

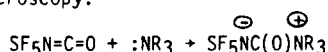
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REACTIONS OF PENTAFLUOROSULFANYL ISOCYANATE WITH NR_3 AND PR_3 COMPOUNDS; PREPARATION AND CHARACTERIZATION OF NOVEL COMPOUNDS $\text{SF}_2\text{NC}(\text{O})\text{NHC}(\text{O})\text{OCH}_3$ AND $1,4\text{-SF}_5\text{NHC}(\text{O})\text{OC}_6\text{H}_4\text{OH}$

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The reaction of Pentafluorosulfanyl Isocyanate, SF_5NCO , with tertiary amines has led to 1:1 adducts which have been shown to be zwitterionic in nature by infrared and NMR spectroscopy.



These adducts are far less thermally stable than the analogous fluorosulfonyl derivatives recently reported by Appel and Montenarch¹. The reaction of SF_5NCO with triphenylphosphine gave some evidence for the zwitterionic derivative, but the product could not be isolated even when SF_5NCO was used in excess. Recently we have also isolated

$\text{F}_2\text{S}=\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{N}}-\text{H}-\text{C}-\text{O}-\text{CH}_3$ from the reaction of $\text{SF}_2\text{NC}(\text{O})\text{NCO}$ with methanol, and $\text{F}_5\text{S}-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{C}_6\text{H}_4-\text{OH}$ from the reaction of SF_5NCO with hydroquinone. Both of these novel compounds were unexpected.

The physical properties of $\text{SF}_5\text{NC}(\text{O})\text{NC}_5\text{H}_5$, $\text{SF}_5\text{NC}(\text{O})\text{N}(\text{C}_2\text{H}_5)_3$, $\text{SF}_2\text{NC}(\text{O})\text{NHC}(\text{O})\text{OCH}_3$, and $1,4\text{-SF}_5\text{NHC}(\text{O})\text{OC}_6\text{H}_4\text{OH}$, prepared during this study, will be discussed in detail.

1 R. Appel and M. Montenarch, Chem. Ber., 110, 2368(1977).

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SOME REACTIONS OF FLUOROIMIDOTETRAFLUROSULFUR

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Fluoroimidotetrafluorosulfur undergoes a number of reactions with strong electrophiles, involving addition to the sulfur-nitrogen double bond. It also reacts readily with fluoride ion, forming the reactive nucleophile SF_5NF^- .

Chlorine(I) fluorosulfate, bromine(I) fluorosulfate, and peroxydisulfuryl fluoride add to $\text{F}_4\text{S}=\text{NF}$, forming the respective *cis* adducts. In the presence of KF, $\text{F}_4\text{S}=\text{NF}$ reacts readily with Br_2 , forming SF_5NBrF , and with acyl fluorides, forming RCONFSF_5 . The SF_5NF^- ion also reacts with $\text{F}_2\text{C}=\text{NF}$ to form $(\text{SF}_5\text{NF})\text{FC}=\text{NF}$, which is isomerized to the unusual azo compound $\text{F}_5\text{S}-\text{N}=\text{N}-\text{CF}_3$ in the presence of CsF.

Self-reaction of $\text{F}_4\text{S}=\text{NF}$ in the presence of KF does not form the expected dimer $(\text{SF}_5\text{NF})\text{F}_3\text{S}=\text{NF}$. Instead, extensive decomposition is observed, along with a low yield of the unusual amine $(\text{SF}_5)_2\text{NF}$.

The structures and possible mechanisms for formation of the various products will be discussed.