Hydrogen Abstraction Reactions of $Hg[ON(CF_3)_2]_2$

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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, $Hg[ON(CF_3)_2]_2$,[1] also readily transfers the $(CF_3)_2NO$ group in reaction with organic and inorganic compounds containing labile halogens,[1] *e.g.*

$$Hg[ON(CF_3)_2]_2 + RX_y \rightarrow R[ON(CF_3)_2]_y + HgX_2$$

[where RX_y = PhCO·Cl, MeI, MeCO·Cl, $COCl_2$, $(COCl)_2$, BCl_3, $OPCl_3$, PCl_5, $SiCl_4$, $GeCl_4$, NOCl, HI, HBr].

However, we have found that $Hg[ON(CF_3)_2]_2$ 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, $(CF_3)_2NOH$, 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 $(CF_3)_2NO\cdot$ has been shown to abstract a proton from $PhCHR_2$[2,3] (where R = H or Me) and protons from benzene[4] at room temperature.

The mercury(II) bis(trifluoromethyl)nitroxide was prepared by shaking mercury and liquid $(CF_3)_2NO\cdot$ in a sealed tube at room temperature.[5] The excess of $(CF_3)_2NO\cdot$ was removed under vacuum. Typically, $Hg[ON(CF_3)_2]_2$ (in excess) reacts with SiH_3Br or SiH_2I_2 to yield essentially quantitative amounts of $(CF_3)_2NOH$ and $Si[ON(CF_3)_2]_4$. The spectra and properties of the latter are identical with those of the product formed in reaction of $Hg[ON(CF_3)_2]_2$ with $SiCl_4$. Mercury and the respective mercury(II) halide remain in the residue along with unchanged $Hg[ON(CF_3)_2]_2$. With GeH_4, reaction proceeds at $< -78°$ resulting in $(CF_3)_2NOH$ and $Ge[ON(CF_3)_2]_4$ 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 Si[ON$(CF_3)_2]_4$ and Ge[ON$(CF_3)_2]_4$ are particularly sensitive to hydrolysis by traces of moisture which gives $(CF_3)_2NOH$ 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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