Highly fluorinated tetrazanes and other polynitrogen compounds

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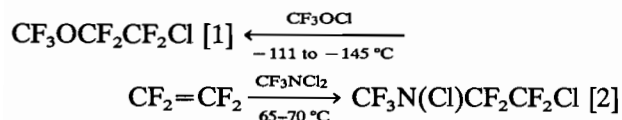
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Abstract

Highly fluorinated tetrazanes and cyclic, polycyclic and acyclic high nitrogen compounds are thermally and hydrolytically stable and, in general, shock insensitive materials. They are slightly volatile, colorless liquids which are only very slightly soluble in most solvents. Their synthetic routes are straightforward but, as is typical of the chemistry of compounds which contain fluorine, there is always sufficient of the unexpected to tweak the imagination.

Introduction

The energies of the nitrogen–chlorine and the oxygen–chlorine bonds in (perfluoroalkyl)chloroamines $((R_f)_2NCl)$ or -dichloroamines (R_fNCl_2) and perfluoroalkyl hypochlorites (R_fOCl) are very similar and their chemistries are not greatly different. However, it is enlightening to compare relative reactivities and the effect of greater charge separation in chloroamines than hypochlorites, e.g. when insertion of either $CF_2=CF_2$ or $CF_2=CFCl$ into CF_3OCl or CF_3NCl_2 occurs, invariably more vigorous conditions are required for N–Cl insertion

$$CF_3OCF_2CF_2Cl \;[1] \xleftarrow[-111 \text{ to } -145\,°C]{CF_3OCl}$$

$$CF_2=CF_2 \xrightarrow[65-70\,°C]{CF_3NCl_2} CF_3N(Cl)CF_2CF_2Cl \;[2]$$

With the exception that a higher temperature is necessary for insertion into the N–Cl bond, the products obtained in either case with $CF_2=CF_2$ are analogous and are formed in high yield. Insertion of olefins into sulfur–chlorine bonds, e.g. SF_5Cl, requires photolytic conditions. Synthesis of new substituted carbimides by insertion of nitriles into the element–chlorine bond of –O–Cl [3], $\rangle$N–Cl [4] and S^{VI}–Cl [5, 6] proceeds readily with the latter two usually via photolysis, but for –O–Cl heating in the presence of an acid is necessary for the insertion reaction to occur.

While no element can compete with carbon in numbers of catenated atoms, stable catenated species of other elements are known, especially if fluorine atoms or fluorinated groups or other electronegative species are present in the molecule, e.g. $CF_3O_nCF_3$ ($n=1-3$)

and O_nF_2 ($n=1, 2, 4$) or $CF_3S_nCF_3$ ($n=1-6$), ClS_nCl ($n=1-100$). Thus, stable catenated nitrogen compounds should be expected to exist and $CF_3N_2CF_3$ and $(CF_3)_4N_2$ are both very stable molecules. Much earlier Dobbie and Eméleus [4] photolytically induced the insertion of cyanogen chloride into the nitrogen–chlorine bond of $(CF_3)_2NCl$. We have taken advantage of this method to prepare similar carbimides which have been used to advantage as reactive precursors to a variety of new highly stable compounds which contain catenated nitrogen atoms [7–10].

Tetrazanes and their precursors

In our work, it has been possible to prepare several carbimides in high yield, e.g.

$$R_f(CF_3)NCl + RC\equiv N \xrightarrow{h\nu} R_f(CF_3)NN=CClR$$
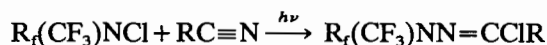
| R_f	R	R_f	R
CCl_2FCF_2	Cl [7]	CF_3CF_2	Cl [7]
$CClF_2CF_2$	Cl [7]	CF_3CF_2	CF_3 [7]
$F_2NCF_2CF_2$	Cl [10]	$F_2NCF_2CF_2$	NF_2CF_2 [10]

Advantage of the susceptibility of the carbon–chlorine bond to nucleophilic attack by polyfluoroalkylalkoxides has been taken to form ether linkages in these compounds, viz.
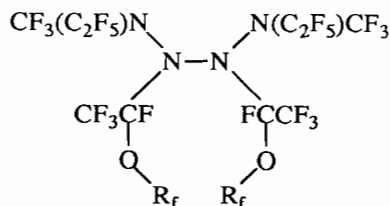
$$CF_3(C_2F_5)NN=C(Cl)CF_3 + LiOR_f \longrightarrow$$

$$CF_3(C_2F_5)NN=C(OR_f)CF_3$$
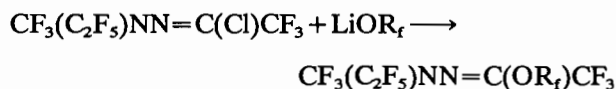
$R_f = CH_2CF_3, \; C(CF_3)_2H$

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Because of the polar nature of the carbon–nitrogen double bond in all of these molecules, chlorine fluoride addition occurs smoothly to form new stable chloroamines

$$R_f(CF_3)NN=CClR + ClF \longrightarrow R_f(CF_3)NN(Cl)CClFR$$
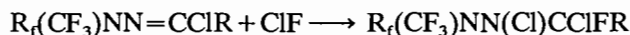
which when photolyzed result in tetrazanes, e.g.

$$CF_3(C_2F_5)NN(Cl)CF(OR_f)CF_3 \xrightarrow[-Cl_2]{h\nu}$$

In some cases, if chlorine is bonded to the carbon atom α to N(Cl), photolysis results in intramolecular dechlorination of the chloroamine to form a new perfluorinated carbimide. Subsequent addition of ClF results in

$$F_2NCF_2CF_2N(CF_3)N(Cl)CClFCF_2NF_2 \xrightarrow[-Cl_2]{h\nu}$$

$$F_2NCF_2CF_2N(CF_3)N=CFCF_2NF_2$$
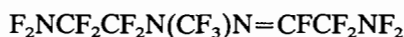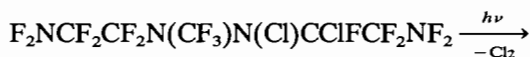
$F_2NCF_2CF_2N(CF_3)N(Cl)CF_2CF_2NF_2$ which loses chlorine upon photolysis and coupling of the nitrogen-containing fragments occurs to give an eight-nitrogen tetrazane in 70% yield [10].
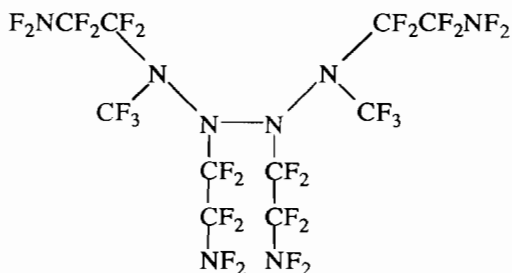
In an effort to replace chlorine with fluorine in these carbimides by using CsF as the fluorinating reagent, two different results were obtained. In the first instance only straightforward fluorination results. The product

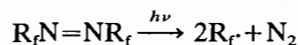$$CF_3(C_2F_5)NN=CClCF_3 + CsF \longrightarrow$$
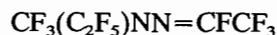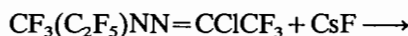
$$CF_3(C_2F_5)NN=CFCF_3$$

can be chlorofluorinated and photolyzed to form a perfluorotetrazane [4, 11, 12]. However, with $CF_3(C_2F_5)NN=CCl_2$, fluorination to $CF_3(C_2F_5)NN=CF_2$ with concomitant dimerization to $CF_3(C_2F_5)NN(CF_3)CF=NN(C_2F_5)CF_3$ occurs. Chlorofluorination of this dimer with chlorine fluoride to form the chloroamine followed by photolysis gives another interesting highly

fluorinated eight-nitrogen tetrazane in 93% yield.
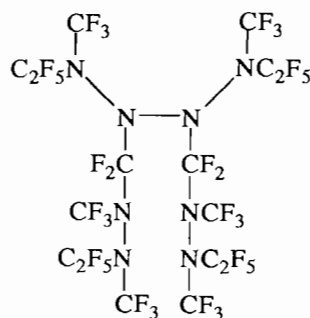
While we are not the first to report the synthesis of fluorinated tetrazanes, previous methods, photolysis at 2537 Å of the respective diazenes, have resulted in low yields [11, 12]. The formation of the tetrazane may result from the reaction of the trifluoromethyl group, formed in the initial decomposition of the diazene, with the parent compound [11], i.e.,

$$R_fN=NR_f \xrightarrow{h\nu} 2R_f\cdot + N_2$$

R_f = polyfluoro- or perfluoromethyl

$$R_f\cdot + R_fN=NR_f \longrightarrow (R_f)_2N\dot{N}R_f$$
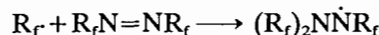
followed either by dimerization

$$2(R_f)_2N\dot{N}R_f \longrightarrow [(R_f)_2NN(R_f)]_2$$
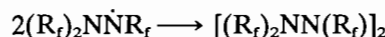
or reaction of the hydrazo radical with the starting diazene to form a tetrazo radical, which subsequently can react with $R_f\cdot$

$$(R_f)_2N\dot{N}(R_f) + R_fN=NR_f \longrightarrow$$
$$(R_f)_2NN(R_f)N(R_f)\dot{N}R_f \xrightarrow{R_f\cdot} [(R_f)_2NNR_f]_2$$
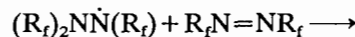
The hexakis(trifluoromethyl)tetrazane $[(CF_3)_2NN(CF_3)]_2$ was also identified as a minor product from the reaction of $[(CF_3)_2NN(CF_3)]_2Hg$ with bromine or chlorine [4]. The formation of the tetrazane very likely results from the decomposition of the photolytically or thermally sensitive halo compounds even in diffuse light at 20 °C.

$$(CF_3)_2NN(CF_3)X \xrightarrow[-X_2]{h\nu \text{ or } \Delta} [(CF_3)_2NN(CF_3)]_2$$
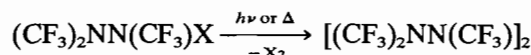
The reported stability of these tetrazanes is surprisingly high. Our results concur and indicate that these substances are highly stable and insensitive to water, air, heat and shock. For example, via differential scanning calorimetry $[CF_3(C_2F_5)NN(C_2F_5)]_2$ and $[F_2NCF_2CF_2N(CF_3)N(CF_2CF_2NF_2)]_2$ are stable to 232 and 177 °C, respectively. On average these stable viscous liquids have densities in the 2.0 to 2.2 g/ml range. Their solubilities in any common, chlorinated, chlorofluorocarbon or fluorinated solvent are very low.

In our work, all of the tetrazanes have been confirmed by excellent elemental analyses as well as characterized

by IR, ^{19}F NMR and mass spectral measurements. Mass spectra are particularly helpful where a molecular ion or M^+ − one substituent group or $M^+/2$ is frequently observed.

The latter observation led to an attempt to thermally induce the insertion of olefins into the N2–N3 bond of a tetrazane. Thus, at 100–110 °C $[CF_3(C_2F_5)NN(C_2F_5)]_2$ can be reacted readily with $CF_2=CFCl$, $CFCl=CFCl$, $CF_2=CH_2$ and $CF_2=CFH$ to form $CF_3(C_2F_5)NN(C_2F_5)\overset{|}{C}\overset{|}{C}N(C_2F_5)N(C_2F_5)CF_3$ in ∼ 30–40% yield [8], e.g.
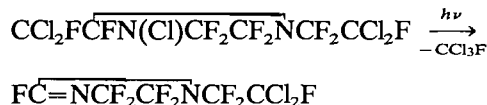
$$CF_3(C_2F_5)NN(C_2F_5)N(C_2F_5)N(C_2F_5)CF_3 \xrightarrow{100-110\,°C}$$
$$2CF_3(C_2F_5)\dot{N}N(C_2F_5)$$

$$CF_3(C_2F_5)N\dot{N}(C_2F_5) + CF_2=CH_2 \longrightarrow$$
$$CF_3(C_2F_5)NN(C_2F_5)CH_2\dot{C}F_2 \xrightarrow{[CF_3(C_2F_5)NN(C_2F_5)]_2}$$
$$CF_3(C_2F_5)NN(C_2F_5)CH_2CF_2N(C_2F_5)N(C_2F_5)CF_3$$

These slightly volatile, colorless liquids are stable with respect to further insertion reactions and exhibit properties similar to the parent tetrazane.

We have attempted to increase the number of catenated nitrogen atoms/molecule by dimerization of a triazane [8]. The insertion of a nitrile into the N–Cl bond of a chlorotris(perfluoroalkyl)hydrazine provided a low yield route to a three-nitrogen compound which

$$CF_3(C_2F_5)NN(Cl)C_2F_5 \,[7] + CF_3CN \xrightarrow[6-10\,h]{h\nu}$$
$$CF_3(C_2F_5)NN(C_2F_5)N=C(Cl)CF_3 +$$
$$5-10\%$$
$$[CF_3(C_2F_5)NN(C_2F_5)]_2$$
$$60-70\%$$

is a stable viscous, water-white, slightly volatile liquid. However, attempts to saturate the carbon–nitrogen double bond with chlorine fluoride led only to fragmentation which precluded dimerization to a higher nitrogen compound.

Cyclic and polycyclic high nitrogen compounds

Cyanogen is always a valuable precursor to a variety of useful reactive starting materials. In this particular case, it undergoes a smooth reaction with chlorine fluoride to form $Cl_2NCF_2CF_2NCl_2$ [13] which, when heated with $CF_2=CFX$ (1:2), gives $ClXCF-CF_2N(Cl)CF_2CF_2N(Cl)CF_2CXClF$ [9]. Subsequent stirring with mercury results in dechlorofluorination

$$ClXCFCF_2N(Cl)CF_2CF_2N(Cl)CF_2CXClF + 2Hg \longrightarrow$$
$$ClXCFCF_2N=CFCF=NCF_2CXClF + 2HgClF$$
$$\mathbf{I}$$

X = Cl (60%); F (50%)

Another polyfluorobisazomethine results upon photolysis of the chlorofluorinated product of the bis(carbimide)

$$CCl_2=NCCl_2CCl_2N=CCl_2 + ClF \longrightarrow$$
$$CF_2ClN(Cl)CFClCFClN(Cl)CF_2Cl \xrightarrow[-2Cl_2]{h\nu}$$
$$CF_2ClN=CFCF=NCF_2Cl$$
$$\mathbf{II}$$

It was then interesting to observe the behavior of these slightly differently substituted bisazomethines with CsF.

$$\mathbf{I} + CsF \xrightarrow{25\,°C}$$

$$\mathbf{III}$$

X = Cl (75%); F (70%)

$$\mathbf{II} + CsF \xrightarrow{100-110\,°C}$$

[14]

$$\mathbf{IV}$$

It is surprising that a small change in the alkyl substituent at nitrogen, CF_2Y (Y = CFXCl in **I**; Cl in **II**) can result in monocyclic and bicyclic products, respectively. Normally in the presence of fluoride ion bisazomethines are isomerized very readily to carbodiimides or perfluorodiazadienes [15], while just the reverse must have occurred prior to cyclization in the case of **I**. The bisazomethine **II** isomerizes first to the α,ω-bisazomethine and the reaction with F$^-$ proceeds according to

The option of the fluoride ion shift between a and b provides a pathway to the bicyclic molecule **IV** that is
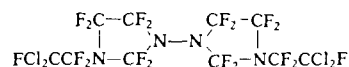
not available for the case where the reactant has a longer chain alkyl substituent at nitrogen (I).

Continuing to take advantage of the polar nature of the carbon–nitrogen double bond in these heterocycles, chlorine fluoride can be utilized to form a new cyclic chloroamine which when photolyzed loses CCl_3F.

$$III + ClF \longrightarrow$$

$$CCl_2F\overline{CFN(Cl)CF_2CF_2}NCF_2CCl_2F \xrightarrow[-CCl_3F]{h\nu}$$

$$F\overline{C=NCF_2CF_2}NCF_2CCl_2F$$

Subsequent saturation with chlorine fluoride and photolysis with concomitant loss of chlorine produces a stable bicyclic hydrazine

$$\begin{array}{cc} F_2C{-}CF_2 & CF_2{-}CF_2 \\ | \quad \rangle N{-}N \langle \quad | \\ FCl_2CCF_2N{-}CF_2 \quad CF_2{-}NCF_2CCl_2F \end{array}$$

A more highly substituted, yet stable, cyclic hydrazine was obtained when **IV** was reacted with chlorine fluoride and then photolyzed losing chlorine [9].
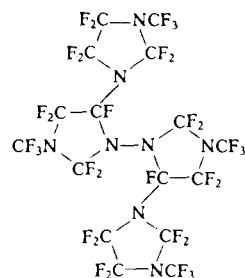
This highly substituted hydrazine has a density of −2.06 g/ml (22 °C), and is stable in stainless steel to at least 210 °C even in the presence of elemental oxygen at greater than one atmosphere pressure.

These compounds are slightly volatile or involatile liquids that display properties of low solubility in a variety of solvents, and of high thermal and hydrolytic stability. They are synthesized in high yields and all are characterized by spectral and elemental analyses.
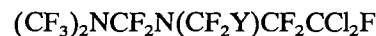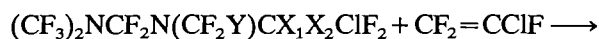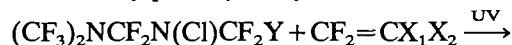
Acyclic difluoromethylenediamines

Perfluoroazaalkenes are readily prepared from appropriately substituted N-chloroamines [2, 16], e.g.

$$CF_3N(Cl)CF_2CCl_2F \xrightarrow{h\nu} CF_3N=CF_2 + CCl_3F$$
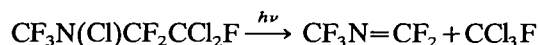
In the presence of F^- or of F^- and ClCN, $CF_3N=CF_2$ dimerizes to $(CF_3)_2NCF=NCF_3$ [17] or gives $(CF_3)_2NCN$ [10] both of which form reactive N-chloro and N,N-dichloro precursors following reaction with chlorine fluoride, viz. $(CF_3)_2NCF_2N(Cl)CF_3$ or $(CF_3)_2NCF_2NCl_2$. Insertion into the nitrogen–chlorine bond(s) occurs readily, e.g.

$$(CF_3)_2NCF_2NCl_2 + CF_2=CClF \xrightarrow{\Delta}$$

$$(CF_3)_2NCF_2N(Cl)CF_2CCl_2F$$
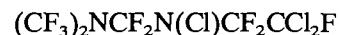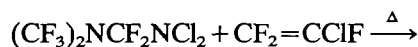
followed by photolytically induced insertion of selected

$$(CF_3)_2NCF_2N(Cl)CF_2Y + CF_2=CX_1X_2 \xrightarrow{UV}$$

$$(CF_3)_2NCF_2N(CF_2Y)CX_1X_2ClF_2 + CF_2=CClF \longrightarrow$$

$$(CF_3)_2NCF_2N(CF_2Y)CF_2CCl_2F$$

$Y = F, CCl_2F; X_1 = X_2 = H; X_1 = F, X_2 = H$

olefins to give several new di(tertiary)amines. These photolytic reactions must be caused to occur in the presence of excess olefin to preclude the formation of the azaalkene or hydrazine, i.e.

$$(CF_3)_2NCF_2N(Cl)CF_2CCl_2F \xrightarrow{UV}$$

$$(CF_3)_2NCF_2N=CF_2 + CCl_3F$$

$$(CF_3)_2NCF_2N(Cl)CF_3 \xrightarrow{UV}$$

$$[(CF_3)_2NCF_2NCF_3]_2 + Cl_2 \text{ [16]}$$
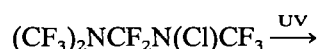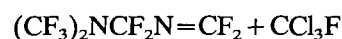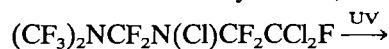
With more complex bis(secondary chloroamines), e.g. $CCl_2FCF_2N(Cl)CF_2CF_2N(Cl)CF_2CCl_2F$, photolysis results in the formation of two moles of the azaalkene, $CF_2=NCF_2CCl_2F$ with concomitant loss of chlorine.

The thermal stability of these di(tertiary)amines, which are invariably liquids, is surprisingly high. While not all have been examined, $(CF_3)_2NCF_2N(CF_2-CCl_2F)CF_3$ has been shown to be stable in Pyrex for at least 3 h at 260 °C and in stainless steel in the presence of oxygen (>one atmosphere) for a least 2 h at 200 °C. Its density is 2.17 g/ml.

Gas phase photolysis is also useful in the introduction of other groups into these diamines, e.g. [16]

$$(CF_3)_2NCF_2N(Cl)CF_3 + R_fCl \xrightarrow{UV}$$

$$(CF_3)_2NCF_2N(R_f)CF_3$$
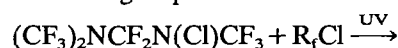
$R_f = CF_3C(O); SF_5$

We are continuing our efforts to obtain high nitrogen compounds with higher numbers of catenated nitrogen atoms as well as those with a variety of functional groups and varying ratios of fluorine and nitrogen. Structure/stability relationships as well as changes in physical properties as a function of structure in poly- and perfluorinated amines, N-chloroamines and polyamines are being examined.

Acknowledgements

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