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Preliminary communication

Displacement of fluorine from perfluoroimines by bis[bis(trifluoromethyl)aminooxy] mercury or *N,N*-bis(trifluoromethyl)hydroxylaminecaesium fluoride

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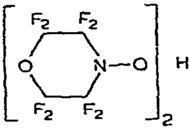
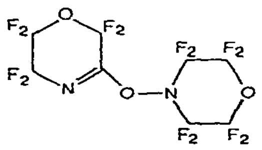
SUMMARY

The mercurial $[(CF_3)_2N{-}O]_2Hg$ reacts with the perfluoroimine $CF_3{-}N{=}CF_2$ to give the mercurial $\{[(CF_3)_2N{-}O{-}CF_2](CF_3)N\}_2Hg$, thermal decomposition of which affords the compounds $CF_3{-}N{=}C[O{-}N(CF_3)_2]{-}O{-}C[O{-}N(CF_3)_2]{=}N{-}CF_3$ and $CF_3{-}N{=}CF{-}O{-}N(CF_3)_2$ as major products, possibly via a series of elimination–addition reactions involving mercury compounds.

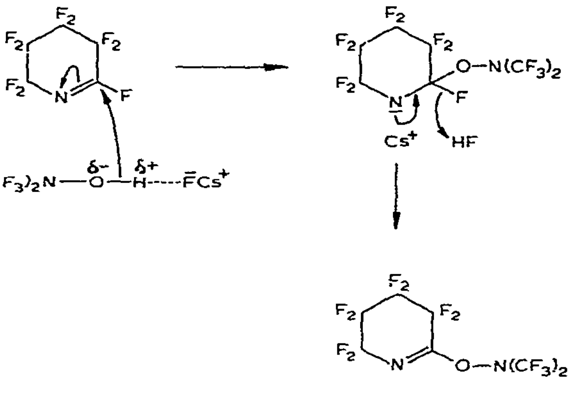
Use of the mercurial $[(CF_3)_2N{-}O]_2Hg$ or the hydroxylamine $(CF_3)_2N{-}OH$ (as its alkalimetal salts or adducts with potassium or caesium fluoride) to introduce the $(CF_3)_2N{-}O$ group into organic, organometallic, or inorganic molecules via halogen exchange reactions has been well exemplified[1]. We have extended the method to perfluoroimines.


(I)


(II)

The work stemmed from the discovery[2] that treatment of the perfluoroimine $CF_2{-}O{-}CF_2{-}CF_2{-}N{=}CF$ with the novel mercurial (I)★ at room temperature resulted in formation of compound (II). Subsequently, reaction of bis[bis(trifluoromethyl)aminooxy]mercury with $CF_2{-}(CF_2)_3{-}N{=}CF$ was shown to give (III), which can also be obtained by treatment of the imine with the sodium salt $(CF_3)_2N{-}O^-Na^+$ or with a $(CF_3)_2N{-}OH{-}CsF$ adduct (see Scheme 1).

★ Prepared from perfluoromorpholine-*N*-oxyl[3] and mercury at room temperature.



(III)

Scheme 1

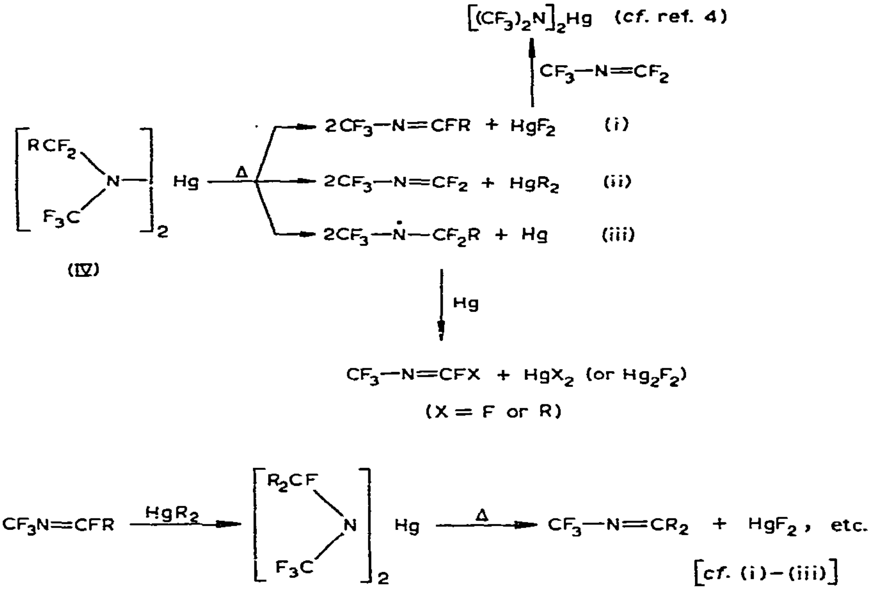
Detailed examination of the reaction between the acyclic compound $CF_3{-}N{=}CF_2$ and bis[bis(trifluoromethyl)aminooxy] mercury at 0° has revealed that a solid adduct forms initially; this adduct has been assigned the structure $\{[(CF_3)_2N{-}O{-}CF_2](CF_3)N\}_2Hg$ (IV) on the basis of elemental analysis, ^{19}F NMR investigations, and the following conversions:

$$\underset{(IV)}{\{[(CF_3)_2N{-}O{-}CF_2](CF_3)N\}_2Hg} \xrightarrow[21^\circ]{Cl_2,\ CFCl_3} HgCl_2 + (CF_3)_2N{-}O{-}CF_2{-}NCl{-}CF_3 \quad (84\%)$$

$$\Big\downarrow \text{HCl, } 21^\circ$$

$$\underset{(IV)}{Cl_2} + (CF_3)_2N{-}O{-}CF_2{-}NH{-}CF_3 \quad (95\%)$$

Thermal decomposition of the mercurial (IV) at 45—100° yields a complex mixture containing the compounds $CF_3{-}N{=}C[O{-}N(CF_3)_2]{-}O{-}C[O{-}N(CF_3)_2]{=}N{-}CF_3$ (V) (59%), $CF_3{-}N{=}CF{-}O{-}N(CF_3)_2$ (9%), $CF_3{-}N{=}C[O{-}N(CF_3)_2]_2$ (traces), $[(CF_3)_2N]_2Hg$, $(CF_3)_2N{-}\dot{O}$, $CF_3{-}N{=}CF_2$, $CF_3{-}NCO$, and Hg_2F_2. The new imine $CF_3{-}N{=}CF{-}O{-}N(CF_3)_2$ can also be obtained (31% yield), together with $(CF_3)_2N{-}O{-}CF_2{-}N{=}CF{-}O{-}N(CF_3)_2$ (22%) and $CF_3{-}NH{-}CF_2{-}O{-}N(CF_3)_2$ (26%), by treatment of $CF_3{-}N{=}CF_2$ with a ca. 2.5/1 (molar) adduct of *N,N*-bis (trifluoromethyl) hydroxylamine with caesium fluoride at room temperature. Possible decomposition modes for the mercurial (IV) are shown in Scheme 2 [R represents the $(CF_3)_2N{-}O$ group]; at present the precise pathway leading to the formation of product (V) is obscure.



Scheme 2

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1 For reviews see: D.P. Babb and J.M. Shreeve, *Intra-Science Chemistry Reports*, 5 (1971) 55; R.E. Banks and M.G. Barlow, *Fluorocarbon and Related Chemistry, Vol. 1*, The Chemical Society, London, 1971; H.J. Emeléus, *Record of Chemical Progress*, 32 (1971) 135.
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