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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  $\text{AsF}_5$  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  $22^\circ\text{C}$ .

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

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

Higher molecular weight polymers of  $\text{CF}_2\text{NF}$  can be generated by reaction with strong acids. With  $\text{SbF}_5$ , 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  $\text{CF}_3\text{NBrF}$  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  $\beta$ -FLUORO- $\alpha$ -AMINO-ACIDS USING  $^{19}\text{F}$  NMR SPECTROSCOPY THROUGH COMPLEXATION BY 18-CROWN-6 ETHER

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Eleven  $\beta$ -fluoro- $\alpha$ -aminoacids or esters ( $\text{RCH}_2\text{CH}(\text{NH})_2\text{COOH}$  with  $\text{R}=\text{CH}_3, \text{C}_6\text{H}_5$  and  $\text{COOH}$ ) were synthesized by dehydrofluorination of the corresponding  $\beta$ -hydroxy- $\alpha$ -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  $^{19}\text{F}$  NMR parameters. For the *erythro* configurations, the  $^3J_{\text{HF}}$  coupling constant increases and a high field  $^{19}\text{F}$  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.