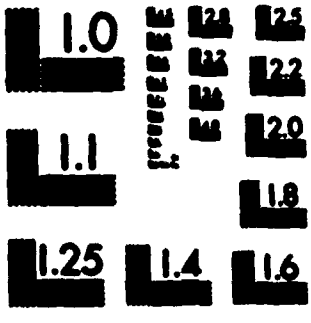
AD-A122 663 SYNTHETIC AND MECHANISTIC STUDIES IN FLUORINE CHEMISTRY 1/1
NEW DEVELOPMENTS I..(U) KANSAS STATE UNIV MANHATTAN
DEPT OF CHEMISTRY D D DESMARTEAU 30 NOV 82
UNCLASSIFIED ARO-14339.11-CH DAAG29-80-C-0102 F/G 7/3 NL

END
DATE FILMED
P 83
DTIC



SYNTHETIC AND MECHANISTIC STUDIES IN FLUORINE CHEMISTRY. NEW DEVELOPMENTS IN OXYGEN-NITROGEN FLUORINE CHEMISTRY

Final Technical Report

Darryl D. DesMarteau

November 30, 1982

U.S. Army Research Office

Grant Number DAAG29-77-G-0071

Contract Number DAAG29-80-C-0102

Kansas State University

Manhattan, Kansas 66506

Approved for Public Release;

Distribution Unlimited

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: One	2. GOVT ACCESSION NO: AD-A	3. RECIPIENT'S CATALOG NUMBER:
4. TITLE (and Subtitle): SYNTHETIC AND MECHANISTIC STUDIES IN FLUORINE CHEMISTRY. NEW DEVELOPMENTS IN ORGANONITROGEN FLUORINE CHEMISTRY	5. TYPE OF REPORT & PERIOD COVERED: Final Technical Report 1/15/77-7/31/82
	6. PERFORMING ORG. REPORT NUMBER:
7. AUTHOR(s): Darryl D. DesMarteau	8. CONTRACT OR GRANT NUMBER(s): DAAG29-77-G-0071 DAAG29-80-C-0102
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Kansas State University, Department of Chemistry, Manhattan, Kansas 66506	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:
11. CONTROLLING OFFICE NAME AND ADDRESS: U. S. Army Research Office, Post Office Box 12211, Research Triangle Park, NC 27709	12. REPORT DATE: November 30, 1982
	13. NUMBER OF PAGES:
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Synthesis of perfluoroorganonitrogen compounds, perfluorooxaziridines, perfluoroimines, reactions of perfluorooxaziridines with nucleophiles, cycloaddition reactions of perfluorooxaziridines, homo and copolymers of perfluorooxaziridines, reactions of perfluoroimines, polymerization of perfluoroimines, fluoride catalyzed reactions of perfluoroimines, fluoride promoted reactions of perfluoroimines.

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, CF_3NCF_2O, (acronym PFAPO-pentafluoroazapropene oxide) is described, PFAPO shows many similarities to HFPO-hexafluoropropene oxide, CF_3CFCF_2O, a commercially important monomer for polymer synthesis. PFAPO undergoes ring opening by many nucleophiles leading to polymers or compounds of the type $CF_3N(Nu)C(O)F$. The latter can be converted to amines $CF_3N(Nu)H$ by reaction with H_2O/NaF and to imines $CF_2{=}NNu$ by reaction with KF. PFAPO also exhibits chemistry unique from that of HFPO in that it undergoes novel cycloadditions with olefins and —>

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. 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, $CF_2=NF$. A novel chlorofluorination of ClCN, followed by dechorination 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 perfluoromethonamine ion CF_3NF^-. The latter is an excellent nucleophile for many reactions leading to novel examples of organonitrogen fluorine compounds. Perfluoromethanimes can also be cationically polymerized to form a unique N-F polymer $(CF_2NF)_n$. Oxidation of CF_3NF^- by halogens provides the first examples of N-bromo-N-fluoroalkanamines. Cyclization of the dimer of $CF_2=NF$ by CsF leads to a novel diaziridine, CF_3NCF_2NF, which undergoes a unique rearrangement to $CF_3N=NCF_3$ in the presence of Fe, Cr and Ni. Considerable chemistry observed for $CF_2=NF$ can be extended to other imines and some nitriles.

PROBLEM STUDIED

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, CF_3NCF_2O, was extensively investigated and a remarkable reaction chemistry has been found for the compound. The compound is designated by the acronym PFAPO (pentafluoroazapropene oxide) and it shows many similarities to the commercially important hexafluoropropene oxide, CF_3CFCF_2O, (HFPO). HFPO is used for the preparation of polymers involving the ring opening of the epoxide by fluoride ion or other bases. Thus HFPO forms the intermediate $CF_3CF_2CF_2O^-$ anion on attack by fluoride ion. Similar behavior is found for PFAPO.

$$HFPO + F^- \longrightarrow "CF_3CF_2CF_2O^-"$$

$$PFAPO + F^- \longrightarrow "CF_3NFCF_2O^-"$$

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.

$$"CF_3CF_2CF_2O^-" \longrightarrow F^- + CF_3CF_2C(O)F$$

$$"CF_3NFCF_2O^-" \longrightarrow F^- + CF_3NFC(O)F$$

In the case of HFPO, the industrial applications are based on the attack of the anion on HFPO 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 CsF, but these have not yet been characterized.

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

$$\text{PFAPO} + Nu^- \longrightarrow CF_3N(Nu)C(O)F + F^-$$

$$\downarrow$$

$$\downarrow + H_2O \xrightarrow{NaF} CF_3N(Nu)H + CO_2 + HF$$

$$\downarrow$$

$$\downarrow + KF \longrightarrow CF_2 = NNu + KF\cdot HF$$

$$\downarrow$$

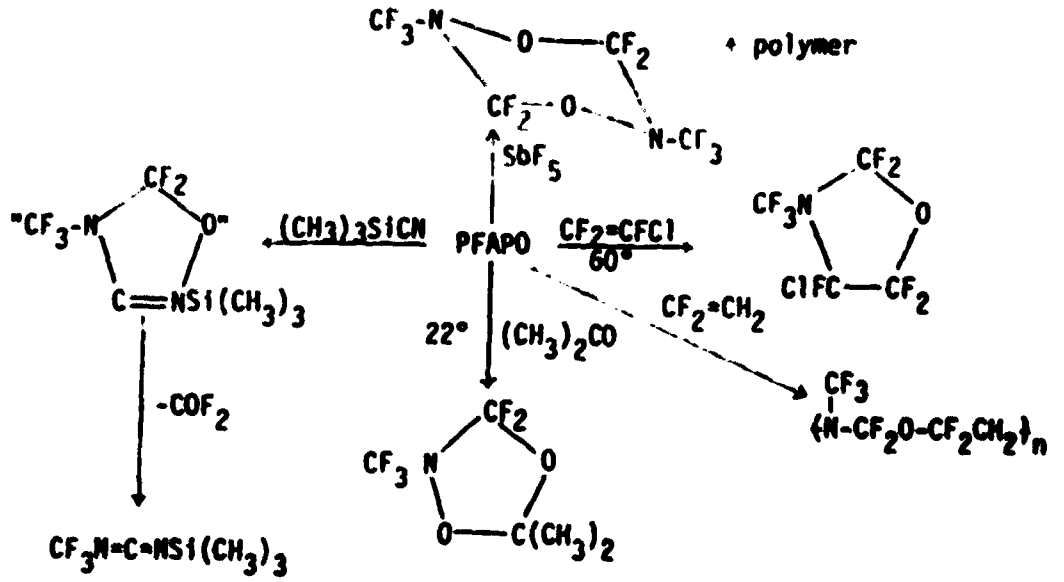
$$\downarrow \xrightarrow{CsF} CF_3N(Nu)CF=NNu$$

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 I.

SCHEME I

Unique PFAPO Chemistry
(HFPO does not readily add to unsaturated systems - PFAPO does.)



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 450°C and is untouched by hot concentrated sulfuric acid or aqueous permanganate. The polymer noted with $CF_2=CH_2$ 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 PFAPO can be made to polymerize with a variety of olefins.

Imines. Another extensively investigated compound is perfluoromethanimine, $CF_2=NF$. The development of a high yield synthesis of this material was a major breakthrough. Starting from readily available ClCN, $CF_2=NF$ can be prepared in over 90% yield.

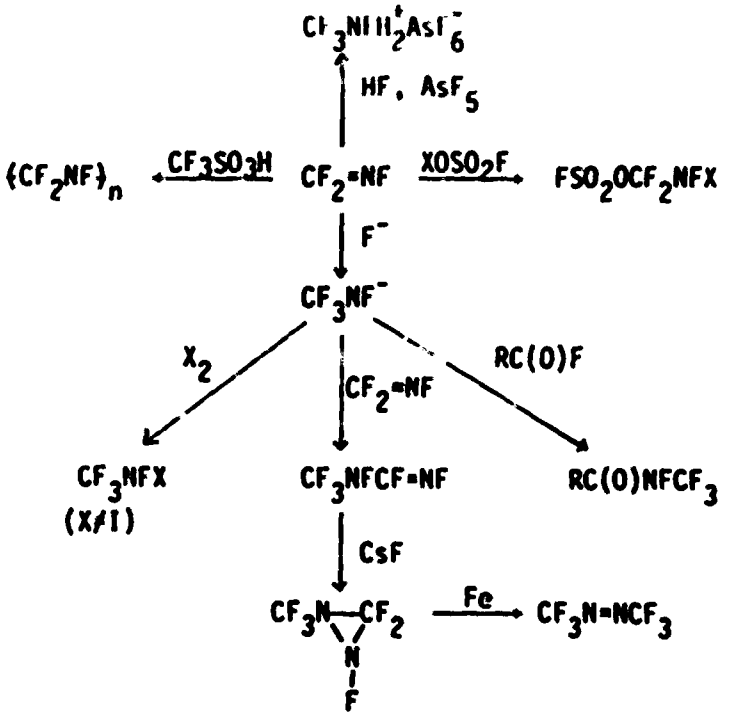
$$ClCN + ClF + F_2 \longrightarrow ClCF_2NClF$$

$$ClCF_2NClF + Hg \xrightarrow{TFAA} CF_2=NF + HgCl_2$$

The chemistry of $CF_2=NF$ leads readily to many new compounds including the first examples of polymeric N-F compounds and perfluoroalkyamonium salts. Some of the remarkable chemistry of $CF_2=NF$ 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 CF_2=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.

LIST OF PUBLICATIONS

1. A. Sekiya and D. D. DesMarteau, "Reaction of $CF_3OONHCF_2OOCF_3$ with Metal Fluorides," Inorg. Chem., 18, 919 (1979).

2. A. Sekiya and D. D. DesMarteau, "The Reaction of 2-Trifluoromethyl-3,3-difluorooxaziridine with Some Fluorinated Nucleophiles, J. Org. Chem. 44, 1131 (1979).

3. A. Sekiya and D. D. DesMarteau, "A Facile Synthesis of 1,1-Bix(fluoroxy)perfluoroethane," Inorg. Nucl. Chem. Letters, 15, 203 (1979).

4. A. Sekiya and D. D. DesMarteau "Novel N-Fluoroamines via the Chlorofluorination of Compounds with Carbon-Nitrogen Triple Bonds," J. Am. Chem. Soc., 101, 7460 (1980).

5. A. Sekiya and D. D. DesMarteau, "The Reaction of 2-Trifluoromethyl-3,3-difluorooxaziridine with Nucleophiles," J. Fluorine Chem., 14, 289 (1979).

6. A Sekiya and D. D. DesMarteau, "Synthesis of 1,1-Bix(fluoroxy)perhaloalkanes by Reaction of Fluorinated Carboxylic Acids with Fluorine in the Presence of Cesium Fluoride," Inorg. Chem., 19, 1328 (1980).

7. A. Sekiya and D. D. DesMarteau, "Synthesis of Trifluoromethyl Amines $CF_3N(X)H$, from $CF_3N(X)C(O)F$," J. Fluorine Chem., 15, 183 (1980).

8. A. Sekiya and D. D. DesMarteau, "Synthesis and Properties of 2-(Pentafluorothio)-3,3-difluorooxaziridine," Inorg. Chem., 19, 1330 (1980).

9. D. D. DesMarteau and K. Seppelt, "N-Fluoroiminosulfur Tetrafluoride," Angew. Chemie, 92, 659 (1980).

10. A. Sekiya and D. D. DesMarteau, "The Chlorofluorination of Nitriles. Preparation of N-Chloro-N-fluoroalkylamines," Inorg. Chem., 20, 1 (1981).

11. A. Sekiya and D. D. DesMarteau, "The Reaction of N-Chloro-N-Fluoroamines with Mercury. A Facile Synthesis of N-Fluoroimines and N-Fluoroamines," J. Org. Chem., 46, 1277 (1981).

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-Alkoxymethanimines," J. Fluorine Chem., 18, 441 (1981).

14. D. D. DesMarteau, H. H. Eysle, H. H. Oberhammer and H. Gunther, "Novel Sulfur-Nitrogen Fluorine Compounds. Synthesis and Properties of SF_5NClF, SF_5NHF and $FN{=}SF_4$ and the Molecular Structure and Vibrational Analysis of $FN{=}SF_4$," Inorg. Chem., 21, 1607 (1982).

15. S.-C. Chang and D. D. DesMarteau, "Perfluoromethanamine Ion," Polyhedron, 1, 129 (1982).

16. W. L. Lam and D. D. DesMarteau, "Unusual Cycloadditions of 3-Trifluoromethyl-2,2-difluorooxaziridine, J. Am. Chem. Soc., 104, 4034 (1982).

Papers In Press (Copies previously provided to ARO)

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.

18. S. C. Chang and D. D. DesMarteau, "Addition Reaction of N-Bromoperfluoromethanamine with Some Olefins," J. Org. Chem.

19. S. C. Chang and D. D. DesMarteau, "Fluoride Catalyzed Reactions of Perfluoromethanimine. Novel Chemistry of the Perfluoromethanamine Ion", J. Org. Chem.

20. S. C. Chang and D. D. DesMarteau, "Oxidation Reactions of Perfluoromethanimine and Related Compounds. Electrophilic Additions to $CF_2=NF$ and Fluoride Promoted Oxidation of Perhaloimines and Nitriles by Cl_2 and BrF_3," Inorg. Chem.

PARTICIPATING SCIENTIFIC PERSONNEL

Dr. Darryl D. DesMarteau, principal investigator
Dr. Akira Sekiya, postdoctoral
Dr. Brian A. O'Brian, postdoctoral
Paul Mulcahy*
Dr. Kamalesh Johri, Ph.D. 1982
Dr. Yataka Katsuhara, postdoctoral*
Dr. William Y. Lam, postdoctoral
Shi-Ching Chang, Ph.D. 1982
Yuan y. Zheng, visiting scholar

*minor participants