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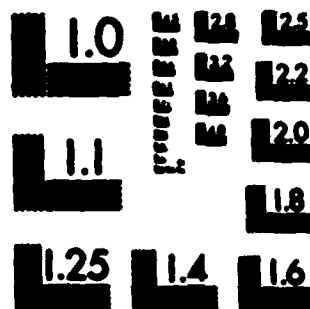
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SYNTHETIC AND MECHANISTIC STUDIES IN
FLUORINE CHEMISTRY. NEW DEVELOPMENTS IN
ORGANONITROGEN FLUORINE CHEMISTRY

Final Technical Report

Darryl D. DesMarteau

November 30, 1982

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The reaction chemistry of the novel oxaziridine 2-trifluoromethyl-3,3-difluorooxaziridine, $\text{CF}_3\text{NCF}_2\text{O}$, (acronym PFAPO-pentafluoroazapropene oxide) is described. PFAPO shows many similarities to HFPO-hexafluoropropene oxide, $\text{CF}_3\text{CF}_2\text{O}$, a commercially important monomer for polymer synthesis. PFAPO undergoes ring opening by many nucleophiles leading to polymers or compounds of the type $\text{CF}_2\text{N}(\text{Nu})\text{C}(\text{O})\text{F}$. The latter can be converted to amines $\text{CF}_2\text{N}(\text{Nu})\text{H}$ by reaction with $\text{H}_2\text{O}/\text{NaF}$ and to imines $\text{CF}_2=\text{NNu}$ by reaction with KF . PFAPO also exhibits chemistry unique from that of HFPO in that it undergoes novel cycloadditions with olefins and		

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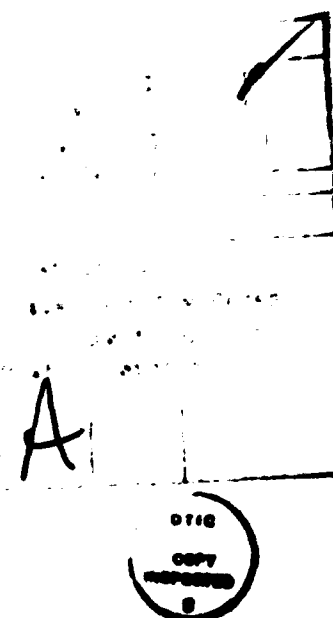
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2. ABSTRACT CONTINUED

ketones, with itself in the presence of SbF_5 and possibly with nitriles. These reactions are very unusual from a mechanistic standpoint and provide novel heterocycles and polymers with potentially useful properties.

New chemistry of perfluoroimines is exemplified by perfluoromethanimine, $\text{CF}_2=\text{NF}$. A novel chlorofluorination of ClCN , followed by dechlorination with Hg^2 in TFAA provides an excellent high-yield synthesis. This imine exhibits a rich chemistry in the presence of fluoride ion, which generates the perfluoromethanimine ion $\text{CF}_2=\text{NF}^-$. The latter is an excellent nucleophile for many reactions leading to novel examples of organonitrogen fluorine compounds. Perfluoromethanimines can also be cationically polymerized to form a unique N-F polymer $(\text{CF}_2\text{NF})_n$. Oxidation of $\text{CF}_2=\text{NF}^-$ by halogens provides the first examples of N-bromo-N-fluoroalkanimines. Cyclization of the dimer of $\text{CF}_2=\text{NF}$ by CsF leads to a novel diaziridine, $\text{CF}_2\text{NCF}_2\text{NF}$, which undergoes a unique² rearrangement to $\text{CF}_2\text{N}=\text{NCF}_2$ in the presence of Fe, Cr and Ni. Considerable chemistry observed for $\text{CF}_2=\text{NF}$ can be extended to other imines and some nitriles.

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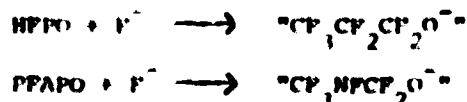


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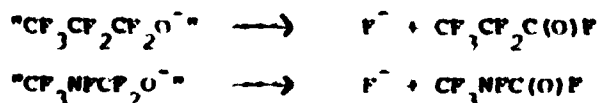
The synthesis and properties of novel organonitrogen fluorine compounds were investigated with emphasis on the chemistry of perfluorinated oxaziridines, imines and amines.

SUMMARY OF IMPORTANT RESULTS

Oxaziridines. The novel oxaziridine, 2-trifluoromethyl-3,3-difluorooxaziridine, $\text{CF}_3\text{NCF}_2\text{O}$, was extensively investigated and a remarkable reaction chemistry has been found for the compound. The compound is designated by the acronym PFAPO (pentafluorooxazepropene oxide) and it shows many similarities to the commercially important hexafluoropropene oxide, $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}$, (HFPPO). HFPPO is used for the preparation of polymers involving the ring opening of the epoxide by fluoride ion or other bases. Thus HFPPO forms the intermediate $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}^-$ anion on attack by fluoride ion. Similar behavior is found for PFAPO.

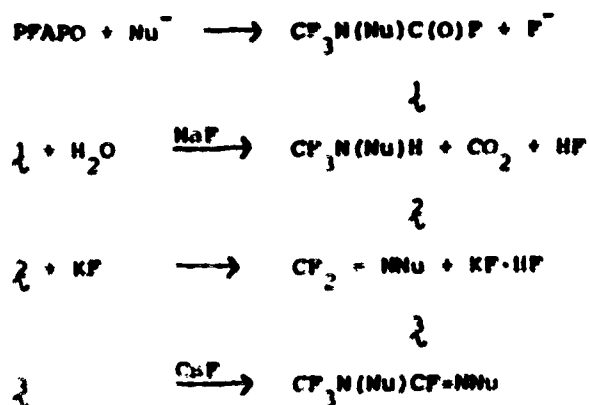


The anion so generated may then react with appropriate substrates or with the epoxide, or under suitable conditions, loss of fluoride occurs leading to isomerization.



In the case of HFPPO, the industrial applications are based on the attack of the anion on HFPPO leading to homopolymerization or on unsaturated fluorocompounds leading to copolymers. The homo and copolymerization of PFAPO in the same way is clearly feasible and homopolymers have been observed in reaction with CaF_2 , but these have not yet been characterized.

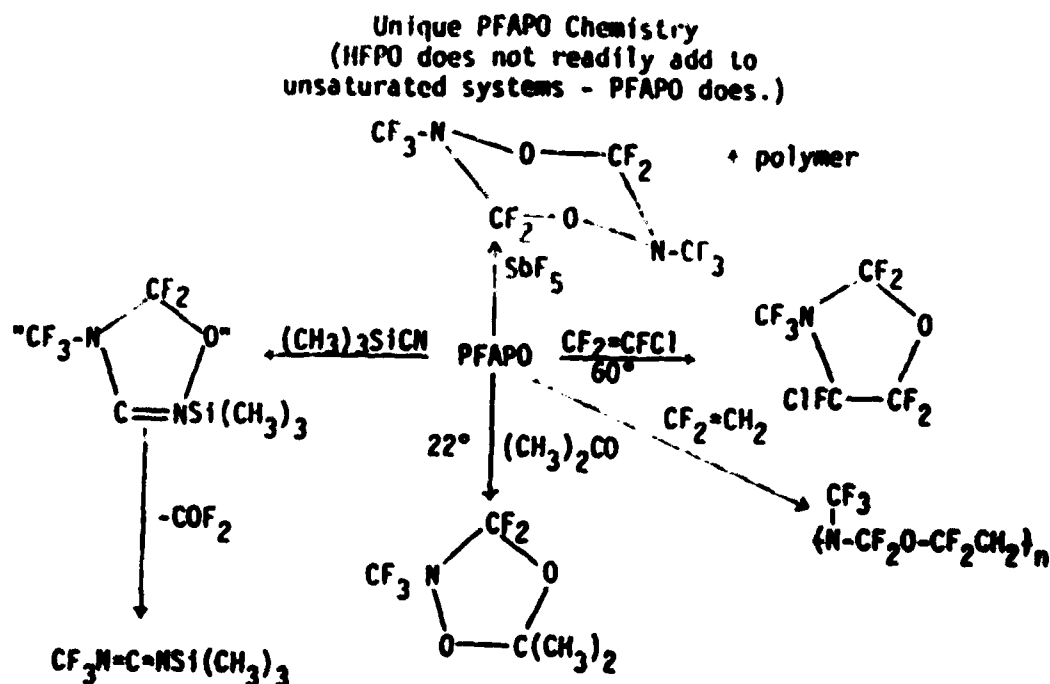
Many nucleophiles attack PFAPO and a series of interesting transformations have been demonstrated.



Nu is an alkoxy or perfluoroalkoxy group and the dimerization of $\downarrow$ occurs only with the latter. The same series of transformation may also be carried out when Nu=F.

PFAPO has been shown to undergo many unique reactions, not observed for HFPO. These reactions are remarkable both from the standpoint of their mechanisms and their preparative value. Some of these reactions are summarized in Scheme 1.

SCHEME 1



A variety of olefins undergo cycloadditions and many polar unsaturates besides ketones and nitriles will undoubtedly react, but have not yet been investigated. Of particular note are the polymers indicated and the perhalogenated 1,3-oxazolidines. The latter are chemically and thermally very inert and the perfluorocompound formed with tetrafluoroethylene is stable to 550°C and is untouched by hot concentrated sulfuric acid or aqueous permanganate. The polymer noted with $\text{CF}_2=\text{CH}_2$ is not yet well characterized but the similarity to fluorinated nitroso rubbers and other elastomers such as Viton is clear. Under appropriate conditions, it seems clear that PFAPU can be made to polymerize with a variety of olefins.

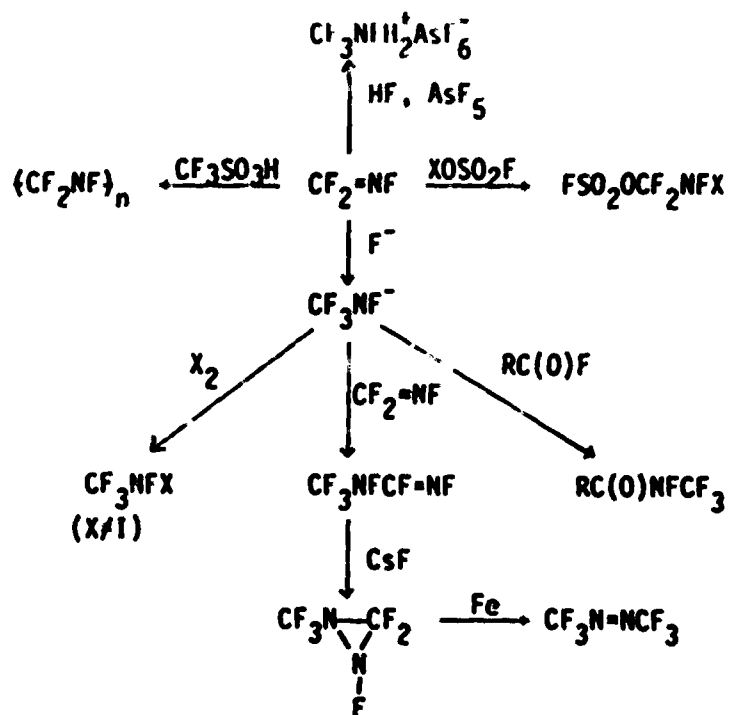
~~PERFLUOROMETHANIMINE~~. Another extensively investigated compound is perfluoromethanimine, $\text{CF}_2=\text{NPF}$. The development of a high yield synthesis of this material was a major breakthrough. Starting from readily available ClCN , $\text{CF}_2=\text{NPF}$ can be prepared in over 90% yield.



The chemistry of $\text{CF}_2=\text{NPF}$ leads readily to many new compounds including the first examples of polymeric N-P compounds and perfluoroalkylammonium salts. Some of the remarkable chemistry of $\text{CF}_2=\text{NPF}$ is summarized in Scheme 2. Much of this work is truly unique and extension to other imines and nitriles is clearly possible based on preliminary work.

SCHEME 2

Some Chemistry of $\text{CF}_2=\text{NF}$



Summary. Details of some of the above work as well as other research are contained in the publication list in the following section. In continuing work in this area, seven additional publications are in various states of preparation, relating to the chemistry of SF_4-NF , CF_2-NCl , other perhalogenated oxaziridines and fluoride catalyzed and fluoride promoted reactions of fluorocarbon nitriles and imines.

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12. A. Sekiya and D. D. DesMarteau, "The Addition of Fluorine to Perhalogenated Compounds Containing Carbon-Nitrogen Double Bonds," *J. Fluorine Chem.*, **17**, 463 (1981).
13. W. Y. Lam and D. D. DesMarteau, "Novel 1,1-Difluoro-2-Akloxymethanimines," *J. Fluorine Chem.*, **18**, 441 (1981).
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15. S.-C. Chang and D. D. DesMarteau, "Perfluoromethanimine Ion," Polyhedron, 1, 129 (1982).
16. W. I. Lam and D. D. DesMarteau, "Unusual Cycloadditions of 3-Trifluoromethyl-2,2-difluorooxaziridine, J. Am. Chem. Soc., 104, 4034 (1982).

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17. D. Christen, H. Oberhammer, R. M. Hammaker, S. C. Chang and D. D. DesMarteau, "The Structure of Perfluoromethanimine by Microwave, Infrared and Raman Spectroscopy, Electron Diffraction and Ab Initio Methods," J. Am. Chem. Soc.
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