 72 $[N(C_2H_5)_2]^+$ (100.0), 71 (18.7), 69 (10.9), 56 (16.1), 55 (12.1), 44 (11.8), 43 (10.9), 42 (9.2); chemical ionization mass spectrum (isobutane) m/e (rel intensity): 298 $[M+H]^+$ (27.2), 278 (20.0), 254 (100.0), 183 (27.3); ^1H NMR (d_6-actone): $\delta(CH_2)$ 3.34 (q), $\delta(CH_3)$ 1.33 (t) (J_{H-H} = 7.0 Hz); ^{13}C NMR (neat): $\delta N{=}C$ 160.0 (m), δCH_2 42.6 (t) ($^1J_{C-H}$ = 138 Hz), δCH_3 11.4 (q) ($^1J_{C-H}$ = 124 Hz). Elemental analysis did not afford satisfactory results.

Preparation of $SF_5N{=}C(OCH_3)N(C_2H_5)_2$

The compound $SF_5N{=}C(OCH_3)N(C_2H_5)_2$ was prepared by allowing $SF_5N{=}C(Cl)N(C_2H_5)_2$ (0.66 g, 2.5 mmol) and $NaOCH_3$ (3 mmol) to react in the same fashion as in the previous reactions. The product (0.50g) was found by NMR and gas chromatographic analyses to be an ~ 3:1 mixture of unreacted $SF_5N{=}C(Cl)N(C_2H_5)_2$ and $SF_5N{=}C(OCH_3)N(C_2H_5)_2$. This mixture could not be separated by liquid chromatography using a 60-200 mesh Type H silica gel column; however, gas chromotagraphy coupled with mass spectrometry utilizing a 10% SP-2100 column gave an excellent separation. The properties of $SF_5N{=}C(OCH_3)N(C_2H_5)_2$ (nc) observed were: v.p. < 1 torr @ 25°C; mass spectrum (70 eV) m/e (rel intensity): 256 M^+ (0.1), 241 $[M-OCH_3]^+$ (4.5), 213 (2.3), 197 (1.1), 184 $[M-N(C_2H_5)_2]^+$ (6.9), 169 (3.0), 150 (1.6), 129 (26.1), 127 (23.0), 89 (7.5), 86 (22.0), 83 (7.4), 81 (20.6), 73 (5.0), 72 $[N(C_2H_5)_2]^+$ (100.0), 58 (61.6), 56 (17.7), 55 (14.3); ^1H NMR: $\delta(OCH_3)$ 3.88 (s), $\delta(CH_2)$ 3.35 (q), $\delta(CH_3)$ 1.19 (t) (J_{H-H} = 7.0 Hz).

Preparation of $SF_5N{=}C(C_6H_5)N(C_2H_5)_2$

This imine was prepared in the same way as the previous ones, by allowing $SF_5N{=}C(Cl)N(C_2H_5)_2$ (0.415 g, 1.6 mmol) to react with C_6H_5Li (1.25 ml of a 1.6 M solution in ether/benzene). After 12 days the reaction mixture was filtered through a glass frit and the ether and benzene removed under vacuum. Unreacted $SF_5N{=}C(Cl)N(C_2H_5)_2$ was distilled into a detachable U-trap held at -196°C. The resulting solid residue was sublimed and resublimed to give $SF_5N{=}C(C_6H_5)N(C_2H_5)_2$ (nc) (0.20 g, 0.66 mmol). The properties of $SF_5N{=}C(C_6H_5)N(C_2H_5)_2$ observed were m.p. 47-48°C; IR (mull): 3000 (wsh), 2975 (m), 2940 (w), 2880 (w), 1550 (s), 1505 (m), 1482 (m), 1438 (m), 1363 (m), 1313 (m), 1288 (m), 1220 (m), 1190 (m), 1098 (m), 1070 (m), 1028 (w), 1000 (w), 955 (m), 895 (s), 840 (vsb), 786 (s), 770 (s), 735 (sb), 650 (s), 620 (m), 585 (msh), 570 (s) cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 303 $[M{+}1]^+$ (1.5), 302 M^+ (0.9), 287 $[M-CH_3]^+$ (2.2), 283 $[M-F]^+$ (32.4), 259 (11.8), 230 $[M-N(C_2H_5)_2]^+$ (51.5), 176 (20.6), 175 $[NC(C_6H_5N(C_2H_5)_2]^+$ (100.0), 132 (14.7), 127 $[SF_5]^+$ (83.8), 105 (13.2), 104 (64.7), 103 (32.4), 77 (32.4), 76 (14.7), 73 (19.1), 72 (58.8), 56 (14.7), 44 (25.0), 42 (16.1); chemical ionization mass spectrum (isobutane) m/e (rel intensity): 303 $[M{+}H]^+$ (28.6), 283 (100.0), 175 (26.3), 72 (28.8); ^1H NMR (d_6-acetone): $\delta(C_6H_5)$ 7.36 (bm), $\delta(CH_2)$ 3.57 (q) and 2.94 (q), $\delta(CH_3)$ 1.27 (t) and 0.96 (t) (J_{H-H} = 7.0 Hz). ^{13}C NMR (d_6-DMSO): $\delta N{=}C$ 163.5 (m), δC_1 134.3, δC_2 128.0 or 127.2, δC_3 127.2 or 128.0, δC_4 129.3, δCH_2 44.7 and 42.5, δCH_3 13.5 and 11.6.



Anal: Calcd or $C_{11}H_{15}N_2SF_5$: C, 43.71; H, 4.97; N, 9.27; S, 10.60. Found: C, 44.21; H, 4.93; N, 8.35; S, 9.38.

Preparation of $SF_5N{=}C(CF_3)N(C_2H_5)_2$

The compound $SF_5N{=}C(CF_3)N(C_2H_5)_2$ was isolated in 97% yield from the reaction of $SF_5N{=}C(Cl)N(C_2H_5)_2$ (0.98 g, 3.8 mmol) and $HN(C_2H_5)_2$ (0.78 ml, 7.5 mmol). The properties of $SF_5N{=}C(CF_3)N(C_2H_5)_2$ observed were: v.p. < 1 torr @ 25°C; IR (capillary film): 2990 (m), 2950 (m), 2890 (w), 1600 (vs), 1482 (m), 1465 (m), 1442 (m), 1393 (m), 1367 (ss), 1307 (m), 1239 (vs), 1220 (s), 1181 (vs), 1157 (vs), 1138 (s), 1100 (m), 1070 (m), 958 (ss), 855 (vsb), 794 (vs), 763 (s), 733 (s), 662 (s), 583 (s) cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 295 $[M{+}1]^+$ (1.4), 294 M^+ (0.5), 293 (0.3), 279 $[M-CH_3]^+$ (4.0), 275 $[M-F]^+$ (24.6), 197 (11.7), 176 (17.1), 172 (11.9), 169 (17.4), 167 $[NC(CF_3)N(C_2H_5)_2]^+$ (88.9), 148 (17.4), 139 (9.8), 127 $[SF_5]^+$

(100.0), 124 (85.2), 119 (19.9), 117 (20.9), 96 (15.9), 89 (19.9), 69 (16.9); *chemical ionization mass spectrum (isobutane) m/e (rel intensity)*: 295 $[M+H]^+$ (100.0), 275 (31.5), 169 (4.4); ^{19}F NMR (neat): δA 90.4 (n), δB 79.9 (d of m), δX -62.4 (qu) (J_{AB} = 153-159 Hz, J_{BX} = 16.9 Hz); ^1H NMR (neat): δ(CH_2) 3.15 (q), δ(CH_3) 0.87 (t) (J_{H-H} = 7.0 Hz); ^{13}C NMR (neat): δN=C 146.3 (m), δCF_3 134.9 (q) ($^1J_{C-F}$ = -287.1 Hz), δCH_2 44.9 (t of q) ($^1J_{C-H}$ = 143 Hz, $^5J_{CH_2-CF_3}$ = 2 Hz), δCH_3 10.7 (q) ($^1J_{C-H}$ = 128 Hz).

Anal: Calcd for $C_6H_{10}N_2SF_8$: C, 24.49; H, 3.40; N, 9.52; S, 10.88. Found: C, 24.36; H, 3.37; N, 9.56; S, 9.59.

Preparation of $SF_5N=C(CH_3)N(C_2H_5)_2$

The compounds $SF_5N=C(Cl)CH_3$ (0.2 mmol) and CCl_3F (standard) were condensed at -196°C into an NMR tube contaiining 1/4 ml of degassed $HN(C_2H_5)_2$. The tube was sealed and allowed to warm slowly to room temperature. A solid precipitate had formed in the tube by the time the reaction mixture reached room temperature. The ^{19}F NMR spectrum of the reaction mixture showed that all of the $SF_5N=C(Cl)CH_3$ had reacted and that a new SF_5 group had appeared. The ^1H NMR spectrum showed evidence of $(C_2H_5)_2NH{\cdot}HCl$ as well as the presence of excess diethylamine. The NMR tube was broken open and the excess diethylamine removed under vacuum. A small quantity of a fairly nonvalatile, clear liquid was then distilled from the tube into a detachachable U-trap held at -196°C. This liquid was identified as $SF_5N=C(CH_3)N(C_2H_5)_2$ (nc) by mass spectrometry. The properties of $SF_5N=C(CH_3)N(C_2H_5)_2$ observed were: v.p. < 1 torr @ 25°C; mass spectrum (70 eV) m/e (rel intensity): 240 M^+ (0.1), 225 $[M-CH_3]^+$ (0.1), 221 $[M-F]^+$ (0.7), 197 (0.3), 168 $[M-N(C_2H_5)_2]^+$ (1.6), 127 (1.3), 115 (7.1), 113 $[NC(CH_3)N(C_2H_5)_2]^+$ (7.5), 85 (4.1), 73 (21.3), 72 (43.2), 71 (10.2), 70 (6.1), 59 (4.8), 58 (100.0), 57 (15.3), 56 (41.7).

Preparation of $SF_5N=C(Cl)OCH_3$

The chlorimine $SF_5N=C(Cl)OCH_3$ was isolated in 16% yield from an approximately equal molar reaction of $SF_5N=CCl_2$ (2.35 g, 10.5 mmol) and $NaOCH_3$ (10 mmol). Repeated distillations gave $SF_5N=C(OCH_3)_2$ (0.09 g, 8% yield - see below) remaining in the initial trap, $SF_5N=C(Cl)OCH_3$ (0.24 g) stopping in the -45°C trap, and unreacted $SF_5N=CCl_2$ (0.78 g, 3.5 mmol) stopping in the -70°C trap. The properties of $SF_5N=C(Cl)OCH_3$ observed were: IR (gas): 3030 (w), 3015 (w), 2980 (w), 1665 (vs), 1450 (mb), 1295 (s), 1245 (s), 1182 (m), 1130 (w), 1097 (w), 1080 (w), 1062 (w), 1028 (m), 954 (s), 900 (vs), 845 (w), 808 (vs), 700 (w), 605 (sb), 580 (ssh) cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 202, 200 $[M-F]^+$ (0.4, 1.1), 190, 188 $[M-OCH_3]^+$ (0.7, 2.2), 184 $[M-Cl]^+$ (22.9), 169 (0.7), 150 (4.7), 127 $[SF_5]^+$ (100.0), 113 (6.5), 99, 97 (6.7, 18.5), 95 (20.0), 94, 92 $[M-SF_5]^+$ (1.5, 5.0), 89 (21.4), 81 (18), 70 (4.7), 67 (6.2), 65 (5.7), 64, 62 (12.5, 34.3), 47 (11.9), 31 (9.4), 30 (8.5), 29 (8.1), 15 (22.9); ^1H NMR (neat): $\delta(OCH_3)$ 3.91 (s); ^{13}C NMR: $\delta N{=}C$ 149.3 (qu) (J_{SF_4-C} = 7.3 Hz), δOCH_3 58.4.

Anal: Calcd for $C_2H_3NSOClF_5$: C, 10.93; H, 1.37; N, 6.38. Found: C, 10.85; H, 1.11; N, 6.42.

Hydrolysis of $SF_5N{=}C(Cl)OCH_3$

The reaction of 0.3 mmol each of $SF_5N{=}C(Cl)OCH_3$ and water was carried out in a 5 ml glass reaction cylinder, the progress of the reaction being monitored by infrared spectroscopy. After 12 h there was no evidence for hydrolysis, but after approximately 35 days, a white solid had formed in the reaction vessel. The volatile products, consisting of HCl, CO_2, NSF_3, SiF_4, and CH_3Cl, were removed under vacuum. The remaining white solid was purified by vacuum sublimation at 25°C to give $SF_5NHC(O)OCH_3$ (0.02 g, 0.1 mmol) in 33% yield. The urethane was identified by infrared and mass spectroscopy -both of which were in excellent agreement with the data previously obtained for this compound from its preparation from SF_5NCO and CH_3OH [5]. The volatile products with the exception of HCl, obviously resulted from the hydrolysis of $SF_5NHC(O)OCH_3$. The methyl chloride was most likely produced by the reaction of HCl with the methanol produced [19].

Preparation of $SF_5N{=}C(OCH_3)_2$

When $SF_5N{=}CCl_2$ (1.30 g, 5.8 mmol) was allowed to react with an excess of $NaOCH_3$ (15 mmol) the compound $SF_5N{=}C(OCH_3)_2$ (nc) (1.10 g, 5.1 mmol) was isolated in 88% yield. The properties of $SF_5N{=}C(OCH_3)_2$ observed were: m.p. 46-48°C; IR (gas): 2980 (w), 1665 (s), 1470 (w), 1445 (w), 1320 (m), 1245 (m), 1180 (m), 1030 (w), 946 (m), 897 (vs), 809 (s), 730 (mb), 600 (m) cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 215 M^+ (13.6), 196 $[M-F]^+$ (10.3), 185 (19.0), 184 $[M-OCH_3]^+$ (12.4), 170 (0.6), 158 (3.7), 150 (6.0), 127 $[SF_5]^+$ (100.0), 112 (2.6), 108 (1.1), 104 (0.4), 93 (38.5), 89 (21.3), 88 (1.0), 81 (25.8), 70 (3.5), 59 (19.2), 58 (100.0), 47 (4.9), 45 (4.1); ^1H NMR ($CDCl_3$): $\delta(OCH_3)$ 4.12 (s); ^{13}C NMR (d_6-acetone): $\delta N{=}C$ 156.1 (qu) (J_{SF_4-C} = 5.9 Hz), δOCH_3 57.2 (q) ($^1J_{C-H}$ = 148.5 Hz).

Anal: Calcd for $C_3H_6NSO_2F_5$: C, 16.74; H, 2.79; N, 6.51. Found: C, 16.76; H, 2.65; N, 6.51.

Reaction of $SF_5N{=}CCl_2$ with $NaOC_6H_5$

After allowing a mixture of $SF_5N{=}CCl_2$ (0.80 g, 3.57 mmol) and $NaOC_6H_5$ (8.0 mmol) to react at room temperature for 2 days, a fairly nonvolatile liquid later identified as $SF_5N{=}C(Cl)OC_6H_5$ (nc) (0.17 g, 0.6 mmol) was distilled from the product mixture. The remaining solid product was then recrystallized from acetone to give $SF_5N{=}C(OC_6H_5)_2$ (nc) (0.37 g, 1.1 mmol).

The properties of $SF_5N{=}C(Cl)OC_6H_5$ observed were: v.p. <1 torr @ 25°C; m.p. 22-23°C; IR (capillary film): 3080 (w), 3060 (w), 1650 (vsb), 1588 (ms), 1491 (ss), 1217 (vsb), 1073 (w), 1027 (w), 960 (s), 864 (vsb), 837 (s), 815 (vs), 750 (m), 687 (ss), 652 (w), 635 (w), 597 (vs), cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 283, 281 M^+ (5.4, 13.5), 264, 262 $[M-F]^+$ (0.8, 2.2), 246 $[M-Cl]^+$ (24.3), 190, 188 $[M-OC_6H_5]^+$ (11.7, 32.4), 156, 154 $[NC(Cl)OC_6H_5]^+$ (16.2, 48.6), 150 (10.8), 127 $[SF_5]^+$ (100.0), 119 (54.1), 112 (9.4), 93 (40.5), 89 (16.2), 77 (59.5), 65 (86.5), 64 (16.2), 63 (10.8), 58 (12.1), 51 (24.3), 50 (10.8), 43 (29.7), 45 (43.2), 42 (10.8), 41 (10.8), 39 (32.4); ^1H NMR (neat): $\delta(C_6H_5)$ 6.98 (bm); ^{13}C NMR (d_6-acetone): δC_2 121.7, δC_4 128.5, δC_3 130.9.

Anal: Calcd for $C_7H_5NSOClF_5$: C, 29.89; H, 1.78; N, 4.98. Found: C, 29.87; H, 1.67; N, 4.99.

The properties of $SF_5N{=}C(OC_6H_5)_2$ observed were: m.p. 66-68°C; IR (mull): 3080 (w), 3060 (w), 1670 (s), 1593 (ss), 1493 (ss), 1302 (sb), 1215 (s), 1187 (s), 1165 (s), 1125 (m), 1077 (m), 1026 (w), 973 (w), 963 (w), 918 (m), 876 (vs), 860 (s), 810 (s), 754 (s), 725 (m), 690 (m), 592 (m) cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 339 M^+ (1.6), 320 $[M-F]^+$ (1.2), 246 $[M-OC_6H_5]^+$ (31.0), 169 (4.8), 150 (9.4), 142 (5.0), 141 (13.6), 127 (1.2), 119 (47.8), 94 (8.9), 93 (4.7), 77 $[C_6H_5]^+$ (100.0), 65 (17.7), 51 (18.1), 39 (12.3); ^1H NMR (acetone): $\delta(C_6H_5)$ 7.40 (m); ^{13}C NMR (d_6-acetone): δC_2 121.6, δC_4 127.9, δC_3 130.7, δC_1 152.4.

Anal: Calcd for $C_{13}H_{10}NSO_2F_5$: C, 46.02; H, 2.95; N, 4.13. Found: C, 45.01; H, 2.70; N, 3.87.

Hydrolysis of $SF_5N{=}C(Cl)OC_6H_5$

The chloroimine $SF_5N{=}C(Cl)OC_6H_5$ (0.3 mmol) and water (0.3 mmol) were allowed to react at room temperature in a 5 ml glass reaction cylinder. Within several days the reaction mixture had become dark brown in color.

After 3 weeks the volatile materials were removed from the reaction vessel and examined by infrared spectroscopy. The presence of HCl, NSF_3, CO_2, and SiF_4 supports the assumption that the chloroimine hydrolyzed to the urethane $SF_5NHC(O)OC_6H_5$ which further hydrolyzed to the above products. The fact that no urethane was isolated is not surprising when one considers that $SF_5NHC(O)OC_6H_5$ was observed by NMR spectroscopy to hydrolyze within one half-hour in the presence of aqueous acetate [5].

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