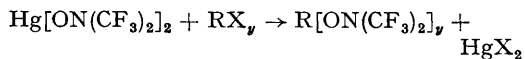


Hydrogen Abstraction Reactions of $\text{Hg}[\text{ON}(\text{CF}_3)_2]_2$

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THE bis(perfluoroalkyl)-, bis(hexafluorodimethylamino)-, and bis(trifluoromethylthio)-mercurials are known to be useful agents for the introduction of perfluoroalkyl, hexafluorodimethylamino-, and trifluoromethylthio-groups into compounds which contain a reactive halogen. The new mercurial, $\text{Hg}[\text{ON}(\text{CF}_3)_2]_2$,¹ also readily transfers the $(\text{CF}_3)_2\text{NO}$ group in reaction with organic and inorganic compounds containing labile halogens,¹ *e.g.*



[where $\text{RX}_y = \text{PhCO}\cdot\text{Cl}$, MeI , $\text{MeCO}\cdot\text{Cl}$, COCl_2 , $(\text{COCl})_2$, BCl_3 , OPCl_3 , PCl_5 , SiCl_4 , GeCl_4 , NOCl , HI , HBr].

However, we have found that $\text{Hg}[\text{ON}(\text{CF}_3)_2]_2$ behaves in a unique manner towards compounds containing silicon-, germanium-, and, in some cases, carbon-hydrogen bonds. Hydrogen atoms are abstracted to form bis(trifluoromethyl)hydroxylamine, $(\text{CF}_3)_2\text{NOH}$, and are replaced by the bis(trifluoromethyl)nitroxide group. The mercurial is reduced to elemental mercury. Reaction occurs generally at or below 20°. These are the first examples of hydrogen abstraction by a

fluorinated mercurial, although the reactive radical $(\text{CF}_3)_2\text{NO}\cdot$ has been shown to abstract a proton from PhCHR_2 ,^{2,3} (where $\text{R} = \text{H}$ or Me) and protons from benzene⁴ at room temperature.

The mercury(II) bis(trifluoromethyl)nitroxide was prepared by shaking mercury and liquid $(\text{CF}_3)_2\text{NO}\cdot$ in a sealed tube at room temperature.⁵ The excess of $(\text{CF}_3)_2\text{NO}\cdot$ was removed under vacuum. Typically, $\text{Hg}[\text{ON}(\text{CF}_3)_2]_2$ (in excess) reacts with SiH_3Br or SiH_2I_2 to yield essentially quantitative amounts of $(\text{CF}_3)_2\text{NOH}$ and $\text{Si}[\text{ON}(\text{CF}_3)_2]_4$. The spectra and properties of the latter are identical with those of the product formed in reaction of $\text{Hg}[\text{ON}(\text{CF}_3)_2]_2$ with SiCl_4 . Mercury and the respective mercury(II) halide remain in the residue along with unchanged $\text{Hg}[\text{ON}(\text{CF}_3)_2]_2$. With GeH_4 , reaction proceeds at $< -78^\circ$ resulting in $(\text{CF}_3)_2\text{NOH}$ and $\text{Ge}[\text{ON}(\text{CF}_3)_2]_4$ which is also produced by reaction of GeCl_4 with the mercurial. Mercury is the only other product.

Although the hydrogen atoms of the methyl group in MeI are not attacked at room temperature, in CH_2I_2 , the methylene protons are slowly replaced. The reaction proceeds more rapidly at 50°. The protons in benzoyl chloride and chlorobenzene are unaffected by the mercurial.

The products of these reactions are liquids of low volatility and $\text{Si}[\text{ON}(\text{CF}_3)_2]_4$ and $\text{Ge}[\text{ON}(\text{CF}_3)_2]_4$ are particularly sensitive to hydrolysis by traces of moisture which gives $(\text{CF}_3)_2\text{NOH}$ as the

only volatile product. Infrared, mass, and n.m.r. spectra and elemental analyses are in agreement with those required for the new compounds.

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