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

Final Technical Report

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A series of 1,1-difluoro-2-aza-perhalo-1-butenes, C\textsubscript{2}F\textsubscript{2}=NCP\textsubscript{2}CFX\textsubscript{1} (X = F, Cl, Br), were prepared by addition of C\textsubscript{2}F\textsubscript{2}=NCl to the olefins C\textsubscript{2}F\textsubscript{2}=CF\textsubscript{1}. These azabutenes were converted in high yield to the novel oxaziridines C\textsubscript{2}X\textsubscript{2}C\textsubscript{2}FCF\textsubscript{2}N\textsubscript{2}C\textsubscript{2}F\textsubscript{2} with CF\textsubscript{3}OOH. The chemistry of these oxaziridines resembles closely that previously found for C\textsubscript{2}F\textsubscript{2}=NCP\textsubscript{2}F\textsubscript{2} and allows the synthesis of a variety of new fluorinated compounds.
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 $\{\text{CF}_2\!\!=\!\!\text{NF}\}_n$.

Fluoride-promoted reactions of halogenated nitriles of the type $\text{R-CN}$ ($\text{R} = \text{CF}_3$, $\text{C}_2\!\!\text{F}_5$, $\text{C}_2\!\!\text{F}_7$, $\text{CCl}_3$) leads readily to $\text{R-CH-CNCl}_2$ and $\text{R-CF}-\text{NBr}$ on oxidation of intermediate anions with the respective halogens. The reactivity of the nitrogen bromine bond of the $\text{N}$-bromoimines can be exploited to prepare a variety of new halogenated azalkenes by addition to both halogenated on non-halogenated olefins. Photolysis of the $\text{N}$-bromoimines gives the respective azines, $\text{R-CF=N-N-CFR}$, 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 \( \text{CF}_3\text{N}=\text{CF}_2 \), 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 \( \text{CF}_2=\text{N}R \).

This was accomplished by a reaction of \( \text{CF}_2=\text{NCl} \) with \( \text{CF}_2=\text{CFX} \) (\( X=\text{F, Cl, Br} \)), which under the right conditions forms the respective imines.

\[
\text{CF}_2=\text{NCl} + \text{CF}_2=\text{CFX} \quad \text{170°C} \quad \text{11 atm} \quad \text{50%}
\]

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 \( \text{CF}_3\text{OOH} \), as previously used to prepare \( \text{CF}_3\text{N}=\text{CF}_2 \).

\[
\text{CF}_2=\text{NCF}_2\text{CF}_X \text{Cl} + \text{CF}_3\text{OOH} \quad \text{O°C} \quad \text{CF}_3\text{OOCF}_2\text{N}((\text{H})\text{CF}_2\text{CFXCl}}
\]

\[
\text{KHF} \quad \text{22°C} \quad \text{ClXCCF}_2\text{N}=\text{CF}_2 \quad \text{CF}_2=\text{COF}_2 + \text{HF} \quad \text{80-90%}
\]
These new oxaziridines are thermally stable at 22°C and show nearly the same remarkable reactivity as CF₃N-CPF₂.⁸

\[
\text{ClXCPF}_2 \xrightarrow{(\text{CH}_3)_2\text{C}=\text{O}} \text{ClXCPF}_2 \xrightarrow{\text{Nu}^-} \text{ClXCPF}_2\text{N(Nu)}\text{C}(\text{O})\text{F} \quad (\text{Nu}=\text{CH}_3\text{O})
\]

\[
60°C \xrightarrow{\text{C}_2\text{F}_4} \quad \text{ClXCPF}_2\text{N} \quad \text{ClXCPF}=\text{NF} + \text{COF}_2
\]

(Nu=F)

+ polymer

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

Polymerization of CF₂=NF

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

\[
\text{CF}_2=\text{NF} \xrightarrow{\text{A}} (\text{CF}_2\text{F}_n)^- \text{N}_n
\]

A=SbF₅, CF₃SO₂H

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, (CH₃)₃N. Again, the material is readily polymerized

\[
\text{CF}_2=\text{NF} \xrightarrow{(\text{CH}_3)_3\text{N}} (\text{CF}_2\text{F}_n)^- \text{N}_n
\]

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 (CF₂-NF)⁺ with n=1-3 and, depending on the ratio of (CH₃)₃N to CF₂=NF, (CF₂-NF)ₙNMe₃⁺ 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 Cl₂ and Br₂ of fluorinated nitrogen anions generated from imines such as CF₂=NF, by reaction with KF or CsF.¹⁰

\[
\text{CF}_2=\text{NF} + \text{F}^\ominus \rightarrow \text{CF}_3\text{NF}^\ominus + \text{X}^2_x \rightarrow \text{CF}_3\text{NF}X^2_x \quad \text{X=Cl, Br}
\]

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

\[
\text{R}_x\text{CN} + \text{F}^\ominus \rightarrow \text{R}_x\text{CFN}^\ominus + \text{Cl}_2 \rightarrow \text{R}_x\text{CF}_2\text{NCl}_2 \quad (90\%)
\]

The N-bromoimines 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.

\[
\text{R}_x\text{CF}=\text{NBr} + \xrightarrow{150-200\degree C} \text{R}_x\text{CF}=\text{N-C-C-Br}
\]

\[
= \text{C}_2\text{F}_4, \text{C}_2\text{F}_3\text{Cl}, \text{C}_2\text{F}_2\text{Cl}_2, \text{C}_2\text{F}_3\text{Br}, \text{C}_2\text{F}_2\text{HBr}, \text{C}_2\text{H}_4, \text{C}_2\text{H}_2\text{F}_2, \text{CH}_3\text{CHCH}_2
\]

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

\[
\text{R}_x\text{CF}=\text{NBr} \xrightarrow{\text{hv}} \text{R}_x\text{CF}=\text{N-N-CFR}_x + \text{Br}_2
\]

Again, it is clear that these materials provide entry into new areas of organonitrogen 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.
REFERENCES


LIST OF PUBLICATIONS


PARTICIPATING SCIENTIFIC PERSONNEL

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