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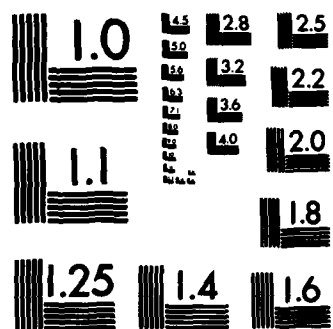
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SYNTHETIC AND MECHANISTIC STUDIES IN
FLUORINE CHEMISTRY. NEW DEVELOPMENTS IN
ORGANONITROGEN FLUORINE CHEMISTRY

Final Technical Report

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A series of 1,1-difluoro-2-aza-perhalo-1-butenes, $\text{CF}_2=\text{NCF}_2\text{CFXCl}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$), were prepared by addition of $\text{CF}_2=\text{NCl}$ to the olefins $\text{CF}_2=\text{CFX}$. These azabutenes were converted in high yield to the novel oxaziridines $\text{CF}_2\text{N}(\text{CF}_2)\text{CFXCF}_2$ with CF_3OOH . The chemistry of these oxaziridines resembles closely that previously found for $\text{CF}_3\text{N}(\text{CF}_2)_2$ and allows the synthesis of a variety of new fluorinated compounds.		

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20. ABSTRACT CONTINUED

The reactive perfluoromethanimine, $\text{CF}_2=\text{NF}$, previously polymerized by strong acids, was shown to also be polymerizable with the base $(\text{CH}_3)_3\text{N}$. Evidence clearly indicates a homopolymer $[\text{CF}_2-\text{N}]_n$.

Fluoride promoted reactions of halogenated nitriles of the type R^xCN ($\text{R}^x = \text{CF}_3, \text{C}_2\text{F}_5, \text{C}_3\text{F}_7, \text{CCl}_3$) leads readily to $\text{R}^x\text{CF}_2\text{NCl}_2$ and $\text{R}^x\text{CF}=\text{NBr}$ on oxidation of intermediate anions with the respective halogens. The reactivity of the nitrogen bromine bond of the N-bromoimines can be exploited to prepare a variety of new halogenated azalkenes by addition to both halogenated on non-halogenated olefins. Photolysis of the N-bromoimines gives the respective azines, $\text{R}^x\text{CF}=\text{N}=\text{N}=\text{CFR}^x$, in good yield. All of these compounds show considerable promise for new chemistry.

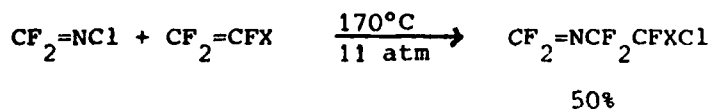


PROBLEMS STUDIED

→ Synthesis and properties of novel organonitrogen fluorine compounds were investigated with emphasis on the synthesis of new perhalogenated oxaziridines, reactions of $\text{CF}_2=\text{NF}$ and $\text{SF}_4=\text{NF}$, and fluoride promoted reactions of imines and nitriles. ←

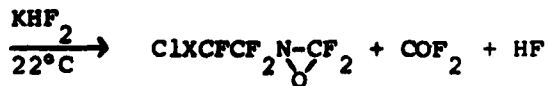
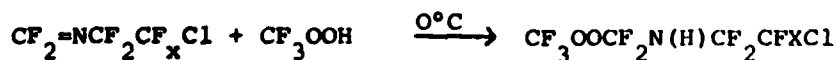
SUMMARY OF IMPORTANT RESULTS

New Oxaziridines. Because of the fascinating chemistry of $\text{CF}_3\text{N}(\text{CF}_2)_2$,¹⁻⁶ it is of importance to prepare other homologs of this class of materials in order to evaluate the potential of this class of compounds in general. For this purpose it was necessary to find a synthesis of imines of the type $\text{CF}_2=\text{NR}_x$. This was accomplished by a reaction of $\text{CF}_2=\text{NCl}$ with $\text{CF}_2=\text{CFX}$ ($X = \text{F}, \text{Cl}, \text{Br}$), which under the right conditions forms the respective imines.⁷



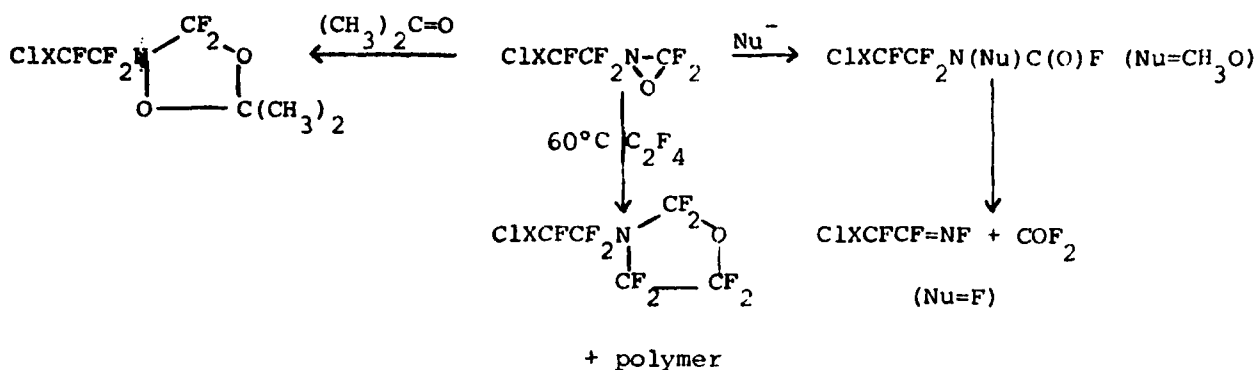
This reaction also leads to significant formation of $\text{CF}_2=\text{N}(\text{CF}_2\text{CFX})_n\text{Cl}$ polymers, varying in properties from viscous liquids to gels and solids. These polymers may be of interest because they still contain the reactive $\text{CF}_2=\text{N}$ group.

With the new imines thus formed, the epoxidation was readily accomplished by oxidation with CF_3OOH , as previously used to prepare $\text{CF}_3\text{N}(\text{CF}_2)_2$.¹



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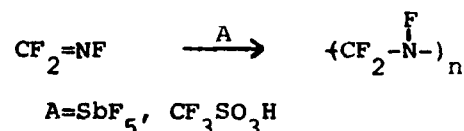
These new oxaziridines are thermally stable at 22°C and show nearly the same remarkable reactivity as $\text{CF}_3\text{N}-\text{CF}_2$.⁸



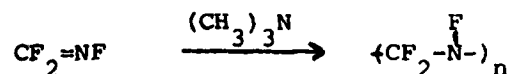
These series of new materials are extremely interesting and reaffirm the industrial potential of perhalogenated oxaziridines.

Polymerization of $\text{CF}_2=\text{NF}$

We have previously discussed the novel acid catalyzed polymerization of the perfluoromethanimine.⁹



This represents the only known polymerization of an N-fluoroimine and this polymer has sparked interest wherever it is discussed. In continuing work on this material, we have investigated the polymerization of the imine by the base, $(\text{CH}_3)_3\text{N}$. Again, the material is readily polymerized

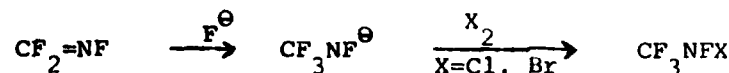


As yet, we have only limited characterization of the viscous liquid to solid polymers. However ¹⁹F-NMR suggests the presence of the polymer (2 broad signals, area 1:2) and mass spectra show fragments of $(\text{CF}_2-\text{NF})_n^+$ with n=1-3 and, depending on the ratio of $(\text{CH}_3)_3\text{N}$ to $\text{CF}_2=\text{NF}$, $(\text{CF}_2\text{NF})_n\text{NMe}_3^+$ are readily seen.

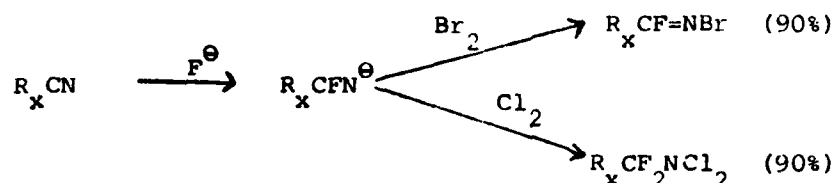
Future plans call for a more detailed characterization of these polymers.

Fluoride Promoted Reactions of Imines & Nitriles

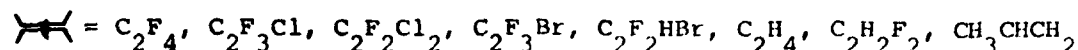
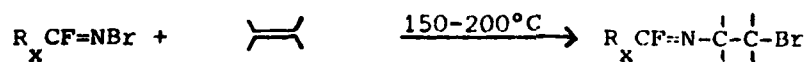
Earlier we had determined the facile oxidation by Cl_2 and Br_2 of fluorinated nitrogen anions generated from imines such as $\text{CF}_2=\text{NF}$, by reaction with KF or CsF .¹⁰



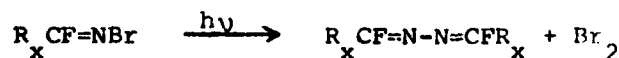
Extension of this work to nitriles has now been highly successful.



The N-bromoisimines are particularly useful materials for a variety of useful reactions. They readily add to a variety of halogenated and non-halogenated olefins in high yield.



They are also readily photolyzed to the azines in excellent yield.



Again, it is clear that these materials provide entry into new areas of organo-nitrogen fluorine chemistry with obvious potential for useful new materials ranging from novel monomers to unusual heterocycles.

Conclusion. This research represents a variety of new developments in organo-nitrogen fluorine chemistry. However we have not closed the door on any particular aspect of this work. On the contrary, we have opened a floodgate to a wealth of new and interesting chemistry.

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