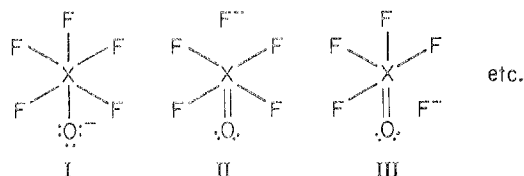
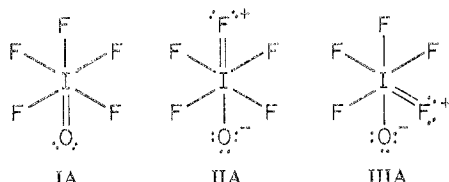


than 2 (f_0 in $\text{SeO}_2\text{F}_2 = 8.00 \text{ mdyne/\AA}$). This can be rationalized by contributions from the resonance structures



with II and III being more dominant than I as expected from the higher electronegativity of F when compared to that of O. The polarization of the X-F bond also explains the strong drop of f_{XF} from XF_6 to XF_5O^- ($f_{\text{Te-F}}$ in TeF_6 , 5.07 mdyne/ \AA ; $f_{\text{Se-F}}$ in SeF_6 , 4.99 mdyne/ \AA).²¹ (ii) Molecular orbital arguments favor II over III, causing f_{R} to become smaller than f_{I} in XF_5O^- . (iii) In IF_5O , however, argument (ii) combined with the resonance structures



causes f_{R} to become slightly larger than f_{I} . (iv) The XF_5 part of XF_5O^- is less electronegative in TeF_5O^- than in SeF_5O^- , thus giving in TeF_5O^- more weight to resonance structure I. This causes f_0 to increase and f_{I} and f_{R} to decrease when going from TeF_5O^- to SeF_5O^- .

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Registry No. TeF_5OCs , 19610-48-1; TeF_5OAg , 50700-88-4; TeF_5O^- , 42503-56-0; SeF_5O^- , 42310-69-0; IOF_5 , 16056-61-4.

Supplementary Material Available. A detailed description of the normal-coordinate analysis of the TeF_5O^- ion will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 \times 148 mm, 24 \times reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number AIC403713.

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Polar and Free-Radical Additions of Fluorinated Species to Unsaturated Carbon-Nitrogen Systems

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Polar and free-radical addition reactions to halo nitriles and imines are examined and compared. The new compounds $\text{CF}_3\text{C}(\text{OSO}_2\text{F})_2\text{N}(\text{OSO}_2\text{F})_2$, $\text{ClC}(\text{OSO}_2\text{F})_2\text{N}(\text{OSO}_2\text{F})_2$, $(\text{CF}_3)_2\text{C}=\text{NCF}_3$, $(\text{CF}_3)_3\text{CN}(\text{CF}_3)_2$, $(\text{CF}_3)_3\text{CNNCF}_3$, $(\text{C}_6\text{F}_5)_2\text{CFN}(\text{CF}_3)\text{Cl}$, $(\text{CF}_3)_2\text{CFN}(\text{CF}_3)\text{H}$, and $\text{ClCCF}_3=\text{NCF}_3$ were prepared and characterized. While polar addition reactions are discussed in terms of the polarization of the reaction site, radical addition products are explained via the formation of a nitrene intermediate. The radical additions to halo nitriles are shown to be synthetically useful, giving yields of up to 80%.

Introduction

In the literature, examples of free-radical addition to carbon-nitrogen unsaturated moieties are rare. In fact, various nitriles have been used as solvents in studies which involve radical reactions. In the presence of methyl radicals, cyanogen reacts to give acetonitrile as well as solid products¹ which were not identified. Hydrogen atoms have been reported to react with RCN ($\text{R} = \text{alkyl}$) to yield the intermediate $\text{RC}(\text{H})=\text{N}\cdot$.² However, the final products were not identified. The additions of H atoms to cyanogen at 25° and to azomethane as well as the addition of CN radicals to CH_3CN to yield the intermediate $\text{CH}_3\text{C}(\text{CN})=\text{N}\cdot$ ³ demonstrate the ease with which radical additions to carbon-nitrogen unsaturated systems may take place. Unfortunately, none of the final products was isolated and identified.

Only a few radical additions of synthetic utility have been reported, e.g., the fluorination with elemental fluorine of materials such as trifluoroacetonitrile gave $\text{CF}_3\text{CF}_2\text{NF}_2$, $\text{C}_2\text{F}_5\text{N}=\text{NC}_2\text{F}_5$, and $\text{CF}_3\text{C}(\text{F})=\text{NF}$.^{4,5} Photolysis of mixtures of SF_5Cl and ClCN or of SF_5Cl and CF_3CN yielded $\text{SF}_5\text{N}=\text{CCl}_2$ or $\text{SF}_5\text{N}=\text{CClCF}_3$, respectively.⁶ The reaction of the phosphazene, $\text{Ph}_3\text{P}=\text{N}-\text{N}=\text{CPh}_2$, and CF_3CN at 25° to yield $\text{Ph}_3\text{P}=\text{N}(\text{CF}_3)\text{C}=\text{NN}=\text{CPh}_2$ was reported to occur via radical addition.⁷ When photolyzed with $(\text{CN})_2$, tetrafluorohydrazine, a good source of difluoramine and fluorine radicals, produced $\text{NF}_2\text{CF}_2\text{CN}$, $(\text{NF}_2\text{CF}_2)_2$, and $\text{C}_2\text{F}_5\text{NF}_2$.⁸

The paucity of radical additions to carbon-nitrogen double and triple bonds suggested that such a study should be undertaken and the results compared with similar polar interactions. Investigation of the reaction of radicals and polar

molecules with several unsaturated carbon-nitrogen systems was initiated to determine the general applicability of the method and the factors which affect such additions.

Experimental Section

Starting Materials. Peroxydisulfuryl difluoride was synthesized by the literature method.⁹ All other starting materials were commercially available and, with the exception of chlorine monofluoride (Ozark Mahoning), were used without further purification.

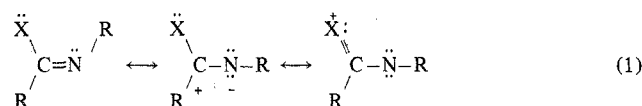
General Procedures. Thermolytic gas-phase reactions were carried out in Pyrex vessels equipped with either Rotaflo TF2/13 Teflon stopcocks or with Kontes high-vacuum Teflon valves. Both 0.3- and 1.8-l. quartz reaction vessels fitted with a Rotaflo TF2/13 Teflon stopcock and a ground-glass stopcock, respectively, were used for photolytic reactions in a Rayonet photochemical reactor equipped with a 2537-Å source.

Conventional vacuum-line techniques were used for handling the volatile materials. Gas-phase infrared spectra were obtained with an 8-cm Pyrex cell fitted with KBr windows using a Perkin-Elmer Model 457 infrared spectrometer. Proton and ¹⁹F nuclear magnetic resonance spectra were recorded on Varian A-60 and HA-100 nuclear magnetic resonance spectrometers with tetramethylsilane and Freon 11 as internal references. A Perkin-Elmer Hitachi RMU-6E mass spectrometer was used for mass spectra. A column constructed of copper tubing, having a 6.35-mm. o.d. and packed with 20% Kel F-3 polymer oil on Chromosorb P, was used for gas chromatographic purification of products. Crude separation of products was accomplished *via* trap-to-trap distillation. Vapor pressure studies were accomplished by using either the method of Kellogg and Cady¹⁰ or a mercury isoteniscope. Molecular weights were determined *via* PVT measurements with a 0.125-l. Pyrex bulb. Some fluoride analyses were made by using an Orion 94-09 fluoride ion electrode after fusion with sodium metal. Other elemental analyses were done by Beller Laboratories in Göttingen, Germany.

Infrared, mass, and nuclear magnetic resonance spectral data are listed in Table I. Elemental analyses, thermodynamic and vapor pressure data, observed molecular weights, starting materials, reaction conditions, products, and yields are summarized in Table II.

Results and Discussion

Nitrile Addition Mechanism. Radical additions to unsaturated carbon-nitrogen systems, although not as readily obtained as radical additions to their carbon-carbon counterparts, proceed well under thermal (80° with fluorosulfate radicals, ·OSO₂F) or photolytic (2537 Å with trifluoromethyl radicals, CF₃·) conditions. When radical additions to the carbon-nitrogen bonds are compared to polar additions at the same sites both the vigor of the reactions and the products obtained vary greatly. Reactions which occur *via* polar addition include those of ClF with compounds such as CF₃CN, ClCN, and (CN)₂, as well as with imines.¹¹ In general, these additions proceed readily, and in each of the above cases, the carbon-nitrogen triple bond is saturated; *i.e.*, no carbon-nitrogen double-bonded intermediates or products are observed, even in the case of large excesses of the unsaturated reactant.¹² This suggests that the carbon-nitrogen double bond is more susceptible to polar addition than is the triple bond. It is possible to rationalize this phenomenon by examining the polarization (or depolarization) of the expected doubly bonded intermediate. Polar addition of compounds, such as ClF, to RCN involves attack by the more electronegative atom or group of atoms on the partially positive carbon atom facilitating the polarization of the carbon-nitrogen bond and increasing its susceptibility to polar addition which gives rise to saturated addition products.¹³



Polar additions to such carbon-nitrogen double bonds do proceed very easily. Chlorine monofluoride reacts with CF₃NCF₂ and CF₃C(O)N=C(CF₃)₂ at 25° to give

CF₃NCICF₃ (80%) and CF₃C(O)NCICF(CF₃)₂ (99%), respectively. Even in the case of (CF₃)₂C=NCF₃, where all the groups attached are equally capable of withdrawing electrons, ClF adds readily at -78° to yield (CF₃)₂CFN(CF₃)Cl (72%).

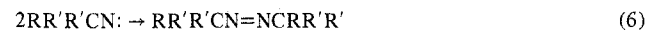
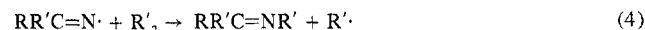
When depolarization of the carbon-nitrogen double bond occurs, the double-bond character of the imine is enhanced,



and polar addition to such systems would be expected to be slow. In fact, addition of ClF to such systems, *e.g.*, (C-F₃)₂C=NCF₃, does not proceed in the absence of a metal fluoride.¹⁴

Radical additions on the other hand tend to give rise to a variety of both saturated and unsaturated products. The first step in the addition to carbon-nitrogen unsaturated moieties (subsequent to radical initiation) is attack at the carbon. This is supported by the identification of the intermediate radical RC(H)=N· from the reaction of H atoms with various hydrocarbon nitriles² and the CH₃C(CN)=N· intermediate from the reaction between CN radicals and acetonitrile.³ Previously, it was shown that S₂O₆F₂ reacted with (CF₃)₂C=N-N=C(CF₃)₂ to yield (CF₃)₂(OSO₂F)C-N=N-C(CF₃)₂(OSO₂F),¹⁵ which also supports initial attack at carbon.

Although greater than 99% of the addition product from the reaction of fluorosulfate radicals (·OSO₂F) with CF₃CN (or ClCN) was the saturated species CF₃C(OSO₂F)₂N(OSO₂F)₂, with trifluoromethyl radicals (CF₃·) approximately 90% of the addition product was the unsaturated imine derivative. However, since we have found that the fluorosulfate radicals do not add readily (if at all) to several imine species, *i.e.*, CF₂NCF₃, (CF₃)₂CNCl, (CF₃)₂CNOSO₂F, and (C-F₃)₂CNH, or to CF₃NCO, the inclusion of an unsaturated species, such as CF₃C(OSO₂F)=N(OSO₂F), in any mechanistic scheme does not appear reasonable, in spite of the favored production of this type of species with CF₃·. Thus we suggest a mechanism which involves the formation of a nitrene, and the reaction pathways of eq 3-7 are proposed to account



for the addition of radicals to the unsaturated carbon-nitrogen systems.

In the case where R' = ·OSO₂F, only a trace of material believed to be CF₃C(OSO₂F)=N(OSO₂F) (I) was observed, and it was not definitely identified. The infrared spectrum of the compound contained an absorption band of medium intensity at about 1786 cm⁻¹ indicating the presence of a carbon-nitrogen double bond. Only very small amounts of this material should be observed since the most reactive species under the reaction conditions used (80°) is ·OSO₂F (although only about 6% of the S₂O₆F₂ would be in the form of ·OSO₂F).¹⁶ In addition, the formation of a second carbon-oxygen bond is energetically more favorable at 80° than the formation of a nitrogen-oxygen bond. The fact that no dimer (the product of reaction 6) was isolated indicates that reaction 5 was not sufficiently rapid to produce a significant concentration of the nitrene at any time during the reaction. However, reaction 5 must be faster than that leading to the dimerization of the CF₃C(OSO₂F)=N· intermediate, since

Table I

Compd	Nmr, ppm	Mass spectrum: mass no., %, fragment (70 eV)	Ir spectrum, cm ⁻¹
ClC(OSO ₂ F) ₂ N(OSO ₂ F) ₂	A -45.6 B -53.2 A/B = 1/1	333, 1, C(OSO ₂ F) ₂ NOSO ₂ F ⁺ ; 288, 1, C(OSO ₂ F) ₂ NOSO ⁺ ; 259, 1, ClC(OSO ₂ F)N(OSO ₂ F) ⁺ ; 237, 1, SOC(OSO ₂ F)-NOSO ⁺ ; 224, 2, C(OSO ₂ F)N(OSO ₂ F) ⁺ ; 159, 1, SOC(OSO ₂ F) ⁺ ; 141, 10, C(OSO ₂ F)NO ⁺ ; 129, 2, ONOSO ₂ F ⁺ ; 127, 7, OCOSO ₂ F ⁺ ; 125, 3, NCOSO ₂ F ⁺ ; 93, 2, ClC(O)-NO ⁺ ; 83, 100, SO ₂ F ⁺ ; 77, 36, ClC(O)N ⁺ ; 70, 6, Cl ₂ ⁺ ; 67, 34, SOF ⁺ ; 64, 33, SO ₂ ⁺ ; 63, 46, ClCO ⁺ ; 60, 4, ClCN ⁺ ; 51, 11, SF ⁺ ^a	1489 vs, 1249 vs, 1050 s, b, 950 m, 840 vs, b, 750 m, 708 m ^b
CF ₃ C(OSO ₂ F) ₂ N(OSO ₂ F) ₂	A -45.9 B -53.0 C +74.0 A/B/C = 2/2/3	293, 2, CF ₃ C(OSO ₂ F)N(OSO ₂ F) ⁺ ; 210, 1, CF ₃ C(OSO ₂ F)-NO ⁺ ; 194, 2, CF ₃ C(OSO ₂ F)N ⁺ ; 191, 1, CF ₃ (OSO ₂)NO ⁺ ; 159, 1, SOC(OSO ₂ F) ⁺ ; 149, 16, CF ₃ SO ₃ ⁺ ; 127, 18, CF ₃ -C(O)NO ⁺ ; 111, 35, CF ₃ C(O)N ⁺ ; 99, 5, SO ₃ F ⁺ ; 97, 75, CF ₃ CO ⁺ ; 92, 12, CF ₃ C(O)N ⁺ ; 83, 100, SO ₂ F ⁺ ; 81, 6, CF ₃ C ⁺ ; 80, 5, CF ₂ CN ⁺ ; 78, 5, CF ₂ CO ⁺ ; 76, 7, CF ₂ CN ⁺ ; 69, 95, CF ₃ ⁺ ; 67, 44, SOF ⁺ ; 64, 37, SO ₂ ⁺ ; 51, 4, SF ⁺	1488 vs, 1293 m, 1246 vs, 1093 vs, 1050 m, 953 m, 898 s, 839 vs, 792 m, 743 s, 712 s
(CF ₃) ₂ C=NCF ₃	A +59.2 quartet B +66.1 overlapping Quartet of quartets C +71.5 quartet <i>J</i> _{A-B} = 12.6 Hz <i>J</i> _{B-C} = 8.2 Hz <i>J</i> _{A-C} ≈ 0.0 Hz A/B/C = 1/1/1	214, 10, (CF ₃) ₂ C=NCF ₃ ⁺ ; 164, 29, (CF ₃) ₂ CN ⁺ ; 145, 1, C ₃ F ₅ N ⁺ ; 114, 4, C ₂ F ₄ N ⁺ ; 76, 4, CF ₂ CN ⁺ ; 69, 100, CF ₃ ⁺ ; 50, 5, CF ₂ ⁺	1736 m, 1333 s, 1278 s, 1244 vs, 1234 vs, 1209 s, 984 s, 879 w, 736 m, 684 w, 640 w
(CF ₃) ₃ CN(CF ₃) ₂		See Discussion	
(CF ₃) ₂ CFN(CF ₃)Cl	A +60.7 doublet of septets B +75.7 doublet of quartets C +148.5 quartet of septets <i>J</i> _{A-C} = 23 Hz <i>J</i> _{A-B} = 4.8 Hz <i>J</i> _{B-C} = 3.0 Hz A/B/C = 3/6/1	214, 17 (CF ₃) ₂ CNCF ₃ ⁺ ; 164, 37, (CF ₃) ₂ CN ⁺ ; 145, 1, C ₃ F ₅ N ⁺ ; 114, 25, C ₂ F ₄ N ⁺ ; 76, 5, CF ₂ CN ⁺ ; 69, 100, CF ₃ ⁺ ; 50, 11, CF ₂ ⁺ ; 36, 3, HCl ⁺ ^a	1275 vs, 1256 vs, 1224 vs, 1197 s, 1162 m, 1121 m, 1094 m, 1079 m, 921 w, 861 vw, 760 w, 727 m, 699 m, 550 w
(CF ₃) ₂ CFN(CF ₃)H	A +53.4 complex B +77.8 doublet of quartets C +139.4 complex ¹ H δ 4.53 broad <i>J</i> _{A-B} = 4.6 Hz <i>J</i> _{B-C} = 4.0 Hz A/B/C = 3/6/1	234, 1, (CF ₃) ₂ CFN(CF ₃)H ⁺ ; 233, 1, (CF ₃) ₂ CFN(CF ₃) ⁺ ; 214, 18, (CF ₃) ₂ CNCF ₃ ⁺ ; 184, 2, (CF ₃) ₂ CFNH ⁺ ; 164, 36, (CF ₃) ₂ CN ⁺ ; 145, 2, C ₃ F ₅ N ⁺ ; 114, 13, C ₂ F ₄ N ⁺ ; 76, 6, CF ₂ CN ⁺ ; 69, 100, CF ₃ ⁺ ; 50, 9, CF ₂ ⁺	3450 s, 1529 s, b, 1354 s, 1287 vs, 1262 vs, 1236 vs, 1205 vs, 1175 s, 990 s, 892 s, 800 m, 749 m, 702 s, 670 s, 550 w
(CF ₃) ₃ CNNCF ₃	A +54.3 decet B +70.8 quartet <i>J</i> _{A-B} = 6.4 Hz A/B = 1/3	219, 1, (CF ₃) ₃ C ⁺ ; 214, 1, (CF ₃) ₂ C(CF ₃)N ⁺ ; 131, 6, CF ₃ CCF ₃ ⁺ ; 116, 5, CF ₄ N ₂ ⁺ ; 97, 2, CF ₃ N ₂ ⁺ ; 93, 1, C ₃ F ₃ ⁺ ; 69, 100, CF ₃ ⁺ ; 50, 6, CF ₂ ⁺ ^c	1314 m, sh, 1289 vs, 1274 vs, 1247 m, 1232 m, 1186 s, 1154 w, 1094 m, sh, 1083 s, 896 w, 734 m, 710 w
CF ₃ C(Cl)=NCF ₃	A +61.8 broad ^d B +73.7 broad	180, 20, ClC(CF ₃)NCF ₃ ⁺ ; 164, 32, CF ₃ CNCF ₃ ⁺ ; 130, 74, ClCNCF ₃ ⁺ ; 85, 34, CF ₂ Cl ⁺ ; 76, 19, CF ₂ CN ⁺ ; 69, 100, CF ₃ ⁺ ; 61, 98, ClCN ⁺ ; 50, 28, CF ₂ ⁺ ^a	1709 m, 1299 s, 1257 vs, 1221 vs, 1194 m, sh, 1059 w, 971 m, 879 w, 859 w, 750 w, 650 w

^a Isotope ratios are correct. ^b Liquid phase. ^c The 17-eV spectrum shows a large peak at P - 19 = 297 mass units. ^d No change with temperature over the range +25 → -80°.

no dimeric material, CF₃C(OSO₂F)=N—N=C(OSO₂F)-CF₃, was observed even when the CF₃CN:S₂O₆F₂ molar ratio was greater than 2. Small amounts of S₂O₅F₂, noncondensable materials, and excess CF₃CN were the only other products observed. A similar reaction sequence may be written for the reaction between S₂O₆F₂ and ClCN.

The major product obtained with CF₃CN when R' = CF₃ is the substituted imine (CF₃)₂C=NCF₃ (I). Only about 1% of the trifluoroacetonitrile reacted to yield the saturated product (CF₃)₃CN(CF₃)₂ (III). Although no (CF₃)₃CN=NC(CF₃)₃ (II) was isolated, (CF₃)₃CN=NCF₃ (V) was found, and its presence can be rationalized by the reaction pathway of Scheme I. Mass spectral evidence for (CF₃)₂C=N—N=C(CF₃)₂ (IV) was obtained midway through the reaction. The overall yield of (CF₃)₂C=NCF₃ (I) was 25% after 48

hr of ultraviolet irradiation. The radical migration proposed which leads to (CF₃)₃CN=NCF₃ (V) and C(CF₃)₄ (VI) has been employed previously to account for the formation of CF₃N=C(F)C₂F₅ from thermolysis of (CF₃)₂NCF=CF₂.¹⁷ Both migrations are to a position γ from the original. No C(CF₃)₄ was isolated. The only additional products observed were C₂F₆, CO, and small amounts of SiF₄.

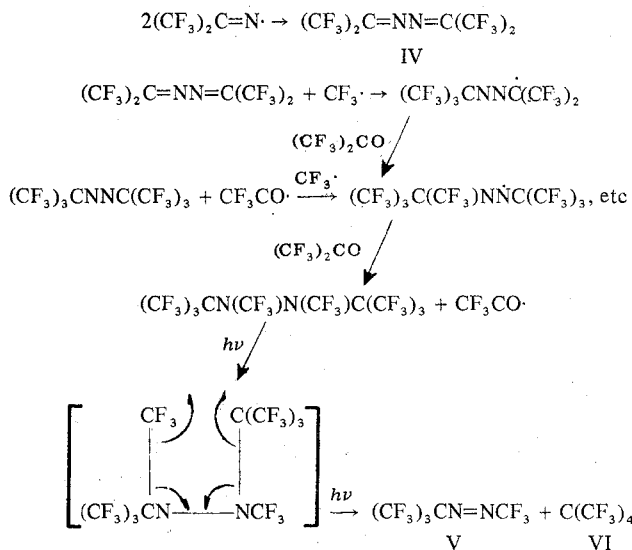
In support of this addition mechanism, a nitrene has been proposed as an intermediate in the fluorination with elemental fluorine of CF₃CN to explain the production of the unsymmetrical azene CF₃CF₂NNCF₃ and several other products.⁵ Another reasonable route to the same products is the subsequent fluorination of a possible intermediate (CF₃CF=N)₂ in the reaction with fluorine. It has been observed that fluorosulfate radicals react with ((CF₃)₂C=N)₂¹⁵ in a reaction

Table II

Compd (yield)	Reactants (mmol)	Conditions	Elemental analyses ^a								ΔH , kcal/ mol	ΔS , eu	Bp, °K	Mol wt		$\log P_{\text{Tot}} =$ $A - B/T$		
			C		N		S		F					Calcd	Found		A	B
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found								
$\text{CF}_3\text{C}(\text{OSO}_2\text{F})_2\text{N}-$ $(\text{OSO}_2\text{F})_2$ (85%)	CF_3CN (1), $\text{S}_2\text{O}_6\text{F}_2$ (2)	80°, 12 hr	4.9	5.1	2.9	2.8	26.1	25.8	27.1	27.4	11.7	28.0	418	9.01	2560			
$\text{ClC}(\text{OSO}_2\text{F})_2\text{N}-$ $(\text{OSO}_2\text{F})_2$ (82%)	ClCN (1), $\text{S}_2\text{O}_6\text{F}_2$ (2)	80°, 12 hr	2.6	2.8	3.1	3.2	28.0	28.7	16.6	16.7	8.0	7.7	424	8.83	2520			
$(\text{CF}_3)_3\text{C}=\text{NCF}_3$ (25%)	CF_3CN (20), $(\text{CF}_3)_2-$ CO (30)	2537 Å, ^b 48 hr							73.3	72.1	6.0	20.7	288	233	236	7.39 1300		
$(\text{CF}_3)_3\text{CFN}(\text{CF}_3)-$ Cl (72%)	$(\text{CF}_3)_2\text{CNCF}_3$ (1), ClF (1)	-78°, 3-12 hr	16.7	16.8							12.2	12.3	325	287	290	8.13 1704		
$(\text{CF}_3)_3\text{CFN}(\text{CF}_3)\text{H}$ (89%)	$(\text{CF}_3)_2\text{CFN}(\text{CF}_3)\text{Cl}$ (1), HCl (1.5)	25°, 12 hr							75.1	76.3	7.6	24.4	309	253	255	8.22 1650		
$(\text{CF}_3)_3\text{CNCNCF}_3$ (2.5%)	CF_3CN (20), $(\text{CF}_3)_2-$ CO (30)	2537 Å, 48 hr							72.2	72.2 ^c	6.4	20.8	309	316	315	7.42 1399		
$\text{CF}_3\text{C}(\text{Cl})=\text{NCF}_3$ (^c 1%)	ClCN (20), $(\text{CF}_3)_2-$ CO (30)	2537 Å, 48 hr							57.4	56.0								

^a Values are percentage composition. ^b Quartz vessels. ^c Average of two determinations: ¹⁹F nmr (74.3%) and fluoride ion electrode (70.0%).

Scheme I



which is analogous to the fluorination of $((\text{CF}_3)\text{CFN})_2$; i.e., two pathways are possible.

Using the proposed mechanism, a rationale for the observed major products from the fluorosulfate and trifluoromethyl radical addition reactions, as well as fluorination, is possible. Under the reaction conditions used here for the trifluoromethyl radical addition (2537 \AA for 48 hr with $(\text{CF}_3)_2\text{CO}$ as a source of trifluoromethyl radicals), only low concentrations of CF_3 radicals are present at any particular time, and the concentration of hexafluoroacetone is constantly high; thus reaction 4 is favored, and formation of the unsaturated species is observed. However, in the case of the fluorosulfate radical addition, under the conditions used (80° , 12 hr), a relatively high steady-state concentration of reactive fluorosulfate radicals exists ($\text{S}_2\text{O}_6\text{F}_2$ is $\sim 4\%$ dissociated to fluorosulfate radicals at 25°),¹⁶ so that reaction 4 is less favored, while formation of the nitrene (reaction 5) and its subsequent reaction to yield the saturated product are enhanced. No product resulting from the dimerization of the nitrene (reaction 6) is observed, since it is energetically less likely and the concentration of nitrene is always small.

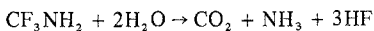
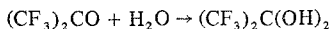
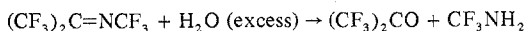
It is proposed that the addition reaction of any radical with a nitrile species may be described by reactions 3–7. For the addition of the three radicals, $\text{F}\cdot$, $\cdot\text{OSO}_2\text{F}$, and $\text{CF}_3\cdot$, the mechanism explains the products very well. It might be expected that for the fluorosulfate radical addition, a change in conditions would allow the isolation of the unsaturated product of reaction 4. Also, in the case of the trifluoromethyl radical addition, if a different source of radicals were used, e.g., one that allowed a constant high concentration of CF_3 radicals to be present, perhaps CF_3NNCF_3 , the major product would be the saturated species. Continuing studies of this type are being undertaken.

Although polar additions to carbon–nitrogen unsaturated systems generally proceed under more moderate conditions, radical additions to the same systems are sufficiently facile to be synthetically useful. While radical additions can be controlled to yield the unsaturated product, or the saturated product, polar additions saturate the carbon–nitrogen system completely.

Characteristic Reactions of Products. The compounds $\text{ClC}(\text{OSO}_2\text{F})_2\text{N}(\text{OSO}_2\text{F})_2$ and $\text{CF}_3\text{C}(\text{OSO}_2\text{F})_2\text{N}(\text{OSO}_2\text{F})_2$ are stable at 150° in glass over a period of 24 hr. At 25° , $\text{CF}_3\text{C}(\text{OSO}_2\text{F})_2\text{N}(\text{OSO}_2\text{F})_2$ reacted slowly with KF (24 hr) and more rapidly with CsF (5 min) to yield the volatile products SO_2F_2 , $\text{CF}_3\text{C}(\text{O})\text{F}$, SO_2 , SiF_4 , $\text{S}_2\text{O}_3\text{F}_2$, and NO . When the temperature was increased to 80° , reaction with KF

remained slow and gave rise to the same products listed above. No other volatile products were observed after fluorination with elemental fluorine of the solid residue remaining after the initial volatile products were removed.

$(\text{CF}_3)_2\text{C}=\text{NCF}_3$ reacted slowly (12 hr) with excess water to yield $(\text{CF}_3)_2\text{C}(\text{OH})_2$, NH_4F , CO_2 , and a nonsublimable solid *via* the route



No SiF_4 was observed. The nonsublimable solid can be accounted for by the reaction between CF_3NH_2 and HF to give the salt $\text{CF}_3\text{NH}_3^+\text{F}^-$. However, insufficient material was available for analysis.

Treatment of $(\text{CF}_3)_2\text{C}=\text{NCF}_3$ with ClF does yield $(\text{CF}_3)_2\text{CFN}(\text{CF}_3)\text{Cl}$. The mass spectrum of the *N*-chloramine at reduced inlet temperature showed several mass fragments containing chlorine. Subsequent reaction with HCl to yield $(\text{CF}_3)_2\text{CFN}(\text{CF}_3)\text{H}$ and Cl_2 confirmed the structure of this compound.

The small yield of $\text{ClC}(\text{CF}_3)=\text{NCF}_3$ obtained in the reaction between trifluoromethyl radicals and ClCN was attributed to the instability of ClCN under the influence of ultraviolet irradiation to give Cl_2 , $(\text{CN})_2$, and $(\text{ClCN})_3$ and to the possible instability of the product itself under the same conditions. No attempts to increase the yield by using a flow system or other techniques were made.

$(\text{CF}_3)_3\text{CN}(\text{CF}_3)_2$. Such small yields of this compound were obtained that it was not possible to purify it satisfactorily. The absence of any infrared absorption bands in the region from 1700 to 1400 cm^{-1} indicated there was no carbon–nitrogen double bond in the molecule. The mass spectrum of the impure compound gave rise to peaks corresponding to $(\text{CF}_2)_3\text{CN}(\text{CF}_3)_2^+$, $(\text{CF}_2)_2\text{CN}(\text{CF}_3)_2^+$, and $\text{CF}_2\text{CN}(\text{CF}_3)_2^+$. Fluorine nuclear magnetic resonance spectra showed two resonances at 49.2 (A) and 63.4 ppm (B) relative to Freon 11. The peaks were in a ratio of 2/3 (A/B). High-resolution spectra showed peak A to be a decet, while B was a septet ($J_{AB} = 9.9$ Hz). Decoupling of peak A from B caused B to collapse to a singlet. The infrared spectrum gave rise to strong absorption bands at 1350, 1270, 1240, 1210, 1177, 1139, 960, 878, and 738 cm^{-1} .

Nuclear Magnetic Resonance. The compound $(\text{CF}_3)_3\text{C}-\text{N}(\text{CF}_3)_2$ gives rise to resonances at 49.2 (decet) and 63.4 (septet) ppm with an area ratio of 2:3, respectively. Thus, the trifluoromethyl groups bonded to nitrogen occur at lower field. Similar assignments are made for the compounds, $(\text{CF}_3)_2\text{CFN}(\text{CF}_3)\text{H}$, $(\text{CF}_3)_2\text{CFN}(\text{CF}_3)\text{Cl}$, and $(\text{CF}_3)_3\text{CNNCF}_3$. In every case, the fluorine atoms of the CF_3 groups bonded to carbon resonate at higher field than those bonded to nitrogen. Based on this, we have assigned the chemical shifts for the

compounds $\text{CF}_3\text{C}(\text{Cl})=\text{NCF}_3$ and $(\text{CF}_3)_2\text{C}=\text{NCF}_3$. For the former compound, peaks which are broad and ill resolved under high resolution down to -80° are observed at 61.8 (*N*- CF_3) and 73.7 (*C*- CF_3) ppm. For $(\text{CF}_3)_2\text{C}=\text{NCF}_3$, at 25° or below, resonances at 66.1 ppm (quartet of quartets) and at 71.5 ppm (quartet) arise from *C*- CF_3 groups. The CF_3 bonded to nitrogen is a quartet at 59.2 ppm. There is some evidence in the literature that suggests coupling between *cis*-trifluoromethyl groups in perfluorinated alkenes is larger than coupling between *trans*-trifluoromethyl groups.¹⁸ Assuming that the same behavior pattern holds in carbon–nitrogen double-bonded systems, the CF_3 bonded to carbon at 71.5 ppm must be *syn* to the CF_3 bonded to nitrogen at 59.2 ppm ($J = 12.6$ Hz). The CF_3 bonded to carbon at 66.1 ppm is then *anti* to the CF_3 bonded to nitrogen ($J \approx 0$). Coupling between the chemically nonequivalent CF_3C groups is 8.2 Hz, a value in line with those reported for similar systems.¹⁹

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Registry No. $\text{CF}_3\text{C}(\text{OSO}_2\text{F})_2\text{N}(\text{OSO}_2\text{F})_2$, 53684-02-9; $\text{ClC}(\text{O}-\text{SO}_2\text{F})_2\text{N}(\text{OSO}_2\text{F})_2$, 53684-03-0; $(\text{CF}_3)_2\text{C}=\text{NCF}_3$, 453-22-5; $(\text{CF}_3)_2\text{CFN}(\text{CF}_3)\text{Cl}$, 53684-04-1; $(\text{CF}_3)_2\text{CFN}(\text{CF}_3)\text{H}$, 53684-05-2; $(\text{CF}_3)_3\text{CNNCF}_3$, 53684-06-3; $\text{CF}_3\text{C}(\text{Cl})=\text{NCF}_3$, 53684-07-4; CF_3CN , 353-85-5; $\text{S}_2\text{O}_6\text{F}_2$, 13709-32-5; ClCN , 506-77-4; $(\text{CF}_3)_2\text{CO}$, 684-16-2; ClF , 7790-89-8; HCl , 7647-01-0; $(\text{CF}_3)_3\text{CN}(\text{CF}_3)_2$, 53684-08-5.

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