

B-10

NEW REACTIONS OF HEXAFLUOROACETONE

N. K. Homsy, H. W. Roesky, J. Lucas and V. W. Pogatzki

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, 3400 Göttingen (F.R.G.)

Dithiocyanogen $(\text{SCN})_2$ reacts with hexafluoroacetone (HFA) without cleavage of the S-S bond, leading to the formation of the cycloaddition product $[-\text{S}-\overset{\text{O}}{\parallel}{\text{C}}=\text{N}-\text{C}(\text{CF}_3)_2-\text{O}-\text{C}(\text{CF}_3)_2-\overset{\text{O}}{\parallel}{\text{C}}]_2 \underline{1}$.

1 can be cleaved at the S-S bond by elemental chlorine to give the sulfenic acid chloride which easily undergoes substitution reactions with lithium salts and Me_3Si -compounds under elimination of LiCl and Me_3SiCl , respectively. Reactions with $n\text{-BuLi}$, $(\text{cyclohexyl})_2\text{NLi}$, $(\text{Me}_3\text{Si})_2\text{NLi}$ and Me_3SiCN are reported. Cycloaddition also takes place by reaction of HFA with $\text{S}(\text{SCN})_2$, $\text{Hg}(\text{SCN})_2$, $\text{P}(\text{NCS})_3$ and $\text{As}(\text{NCS})_3$. Reaction of $\text{Hg}(\text{SCN})_2 \cdot 4 \text{HFA}$ with CF_3SCl , $\text{ClSC}_2\text{F}_4\text{SCl}$ and Br_2 leads under elimination of mercury halide to various disulfenes. Treating $\text{Hg}(\text{SCN})_2 \cdot 4 \text{HFA}$ or $\text{Hg}(\text{CN})_2 \cdot 4 \text{HFA}$ with Ph_2PCl results in the formation of bicyclic phosphoranes. The products of the reaction of HFA with Me_3SiCN are discussed.

The reaction of NWCl_3 with HFA is investigated. In the presence of Ph_4AsCl the new crystalline compound $(\text{Ph}_4\text{As})_2[\text{Cl}_5\text{WNC}(\text{CF}_3)_2\text{NWCl}_5]$ is formed. The two tungsten atoms are linked through a nitrogen-carbon-nitrogen bridge. X-ray structure analyses of various compounds are reported.