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NOVEL CHEMISTRY OF TRIFLUOROMETHYLENIMINE

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The reaction chemistry of $\text{CF}_2=\text{NF}$ has been examined and a variety of novel N-fluoro compounds were found.

Reaction with AsF_5 in HF yields an ammonium salt, $\text{CF}_3\text{NFH}_2^+\text{AsF}_6^-$. The salt is a solid with a dissociation pressure of 7 torr at 22°C .

Electrophilic reagents (XOSO_2F , $\text{X}=\text{Br}, \text{Cl}, \text{OSO}_2\text{F}$) add across the carbon-nitrogen double bond to form the corresponding N-halo-N-fluoroamines.

Reactions with metal fluorides (KF or CsF) at ambient temperature generated the perfluoromethanamine ion, CF_3NF^- . This ion undergoes nucleophilic substitution reactions with CF_2NF , RfCOF ($\text{Rf} = \text{F}, \text{CF}_3, \text{C}_2\text{F}_5$) and it is oxidized by halogens to CF_3NXF ($\text{X}=\text{Br}, \text{Cl}$).

Higher molecular weight polymers of CF_2NF can be generated by reaction with strong acids. With SbF_5 , an air-sensitive polymer film is formed in a glass reactor. With $\text{CF}_3\text{SO}_3\text{H}$, a water-resistant viscous liquid is formed. Preliminary evidence indicates a structure $-(\text{CF}_2\text{NF})_n-$.

Reaction of CF_3NBrF with olefins ($\text{CF}_2=\text{CF}_2$, $\text{CF}_2=\text{CFC1}$, $\text{CF}_2=\text{CBr}_2$, $\text{CF}_2=\text{CH}_2$ and $\text{CH}_2=\text{CH}_2$) at elevated temperature cleaves the N-Br bond and results in addition to the olefin. The reaction mechanism is believed to be free radical and only a single regioisomer is observed with the unsymmetrical olefins.

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CONFIGURATIONAL ASSIGNMENT OF SEVERAL β -FLUORO- α -AMINO-ACIDS USING ^{19}F NMR SPECTROSCOPY THROUGH COMPLEXATION BY 18-CROWN-6 ETHER

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Eleven β -fluoro- α -aminoacids or esters ($\text{RCHFCH}(\text{NH})_2\text{COOH}$ with $\text{R}=\text{CH}_3, \text{C}_6\text{H}_5$ and COOH) were synthesized by dehydrofluorination of the corresponding β -hydroxy- α -amino acids or esters using sulfur tetrafluoride (J. Kollonitsch) or diazotation of diamino-dicarboxylic acid in liquid hydrogen fluoride (K. Matsumoto).

The *erythro* or *threo* configurational assignments is made using effect of complexation of the ammonium group by 18-crown-6 ether on ^{19}F NMR parameters. For the *erythro* configurations, the $^3J_{\text{HF}}$ coupling constant increases and a high field ^{19}F chemical shift is generally observed; these phenomena are accompanied by a decrease of the $^3J_{\text{HH}}$ and $^3J_{\text{CF}}$ coupling constants. The opposite effects are observed for the *threo* configurations. These observations may be explained by a change of relative population of the conformers around the $\text{C}_\alpha\text{-C}_\beta$ bond through complexation of the ammonium group. This complexation impairs the interactions between ammonium and fluorine groups and concomitantly the steric hindrance between ammonium and R (methyl, phenyl or carboxylate) groups is increased.