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Reactions and Photochemistry of Some Fluorinated Amines and Imines

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Treatment of $CF_3C(O)N=C(CF_3)_2$ (I) and $CF_3C(O)NClCF(CF_3)_2$ (III) with PCl_5 readily produces the imines $CF_3CCl_2N=C(CF_3)_2$ (II) and $CF_3CCl=NCF(CF_3)_2$ (V), respectively. Catalytic chlorofluorination of II yields $CF_3CF_2NClCF(CF_3)_2$ (VIII) via a series of ClF addition and subsequent dechlorination steps. Polar addition of ClF to $CF_3CF_2N=CFCF_3$ (XI) results in $(CF_3CF_2)_2NCl$ (XIII). The two chloramines VIII and XIII are converted to the perfluoroalkyl secondary amines $CF_3CF_2NHCF(CF_3)_2$ and $(CF_3CF_2)_2NH$ with HCl. Photolytic decomposition products of the chloramines, which include a new perfluoroalkyl asymmetric amine, $CF_3(CF_3CF_2)NCF(CF_3)_2$ (XII), are identified. The mechanistic pathway for the photolytic decomposition of I is also presented.

Perhaloacetones are reported to be extremely resistant to chlorination by phosphorus pentachloride; e.g., temperatures in excess of 250° were required for reaction to occur.[1] The resistance of the carbonyl function to chlorination via this route has been attributed to the negative inductive effects of surrounding halogenated clusters which reduce electron availability at the carbonyl thus inhibiting attack by the chlorophosphonium ion, PCl_4^+.[1,2] However, despite the presence of the electron-withdrawing trifluoromethyl substituent on the acyl carbon of N-trifluoroacetylhexafluoroisopropylidenimine and trifluoroacetylheptafluoroisopropylchloramine, phosphorus pentachloride readily chlorinates the carbonyl group at 25° due to greater electron availability at the carbonyl oxygen.

Chlorine monofluoride is a very versatile reagent which may act as a chlorinating, fluorinating, or chlorofluorinating reagent for a wide variety of systems. We and others have found earlier that ClF undergoes uncatalyzed polar additions to the carbon–nitrogen double bond of fluoroalkylimines to give the corresponding N-chloramines.[3-6] However, in some cases, addition of ClF across the C=N bond occurs only in the presence of a catalyst.[6] A recent report[7] discusses polar additions to C=N bonds in terms of the polarization of the reaction site ($^{\delta+}C=N^{\delta-}$) by inductive and resonance contributions of the imine substituents. While this is a useful guideline for estimating relative ease of saturation, we observed that the rates of chlorofluorination may differ considerably for highly polarized imines.

Compounds which result from the saturation of the carbon–nitrogen multiple bond with ClF and which contain chlorine bonded to the α carbon have been shown to dechlorinate readily either by thermal means or in the presence of mercury.[6,8] The N-chloramines in this work which contain chlorine bonded to the α carbon have not been isolated, due to the thermally induced elimination of chlorine at 25°.

In the present study, the mechanism has been elucidated whereby $CF_3CCl_2N=C(CF_3)_2$ reacts with excess ClF in the presence of CsF to yield the asymmetric tertiary N-chloramine $CF_3CF_2NClCF(CF_3)_2$ via a series of ClF addition and subsequent dechlorination steps. Another N-chloramine, $(CF_3CF_2)_2NCl$, has been synthesized via the uncatalyzed polar

addition of ClF to its imine precursor. The polar character of the nitrogen–chlorine bond[3,9-11] has been demonstrated by reaction of the N-chloramines with HCl to give the secondary amines and chlorine gas.

Under appropriate thermal and photolytic conditions, chloramines have been shown to give rise to hydrazines via generation of the intermediate radical $(R_f)_2N\cdot$.[4,11-13] We have found that although the N–Cl bond is susceptible to photolytic cleavage, when a CF_3 substituent exists on the α carbon, additional loss of the $\cdot CF_3$ radical provides a new photolytic pathway which results in formation of an imine which precludes the subsequent formation of a hydrazine. Also, the newly generated $\cdot CF_3$ radical may couple with an intermediate $(R_f)_2N\cdot$ to yield the tertiary amine.

Photolyses of compounds containing the trifluoroacetyl group are known to produce $\cdot CF_3$ radicals,[2,3] and N-trifluoroacetylhexafluoroisopropylidenimine is no exception. However, the counterradical which also contains an unsaturated function may undergo intermolecular rearrangement or elimination. The major process via which the acetylimine is photolytically decomposed provides a new, simple, high-yield synthesis of isocyanates.

Experimental Section

Materials. Literature methods were used to prepare $CF_3C(O)-N=C(CF_3)_2$ and $CF_3C(O)NClCF(CF_3)_2$.[3] Photolysis of $CF_3-F_2NClCF(CF_3)_2$, as described in this paper, provided $CF_3CF=N-CF_2CF_3$. Phosphorus pentachloride and aluminum chloride (J. T. Baker Co.) were handled in an inert-atmosphere box and used as received. Chlorine monofluoride (Ozark-Mahoning Co.) and HCl (Matheson) were used as received without further purification. CsF (ROC/RIC) was dried in vacuo at 135° prior to use.

General Methods. Most gases and volatile liquids were handled in a conventional Pyrex vacuum apparatus equipped with a Heise Bourdon tube gauge. Volatile starting materials and purified products were measured quantitatively by *PVT* techniques. Photolytic reactions were normally run in a Rayonet photochemical reactor maintained at 30° by a forced-air cooling system. For the photolyses standard 2537- or 3500-Å lamps and quartz vessels of suitable size were used. Volatile products were purified by trap-to-trap distillation or by gas chromatography. For gas chromatographic separations, the columns were constructed of 0.25-in. copper tubing packed with 15% Fluorolube

Table I. Products, Reactants, and Conditions

Compd, % yield	Reactants, mmol	Conditions	Comments
$CF_3CCl_2N=C(CF_3)_2$, >99	$CF_3C(O)N=C(CF_3)_2$, 5.4; PCl_5, 12	6 hr, shake^a	$POCl_3$ removed by $AlCl_3$; trap to trap, $-65°$, $-30°$
$CF_3CCl=NCF(CF_3)_2$, >99	$CF_3C(O)NClCF(CF_3)_2$, 7; PCl_5, 15	8 hr, shake^a	Trap to trap, $-98°$, $-65°$
$(CF_3CF_2)NClCF(CF_3)_2$, >99	$CF_3CCl_2N=C(CF_3)_2$, 4; ClF, 13; CsF, 10 g	12 hr, shake^a	Trap to trap, $-65°$, $-30°$
$(CF_3CF_2)_2NCl$, ~98	$CF_3CF=NCF_2CF_3$, 6; ClF, 11	6 hr^a	b
$CF_3CF_2NHCF(CF_3)_2$, ~93	$CF_3CF_2NClCF(CF_3)_2$, 1.4; HCl, 2.0	8 hr^a	c; trace of $CF_3CF=NCF(CF_3)_2$
$(CF_3CF_2)_2NH$, ~97	$(CF_3CF_2)_2NCl$, 2.0; HCl, 3.5	8 hr^a	d
$CF_3CF=NCF(CF_3)_2$, >99	$CF_3CF_2NHCF(CF_3)_2$, 1.2; $(CH_3)_3N$, 1.2	3 hr^a	$(CH_3)_3NHF$ residue
	$(CF_3CF_2)NCl$, 1.7	3500 Å, 3.5 hr	b; $[(CF_3CF_2)_2N]_2$, 0.4;^{e} $CF_3CF_2N=CF_2$, 0.2; CF_3Cl, Cl_2, $(CF_3CF_2)_2NCF_3$, trace; $CF_3CF_2N=CFCF_3$, trace
	$CF_3CF_2NClCF(CF_3)_2$, 5	3500 Å, 1.5 hr	d; $CF_3(CF_3CF_2)NCF(CF_3)_2$, 0.7; $CF_3CF_2N=CF(CF_3)$, 2.2; Cl_2; CF_3Cl
	$CF_3C(O)N=C(CF_3)_2$, 3.7	2537 Å, 18 hr	b; $(CF_3)_3CNCO$, 2.1; $(CF_3)_2C=NC(CF_3)_2NCO$, 0.6; $(CF_3)_2C=NCF_3$, 0.3; C_2F_6, 0.6; CO, 0.9

^{a} At 25°. ^{b} Six-foot FS-1265 column. ^{c} Eight-foot Fluorolube GR-90 column. ^{d} Eight-foot Kel F No. 3 oil column. ^{e} All amounts in millimoles.

Table II. Reactions of Chlorine Monofluoride with Imines

Imine, mmol	Amt of ClF, mmol	Products, mmol
$CF_3CCl_2N=C(CF_3)_2$, 4.0	13.0^a	$CF_3CF_2NClCF(CF_3)_2$, 4.0
$CF_3CCl=NCF(CF_3)_2$, 5.0	11.5^a	$CF_3CF_2NClCF(CF_3)_2$, 5.0
$CF_3CF=NCF(CF_3)_2$, 4.0	4.0^a	$CF_3CF_2NClCF(CF_3)_2$, 3.8
$CF_3CCl_2N=C(CF_3)_2$, 3.0	3.0^a	$CF_3CF_2NClCF(CF_3)_2$, varying yields; $CF_3CF=NCF(CF_3)_2$
$CF_3CCl=NCF(CF_3)_2$, 0.5	0.0^a	$CF_3CF=NCF(CF_3)_2$, 0.5^c
$CF_3CF=NCF(CF_3)_2$, 0.6	2.3^b	$CF_3CF_2NClCF(CF_3)_2$, 0.6^d
$CF_3CCl_2N=C(CF_3)_2$, 4.0	8.0^b	No reaction
$CF_3CCl=NCF(CF_3)_2$, 1.0	1.5^b	$CF_3CF=NCF(CF_3)_2$, 0.2^e

^{a} Ten grams of CsF. ^{b} No CsF. ^{c} Fluorination occurs via nucleophilic attack by the fluoride ion of CsF. ^{d} After 6 hr the reaction is <40% complete. After 48 hr the addition is nearly quantitative. ^{e} Yield is for reaction time of 6 hr (i.e., <20% complete).

GR-90 on Chromosorb P, 25% Kel-F No. 3 oil on Chromosorb P, or 37% FS-1265 on Chromosorb P. Helium was used as a carrier gas. Vapor pressure studies were made by using the method of Kellogg and Cady[14] or by an isoteniscopic method.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer by using a 50-mm Pyrex glass cell equipped with KBr windows. ^{19}F and ^{1}H NMR spectra were obtained on a Varian HA-100 spectrometer by using CCl₃F and tetramethylsilane as internal standards. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E spectrometer operating at an ionization potential of 70 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

General Synthetic Procedures. In Table I are the detailed experimental data for the synthesis of the compounds discovered in this study. In general, CsF, PCl₅, or AlCl₃ was added to a Pyrex vessel in an inert-atmosphere box and, after evacuation of the vessel, the other reactant was condensed onto the solid at −183°. The contents of the vessel were held at ambient temperature for a given time period and separated by fractional condensation. Final purification was obtained by using gas chromatography.

When the reactants were both volatile, they were condensed into the reaction vessel at −195° and reaction was allowed to occur as the mixture warmed. Photolysis reactions of the chloramines and the N-trifluoroacetylimine were carried out in the gas phase in either Pyrex or quartz vessels at either 2537 or 3500 Å. Separation and purification were obtained as above.

Reactions of Chlorine Monofluoride with Imines. In Table II are listed several reactions which serve to support the mechanism proposed in Scheme II. Generally, ClF and the imine were condensed at −183° into an evacuated 100-ml Pyrex vessel. The vessel was allowed to warm to 25° and stand for 6–12 hr after which the products were purified by trap-to-trap distillation.

Table III. Infrared Data (cm^{-1})

$CF_3CCl_2N=C(CF_3)_2$	1721 ms, 1690 sh, 1301 s, 1272 vs, 1242 vs, 1193 vs, 1085 ms, 978 s, 960 ms, 750 m, 730 m, 650 w, 520 w
$CF_3CCl=NCF(CF_3)_2$	1751 sh, 1724 s, 1706 sh, 1331 m, 1273 vs, 1260 vs, 1236 vs, 1190 vs, 1147 s, 1094 s, 993 s, 953 ms, 746 m, 731 m, 644 w, 522 w
$CF_3CF_2NClCF(CF_3)_2$	1250 vvs, br, 1173 s, 1112 s, 1062 m, 976 m, 905 w, 814 w, 725 ms, 704 m, 536 w
$CF_3CF_2NHCF(CF_3)_2$	3430 m, 1559 m, 1383 w, 1278 vvs, 1254 vvs, 1224 vs, 1194 vs, 1174 s, 1144 ms, 1072 s, 1016 w, 990 m, 834 w, 695 m, 535 w, br
$(CF_3CF_2)_2NCl$	1350 w, 1260 sh, 1239 vs, 1203 s, 1160 s, 1107 s, 1065 m, 927 w, 842 m, 755 w, 725 ms, 697 w, 530 w
$(CF_3CF_2)_2NH$	3450 m, 1532 ms, 1339 ms, 1248 vs, 1235 vs, 1157 s, 1130 sh, 1078 s, 867 w, 820 w, 735 m, 698 s, 527 w, 485 vw
$CF_3(CF_3CF_2)NCF(CF_3)_2$	1350 s, 1303 vs, 1285 vs, 1262 vs, 1242 vs, 1202 s, 1184 sh, 1150 s, 1132 ms, 1083 s, 1017 w, 970 s, 942 s, 850 s, 743 s, 731 s, 660 w, 533 w

All of the previously known compounds were identified by comparison of recorded infrared, ^{19}F NMR, and mass spectral data with reported literature data where available.

Infrared, ^{19}F and ^{1}H NMR, elemental analysis, and thermodynamic data of the new compounds are summarized in Tables III–V, respectively. Mass spectral data have been tabulated and are available upon request.
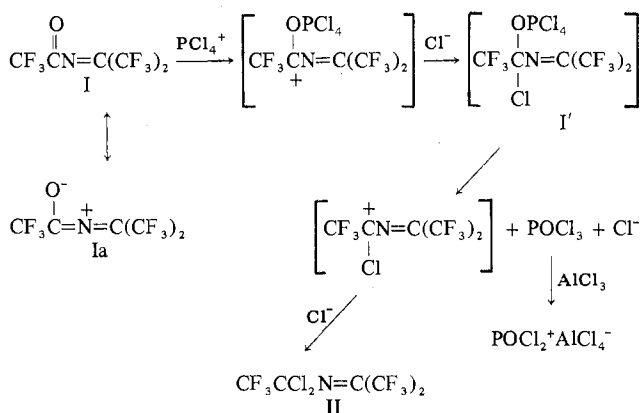
Results

N-Trifluoroacetylhexafluoroisopropylidenimine[3] was converted readily into the *gem*-dichloride upon treatment with phosphorus pentachloride in a reaction which involved electrophilic attack of the halogen reagent on the carbonyl group, followed by reaction with chloride ion, decomposition to the chlorocarbonium ion, and finally the formation of the *gem*-dichloride II.[15] However, it is not possible to rule out completely an intramolecular elimination reaction to form II from I'. (See Scheme I.) The high reactivity of I toward PCl₅ can be attributed to a large contribution from resonance structure Ia which increases electron availability at the carbonyl oxygen. Preliminary evidence for the reaction having occurred

Table IV. ^{19}F and ^{1}H NMR Data^c

73.2^a			75.1
CF$_3$	CCl$_2$	N=C	(CF$_3$)$_2$
s			s

73.7		160	79.0
CF$_3$	CCl=N	CF	(CF$_3$)$_2$
s		sept	d

└—4.2^b—┘

┌———— 6.4 ————┐
d   q

82.1	95.2			145	75.1
CF$_3$	CF$_2$	N	Cl	CF	(CF$_3$)$_2$
	sept d			t sept	d t

└—— 32.6 ——┘ └—2.6—┘
└———————— 7.4 ————————┘

87.2	93.8		3.95	144	78.8
CF$_3$	CF$_2$	N	H	CF	(CF$_3$)$_2$
s	sept d d		br	br	d t

└— 10.6 —┘└—?—┘└—4.0—┘
└———————— 15.0 ————————┘
└———————————— 7.5 ————————————┘

81.9	95.7		
(CF$_3$	CF$_2$)$_2$	N	Cl
p	sept		

└— 3.2 —┘

87.4	95.1		4.52
(CF$_3$	CF$_2$)$_2$	N	H
p	sept d		br

└—1.4—┘ └—9.2—┘

| 50.0	83.0	91.0		156	76.8
CF$_3$	(CF$_3$	CF$_2$)	N	CF	(CF$_3$)$_2$

^{a} ϕ (ppm). ^{b} J (Hz). ^{c} Key: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; sept, septet. Reference: internal CFCl$_3$ and (CH$_3$)$_4$Si.

Scheme I

Scheme II. Catalyzed Chlorofluorination of N-1,1-Dichloro-2,2,2-trifluoroethylhexafluoroisopropylidenimine
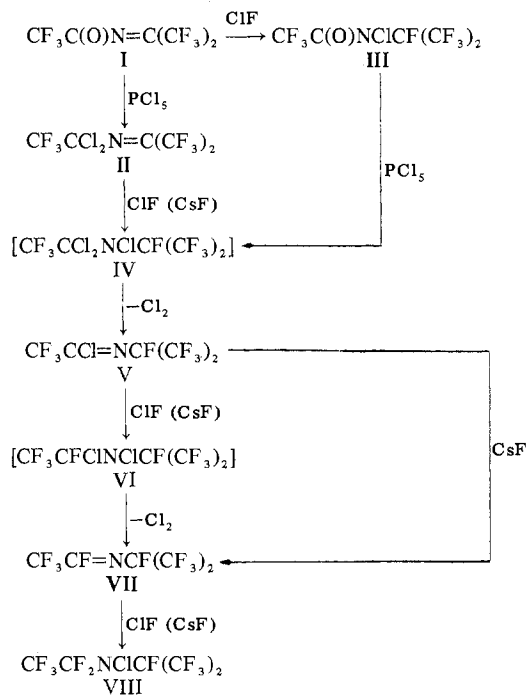

is the shift of the stretching frequency of the carbon–nitrogen double bond to lower energy and concomitant disappearance of the carbonyl stretching frequency of the precursor I. Separation of the *gem*-dichloride II from POCl$_3$ was accomplished by complexing the latter with AlCl$_3$.

The *gem*-dichloride II was not susceptible to uncatalyzed ClF addition at ambient temperature. However, in the presence of CsF, II reacted with excess ClF (1:3) to give a quantitative yield of perfluoro(ethylisopropyl)chloramine (VIII) and chlorine gas. The likely mechanism by which this occurs is shown in Scheme II whereby it can be rationalized that II undergoes a series of ClF addition reactions with subsequent dechlorination steps to give the imidoyl fluoride VII[16] which further adds ClF in a final step to produce the chloramine VIII. Lowering the ratio ClF:II afforded both the imidoyl fluoride VII and the chloramine VIII. It was not possible to adjust experimental conditions to allow the isolation of the imidoyl chloride V from the CsF-catalyzed reaction of ClF and II, e.g., ClF (CsF):II < 1. However; the imidoyl chloride V was obtained by reaction of trifluoroacetylheptafluoroisopropyl-chloramine[3] (III) with PCl$_5$ via intermediate IV. A resonance contribution to III analogous to that of Ia

$$\underset{C-N}{\overset{O}{\overset{\|}{}}} \longleftrightarrow \underset{C=N}{\overset{O^-}{\overset{|}{}}{\overset{+}{}}}$$
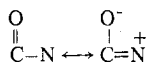
accounts for the high reactivity of III toward PCl$_5$. Inter-

mediates IV and VI were not isolated due to the rapid dechlorination of the species at ambient temperature. The imidoyl chloride V could readily be converted to the imidoyl fluoride VII by direct nucleophilic attack of F$^-$. This alternative pathway accounts for the fact that no CF$_3$CCl=NCF(CF$_3$)$_2$ (V) can be isolated upon chlorofluorination of II in the presence of CsF even at low ratios of ClF:II.

Although II was not susceptible to uncatalyzed addition of ClF, V and VII were found to add ClF slowly at ambient temperatures in the absence of CsF. The highly polar ClF molecule (0.88 D)[4] added more readily to V since the chlorine permits a resonance contribution (A) which will polarize the C=N bond. VII added ClF mainly because the imidoyl fluorine provides a strong inductive effect which polarizes the

C=N bond (B).[7]

$$\underset{A}{\overset{Cl}{\underset{CF_3}{>}}C=N-} \;\longleftrightarrow\; \overset{\overset{\delta+}{Cl}}{\underset{CF_3}{>}}C\overset{\delta-}{-N-} \qquad \underset{B}{\overset{F}{\underset{CF_3}{>}}\overset{\delta+\;\delta-}{C=N-}}$$

In like manner, $CF_3CF=NCF_2CF_3$[17] (XI), which is generated in the photolysis of $CF_3CF_2NClCF(CF_3)_2$ (Scheme III), added ClF very readily due to the very polar nature of the C=N bond similar to that of the imidoyl fluoride VII. The fact that polar addition of ClF to XI occurred much more rapidly than to VII suggests that there must be considerable kinetic as well as thermodynamic control of these systems.

Each of the two chloramines VIII and XIII was photolyzed in an attempt to form fluoroalkylhydrazines.[4,11-13] However, as shown in Scheme III, in addition to N–Cl cleavage, there was considerable cleavage of the C–CF3 bond. Consequently, two major pathways were observed for each of the chloramines VIII and XIII. Pathway L in Scheme III was the major route of photolytic decomposition of chloramine VIII. A radical (IX) was formed by homolytic cleavage of the N–Cl bond. This radical readily underwent a β elimination (X) with a concerted loss of ·CF3 to form the imidoyl fluoride XI. Alternatively, generation of the radical $CF_3CF_2NCF(CF_3)_2$ (IX) provided a minor route (R) which resulted in the new asymmetric perfluoroalkylamine XII via coupling of IX with the ·CF3 radical.
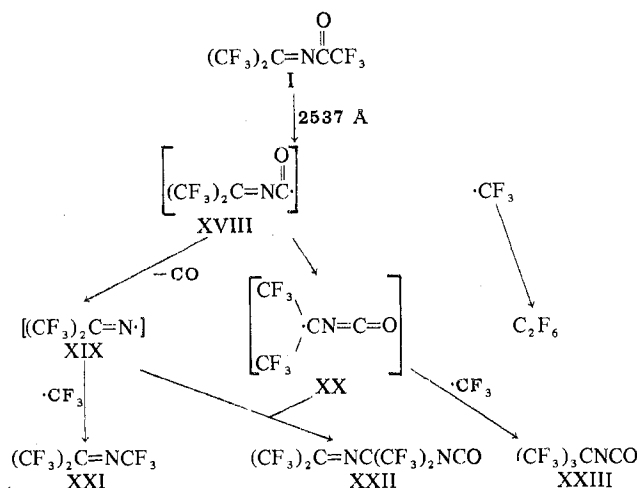
The fact that no C_2F_6 was observed among the products indicates that the ·CF3 radical concentration must be low throughout the photolysis. Upon generation, ·CF3 radicals couple immediately with the more highly concentrated species, $CF_3CF_2NCF(CF_3)_2$ or ·Cl radicals. No evidence for the formation of the perfluoro(1,2-diethyl-1,2-diisopropyl)-hydrazine was observed.

As mentioned above, XI readily undergoes uncatalyzed polar addition of ClF to produce the *N*-chloramine XIII which upon photolysis is decomposed via two significant pathways with

Scheme III. Photolysis of Chloramines

$$\underset{VIII}{CF_3CF_2\overset{Cl}{\overset{|}{N}}CF(CF_3)_2}$$

$$\downarrow 3500\,\text{Å}$$

$$\underset{IX}{[CF_3CF_2NCF(CF_3)_2]\;\cdot Cl}$$

$$\underset{X}{\left[CF_3CF_2N\overset{CF_3}{\cdots}CFCF_3\right]} \overset{L}{\swarrow} \qquad \overset{\cdot CF_3}{\searrow}{}^{R} \;\; \underset{XII}{CF_3(CF_3CF_2)NCF(CF_3)_2}$$

$$\downarrow{}^{-\cdot CF_3}$$

$$\underset{XI}{CF_3CF_2N=CFCF_3} \overset{ClF}{\longrightarrow} \underset{XIII}{CF_3CF_2\overset{Cl}{\overset{|}{N}}CF_2CF_3}$$

$$\downarrow 3500\,\text{Å}$$

$$\underset{XIV}{\left[CF_3CF_2\dot{N}CF_2CF_3\right]\cdot Cl}$$

$$\underset{XV}{\left[CF_3CF_2N\overset{CF_3}{\cdots}CF_2\right]} \overset{L'}{\swarrow} \qquad \searrow{}^{R'} \;\; \underset{XVII}{[(CF_3CF_2)_2N]_2}$$

$$\downarrow{}^{-\cdot CF_3}$$

$$\underset{XVI}{CF_3CF_2N=CF_2}$$

Table V. Elemental Analyses and Thermodynamic Data

	C		H		N		F		Cl		Thermodynamic data				
											Bp, °C	ΔH_{vap}, kcal/mol	ΔS_{vap}, eu	$\log P_{Torr} = A - B/T$
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found				A	B
$CF_3CCl_2N=C(CF_3)_2$	18.99	19.00			4.43	4.42	54.1	54.4	22.44	22.31	88.4	8.43	23.3	7.97	1841
$CF_3CCl=NCF(CF_3)_2$	20.03	19.96			4.67	4.74	63.4	63.3	11.85	12.10	58.2	7.72	23.3	7.97	1686
$CF_3CF_2NClCF(CF_3)_2$	17.78	17.78			4.15	4.30	67.6	67.4	10.52	10.62	73.4	8.05	23.2	7.96	1759
$CF_3CF_2NHCF(CF_3)_2$	19.80	19.76	0.33	0.40	4.62	4.54	75.2	75.0			51.7	7.63	23.5	8.01	1667
$(CF_3CF_2)_2NCl$	16.70	17.12			4.87	4.70	66.1	67.0	12.35	11.63	52.0	7.35	22.6	7.82	1606
$(CF_3CF_2)_2NH$											33.0	7.12	23.3	7.97	1556
$CF_3(CF_3CF_2)NCF(CF_3)_2$	19.41	19.45			3.77	3.79	76.8	77.0			65.1	7.33	21.7	7.62	1601

Scheme IV. Photolysis of
*N*-Trifluoroacetylhexafluoroisopropylidenimine

L' as the minor and R' as the major routes as shown in Scheme III. Pathway L' provides the radical XIV which undergoes a β elimination (XV) with loss of the ·CF₃ radical to form the imidoyl difluoride XVI.[18,19] In the alternative route R', the symmetrical amine radical XIV dimerizes to form the hydrazine XVII.[20] Photolysis of each of the chloramines VIII and XIII shows a strong dependence of reaction products on the ease and rate of formation of ·CF₃ radicals as illustrated by R and R'. Another factor which enhances the formation of the hydrazine is the smaller degree of steric interaction for dimerization of $(CF_3CF_2)_2N\cdot$ than for dimerization of $CF_3CF_2\dot{N}CF(CF_3)_2$. Thus, VIII and XIII represent two nearly identical chloramines which are decomposed photolytically by similar routes but which give rise to different major products.

The polar nature of the N–Cl bond,[9-11] was further illustrated in this work by reaction of the chloramines VIII and XIII with HCl. In each case, high yields of the secondary amines $CF_3CF_2NHCF(CF_3)_2$ and $(CF_3CF_2)_2NH$ were obtained. With $CF_3CF_2NHCF(CF_3)_2$, the product mixture also contained small amounts of $CF_3CF=NCF(CF_3)_2$ and SiF₄, which could result from the thermally induced elimination of small amounts of HF, typical of other bis(perfluoroalkyl)-amines.[10,21] Both of the perfluoroalkyl secondary amines were thermally stable at least to temperatures slightly greater than their boiling points.

Primary or secondary amines which contain fluorine attached directly to the α-carbon atoms are known to be relatively unstable and subject to the base-catalyzed loss of HF.[22,23] When $CF_3CF_2NHCF(CF_3)_2$ was treated with trimethylamine, dehydrofluorination occurred with loss of the ethyl α fluorine, rather than the isopropyl α fluorine, to form $CF_3CF=NCF(CF_3)_2$.

Trifluoromethylacetyl groups generate ·CF₃ radicals readily under photolytic conditions.[2,3] Therefore, photolysis of *N*-trifluoroacetylhexafluoroisopropylidenimine (I) (Scheme IV) could lead to a symmetric urea via loss of CO from an oxalyl intermediate. However, presence of the unsaturated imine function in conjugation with the unpaired electron of the acyl radical XVIII permits a resonance-stabilizing contribution of the tertiary radical XX which couples more readily with the ·CF₃ radical to form perfluoro(*tert*-butyl) isocyanate (XXIII).[24] This rearrangement provides the major pathway for photolytic decomposition. Alternately, the acetyl radical XVIII may lose CO to form the reactive imine radical XIX which can couple with either the tertiary radical XX to form the isocyanate XXII[25] or couple with a ·CF₃ radical to form the *N*-trifluoromethylhexafluoroisopropylidenimine (XXI).[7]

Hexafluoroethane, formed from coupling of ·CF₃ radicals, is the other major product. While numerous methods for preparation of isocyanates already exist,[26] the major route to photolytic decomposition shown in Scheme IV suggests that an additional new, simple, high-yield synthesis of a variety of isocyanates may be possible using variously substituted *N*-trifluoroacetylimines as the precursors, e.g.

$$RR'C=NC(O)CF_3 \xrightarrow{h\nu} RR'(CF_3)CNCO$$
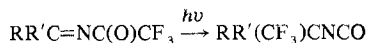
The two new imines $CF_3CCl_2N=C(CF_3)_2$ and $CF_3C-Cl=NCF(CF_3)_2$ were identified by the strong characteristic infrared $\nu C=N$ stretching frequencies at 1690 and 1757 cm⁻¹, respectively. The secondary amines $CF_3CF_2NHCF(CF_3)_2$ and $(CF_3CF_2)_2NH$ were easily recognized by the presence of respective N–H stretching frequencies, 3430 and 3450 cm⁻¹, and the N–H deformation modes at 1559 and 1532 cm⁻¹. The infrared spectra of the new *N*-chloramines VIII and XIII and of the asymmetric tertiary perfluoroalkylamine XII served to support the structures of these compounds.

The ¹⁹F NMR chemical shifts were typical and in the regions expected for each type of fluorine environment.[27-30] No hyperfine splitting was observed across the C=N bond. In contrast, strong spin–spin coupling was noted over the nitrogen between the fluorines of the amine substituents. The coupling pattern of $CF_3CF_2NHCF(CF_3)_2$ could only be resolved with extensive spin–spin decoupling experiments. Charge asymmetry about the nitrogen resulted in dipole–quadrupole interactions which led to line broadening in the ¹H NMR spectra of the secondary amines.[31] The ¹⁹F NMR spectrum of perfluoro(methylethylisopropyl)amine, an interesting molecule with three different fluoroalkyl substituents, could not be totally resolved due to extensive spin–spin interactions as well as significant induced quadrupolar broadening of several of the peaks by the nitrogen. Analysis of this spectrum will be reported later. The mass spectra confirmed the given structures for all of the compounds although a molecular ion was observed for $CF_3CCl_2N=C(CF_3)_2$ and $(CF_3CF_2)_2NCl$ only.

Registry No. CF₃C(O)N=C(CF₃)₂, 52225-57-7; PCl₅, 10026-13-8; CF₃CCl₂N=C(CF₃)₂, 54566-77-7; CF₃C(O)NClC-F(CF₃)₂, 52225-59-9; CF₃CCl=NCF(CF₃)₂, 54120-14-8; ClF, 7790-89-8; CsF, 13400-13-0; (CF₃CF₂)NClCF(CF₃)₂, 54566-78-8; CF₃CF=NCF₂CF₃, 380-66-5; (CF₃CF₂)₂NCl, 54566-79-9; HCl, 7647-01-0; CF₃CF₂NHCF(CF₃)₂, 54566-80-2; (CF₃CF₂)₂NH, 54566-81-3; (CH₃)₃N, 75-50-3; CF₃CF=NCF(CF₃)₂, 2344-11-8; CF₃(CF₃CF₂)NCF(CF₃)₂, 54566-82-4; CF₃CF₂N=CF₂, 428-71-7; [(CF₃CF₂)₂N]₂, 651-29-6; (CF₃)₂C=NCF₃, 453-22-5; (CF₃)₃CNCO, 33959-33-0; (CF₃)₂C=NC(CF₃)₂NCO, 34556-42-8.

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Fluorine-19 Nuclear Magnetic Resonance Spectrum of Trifluoromethyl(pentafluoroethyl)sulfur Difluoride

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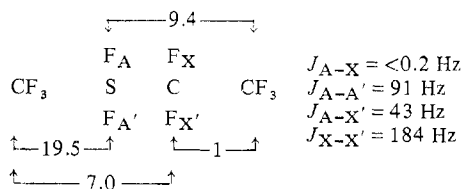
A study of the ¹⁹F nuclear magnetic resonance spectrum of trifluoromethyl(pentafluoroethyl)sulfur difluoride, $CF_3SF_2CF_2CF_3$, shows that the geminal fluorine atoms of the methylene group as well as the geminal fluorine atoms bonded to sulfur are magnetically nonequivalent. Thus this molecule may be described in terms of an $AA'XX'Y_3Z_3$ system. Chemical shifts and coupling constants of all fluorine nuclei are reported.

There are many reports of magnetic nonequivalence of geminal nuclei on vicinal atoms, such as in $CF_2=CH_2$ which is the classical example of an $AA'XX'$ spin system.² However, we report here the first example of magnetic nonequivalence of two geminal fluorine atoms bonded to S(IV) and the concomitant magnetic nonequivalence of the geminal fluorine atoms on the adjacent methylene carbon in trifluoromethyl(pentafluoroethyl)sulfur difluoride, $CF_3SF_2CF_2CF_3$. The chemical shifts of the members of each pair of nuclei are identical and are in the region characteristic for fluorine bonded to S(IV) or to methylene carbon.

Results

The trifluoromethyl(pentafluoroethyl)sulfur difluoride was prepared by the literature method³ and the ¹⁹F nuclear resonance spectral studies were obtained using a Varian HA-100 nmr spectrometer operating at 94.1 MHz. Freon 11 was the internal reference. The chemical shift and spin–spin coupling data are as indicated. This molecule gives a typical spectrum for an $AA'XX'Y_3Z_3$ system which can be analyzed by examining the CF_2 and SF_2 regions separately. Basically these two portions of the spectrum are identical with those described for such a system⁴ but appear to be dissimilar due to the different spin–spin couplings with the fluorine atoms of CF_3 and CF_3S, e.g., between $CF_3S–SF_2$ ($J = 19.5$ Hz) and $CF_3S–CF_2$ ($J = 7.0$ Hz) and between $CF_3C–SF_2$ ($J = 9.4$ Hz)

$$\phi, \text{ppm} \quad 55.8 \quad 13.2 \quad 100.7 \quad 80.2$$

With coupling constants:
$J_{A-X} = <0.2$ Hz, $J_{A-A'} = 91$ Hz, $J_{A-X'} = 43$ Hz, $J_{X-X'} = 184$ Hz

Table I

Compd	Chem shift	
	SF_{ax}	SF_{eq}
$CF_3SF_3$⁷	-47	49
$(CF_3)_2CFSF_3$⁶	-61	54
$CF_3SF_2CF_3$³	14	
$CF_3SF_2C_2F_5$³	13	
$CF_3SF_2CF_2CF_2CF_3$³	11	
$CF_3SF_2CF(CF_3)_2$⁶	14	
$[(CF_3)_2CF]_2SF_2$⁶	11	
$c\text{-}C_4F_8SF_2$⁸	11	

and $CF_3C–CF_2$ ($J = 1$ Hz). The experimentally and computer-generated CF_2 portions of the spectrum are identical. As is expected, the peaks at the center of the spectrum are much more intense than the components of the basic quartets farthest removed from the center. Although the pair of quartet of quartets separated by 195 Hz was sufficiently intense to be recorded during a normal scan, it was necessary to use time-averaging techniques to observe the pair separated by 552 Hz. That the quartets are not ¹³C satellites follows from two observations: (1) the structure is the expected quartet of quartets, rather than the more complicated pattern expected of ¹³C satellites; (2) there is self-consistency within the $AA'XX'$ scheme, which determines four coupling constants from five pieces of data.

Discussion

As expected, the ¹⁹F NMR spectra of the bis(perfluoroalkyl) sulfides, e.g., CF_3SCF_3,⁵ $CF_3SCF_2CF_3$,³ and $CF_3SCF_2CF_2CF_3$,³ are straightforward textbook examples. These sulfides which are likely to have a skewed tetrahedral structure with the unshared electron pairs at two of the apices are easily fluorinated with chlorine monofluoride at $-78°$ to the respective bis(perfluoroalkyl) sulfur difluorides, $R_fSF_2R_f'$. The ¹⁹F NMR spectrum of the sulfur difluoride where $R_f = R_f' = CF_3$ is again