The synthesis and chemistry of N-chlorosulfenylaziridines

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Title: The Synthesis and Chemistry of N-chlorosulfenyl-aziridines.

APPROVED BY MEMBERS OF THE THESIS COMMITTEE:

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Thiazyl chloride, the monomer of trichlorotriothiazene, reacts with fluorinated olefins to form N-chlorosulfenyl-aziridines. Four members of this new class of compounds, CF$_3$CFCF$_2$NSCl, SF$_2$CFCF$_2$NSCl, C$_4$F$_9$CFCF$_2$NSCl, and CF$_3$CFCF(CF$_3$)NSCl have been prepared. Fluorine NMR, carbon-13 NMR, mass spectrometry, infrared spectroscopy, and elemental analysis
analysis have been used to characterize these compounds.

The mechanism proposed for the formation of the aziridines involves an attack on the double bond of the olefin by the thiazyl chloride, which acts as a sulfenylnitrene. This mechanism is consistent with previously reported reactions of aziridine formation by sulfenylnitrenes.

Thiazyl chloride does not react with the cyclic olefins perfluorocyclopentene and perfluorocyclobutene. A fluoroolefin with a proton in the allylic position was found to react rapidly in the presence of thiazyl chloride, apparently polymerizing by radical mechanism.

The disulfide derivative of CF₃CFCF₂NSCl was prepared by dechlorination in the presence of mercury. Other attempts to form derivatives of N-chlorosulfenylaziridines are described.

The dimer of trifluorovinylsulfur pentafluoride, formed by a low-temperature reaction catalyzed by (Me₂N)₃S⁺Me₃SiF₂⁻ (TASF), has been analyzed by fluorine and carbon NMR, infrared spectroscopy, and mass spectrometry. The structure of the dimer has now been assigned.

A computer program written to assist in the analysis of mass spectra is presented and described.
THE SYNTHESIS AND CHEMISTRY OF
N-CHLOROSULFENYLAZIRIDINES

by

MICHAEL CLAUDE HARE

A thesis submitted in partial fulfillment of the
requirements for the degree of

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in
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TO THE OFFICE OF GRADUATE STUDIES:

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CHAPTER I

INTRODUCTION

This work describes the preparation and chemistry of fluorinated \(\textit{N}\)-chlorosulfenylaziridines. We have prepared a number of these compounds by reacting the monomer of trichlorotrithiazene with the appropriate fluoroalkene as shown in Equations 1 and 2.

\[
\text{(1)} \quad \begin{array}{c}
\text{Cl} \quad \text{N} \quad \text{N} \\
\text{S} \quad \text{N} \\
\text{N} \quad \text{S} \\
\text{Cl}
\end{array} \xrightarrow{45-50^\circ \text{C}} \text{CFCl}_3 \xrightarrow{} 3 \text{[NSCl]}
\]

\[
\text{(2)} \quad \text{[NSCl]} + \begin{array}{c}
\text{F} \\
\text{C} = \text{C} \\
\text{Y}
\end{array} \xrightarrow{} \quad \begin{array}{c}
\text{C} \\
\text{F} \\
\text{N} \\
\text{SCl}
\end{array}
\]

(\text{I-VI})

\(\text{I}, \text{X} = \text{CF}_3, \text{Y} = \text{F}\)
\(\text{II}, \text{X} = \text{SF}_6, \text{Y} = \text{F}\)
\(\text{III}, \text{X} = \text{OC}_2\text{F}_5, \text{Y} = \text{F}\)
\(\text{IV}, \text{X} = \text{CF}_3, \text{Y} = \text{CF}_3\)
\(\text{V}, \text{X} = \text{F}, \text{Y} = \text{F}\)
\(\text{VI}, \text{X} = \text{Cl}, \text{Y} = \text{F}\)

Compounds (I), (II), and (III) have been prepared in our lab and completely characterized by infrared spectroscopy, \(\text{^{13}}\text{C}\).
NMR, $^{19}$F NMR, mass spectra, and elemental analysis. Compound (IV) has also been prepared in our lab and characterized by IR and $^{19}$F NMR analysis. Compounds (V) and (VI) were prepared and characterized by our colleagues at the Universität Bremen, and their properties are discussed below.

We have also shown that the disulfide derivative (VII) of compound (I) can be prepared by dechlorination in the presence of mercury according to Equation 3.

\[
\begin{align*}
\text{(3)} \quad & \quad \begin{array}{c}
\text{CF}_{3} \quad \text{F} \\
\text{F} \quad \text{N} \quad \text{F} \\
\text{SCl}
\end{array} \quad \begin{array}{c}
\text{Hg}_{25^\circ} \rightarrow \\
\text{CF}_{3} \quad \text{F} \\
\text{F} \quad \text{N} \quad \text{S} \quad \text{S} \quad \text{N}
\end{array} \\
\text{(VII)}
\end{align*}
\]

Preliminary results of reactions that give a further indication of the chemistry of $N$-chlorosulfenylaziridines will be presented and discussed.

The mechanism proposed for the formation of the aziridines involves the sulfenylnitrene resonance structure of thiazyli chloride (NSCl):

\[
\begin{align*}
\text{(4)} \quad & \quad \begin{array}{c}
\text{Cl} \\
\text{S} \quad \text{N}
\end{array} \quad \text{Cl} \quad \text{Cl} \\
\text{S} \quad \text{N} \quad \text{Cl} \quad \text{S} \quad \text{N}
\end{align*}
\]

Aziridines are commonly prepared by nitrene reactions with alkenes. Only a few reactions of sulfenylnitrenes have been
previously reported, however, and aziridines formed from NSCl have been reported only as unstable intermediates.

The formation and chemistry of this new class of aziridines may be understood by reference to previous studies of the formation and chemistry of aziridines, nitrenes, and fluoroolefins. This Thesis will accordingly give a short historical overview of these topics before describing the preparation and reactions of \( N \)-chloro-sulfenylaziridines. This will be followed by a discussion of their properties and chemistry.

An appendix to this Thesis will describe and list MASPEC, a computer program written during the course of these studies which has been found useful in the analysis of mass spectra.
CHAPTER II

REVIEW OF THE LITERATURE

AZIRIDINES

Aziridines are three-membered heterocycles, the nitrogen analogs of epoxides, with which they share an extensive chemistry (1). The first reported synthesis of what was almost certainly an aziridine, although a different structure was initially proposed, was by Gabriel in 1888 (2). Gabriel prepared ethyleneimine, the parent aziridine, by rearrangement of 2-bromoethylamine and treatment with potassium hydroxide to liberate the free base:

\[
\text{BrCH}_2\text{CH}_2\text{NH}_2 \rightarrow \text{N}^+ \xrightarrow{\text{KOH}} \text{N} \\
\]

Since then, aziridines have been extensively studied and are commercially valuable in pharmaceuticals and materials.

Many aziridines are known to have physiological effects (3). Investigation into the physical chemistry of aziridines and aziridine precursors was propelled during World War II by the discovery of the involvement of quaternary aziridinium salts in the toxicology of mustard
gas. The toxicity of aziridines has limited their commercial use in polymers to some extent. They have been found to have antitumor properties, however, and continue to be intensively studied on that account. The physiological effects of sulfenylaziridines are, of course, unknown.

Synthesis

Aziridines are commonly made by either intramolecular displacement of a vicinal leaving group by an amine or by reaction of an electron-rich olefin with a nitrene.

Conditions which favor intramolecular cyclization to aziridines have been summarized by Dermer and Ham (4) and are of interest in showing factors which influence aziridine reactivity. Among these factors are the presence of a solvent of high dielectric constant to stabilize the initially formed aziridinium salt, a good leaving group, and the nucleophilicity of the amino nitrogen.

Addition of an amine to an epoxide to form a vicinal amino alcohol, followed by intramolecular ring closure is one of the most common preparations of aziridines (5).

Formation of the aziridine ring by addition to carbon-carbon double bonds is also synthetically useful, and generally involves the use of azides. The azides may react either by loss of nitrogen to form a nitrene, or by formation of a 1,2,3-triazoline adduct which in some cases may be isolated before pyrolysis or photolysis to the aziridine (Equation 6). Ring formation by nitrenes will be
The extensive chemistry of aziridines is due to the presence of at least two reactive features, the amine nitrogen and the strained ring. Aziridines undergo both ring opening reactions and reactions which preserve the three-membered ring. These reactions make aziridines versatile synthetic precursors in heterocyclic chemistry.

Ring-opening reactions may involve either nucleophilic attack at a ring carbon or a unimolecular ring opening followed by cycloaddition. Ring-opening cycloadditions have been reviewed by Lown (6). Equation 7 gives an example of this type of reaction in which the unimolecular cleavage of the aziridine carbon-carbon bond forms an azomethine ylid, which is captured by a dipolarophile in a cycloaddition reaction:
Ring opening of the aziridine is in many cases (7) concerted and conrotatory as predicted for a four-electron system by Woodward and Hoffman (8). The stereospecificity of this reaction is often obscured by bond rotation after ring opening when reaction with the dipolarophile is slow, but only one isomer is formed with more reactive dipolarophiles such as tetracyanoethylene (9).

Ring opening by nucleophilic attack at a ring carbon under neutral conditions generally requires substituents with lone electron pairs which can stabilize the negative charge on the nitrogen in the transition state. In acidic conditions, however, the protonated nitrogen facilitates ring opening and very mild nucleophiles may be used (10). If the nucleophile is another aziridine, polymerization may result.

If the ring nitrogen is not conjugated with ring substituents having lone pairs and care is taken to avoid
ring opening conditions, aziridines may undergo the usual reactions of amines (11). These reactions include formation of quaternary salts, formation of metal complexes, addition to alkenes, and nucleophilic substitution reactions.

NITRENES

Nitrenes (R-Ñ:\textsuperscript{N}) are the neutral and monovalent nitrogen analogues of carbenes. Their properties and reactivity are strongly dependant on the substituent, and nitrenes with different substituents usually must be considered separately due to these differences (12). Nitrenes are most commonly generated by thermal or photolytic degradation of alkyl, aryl, acyl, or sulfonyl azides (13).

Reactions of nitrenes are very fast, and for reactions with a nitrene mechanism, formation of the nitrene is normally the rate-determining step. Intramolecular reactions and rearrangements are far more common than intermolecular reactions. Neighboring groups often play a large role in stabilizing the nitrene by resonance or by formation of transient ring structures, so that the existence of the nitrene as a discrete species is often in question.

Nitrenes may exist in either the triplet or the singlet state. A theoretic study of the simplest nitrene NH (sometimes called imidogen) concluded that its ground state is a triplet, with an energy 41 kcal/mol less than the
singlet form (14). Theoretic and experimental evidence suggests that most other nitrenes are also ground state triplets (15). Reactions of singlet nitrenes are well known, however, since it is often the initially formed state, and is known to be the ground state in some cases. Singlet nitrenes, with an empty orbital, are powerful electrophiles and generally undergo single step reactions with a π system or other available electron pair. Triplet nitrenes behave like diradicals and characteristically react in a two-step mechanism (16). The addition of singlet nitrenes to alkenes is generally stereospecific, while triplet nitrenes typically react with a two-step mechanism which allows for loss of stereochemistry (17).

While alkyl and aryl nitrenes generally rearrange rapidly, unless they are constrained in an unusually favorable geometry, nitrenes with neighboring electron withdrawing groups such as RCO-, ROCO-, or RSO₂⁻ can undergo insertion or addition reactions, often with good selectivity (18). This was illustrated by the results of an early experiment (19), given in Equation 8.
Nitrenes with neighboring lone pairs such as aminonitrenes, alkoxynitrenes, and sulfenyl nitrenes have a different electronic structure than other nitrenes due to double-bonded resonance structures (20). This is shown for a prototypical aminonitrene in Equation 9:

In order for nitrene behavior to be observed in aminonitrenes, the amine substituents must be electron withdrawing so that electron density available for double bond formation is reduced. Nitrenes derived from the oxidation of N-aminophthalimide with lead tetraacetate (LTA) have been well studied, and their reactions may be expected to bear some similarities to the reactions of sulfenyl nitrenes. An example from the literature (21) is given in Equation 10:
The existence of the aminonitrene as a discrete species (as opposed to a nitrenoid complex) has been convincingly demonstrated by the formation of the same products from nitrenes generated by three different methods (22).

Aminonitrenes add stereospecifically in every known reaction, indicating that the reactive species is a singlet. Calculations of the electronic states of aminonitrenes also indicate that the singlet is the ground state (23). Aminonitrenes react with electron-poor as well as electron-rich alkenes due to the existence of the diazene resonance structure. Aminonitrenes do not insert into σ bonds, a major side reaction in many aziridine syntheses with nitrenes, so they are among the cleaner reagents for making aziridines (24).

Of the class of nitrenes with neighboring lone pairs, alkoxy- and sulfenyl-nitrenes are less well studied than the aminonitrenes. An example of a successful synthesis using an alkoxy nitrene is the reported (25) preparation of 1-methoxy-2,2,3,3-tetramethylaziridine by oxidation of methoxyamine with lead tetraacetate in the presence of tetramethylethylene:
Only a few reactions of sulfenynitrenes have been reported. In 1979 Atkinson and Judkins (26) described the oxidation of arylsulfenamides with LTA and the reaction of the resultant nitrene with several alkenes:

\[
\text{NO}_2 \text{Ph} \text{SNH}_2 \xrightarrow{\text{LTA}} [\text{ArSN}]
\]

\[
[\text{ArSN}] + \text{Ph} = \text{Me} \rightarrow \text{ArSN} \xrightarrow{\text{Ph} + \text{Me}} \text{ArSN} \xrightarrow{\text{Me}} \text{ArSN} \xrightarrow{\text{Me}}
\]

ratio: 3 1

\[
[\text{ArSN}] + \rightarrow \text{ArSN}
\]

\(\text{o-Nitro substituents on the aryl ring were found to be essential for aziridine formation in this reaction. Divalent sulfur is known to trap nitrenes, and the electron-withdrawing nitro groups lower the availability of the}\)
sulfur to nitrene attack (27). In spite of the non-
stereospecificity of the reaction with cis-β-methylstyrene
the authors concluded that the nitrene ArSN is a ground
state singlet (28). This conclusion was reached from the
observation that the stereoselectivity was not affected by
changing concentrations of the alkene, as would be expected
if the singlet were a transient state. The isomerization is
ascribed instead to a reversible reaction of unreacted
alkene with a radical byproduct present in the reaction
mixture.

A more efficient method of generating arylsulfonyl
nitrenes was described by Atkinson et al. in 1984 (29),
as shown in Equation 13. By extruding the nitrene from
1,4-dihydro-1,4-iminonaphthalene derivatives, which is
energetically very favorable due to formation of a
naphthalene molecule, this method avoids the acidic and
strongly oxidizing conditions which prevail in using lead
tetraacetate. Competing reactions are less prevalent when
this method is followed, and quantitative yields are
reported for products (VIII) and (IX). Reaction with an
electron poor alkene to form product (X) is paralleled only
with aminonitrenes.
The N-S bond in arylsulfenylaziridines may be cleaved without ring opening with sodium borohydride to give the corresponding N-H aziridine (30). This reaction may be used for characterization of the aziridine, and also provides another pathway to synthetically useful aziridines.

Sulfenylnitrenes were proposed as intermediates in a study by Bludssus, Mews, Glemser, and Alange published in 1978 (31). Their investigation into the use of thiazyl fluoride (NSF) for the introduction of the thiazyl group led them to react NSF with perfluoropropene in the presence of cesium fluoride. The expected product was S-perfluoroisopropylthiazene (XI), formed according to Equation 14:
Instead of the expected product (XI), however, they found a complex mixture of products which could be most readily explained by initial formation of the thiazene (XI) as an unstable intermediate, and subsequent reaction to give products (XII), (XIII), and others by a nitrene mechanism:

\[
\text{CF}_3\text{CFCF}_2 + \text{CsF} \rightarrow \left[ (\text{CF}_3)_2\text{CF}^- \text{Cs}^+ \right]
\]

\[
\left[ (\text{CF}_3)_2\text{CF}^- \text{Cs}^+ \right] + \text{NS} \rightarrow \text{F} \rightarrow \left[ (\text{CF}_3)_2\text{CF}^- \text{SN} \right]
\]  

(XI)

Other early results by Bludssus and Mews (32) indicated that NSF in the absence of the fluoride ion reacts through its \( \pi \) system to give a [4+2] cycloaddition product:
This reaction was only successful with perfluorobutadiene; alkylbutadienes such as 2,3-dimethylbutadiene were found to react explosively.

The reactivity of thiazyltrifluoromethane, CF$_3$SN, has been discussed in a 1987 paper by Haas and Mischo (33). Attempts to trap the nitrene decomposition product of CF$_3$S(Cl)=NSi(CH$_3$)$_3$, failed, as only unreacted alkene, polymeric CF$_3$SN, and (CH$_3$)$_3$SiCl were recovered, leading to the conclusion that the nitrene is not formed from this reagent. However, Haas and Mischo were able to form the thiazyltrifluoromethane intermediate from both CF$_3$SNH$_2$ and CF$_3$SN$_3$ and trap it with hexachlorocyclopentadiene (Equation 18).
In the first reported instance of a thiazylic chloride (NSCl, also known as chlorothiazine) reaction as a nitrene (34), Haas and Mischo decomposed \( S_3N_3Cl_3 \) in refluxing toluene to form NSCl and found that it also could add to hexachlorocyclopentadiene:

\[
\begin{align*}
\text{Cl} & \text{S} \equiv \text{N} & \text{S} \equiv \text{Cl} \\
\text{N} & \equiv \text{S} & \text{N} \\
\text{S} & \equiv \text{N} & \text{Cl}
\end{align*}
\]

\[
\text{110°} \quad 3 \text{ hr} \quad 3 [\text{NSCl}]
\]

(19)

\[
[\text{NSCl}] + \begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array}
\quad \rightarrow \quad \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl}
\end{array}
\equiv \text{NSCl}
\]

The structure of (XIV) was verified from its x-ray crystal structure. Several derivatives of (XIV) were later synthesized (35):
Attempts to make a fluoride analogous to (XIV) from NSF were not successful (36), as the addition product was unstable and reacted further with C₂Cl₄ to give C₂Cl₅F and (XIV). Reaction of NSF with perfluorocyclopentadiene caused decomposition to S₄N₄, S₈, and decomposed or polymerized C₅F₆. Under other conditions, C₅Cl₆ reacted with 2 moles of NSF to form an N-S-N=SF₂ linkage, as did perfluoropropene in the following photochemical reaction:

\[
\text{CF}_3\text{CF} = \text{CF}_2 + \text{NSF} \xrightarrow{\text{hv}} \left[ \begin{array}{c} \text{CF}_3 \\ \text{F} \\ \text{F} \\ \text{NSF} \end{array} \right] \xrightarrow{\text{NSF}} \left[ \begin{array}{c} \text{CF}_3 \\ \text{F} \\ \text{F} \\ \text{NS} - \text{N}=\text{SF}_2 \end{array} \right]
\]
FLUOROOLEFINS

All of the \( N \)-chlorosulfenylaziridines synthesized to date have utilized fluorinated alkenes. The properties of fluoroalkanes have been the subject of great interest and some controversy for many years, and these properties have direct bearing on this study. Fluorinated organic molecules have been reviewed by Smart (37). A few of their properties will be mentioned here, along with the results of some more recent studies.

Many of the properties of fluorinated compounds may be explained by the overlap of fluorine 2s and 2p orbitals with the valence orbitals of carbon and other second-row elements. This leads to efficient back-donation of electron density from fluorine lone pairs to \( \sigma^* \) antibonding orbitals, and may be represented by the following resonance structures:

\[
\begin{align*}
\text{F}^- & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad
\end{align*}
\]

This picture of the unusual effects of fluorine substituents is supported by ab initio calculations (38). Another valence bond argument predicts that the highly electronegative fluorine would cause a change in the hybridization of the carbon-fluorine bond, increasing the \( p \) character. This would have the effect of narrowing the
fluorine-carbon-fluorine bond angles. This prediction is qualitatively in agreement with experiment. The F-C-F bond angle in CF$_3$CF=CF$_2$, for example, is 112.2°, close to the sp$^3$ bond angle. Several workers have argued that this effect is better explained by non-bonded attractions between the fluorine atoms than by hybridization effects (39).

Addition reactions of gem-difluoroolefins are more exothermic than the reactions of the corresponding hydrocarbon. Examples are the heat of polymerization of CF$_2$=CF$_2$, 17 kcal/mol more exothermic; and the cyclodimerization of CF$_2$=CF$_2$, 35 kcal/mol more exothermic than comparable reactions of CH$_2$=CH$_2$ (40). The cause of this apparent destabilization of double bonds by fluorine lies in the greater stability of an alkyl CF$_2$ group as compared to a vinyl CF$_2$ group (41). This may be explained in terms of the narrow bond angles preferred by the CF$_2$ group and its preference for pyramidal geometry. W. T. Borden and coworkers have calculated that the difference in the $\pi$ bond energy between CH$_2$=CH$_2$ and CF$_2$=CF$_2$ corresponds closely to the amount of energy needed to bring the CF$_2$ group into the planar configuration necessary for maximal $\pi$ bonding (42).

Several studies have focused on the different reactivity patterns of fluorinated olefins and non-fluorinated olefins in electrocyclic reactions. By studying a series of reactions of 1,1-difluoroallene, shown in
Equations 24, 25, and 26, Dolbier and Burkholder were able to compare the differences in reactivity directly (43).

From these reactions, it is clear that [2+2] reactions are regioselective and give as major product the one with the CF₂ group in the ring. This is consistent with the proposition that alkyl CF₂ groups are more thermodynamically stable than alkene CF₂ groups, and prefer sp³ hybridization. In [2+4] cycloadditions, the CF₂ group is invariably not
involved in ring formation, and it is noted that difluoroallene is much more reactive toward dienes than allene itself, which requires far harsher conditions (200°C, 6 hr) than those of reaction 22. This indicates that the CF₂ group has increased the electrophilicity of the C₂-C₃ π bond but not of the C₁-C₂ π bond. The product ratio of the acrylonitrile reaction, and the fact that Dolbier was unable to react difluoroallene with any electron-rich olefin, indicate that the C₁-C₂ π bond is the more nucleophilic in character.

Dolbier concluded from his product ratio study that the [2+2] reactions of difluoroallene involve a biradical intermediate. A theoretical study by Getty and Borden suggest that the CF₂ group promotes [2+2] additions by stabilizing radical intermediates (44). This paper arose from the observation that while vinylcyclobutane is formed in only trace amounts in the reaction of ethylene with butadiene, the rest being cyclohexene, the reaction of tetrafluoroethylene (TFE) with butadiene gave only 1,1,2,2-tetrafluoro-3-vinylcyclobutane. The Diels-Alder transition state was found to have similar geometry and energy for both ethylene and TFE. The 1,4-diradical formed from TFE was found to be 25-26 kcal/mol more stable than the diradical formed from ethylene, however, giving a kinetic advantage to the formation of the cyclobutane product. The energy advantage of the diradical formed from TFE is
attributed primarily to the pyramidalized CF$_2$ group and weak π bond in TFE itself.

Conclusions relevant to the formation of $N$-chlorosulphenylaziridines which may be drawn from these studies of fluoroolefins are: 1) the π bond is expected to be weaker than the π bond in a hydrocarbon, and the formation of an sp$^3$ carbon at the CF$_2$ group more exothermic; 2) the π bond is electron rich due to back donation of electron density from a fluorine lone pair, and will be reactive towards an electrophilic species such as a nitrene; and 3) the stabilization of radicals by the CF$_2$ group will promote a non-concerted reaction mechanism.
CHAPTER III

EXPERIMENTAL METHODS

APPARATUS

Volatile materials were handled in a standard vacuum apparatus. The vacuum system was equipped with a Televac thermocouple pressure gauge and a mercury manometer. Pressure in the apparatus was maintained at $10^{-3}$ to $10^{-2}$ torr. Glass stopcocks were lubricated with Fluorolube grease.

Separation and purification of products were accomplished in a fractional condensation apparatus in which the volatile crude products were passed from the reaction vessel, at low pressure, through a successive series of cold traps, generally maintained at $-30^\circ$, $-78^\circ$, $-198^\circ$, and $-198^\circ$ C.

Moisture sensitive solids were manipulated in a dry box purged with nitrogen and dried with phosphorous pentoxide. All glassware was oven dried before use.
REAGENTS

The cyclic trimer of NSCl, $S_3N_3Cl_3$, may be prepared either by chlorination of $S_4N_4$ (45) or by chlorination of $S_3N_2Cl_2$ (46). The latter method is preferred in many cases because of the more ready availability of $S_3N_2Cl_2$ (47). $S_3N_3Cl_3$ is a yellow solid at room temperature, with a melting point found to be sharp but variable between $73^\circ$ and $93^\circ$ depending on conditions of crystallization (48). In the infrared spectrum, SN ring modes occur at 1017 vs, 698 ms, and 621 w cm$^{-1}$, with other peaks at 514 m, 493 m, 385 m, and 320 m cm$^{-1}$ (49). (See Analysis section for definition of abbreviations). It is moisture-sensitive and must be handled in dry air. Patton and Jolly showed in a thermodynamic study (50) that $S_3N_3Cl_3$ is stable to sublimation and more importantly that it dissolves to form a mint green solution in hot chlorinated solvent (CCl$_4$) at $55^\circ$, which reformed yellow crystals when cooled.

The trichlorotrithiazene used in this study was a generous gift from Professor Rudiger Mews. Its purity was established by infrared spectroscopy.

CF$_3$CF=CF$_2$ and CF$_3$CF=CFCF$_3$ were purchased from PCR Chemicals and used as received.

SF$_5$CF=CF$_2$ was made by dehydrohalogenation of SF$_5$CFHCF$_2$Br with potassium hydroxide according to published procedures (51). It was dried over P$_2$O$_5$ before use.

C$_4$F$_9$OCF=CF$_2$ was a generous gift from the 3M company, and
was used as received.

Mercury, reagent grade, was purchased from American Scientific Chemical and Supply, and was used as received.

Freon-11 (CFCl₃) was used as received from Dupont.

ANALYSIS

Infrared spectra were taken on either a Nicolet 20DX or a Perkin-Elmer 1600 series FTIR. Spectra of liquids were taken as a capillary film between potassium bromide plates. Spectra of trichlorotrithiazene were taken as a mineral oil mull. Other spectra of solid samples were taken as KBr pellets. Abbreviations used are w, weak; m, medium; s, strong; vs, very strong; sh, shoulder.

¹⁹F NMR spectra were taken either on a Varian EM390 operating at 84.67 MHz, a Bruker AMX400 operating at 376.5 MHz, or a Bruker WP 80 SY operating at 75.39 MHz, as indicated. Chemical shifts in fluorine spectra are reported relative to CFCl₃. Downfield shifts are reported as positive values. Abbreviations used are s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet.

¹³C NMR spectra were taken on a Bruker AMX400 instrument, operating at 100.6 MHz, or on a Bruker WH-360, operating at 90.54 MHz, as indicated, with CDCl₃ as lock solvent and TMS as an internal standard.

Elemental analysis was done by Mikroanalytisches Laboratorium Beller, Göttingen, Germany.
Boiling point determinations were made using a Kontes Bantamware distillation apparatus at low pressure.

REACTIONS OF TRICHLOROTHIAZENE

Reaction with CF₃CF=CF₂

In a 100 ml, thick-walled, airtight Pyrex glass vessel equipped with a Teflon stopcock and a Teflon stir bar was placed 1.1 g (4.7 mmol) of (NSCl)₃. CF₃CF=CF₂ (3.1 g, 21 mmol) and 12.3 g of CFCl₃ were vacuum-transferred into the vessel. The vessel was placed in an oil bath and warmed to 45-50°C. At this temperature the solution turned lime-green. The vessel was heated for 65 hours, with constant stirring. Separation by fractional condensation yielded in the -78°C trap 2.6 g of a yellow malodorous liquid, representing 80% yield. This material was shown by ¹⁹F NMR spectroscopy to be practically pure 2-trifluoromethyl-2,3,3-trifluoro-1(chlorosulfenyl)aziridine, with CFCl₃ as minor impurity.

This material may be stored in a stoppered vial with no major decomposition after several months. Heating to 100°C in toluene for ten minutes caused no degradation apparent in the ¹⁹F spectrum. Reaction with water is rapid, however.

A sample prepared by our colleagues in Germany in 78% yield by the same method was used for NMR, elemental analysis, and boiling point determination. Our results (¹⁹F NMR and IR) are in agreement with their results. These data
have been previously reported (52).

$^{19}$F NMR: Bruker WP 80 SY spectrometer, 75.39 MHz, CDCl$_3$/CFCl$_3$

\[
\begin{align*}
\text{(a)}
\hspace{1cm}
& \begin{array}{c}
\text{CF}_3 \quad \text{(b)} \quad \text{(c)} \quad \text{F(N)} \\
\text{C} & \text{F} & \text{N} & \text{F(M)} \\
\text{SCl}
\end{array} \\
\text{(Z)} \quad \text{F} & \text{M} & \text{F}
\end{align*}
\]

$\delta F_A = -75.25$ ppm, d-d-d

$\delta F_M = -114.25$ ppm, d-d-q

$\delta F_N = -123.07$ ppm, d-d-q

$\delta F_2 = -176.10$ ppm, m

$J_{A-M} = 7.5$ Hz

$J_{A-N} = 0.6$ Hz

$J_{A-Z} = 5.5$ Hz

$J_{M-N} = 81.0$ Hz

$J_{M-Z} = 19.8$ Hz

$J_{N-Z} = 15.6$ Hz

Elemental Analysis: C$_3$F$_6$NSCl, MW 231.5

Found: N 6.05%, S 13.80%

Calculated: N 6.14%, S 14.33%

Boiling Point: 85°C, extrapolated

Infrared Spectrum: Neat capillary film on KBr, cm$^{-1}$: 1455, s; 1342, s; 1237, vs; 1216, vs; 1188, s; 1166, s; 1110, s; 1040, s; 927, w; 835, m; 794, m; 752, m; 688, m; 632, m; 569, m.
$^{13}$C NMR: Bruker WH-360, 90.54 MHz, CDCl$_3$/CFCl$_3$

(a) 
(b) 
(c)

$\delta_a = 118.1 \text{ q-d-d-d}$
$\delta_b = 80.7 \text{ d-d-d-q}$
$\delta_c = 99.5 \text{ d-q-d-d}$
$J_{a-A} = 282.7$
$J_{a-M,N} = 4.0, 2.0$
$J_{a-Z} = 41.2$
$J_{b-A} = 45.0$
$J_{b-M,N} = 20.0, 17.0 \text{ (assignment not possible)}$
$J_{b-Z} = 293.8$
$J_{c-A} = 2.0$
$J_{c-M,N} = 308.2, 301.6 \text{ (assignment not possible)}$
$J_{c-Z} = 18.0$

Reaction with SF$_5$CF=CF$_2$

Into a 100 ml heavy-walled Pyrex glass vessel with an airtight Teflon stopper and containing 2.67 g (10.9 mmol) of (NSCl)$_3$, 5.5 g (26.4 mmol) SF$_5$CF=CF$_2$ was condensed. The vessel was heated at 45-47°C for 25 hours. Separation by fractional condensation was repeated four times, the fourth fractional condensation run yielding 5.0 g (65.3% of theory) of 2-pentafluorothio-2,3,3-trifluoro-1(chlorosulfenyl)-
aziridine, a yellow malodorous liquid.

**Boiling point:** 45-46°C at 70 mm Hg

\(^{19}\text{F NMR:} \) Bruker AMX400 spectrometer, 376.5 MHz, CDCl\(_3\)/CFCl\(_3\)

\[(A) (B)
\begin{array}{c}
\text{F-SF}_4 \quad (a) \quad (b) \quad \text{F (M)}
\end{array}
\]

\[(Z) \text{F} \quad \text{N} \quad \text{F (N)}
\]

\text{SCl}

AB\(_4\)MNZ

\(\delta_A = 66.0 \text{ ppm, d of 9-line pattern, intensity } = 0.99\)

\(\delta_B = 50.88 \text{ ppm, d of multiplet, } 4.00\)

\(\delta_M = -118.14 \text{ ppm, d-d, } 1.00\)

\(\delta_N = -110.95 \text{ ppm, p-d-d, } 1.00\)

\(\delta_z = -144.13 \text{ ppm, d-p-d-d, } 0.99\)

\(J_{A-B} = 146.9 \text{ Hz}\)

\(J_{A-N} = 0.0 \text{ Hz}\)

\(J_{A-N} = 0.0 \text{ Hz}\)

\(J_{A-N} = 5.8 \text{ Hz}\)

\(J_{B-N} = 0.0 \text{ Hz}\)

\(J_{B-N} = 11.1 \text{ Hz}\)

\(J_{B-N} = 13.3 \text{ Hz}\)

\(J_{M-N} = 68.8 \text{ Hz}\)

\(J_{M-N} = 16.3 \text{ Hz}\)

\(J_{N-z} = 18.4 \text{ Hz}\)
$^{13}$C NMR: Bruker AMX400 spectrometer, 100.5 MHz, CDCl$_3$/CFC$_3$

\[
\begin{array}{c}
\text{(A)} \quad (\text{B}) \\
\text{F-SF}_4 \quad (\text{a}) \quad (\text{b}) \quad \text{F (M)} \\
\end{array}
\]

\[
\begin{array}{c}
\quad (\text{Z}) \quad \text{F} \\
\quad \text{N} \\
\quad \text{C} \\
\quad \text{F (N)} \\
\quad \text{SCl}
\end{array}
\]

$\delta_a = 100.1$ ppm, d-d-d-p-t

$\delta_b = 101.5$ ppm, d-d-d

(some couplings not exactly determinable due to overlap of peaks)

$J_{a-z} = 338$ Hz

$J_{a-b} = 31.2$ Hz

$J_{a-A} = 2.5$ Hz

$J_{a-M} = 19.6$ Hz

$J_{b-z} = 18.5$ Hz

$J_{b-N} = 310$ (332) Hz

$J_{b-M} = 332$ (310) Hz

$J_{b-B} = 1.9$ Hz

$J_{b-A} = 0.0$ Hz

Mass spectrum: Electron impact, 70 eV. Peaks greater than 5% of parent peak listed (M/e, type, relative intensity): 254, (M-Cl)$^+$, 1.0%; 208, (M-NSCl)$^+$, 18.5; 202, 200, (M-3F)$^+$, 9.5; 162, 164, (M-SF$_3$)$^+$, 20.0; 150, 152, CClF$_3$NS$^+$ (rearr.), 6.4; 134, CF$_4$NS$^+$, 78.9; 127, SF$_5^+$, 32.2; 114, CF$_5^+$, CF$_2$S$_2$ $^+$ (rearr.), 5.2; 101, CF$_3S^+$ (rearr.), 8.5; 100, CF$_4^+$ (rearr.), 8.0; 95, CF$_3N^+$ (rearr.), 9.3; 89, SF$_3^+$, 100.0; 85, 87, CClF$_2^+$,
10.4; 81, C₂F₃⁺, 31.2; 76, C₂F₂N⁺, 5.0; 70, SF₂⁺, C₂NS⁺, 16.1; 67, 69, ClS⁺, 38.6; 64, CF₃⁺, 20.4; 50, CF₂⁺, 20.2.

Infrared spectrum: Neat sample on KBr, cm⁻¹: 1508, w; 1428, vs; 1377, sh, m; 1345, m-s, sh; 1284, w, sh; 1227, vs; 1190, vs; 1149, vs; 1126, s-vs, sh; 1089, m-s, sh; 1033, s; 893, vs; 860, vs; 837, s-vs; 775, s; 760, m; 698, m; 680, m; 636, m; 606, s-vs; 574, s; 493, s.

Elemental analysis: C₂ClF₆NS₂, MW 289.59
Calculated: N 4.84%, S 22.14%
Found: N 4.87%, S 22.27%

Reaction with C₄F₉OCF=CF₂

To a dry heavywalled 100 ml Pyrex glass vessel with an airtight Teflon stopcock, containing a Teflon stir bar and 1.07 g (4.38 mmol) (NSCl)₃, 5.17 g (16.4 mmol) C₄F₉OCF=CF₂ and 13.4 g CFCl₃ were added by vacuum transfer. This mixture was heated overnight at 42-51°C. Two successive separations by fractional condensation yielded 2.76 g (53% of theory) of product in a -40°C trap.

Infrared spectrum: neat liquid, KBr plates, cm⁻¹: 1462, s; 1307, s; 1230, vs; 1145, vs; 1061, m, sh; 990, w; 952, m; 915, m, sh; 898, m; 877, m; 840, w; 790, w; 748, m; 732, m, sh; 703, w, sh; 682, w, sh; 594, w; 553, w; 536, w; 499, m; 420, w.
$^{19}$F NMR: Varian EM390, 84.67 MHz, CFC$_3$

\[
\begin{align*}
(a)(b)(c) & \quad \text{F(d)} \\
\text{CF}_3\text{CF}_2\text{CF}_2& \quad \text{C} - \text{O} \\
(e) & \quad \text{F} \\
(f) & \quad \text{N} \\
\text{ScI} & \quad \text{F(g)}
\end{align*}
\]

$\delta_a, \delta_d = -82.5, \text{d-m, area} = 4.1$ (overlapped peaks)
$\delta_b, \delta_c = -127, \text{m, area} = 4.1$ (overlapped peaks)
$\delta_e = -87.5, \text{d-t, area} = 1.0$
$\delta_f, \delta_g = -121, \text{area} = 1.95$ (overlapped peaks)
$\delta_h = -123, \text{d-d, area} = 0.90$

$^{19}$F NMR: Bruker AMX400, 376.5 MHz, CDCl$_3$/CFC$_3$

$\delta_a = -81.7, \text{t}$
$\delta_b = -126.4, \text{q-t}$
$\delta_c = -126.8, \text{t,t,d} \text{d}$
$\delta_d = -82.7, \text{t-t-d}$
$\delta_e = -86.1, \text{d-t}$
$\delta_f = -119.3, \text{m}$
$\delta_g = -118.9, \text{d-m}$
$\delta_h = -121.0, \text{d-m}$
$J_{a-b} = 10 \text{ Hz}$
$J_{b-c} = 9 \text{ Hz}$
$J_{c-d} = 11 \text{ Hz}$
$J_{c-e} = 7 \text{ Hz}$
$J_{d-e} = 147 \text{ Hz}$
$J_{d-g} = 11$ Hz

$J_{h-g} = 76$ Hz

$\text{${}^{13}$C NMR: Bruker AMX400, 100.6 MHz, CDCl}_3$/CFCl$_3$, (capital letters indicate carbon atoms, lower case fluorine)

\begin{align*}
\delta_A &= 118.1 \text{ ppm, q-t} \\
\delta_{B,C} &= 109.1, \text{ t-m} \\
\delta_D &= 117.1, \text{ t-t} \\
\delta_F &= 95.0, \text{ d-d-d-d} \\
\delta_G &= 101.6, \text{ d-d-d} \\
J_{A-a} &= 287.3 \\
J_{A-b} &= 33.0 \\
J_{B-b}, J_{C-c} &\approx 270 \text{ (overlapping peaks)} \\
J_{D-d}, J_{D-e} &= 287.6 \\
J_{D-c} &= 32.1 \\
J_{F-f} &= 319.0 \\
J_{F-h}, J_{F-g} &= 19.6 \\
J_{F-(d or e)} &= 2.8 \\
J_{G-h}, J_{G-g} &= 317 \text{ (approximate coupling)} \\
J_{G-f} &= 20 \text{ (approximate coupling)}
\end{align*}
Reaction of ClCH₂CH₂CHClCF₂=CF₂

Preliminary investigation indicates that (NSC1)₃ will add to a fluoroalkene with a partially protonated side chain to form an aziridine.

To a dry 100 ml Pyrex glass vessel with an airtight Teflon stopcock containing a Teflon stir bar, 1.03 g (4.22 mmol) (NSC1)₃ was added. 1.91 g (5.84 mmol) of ClCH₂CH₂CHClCF₂=CF₂ and 7.7 g CFCl₃ were then added by vacuum transfer. This was reacted for two days at 42°C. Attempted separation by fractional condensation yielded only CFCl₃ and yellow decomposition products in the traps, but 2.26 g of a dark red liquid (non-volatile at 2 x 10⁻² torr, room temperature) was recovered from the reaction vessel. This material was not purified further, but preliminary proton and ¹⁹F NMR and IR evidence indicates that the aziridine was formed.

In the ¹⁹F spectrum, there is no evidence of any remaining starting alkene. Peaks in regions centered at -109, -116, -124, and -172 ppm, with relative areas of 2.0, 1.0, 1.1, and 1.0, respectively, are strongly suggestive of a fluoroaziridine.

The proton spectrum (EM390, 90MHz, TMS) of the recovered product is virtually unchanged from that of the starting alkene, indicating that the side chain did not take part in the reaction. The spectrum shows complex resonances centered at 2.8, 3.7, and 4.3 ppm, with relative areas of
2.3, 2.5, and 1.0, respectively.

The IR spectrum has a strong, prominent peak at 1445 cm\(^{-1}\), which is characteristic of fluoroaziridines. Other strong peaks occur at 1220 and 1111 cm\(^{-1}\).

**Reaction with perfluoro-2-butene**

To a dry 100 ml Pyrex glass vessel with an airtight Teflon stopcock containing a Teflon stir bar, 1.0 g (4.1 mmol) of (NSCl), was added. 7.4 g (37 mmol) of CF\(_3\)CF=CFCF\(_3\) and 13.4 g CFCI\(_3\) were added by vacuum transfer. After four days of heating at 40-47°C, the reaction mixture turned reddish-brown. After two successive fractional condensations, 0.57 g of a yellow liquid, 17% of theoretic yield, was recovered from the -78°C trap. This product is relatively unstable; it quickly decomposed to yellow solid in the trap-to-trap apparatus, and samples refrigerated in sealed flasks developed yellow sediment within days.

Peaks assigned to the major aziridine product account for 54% of the total area under peaks in the \(^{19}\)F NMR spectrum, indicating that the sample as run had decomposed. Other peaks (amounting to 14% of total peak area) are suggestive of isomeric aziridines, but are poorly resolved.
$^{19}$F NMR: Bruker AMX400, 376.5 MHz, CDCl$_3$/CFC$_3$,

\begin{equation}
\begin{array}{c}
(A) \ce{CF_3} & \ce{F} & (B) \\
\ce{F} & \ce{N} & \ce{CF_3} \\
(B) & \ce{SCl} & (A)
\end{array}
\end{equation}

$\delta_a = -73.9$

$\delta_b = -168$

$J_{A-B} = 6.1$ Hz

Only one coupling is observed in spectra with a resolution of about 2 Hz. This is more consistent with the trans-substituted aziridine. In CF$_3$CFCF$_2$NSCl, for comparison, the coupling of the trifluoromethyl group is 7.5 Hz with the trans fluorine, 0.6 Hz with the cis fluorine, and 5.5 Hz with the fluorine which is geminal to the trifluoromethyl group. We would therefore anticipate a more complex spectrum than that observed if a fluorine were trans to the trifluoromethyl group.

Infrared spectrum: Nicolet 20DX, neat sample on KBr plates, cm$^{-1}$: 3149 w, 3051 w, 1462 s, 1420 m, sh, 1325 vs, 1306 vs, 1271 s, 1227 vs, 1192 vs, 1148 s, sh, 1133 s, 1069 m, sh, 1030 s, 941 m, 823 w, sh, 813 m, 793 w, 773 vw, 754 m, 730 m, 719 w, sh, 704 vw, 660 m, sh, 645 s, 606 w, 591 vw, sh, 522 m, sh, 512 m, sh, 497 s, 453 m, 438 w, sh, 409 w.
Reaction with CH₂=CHCH₂CF=CF₂

In an attempt to discover whether (NSCl)₃ would react preferentially with a fluoroolefin in the presence of a protonated olefin, CH₂=CHCH₂CF=CF₂ (2.89 g, 23.7 mmol) was condensed into a 100 ml Pyrex glass vessel equipped with an airtight Teflon stopcock and containing 1.12 g (4.48 mmol) of (NSCl)₃, and 13.5 g of CFCl₃. This mixture reacted immediately, with blackening, upon warming. Fractional condensation removed only clear liquid, leaving 1.78 g of a brown-black solid which smelled of burned rubber in the reaction vessel. A second reaction using 1.0 g (4.2 mmol) of (NSCl)₃, and 2 g of CH₂CHCH₂CFCF₂ was held at 0°C for several hours before warming, with other conditions as above. This resulted in less charring, but otherwise similar results. Comparison of the IR spectra of these two products with that of the starting material shows considerable diminution of the -CF=CF₂ peak which occurs at 1801 cm⁻¹ in the starting material.

This reaction may be explained by removal of one of the doubly allylic hydrogen atoms from the alkene by the nitrene, giving a stabilized radical which may undergo polymerization reactions from either the -CH=CH₂ or the -CF=CF₂ end.
Reaction with Perfluorocyclobutene

In the manner described above, 0.72 g (2.95 mmol) of (NSCl), was reacted with 1.29 g (7.96 mmol) of perfluorocyclobutene in 10.4 g of CFCl₃. After heating to 50°C, the reaction mixture became the greenish-yellow color indicative of NSCl monomer. Separation by fractional condensation after 2 days of heating yielded 0.58 g of non-volatile material, which remained in the reaction vessel, and some yellow solid in the -78°C trap. None of the fractions was found to contain the aziridine group. No evidence of aziridine formation was found by ¹⁹F NMR analysis after an additional 3 days of heating. No further studies of this system were attempted.

Reaction with Perfluorocyclopentene

Using the same apparatus as described for the preparation of CF₃CFCE₂NSCl, 1.13 g (4.62 mmol) of (NSCl), was reacted with 3.53 g (16.6 mmol) of perfluorocyclopentene in 13 g CFCl₃. After heating overnight at 44-48°C for 3 days, the reaction mixture was separated by fractional condensation. Analysis of the products were as follows: a small quantity of a yellow solid decomposition product in the -30°C trap; a deep red liquid which had no fluorine NMR resonance in the -78°C trap; and unreacted perfluorocyclopentene in the -198°C trap. No further analysis was attempted.
Reaction with Iodotrifluoroethylene

Using the same apparatus as was used for preparing \( \text{CF}_2\text{CFCF}_2\text{NSCl} \), 1.13 g (5.36 mmol) \( \text{NSCl} \), was reacted with 3.84 g (18.5 mmol) of \( \text{CF}_2=\text{CFI} \) in 14 g of \( \text{CFCl}_3 \). Heating to 46-48°C resulted in a series of color changes from purple to dark brown to yellow. Heating was continued for 3 days. Analysis of low-boiling fractions gave no indication of aziridine formation. The \( ^{19}F \) NMR spectra of higher volatility fractions were identical to the spectrum of iodotrifluoroethylene.

REACTIONS OF \( N \)-CHLOROSULFENYLAZIRIDINES

Formation of a Disulfide

To a 100 ml dry, airtight Pyrex glass vessel containing 3.16 g (15.6 mmol) of mercury and a Teflon stir bar, 1.38 g (5.96 mmol) of \( \text{CF}_3\text{CFCF}_2\text{NSCl} \) was added by vacuum transfer. This mixture was stirred at room temperature for 2 days. Separation by fractional condensation yielded 0.73 g (1.85 mmol, 62% of theory) of bis(2-trifluoromethyl-2,3,3-trifluoroaziridine)disulfide in the -40°C trap. This sample was characterized by \( ^{19}F \) NMR and infrared spectroscopy.

This product was also prepared by our coworkers at the Universität Bremen by reacting 5.85 g mercury and with 2.7 g \( \text{CF}_3\text{CFCF}_2\text{NSCl} \) in n-pentane. After stirring at room temperature overnight, the disulfide, a clear liquid, was produced in 72% yield after separation by fractional
condensation. Their sample was characterized by elemental analysis, infrared spectroscopy, mass spectroscopy, and high-field $^{19}$F and $^{13}$C NMR. These results have been previously reported (53) and are given below. The IR and $^{19}$F NMR given here are in close agreement with my results.

**Elemental analysis:** $C_6F_{12}N_2S_2$, MW 392

Calculated: N 7.14% S 16.33%

Found: N 7.19% S 16.92%

**Infrared spectrum:** gas cell, KBr windows, cm$^{-1}$: 1459 vs, 1337 vs, 1250 vs, 1219 vs, 1201 s, 1171 s, 1117 s, 1100 s, sh, 1043 s, 841 w, 794 w, 750 w, 694 w, 636 w, 598 vw, 573 w, 471 w.

**Mass spectrum:** electron impact, 70 eV; m/e, fragment, relative intensity: 392, $M^+$, 9%; 242, $C_3F_6N_2S_2^+$, 10; 228, $C_3F_6NS_2^+$, 31; 196, $C_3F_6NS^+$, 3; 178, $C_3F_6NS_2^+$, 32; 164, $C_3F_6N^+$, 79; 150, $C_3F_6^+$, 3; 114, $C_2F_4N^+$, 100; 100, $C_2F_4^+$, 8; 69, $CF_3^+$, 46; 64, $S_2^+$, 41; 46, $NS^+$, 57.
$^{19}$F NMR: Bruker WP 80 SY, 75.4 MHz, CDCl$_3$/CFCl$_3$

The $^{19}$F NMR spectrum is complex due to the existence of two diastereomers of the disulfide, with overlapping peaks. Only the largest couplings can be determined for this compound.

\[\begin{align*}
(A) \text{CF}_3, & \quad (b) (c) \quad F (M) \\
(Z) F & \quad N \quad F (N) \\
S
\end{align*}\]

\[\begin{align*}
\delta_A &= -75.5, \text{ multiplet} \\
\delta_x &= -121.4 \text{ and } -122.5, \text{ multiplets} \\
\delta_y &= -113.8, \text{ multiplet} \\
\delta_z &= -173.8, \text{ multiplet} \\
J_{x-y} &= 85.3 \text{ Hz} \\
J_{x-z} &= 18.5 \text{ Hz}
\end{align*}\]

$^{13}$C NMR: Bruker WH360, 90.54 MHz, CDCl$_3$/CFCl$_3$

\[\begin{align*}
\delta_a &= 118.1 \text{ ppm } q-d-d-d \\
\delta_b &= 81.8 \text{ d-q-d-d} \\
\delta_c &= 100.5 \text{ d-d-d-q} \\
J_{a-b} &= 280.0 \text{ Hz} \\
J_{a-z} &= 41.7 \\
J_{a-x}, J_{a-y} &= 4.0, 2.2 \text{ (assignment not possible)} \\
J_{b-z} &= 288.7 \\
J_{b-a} &= 45 \\
J_{b-x}, J_{b-y} &= 20.2, 17.2 \text{ (assignment not possible)} \\
J_{c-x}, J_{c-y} &= 306.5, 301.2 \text{ (assignment not possible)}
\]
\(J_{c-z} = 17.5\)

\(J_{\gamma-\delta} = 2.0\)

**Reaction with ethylene**

Several attempts were made to react the sulfinyl chloride group of the aziridine with an alkene to form a sulfide according to Equation 27.

\[
\text{(27)} \quad \text{RS-Cl} + \text{CH}_2=\text{CH}_2 \rightarrow \text{Cl} \quad \text{SR}
\]

As a first attempt \(\text{CH}_2=\text{CH}_2\) was bubbled into neat \(\text{CF}_3\text{CFCF}_2\text{NSCl}\) at \(-30^\circ\text{C}\) for 2 hr. A proton NMR spectrum of this mixture showed a single peak at 5.32 ppm consistent with dissolved ethylene, and no evidence of reaction. No reaction was evident when this procedure was repeated at room temperature.

In a closed 3 liter Pyrex glass vessel, \(\text{CF}_3\text{CFCF}_2\text{NSCl}\) was irradiated by a sun lamp along with 700 torr ethylene for 3 days. A \(^{19}\text{F}\) NMR spectrum of the liquid product contained a weak signal reminiscent of badly decomposed \(\text{CF}_3\text{CFCF}_2\text{NSCl}\). The proton NMR spectrum showed a broad signal at 2.7-4.0 ppm, indicative of polymerization. Some solid material was recovered from the walls of the vessel. The proton NMR spectrum of this material dissolved in \(\text{CH}_2\text{Cl}_2\) showed two triplets of equal area at 3.1 and 3.8 ppm, with a coupling between them of 7.5 Hz. This is consistent with a product containing the \(-\text{CH}_2\text{CH}_2-\) group. The weak \(^{19}\text{F}\) NMR
spectrum indicated a complex mix of products, with only a small \(-\text{CF}_3\) peak. These results indicate that the aziridine did not add to ethylene in these reactions but served as a free radical source for polymerization.

In a third attempt, a 100 watt ultraviolet Hanovia lamp with a Corex glass filter in a water-cooled immersion well was used for irradiation, and 3.0 g (13 mmol) \(\text{CF}_3\text{CFCF}_2\text{NSCl}\), 530 torr \(\text{CH}_2\text{CH}_2\), and 3 g \(\text{CFCl}_3\) (solvent) were contained in a 5 liter Pyrex glass bulb surrounding the lamp. The reaction vessel was connected to the vacuum line in order to allow for vacuum transfers and to monitor the pressure. Irradiation was continued for 26 minutes, after which the pressure in the vessel was constant. Analysis of the volatile products, which existed as a pale yellow liquid, shows an \(^{19}\text{F NMR spectrum similar to CF}_3\text{CFCF}_2\text{NSCl}\), and the \(-\text{CH}_2\text{CH}_2-\) group in the proton NMR spectrum. A non-volatile yellow liquid was also recovered which contained a \(-\text{CH}_2\text{CH}_2-\) group but no evidence of fluorine was found in this material. A clear polymer film was also recovered from the bottom of the reaction vessel. The IR spectrum of this material shows strong peaks at 2954, 1405, and 1265 cm\(^{-1}\), and also very strong and broad peaks between 700 and 1200 cm\(^{-1}\), indicating that it is a copolymer containing monomer from ethylene and undetermined residues of the aziridine.
**Reaction with Water**

To a 50 ml round-bottomed Pyrex glass flask equipped with a Teflon stir bar and a reflux condenser were added 1.06 g (4.6 mmol) CF₃CF₂NSCl, 0.50 g (27.8 mmol) of distilled water, and 5 g of diethyl ether. After refluxing for 15 minutes, the ether was removed by distillation. Solid products recovered from the resulting crude mixture were 0.046 g of a yellow paste and 0.427 g of white crystals. The yellow paste is thought to be elemental sulfur. (0.046 g represents 1.4 mmol sulfur, 30% yield based on starting aziridine. Not all of the yellow paste could be separated from the white crystals). After washing with water, the white powder was sublimed at 95°C, 2 x 10⁻² torr to yield 0.93 g white powder, mp 117-119°C.

Proton NMR (Bruker AMX400, 400.1 MHz, CDCl₃) of the white solid shows two peaks at 7.32 and 7.55 ppm, relative areas 1.023 and 0.992, respectively. On a continuous wave instrument (Varian EM390, 90 MHz, CDCl₃) there is also a very broad peak centered at 5.5 ppm, and integration gives relative areas 4.3, 1, 1 for peaks at 5.5, 7.3, and 7.5 ppm, respectively. Fluorine NMR shows a single peak at -83.1 ppm relative to CFCl₃. ¹³C NMR shows 3 peaks: δ 169.1 ppm, s; δ 122.4, q, J 292 Hz; δ 90.6 ppm, q, J = 31.0 Hz.

The IR spectrum of the white solid was taken as a KBr pellet. The peaks are as follows: 3442 s, 3332 s, 3284 s, 3213 m, 3107 m, 2802 w, 1690 vs, 1618 m, 1458 w, 1405 m,
1265 m, 1198 vs, 1151 vs, 1114 s, 977.7 m, 796.3 w, 761.3 w,
659.8 m, 541.8 m.

Positive identification of this material has not been
made as of this time.
CHAPTER IV

DISCUSSION OF N-CHOROSULFENYL AZIRIDINES

NMR OF AZIRIDINES

The chemical shifts and coupling constants of atoms on small-ring heterocycles are strongly dependant on the electronic properties of the molecule. These properties are most strongly affected by the heteroatom, but electronic and steric effects of the substituents also play a large role. Comparison of NMR data for N-chlorosulfenylaziridines with published studies of other three-membered rings may therefore give insight into the structure of these molecules.

Early studies by Ernst (54) and others (55) established a close relationship between the fluorine-fluorine coupling constants and the dihedral fluorine-carbon-fluorine angle of trifluorocyclobutanes and trifluorocyclopentanes. In heterocycles, however, this relationship is obscured by the existence of some degree of carbon-carbon double bond character in the ring.

Early proton NMR studies of protonated aziridines observed that the chemical shifts of ring protons are strongly dependant on ring substituents (56). Values of
proton coupling constants for ethylenimine are larger than the couplings in cyclopropane and smaller than those of ethylene oxide, which reflects changes in the hybridization and electronic structure of the molecule due to the different electronegativities of the heteroatoms (57).

The ring fluorine shifts and coupling constants of \( N \)-chlorosulfenylaziridines are summarized in Table I. The fluorine NMR of several compounds derived from hexafluoropropene are listed in Table II. Table III is a comparison of the \(^{19}\text{F}\) NMR of several chlorotrifluoro 3-membered ring systems. Available \(^{13}\text{C}\) NMR data of \( N \)-chlorosulfenylaziridines is listed in Table IV.

**TABLE I**

RING FLUORINE CHEMICAL SHIFTS AND COUPLING CONSTANTS OF \( N \)-CHLOROSULFENYLAZIRIDINES

\[
\begin{array}{cccccc}
X &=& CF_3 & SF_5 & Cl & F & OC_4F_3 \\
\delta_X &= -114.2 & -111.0 & -124.4 & -119.5 & -119 \\
\delta_N &= -123.1 & -118.1 & -121.3 & - & -121 \\
\delta_Z &= -176.1 & -144.1 & -106 & - & -119 \\
J_{MN} &= 81.0 & 68.8 & 72.4 & - & 76 \\
J_{NZ} &= 19.8 & 18.4 & 18.0 & - & - \\
J_{NZ} &= 15.6 & 16.3 & 12.0 & - & - \\
\text{ref.}(58) &= (a) & (a) & (a) & (a) & (b)
\end{array}
\]
TABLE II

FLUORINE NMR DATA OF PERFLUOROPROPENE AND SOME DERIVATIVES

(A) $\text{CF}_3 \text{CFCF}_2 \text{F} (N)$

(Z) $\text{F} \text{CFCF}_2 \text{F} (M)$

<table>
<thead>
<tr>
<th>CF$_3$CFCF$_2$</th>
<th>R = NSCl</th>
<th>NH</th>
<th>NSNSF2</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_A$</td>
<td>-74.5</td>
<td>-75.2</td>
<td>-76.5</td>
<td>-75.6</td>
</tr>
<tr>
<td>$\delta_B$</td>
<td>-99.5</td>
<td>-114.2</td>
<td>-122.0</td>
<td>-115.5</td>
</tr>
<tr>
<td>$\delta_C$</td>
<td>-113.1</td>
<td>-123.1</td>
<td>-122.0</td>
<td>-121.4</td>
</tr>
<tr>
<td>$\delta_D$</td>
<td>-198.5</td>
<td>-176.1</td>
<td>-174.9</td>
<td>-173.0</td>
</tr>
<tr>
<td>$J_{AM}$</td>
<td>8.5</td>
<td>7.5</td>
<td>-</td>
<td>8.0</td>
</tr>
<tr>
<td>$J_{AN}$</td>
<td>22.6</td>
<td>0.6</td>
<td>-</td>
<td>0.7</td>
</tr>
<tr>
<td>$J_{AZ}$</td>
<td>14.1</td>
<td>5.5</td>
<td>-</td>
<td>5.4</td>
</tr>
<tr>
<td>$J_{MN}$</td>
<td>59.3</td>
<td>81.0</td>
<td>102</td>
<td>82.0</td>
</tr>
<tr>
<td>$J_{MZ}$</td>
<td>40.9</td>
<td>19.8</td>
<td>-</td>
<td>19.6</td>
</tr>
<tr>
<td>$J_{NZ}$</td>
<td>118</td>
<td>15.6</td>
<td>-</td>
<td>16.5</td>
</tr>
<tr>
<td>ref. (59)</td>
<td>(a)</td>
<td>(b)</td>
<td>(c)</td>
<td>(d)</td>
</tr>
</tbody>
</table>
TABLE III

FLUORINE NMR OF SOME 3-MEMBERED RINGS

\[
\begin{align*}
\text{Cl} & \quad \text{F (N)} \\
\text{C} & \quad \text{C} \\
(Z)\text{F} & \quad \text{R} \\
\text{F (M)}
\end{align*}
\]

<table>
<thead>
<tr>
<th>( R = \text{O} )</th>
<th>NSCL</th>
<th>CCl(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta_\text{M} )</td>
<td>-110.6</td>
<td>-124.4</td>
</tr>
<tr>
<td>( \delta_\text{N} )</td>
<td>-94.9</td>
<td>-121.3</td>
</tr>
<tr>
<td>( \delta_\text{z} )</td>
<td>-115.5</td>
<td>-106.6</td>
</tr>
<tr>
<td>( J_{\text{MN}} )</td>
<td>+21</td>
<td>72.4</td>
</tr>
<tr>
<td>( J_{\text{MZ}} )</td>
<td>+34.5</td>
<td>18.0</td>
</tr>
<tr>
<td>( J_{\text{NZ}} )</td>
<td>-15.5</td>
<td>12.0</td>
</tr>
</tbody>
</table>

ref. (60) (a) (b) (c)
TABLE IV
CARBON-13 NMR DATA FOR N-CHLOROSULFENYLAZIRIDINES

\[ X \quad (a) \quad (b) \quad F \quad (N) \]
\[ \text{SCl} \]

<table>
<thead>
<tr>
<th>X =</th>
<th>CF₃</th>
<th>SF₃</th>
<th>Cl</th>
<th>F</th>
<th>OC₂F₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>δₐ</td>
<td>80.7</td>
<td>100.1</td>
<td>91.6</td>
<td>101.1</td>
<td>95.0</td>
</tr>
<tr>
<td>δₐ</td>
<td>99.5</td>
<td>101.5</td>
<td>101.6</td>
<td>101.1</td>
<td>101.6</td>
</tr>
<tr>
<td>Jₐ₋ₐ</td>
<td>20.0</td>
<td>19.6</td>
<td>22.0</td>
<td>22.0</td>
<td>19.6</td>
</tr>
<tr>
<td>Jₐ₋ₐ</td>
<td>17.0</td>
<td>19.6</td>
<td>20.7</td>
<td>22.0</td>
<td>19.6</td>
</tr>
<tr>
<td>Jₐ₋ₐ</td>
<td>293.8</td>
<td>338</td>
<td>330.3</td>
<td>319.9</td>
<td>319.0</td>
</tr>
<tr>
<td>Jₐ₋ₐ</td>
<td>308.2</td>
<td>332</td>
<td>319.1</td>
<td>319.9</td>
<td>317</td>
</tr>
<tr>
<td>Jₐ₋ₐ</td>
<td>301.6</td>
<td>310</td>
<td>313.9</td>
<td>319.9</td>
<td>317</td>
</tr>
<tr>
<td>Jₐ₋ₐ</td>
<td>18.0</td>
<td>18.5</td>
<td>18.7</td>
<td>22.0</td>
<td>20</td>
</tr>
<tr>
<td>ref.</td>
<td>(a)</td>
<td>(b)</td>
<td>(a)</td>
<td>(a)</td>
<td>(b)</td>
</tr>
</tbody>
</table>

*carbon-fluorine couplings of the geminal fluorines are not distinguishable.

INFRARED SPECTROSCOPY

Aziridines have several absorptions which are due to deformations of the three-membered ring. Ethyleneimine itself has absorptions at 1210 cm⁻¹ (ring breathing), 856 cm⁻¹ (symmetrical ring deformation), and 1268 cm⁻¹ (asymmetrical ring deformation) (61).

A strong peak in the region of 1450 cm⁻¹ is taken to be characteristic of fluorinated aziridines. It is generally quite distinctive because of the absence of other peaks in
this region. This resonance is reported to occur at 1431 cm\(^{-1}\) for the 1-H fluoro-aziridine \(\text{CF}_3\text{CFCFC1NH}\) (62). Table V lists the occurrence of this resonance for \(N\)-chlorosulfenylaziridines reported in this work and by our coworkers in Germany.

**TABLE V**

**INFRARED ABSORPTIONS OF**

**\(N\)-CHLOROSULFENYLAZIRIDINES**

\[
\begin{array}{ccc}
\text{X} & \text{Y} & \text{peak, cm}^{-1} \\
\text{CF}_3 & \text{F} & 1455 \\
\text{SF}_5 & \text{F} & 1428 \\
\text{ClCH}_2\text{CH}_2\text{CHClCF}_2 & \text{F} & 1445 \\
\text{C}_4\text{F}_9\text{O} & \text{F} & 1462 \\
\text{CF}_3 & \text{CF}_3 & 1462 \\
\text{Cl} & \text{F} & 1435 \\
\text{F} & \text{F} & 1485 \\
\end{array}
\]

**Inversion of Stereochemistry**

In none of the \(N\)-chlorosulfenylaziridines produced from fluorooolefins is there evidence of separate isomers caused by slow inversion of configuration at the ring nitrogen. Slow inversion would be apparent in the NMR spectra. For example, 1-methoxy-2,2,3,3-tetramethylaziridine was found (64) to invert slowly on the NMR time scale at room temperature, resulting in non-equivalent geminal methyl
groups at temperatures as high as 130°C, with peaks at 1.04 and 0.92 ppm. Inversion is expected to be slower in aziridines than in comparable acyclic compounds because of the destabilization of the transition state due to ring strain.

Explanations of differing inversion rates at nitrogen have focused on neighboring lone pairs and the extent of double bond formation between the nitrogen and its neighbor. One such study (65) determined the barrier to pyramidal inversion by examining a series of N-aryl-2,2-dimethyl-aziridines using a temperature dependant NMR study. The barrier was found to be quite sensitive to aryl group substituents, having a range of rate constant of $10^4$ at -60°C. An analysis of these barriers showed a good correlation with the Hammett substituent constant $\sigma^-$, with a $\rho$ value of 2.8 at -60°C. The positive $\rho$ value indicates that the rate of inversion is increased by electron withdrawal. The authors of this study propose that electron withdrawal from the ring enhances the interaction of the nitrogen lone pair with the ring $\pi$ system. This brings the geometry of the system closer to planarity, and consequently reduces the barrier to inversion.

Inversion in sulfenylaziridines is accompanied by torsion about the S-N bond:
The rates and relative importance of inversion at nitrogen and torsion about the S-N bond for a series of sulphenylaziridines is discussed in a paper by Kost and Raban (66). Acyclic sulfenamides are nearly planar and torsion has a higher activation energy than inversion. In sulphenylaziridines the order of energies is reversed due to the effect of ring strain but inversion is still much more rapid than in N-alkylaziridines. There was no linear free energy relationship clearly evident in a series of substituted N-arenesulphenylaziridines. Kost and Raban concluded that a π bonding effect similar to that found in the N-arylaiziridines does not play an important role in lowering the barrier to inversion in sulphenylaziridines. Since the barrier was very low with electronegative substituents such as CF₃ and CCl₃ on the sulfur, the authors propose resonance structures which would have the effect of reducing the bond angles at nitrogen and lowering the barrier to inversion.
The ionized resonance structure could be very important for a sulfenylaziridine in which $R$ is a halogen, giving an indication of possible sites of reactivity for $N$-chlorosulfenylaziridines.

**MECHANISM OF FORMATION**

Further experiments are necessary before full elucidation of the mechanism of formation of $N$-chlorosulfenylaziridines from fluoroolefins will be possible, but some preliminary conclusions may be drawn. Analogy with the relatively well-studied aminonitrenes and sulfenylnitrenes leads to the conclusion that the NSCl nitrene is in the singlet state. The studies of fluoroolefins cited previously indicate that the reaction has a radical intermediate which could be stabilized by the CF$_2$ group. The supposition that the reaction is a non-concerted reaction of a singlet nitrene is unusual, since non-concerted reactions are more characteristic of triplets. It is not improbable, however, since the nitrene is made less reactive by the neighboring divalent sulfur atom, and the radical transition state is stabilized by the fluorine atoms.
These conclusions are supported by a preliminary MINDO calculation done by our coworkers in Germany (67). These calculations indicate that the singlet reaction is highly unsymmetrical, with a well-defined diradical transition state before ring closure.
CHAPTER V

ANALYSIS OF (SF₃CF=CF₂)₂

DISCUSSION

The synthesis of internally unsaturated perfluoroolefins by halide-catalyzed dimerization and trimerization of terminally unsaturated fluoroolefins was patented by Brehm et al. of the du Pont corporation in 1959 (68). Brehm et al. described the dimerization of CF₃CF=CF₂ using a variety of catalysts and conditions. The products found were primarily (CF₃)₂CFCF=CFCF₃ and (CF₃)₂C=CFCF₂CF₃, along with several isomers of the trimer and detectable amounts of terminally unsaturated olefins. This reaction was also discussed by Chambers (69), who found that the major isomer was (CF₃)₂C=CFCF₂CF₃, formed by rearrangement of the carbanion formed in Equation 31 to the isomer which gives the more substituted double bond:
Like other perfluoroolefins, perfluorovinylsulfur pentafluoride dimerizes in the presence of fluoride ion. A sample of the dimer was prepared by G. L. Gard at the Universität Bremen according to Equation 34:

\[
\text{CH}_3\text{CN} \quad \text{SF}_5\text{F} \quad \text{C} = \text{C} \quad \text{SF}_5
\]

\[
\text{C} \quad \text{C} \quad \text{F}_3 \quad \text{C} \quad \text{C} \quad \text{F}_3
\]

Dimerization of SF$_5$CF=CF$_2$ has been previously reported by Canich (70). Canich reacted SF$_5$CF=CF$_2$ with a catalytic amount of cesium fluoride in a closed vessel for several hours at temperatures up to 100°C. The product was isolated in 78% yield, and was found to be 96% pure by GC analysis with a boiling point of 38-39°C at 24.6 torr. Elemental analysis of this product gave: C 11.54%, S 15.38%,
F 73.08%; compared with C 11.67%, S 15.26%, F 73.1%
calculated for C₄F₁₆S₂. Positive structure determination of
this product was not made.

Comparison of the products of these two syntheses
reveals significant differences, particularly in the ¹⁹F
NMR spectra, indicating that the two products are structural
isomers. The formation of two different products is not
unexpected, given the radically different reaction
conditions. The use of a different source of fluoride ion
can also affect the product formed (71).

¹³C and ¹⁹F NMR analysis of the product prepared by Gard
allows positive identification as perfluoro-1,3-
dipentafluorothio-1-butene, as shown in Equation 34.

**ANALYSIS**

**Boiling point**

52.5-53.5 at 78 torr

**Infrared spectrum**

Neat liquid on KBr plates, cm⁻¹: 1791 w, 1704 w, 1580 w,
1499 w, 1404 w, 1325 m, 1279 s, sh, 1253 vs, 1226 s, 1204
vs, 1161 s, 1097 w, 1052 s, 1021 w, sh, 950 w, sh, 916 s,
sh, 873 vs, 840 s, 792 m, 749 s, 708 m, 685 m, 665 s, 605 s,
589 m, 571 s, 536 s, 475 m.
\[^{13}\text{C} \text{ NMR}\]

**Bruker AMX400, 100.6 MHz, CDCl₃/CFCl₃**

\[
\begin{align*}
\text{F-SF}_4 & \quad \text{A} & \quad \text{B} & \quad \text{F} \\
\text{C}=\text{C} & \quad \text{C} & \quad \text{D} \\
\text{F} & \quad \text{C}-\text{CF}_3 & \quad \text{(m)} \\
\text{F} & \quad \text{C} & \quad \text{F} \\
\text{SF}_4 & \quad \text{(d)} \\
\text{F} & \quad \text{C} & \quad \text{F} \\
\text{SF}_4 & \quad \text{(c)}
\end{align*}
\]

\[\delta_a = 159.5; \; d,d,p\]
\[\delta_b = 140.8; \; d,d,d\]
\[\delta_c = 110.0; \; d,p,q,d\]
\[\delta_d = 120.1; \; q,d\]

\[J_{a-x} = 312.5\]
\[J_{a-y} = 43.6\]
\[J_{a-b} = 31.5\]
\[J_{b-x} = 29.5\]
\[J_{b-y} = 268.9\]
\[J_{b-z} = 29.5\]
\[J_{c-x} = 258.2\]
\[J_{d-x} = 289.0\]
\[J_{d-z} = 25.5\]
$^{19}$F NMR

75.4 MHz

\[
\begin{align*}
\text{(a)} & \quad \text{(b)} \\
\text{F-SF}_4 & \quad \text{C=C} \\
\text{(x)} & \quad \text{F-C-} \text{CF}_3 \quad \text{(m)} \\
\text{(z)} & \quad \text{SF}_4 \quad \text{(d)} \\
\text{(c)} & \\
\end{align*}
\]

\[\delta_a = 66.08 \text{ ppm; d,d of 9-line pattern}\]

\[\delta_b = 56.27; \text{ d,d of 6-line pattern}\]

\[\delta_c = 65.13; \text{ m}\]

\[\delta_d = 51.1; \text{ m}\]

\[\delta_m = -73.45; \text{ d,p,d,d,d}\]

\[\delta_x = -127.9; \text{ d,d,m}\]

\[\delta_y = -147.0; \text{ d,m}\]

\[\delta_z = -148.0; \text{ d,m}\]

\[J_{a-b} = 150.0 \text{ Hz}\]

\[J_{b-y} = 23.5\]

\[J_{b-x} = < 1\]

\[J_{c-d} = 143\]

\[J_{d-m} = 10.85\]

\[J_{m-x} = 1.7\]

\[J_{m-y} = 16.5\]

\[J_{m-c} = 0.8\]

\[J_{m-z} = 6.4\]

\[J_{x-y} = 131.5\]

\[J_{x-z} = 65.2\]
Mass spectrum

M/e, ion, relative intensity: 63.0, CSF, 3.99; 69.0, CF₃, 44.57; 70.0, SF, 6.36; 74, C₂F₂, 3.03; 89.0, SF₃, 62.1; 93.0, C₃F₃, 34.29; 100.0, C₂F₄, 6.65; 112.0, C₃F₄, 5.32; 113, C₂SF₂, 4.35; 119.0, C₃F₅, 14.14; 127.0, SF₅, 31.95; 131.0, C₃F₅, 100.00; 132, C₂SF₄, 3.70; 143.0, C₄F₅, 4.62; 150.0, C₂F₆, 15.00; 162.0, C₄F₆, 10.89; 181, C₄F₇, 72.00; 251, C₄SF₅, 3.10; 289, M-SF₅, 9.82; 397, M-F, 2.06.
REFERENCES CITED


2. S. Gabriel, Ber., 21, 2664 (1888).


63. (a) data from this work; (b) data from A. Lork, Master’s Thesis, Universität Bremen, 1991.
APPENDIX A

MASPEC: A COMPUTER PROGRAM
This program has been found useful in analysis of mass spectra. MASPEC reports the possible combinations of atoms for which the sum of molecular weights is within a small range of target values specified by the user. Many target values may be entered, so that all the peaks of mass spectrum may have combinations assigned to them.

MASPEC calculates all possible molecular weights and discards those which are not within the specified range of the target values. This procedure, while inefficient, does not result in excessive computation time (typical runs take less than ten seconds). Although many improbable "fragments" are sometimes reported by this program, it has the advantage of reporting rearranged fragments. (Commercial programs are available which operate on fragmentation principles, but have no capacity for rearrangements, a significant practical disadvantage).

MASPEC recognizes ten of the most common elements by their symbol and automatically assigns the correct atomic weight. The program prompts the user to supply the atomic weight of symbols it does not recognize. This program treats the isotopes of bromine and chlorine separately, and reports all combinations of isotopes if more than one is present.

The computer code for the program, written in C
language mostly in the Spring of 1991, is included here,
followed by sample output.

/*MASPEC: mass spectrum analysis program, revised 6/23/92*/
#include <stdio.h>
#include <stdlib.h>
#include <ctype.h>
float *vector(int nl,int nh);
int **imatrix(int nrl,int nrh,int ncl,int nch);
int *ivector(int nl,int nh);
void free_vector(float *v,int nl,int nh);
void free_imatrix(int **m,int nrl,int nrh,int ncl,int nch);
void free_ivector(int *v,int nl,int nh);
void nrerror(char error_text[]);
void sort2(int n,float *ra,float *rb);
void formentry();
void weights();
void specify();
void compute();
void quitquery();
int **symbol,**forml,stag,natag,targtag,*na,isotag;
char form[50],targstring[80];
float *mw,*targets,*mass,*list,qq;

main()
MASPEC: mass spectrum analysis program revised 6/23/92

This program reports the possible combinations of

atoms for which the sum of molecular weights is within

a small range of target values specified by user. Many

target values may be entered, so that all the peaks of

mass spectrum may have combinations assigned to them.

formentry();

void formentry

/* formula entry routine */

{
    char temp[5];
    int i;
    symbol=imatrix(1,20,1,3);
    na=ivector(1,20);
    qq=sin(l);
    natag=stag=1;

    /* formula entered into array 'form', program is not
case-sensitive */
printf("\n\nEnter formula: ");
scanf("%[0-9a-zA-Z]",form);

/* symbols entered into array 'symbols', two-letter symbols are accounted for */
for(i=0;i<20;i++) {
    if(form[i]==\0) break;
    if (isdigit(form[i])==0) {
        symbol[stag][1]=toupper(form[i]);
        if(isdigit(form[i+1])==0) {
            symbol[stag][2]=tolower(form[i+1]);
            i+=1;
        }
        else symbol[stag][2]=\0;
    }
    else symbol[stag][2]=\0;
    symbol[stag][3]=\0;
    stag+=1;
}
/* digits are entered into array 'temp' */
if(isdigit(form[i])!=0) {
    temp[0]=form[i];
    if(isdigit(form[i+1])!=0) {
        temp[1]=form[i+1];
        temp[2]=\0;
        i+=1;
    }
}
else temp[1] = '0';
/* sequence of digits in 'temp' entered as number in 'na' */
n[na] = atoi(temp);
natag += 1;
}
}
/* error message if number of symbols and number of numbers is not the same */
if (natag != stag) {
    printf("---error in formula entry---");
    exit(0);
}

natag -= 1;
weights();
}

void weights()
/* routine assigns molecular weights to atoms */
{
    char reply[3], jk[3];
    int i, j, k;
    mw = vector(1, 20);
    isotag = 0;
    /* common symbols are recognized */
    for (i = 1; i < natag + 1; i++) {

if(symbol[i][1]=='H'&&symbol[i][2]==' ') mw[i]=1.00783;
else if(symbol[i][1]=='C'&&symbol[i][2]==',')
    mw[i]=12.0000;
else if(symbol[i][1]=='N'&&symbol[i][2]==',')
    mw[i]=14.0031;
else if(symbol[i][1]=='O'&&symbol[i][2]==',')
    mw[i]=15.9949;
else if(symbol[i][1]=='F'&&symbol[i][2]==',')
    mw[i]=18.9984;
else if(symbol[i][1]=='S'&&symbol[i][2]=='i')
    mw[i]=27.9769;
else if(symbol[i][1]=='P'&&symbol[i][2]==',')
    mw[i]=30.9738;
else if(symbol[i][1]=='S'&&symbol[i][2]==',')
    mw[i]=31.9721;
/* two isotopes of Cl and Br are treated separately */
else if(symbol[i][1]=='C'&&symbol[i][2]=='l') {
    mw[i]=34.9689;
    isotag+=na[i];
    for(j=0;j<natag-i;j++) {
        mw[natag+1-j]=mw[natag-j];
        na[natag+1-j]=na[natag-j];
        symbol[natag+1-j][1]=symbol[natag-j][1];
        symbol[natag+1-j][2]=symbol[natag-j][2];
        symbol[natag+1-j][3]=symbol[natag-j][3];
    }
}
na[i+1]=na[i];
mw[i+1]=36.9659;
symbol[i+1][1]='C';
symbol[i+1][2]='l';
symbol[i+1][3]='*';
i+=1;
natag+=1;
}

} else if(symbol[i][1]=='B'&&symbol[i][2]=='r') {
    isotag+=na[i];
mw[i]=78.9183;
for(j=0;j<natag-i;j++) {
    mw[natag+1-j]=mw[natag-j];
    na[natag+1-j]=na[natag-j];
symbol[natag+1-j][1]=symbol[natag-j][1];
symbol[natag+1-j][2]=symbol[natag-j][2];
symbol[natag+1-j][3]=symbol[natag-j][3];
}
na[i+1]=na[i];
mw[i+1]=80.9163;
symbol[i+1][1]='B';
symbol[i+1][2]='r';
symbol[i+1][3]='*';
i+=1;
natag+=1;
}
else if(symbol[i][1]=='I'&&symbol[i][2]==' ')
    mw[i]=126.9045;
/* symbols not recognized may have atomic weights
assigned to them */
else {
    printf("\nProgram does not recognize
" "%c%c".",&symbol[i][1],symbol[i][2]);
    printf("\nChoose: (1) define %c%c as an
    element", symbol[i][1],symbol[i][2]);
    printf("\n    (2) start over");
    printf("\n    (3) quit");
    printf("\n    (press 1, 2, or 3) ");
    scanf("%ls",reply);
    if(reply[0]=='1') {
        printf("\nEnter mw of %c%c ",&symbol[i][1],
                symbol[i][2]);

        gets(jk);
        scanf("%f",&mw[i]);
    }
    else if(reply[0]=='2') {
        gets(jk);
        formentry();
        exit(0);
    }
    else exit(0);
```c
void specify()
/* routine to enter target weights */
{
    int i, j, k;
    char jk[2], temp2[5];
    targets=vector(1, 20);
    gets(jk);
    /* string of digits and commas entered into 'targstring' then as numbers in array 'targets' */
    printf("Enter target weights: ");
    scanf("%[ 0-9,.]", targstring);
    for(i=0, k=0, targtag=1; i<81; i++) {
        if(targstring[i]==',' || targstring[i]=='\0') {
            for(j=0; j<i-k; j++)
                temp2[j]=targstring[k+j];
            temp2[j]="\0";
            k=i+1;
            targets[targtag]=atof(temp2);
            targtag+=1;
        }
    }
    if(targstring[i]=='\0') break;
```
void compute()
{
    /* routine computes all fragment MW's, stores those close to a target weight */
    int i,j,k,f,go,*tally,isototal;
    float tempmass;
    char reply[3];
    tally=ivector(l,20);
    mass=vector(l,1000);
    list=vector(l,1000);
    for (i=l;i<l000;i++) list[i]=i;
    forml=imatrix(l,1000,1,20);
    for(i=1;i<natag+1;i++) tally[i]=0;
    f=go=1;
    while(go==1) {
        tempmass=0;
        /* loop which computes fragment weights */
        for(i=1;i<natag+1;i++) {
            tempmass+=tally[i]*mw[i];
            if(symbol[i][3]=='*')
                isototal=tally[i]+tally[i-1];
for(i=1;i<targtag;i++) {
    if(tempmass>targets[i]-0.5 &&
       tempmass<targets[i]+0.5 &&
       isototal<isotag+l) {
        mass[f]=tempmass;
        for(j=1;j<natag+1;j++)
            forml[f][j]=tally[j];
        f+=1;
    }
}
go=0;
/* loop which decides when to stop for each atom */
for(j=0;j<natag;j++) {
    if(tally[natag-j]<na[natag-j]) {
        tally[natag-j]+=1;
        for(k=natag-j+1;k<natag+1;k++)
            tally[k]=0;
        go=1;
        break;
    }
}
/* calls sort routine which sorts fragments by MW */
if(f>4) sort2(f-1,mass,list);
/* loop to print data to screen */

k=0;
for(i=1;i<f;i++) {
    if(k==0) {
        printf("\n\n          ");
        for(j=1;j<natag+1;j++)
            printf("%c%c%c ",
                symbol[j][1],symbol[j][2],symbol[j][3]);
        printf("\n          ");
        for(j=1;j<natag+1;j++)
            printf(" --- ");
    }
    printf("\n%6.3f ",mass[i]);
    for(j=1;j<natag+1;j++)
        printf(" %2d ",form1[list[i]][j]);
    k+=1;
    if(k==20) {
        printf("\n        ----press any key for more
         data---");
        getch();
        k=0;
    }
}

/* prints data to hardcopy, if desired */

printf("\n\nDo you want to print data? (y/n) ");
scanf("%ls",reply);
if(reply[0]=='y'|reply[0]=='Y') {
    fprintf(stdprn, "\n\nformula entered:
    %s\n", form);
    fprintf(stdprn, "\ntarget weights:
    %s\n", targstring);
    k=0;
    for(i=1;i<f;i++) {
        if(k==0) {
            fprintf(stdprn, "\n\n        for(j=1;j<natag+1;j++)
                fprintf(stdprn, "%c%c%c ",
                    symbol[j][1],symbol[j][2],symbol[j][3]);
            fprintf(stdprn, "\n\n        for(j=1;j<natag+1;j++)
                fprintf(stdprn," --- ");
        }
        fprintf(stdprn, "\n%6.3f ",mass[i]);
        for(j=1;j<natag+1;j++)
                fprintf(stdprn, "%2d ",forml[list[i]][j]);
        k+=1;
        if(k==20)  k=0;
    }
    fprintf(stdprn, "\n\r");
}
free_vector(mw,1,20);
free_vector(targets,1,20);
free_vector(mass,1,1000);
free_vector(list,1,1000);
free_ivector(tally,1,20);
free_imatrix(symbol,1,20,1,3);
free_imatrix(form1,1,1000,1,20);
free_ivector(na,1,20);
quitquery();
}

void quitquery()
/* gives option of continuing or quitting */
{
    char reply[3],jk[3];
    gets(jk);
    printf("\n\nPress "c" to continue, "q" to quit: ");
    scanf("%ls",reply);
    if(reply[0]=='c'||reply[0]=='C') {
        gets(jk);
        formentry();
    }
}

/* the following routines were taken from W. H. Press, B. P.
Flannery, S. A. Teukolsky and W. T. Vetterling,
Numerical Recipes in C: The Art of Scientific
Computing, Cambridge, Cambridge University Press
(1988). */
float *vector(nl,nh)
int nl,nh;
{
    float *v;
    v=(float *)malloc((unsigned) (nh-nl+1)*sizeof(float));
    return v-nl;
}
void free_vector(v,nl,nh)
float *v;
int nl,nh;
{
    free((char*) (v+nl));
}
int *ivector(nl,nh)
int nl,nh;
{
    int *v;
    v=(int *)malloc((unsigned) (nh-nl+1)*sizeof(int));
    return v-nl;
}
void free_ivector(v,nl,nh)
int *v,nl,nh;
{
    free((char*) (v+nl));
}
int **imatrix(nrl,nrh,ncl,nch)
```c
int nrl, nrh, ncl, nch;
{
    int i, **m;
    m = (int **) malloc((unsigned) (nrh-nrl+1) * sizeof(int*));
    m -= nrl;
    for (i = nrl; i <= nrh; i++) {
        m[i] = (int *) malloc((unsigned) (nch-ncl+1) * sizeof(int));
        m[i] -= ncl;
    }
    return m;
}

void free_imatrix(m, nrl, nrh, ncl, nch)
{
    int **m;
    int nrl, nrh, ncl, nch;
    {
        int i;
        for (i = nrh; i >= nrl; i--) free((char*) (m[i] + ncl));
        free((char*) (m + nrl));
    }
}

void nrerror(error_text)
char error_text[];
{
    void exit();
    fprintf(stderr, "\n", error_text);
}
exit(1);
}
void sort2(n,ra,rb)
int n;
float ra[],rb[];
{
    int l,j,ir,i;
    float rrb,rra;
    l=(n >> 1)+1;
    ir=n;
    for(;;) {
        if (l > 1) {
            rra=ra[--l];
            rrb=rb[l];
        } else {
            rra=ra[ir];
            rrb=rb[ir];
            ra[ir]=ra[l];
            rb[ir]=rb[l];
            if (--ir == 1) {
                ra[l]=rra;
                rb[l]=rrb;
                return;
            }
        }
    }
    i=1;
j = l << 1;
while (j <= ir) {
    if (j < ir && ra[j] < ra[j+1]) ++j;
    if (rra < ra[j]) {
        ra[i] = ra[j];
        rb[i] = rb[j];
        j += (i = j);
    }
    else j = ir+1;
}
ra[i] = rra;
rb[i] = rrb;
APPENDIX B

SPECTRA
Infrared Spectrum of $\text{CF}_3\text{CFCF}_2\text{NSCl}$
Infrared Spectrum of SF₃CFCF₂NSCl
Infrared Spectrum of C$_4$F$_9$OCFCF$_2$NSCl
Infrared Spectrum of CF₅CF(CF₂)₂NCl
Infrared Spectrum of \(\text{CF}_3\text{CFCF}_2\text{NS}^-\)\(_2\)
Infrared Spectrum of product of CF<sub>3</sub>CF<sub>3</sub>NCS + H<sub>2</sub>O
Fluorine NMR of (SF$_2$CF=CF$_2$)$_2$
Fluorine NMR of \((SF_2\text{CF}=\text{CF}_2)_2\) (detail)
Fluorine NMR of \( \text{SF}_3\text{CF} = \text{CF}_2 \)_2 (detail)
Fluorine NMR of \((\text{SF}_2\text{CF=CF}_2)_2\) (detail)
Fluorine NMR of \((\text{SF}_3\text{CF}=\text{CF}_2)_2\) (detail)
Carbon-13 NMR of (sp^3-CP=CP)^2

100

ppm

78.2
77.9
77.6
1.1
0.0
Carbon-13 NMR of (SF₃CF=CF₂), (detail)
Carbon-13 NMR of (SF₂CF=CF₂)₂ (detail)