bromide were added 10 mmol at a time every 2 h.

Acknowledgment. This work was supported by the Centre National de la Recherche Scientifique, France, which is gratefully acknowledged for financial aid. The authors are very grateful to one of the referees for helpful suggestions for improvement of the manuscript.

Registry No. Sodium hydride, 7646-69-7; *tert*-amyl alcohol, 75-85-4; sodium *tert*-amyl alcohol, 14593-46-5; octyl bromide, 111-83-1; 1-octene, 111-66-0; Cp_2TiCl_2, 1271-19-8; VCl_3, 7718-98-1; $FeCl_3$, 7705-08-0; $Co(OAc)_2$, 71-48-7; $Ni(OAc)_2$, 373-02-4; $ZnCl_2$, 7646-85-7; $CdCl_2$, 10108-64-2; $ZrCl_4$, 10026-11-6; $MoCl_5$, 10241-05-1; WCl_6, 13283-01-7; octane, 111-65-9; octyl chloride, 111-85-3; octyl iodide, 629-27-6; 2-bromooctane, 557-35-7; bromocyclohexane, 108-85-0; chlorocyclopentane, 930-28-9; 1-bromoadamantane, 768-90-1; 1-chloroadamantane, 935-56-8; 2-bromo-2-methyldodecane, 76402-83-0; 2-chloro-2-methyldodecane, 4325-53-5; 1-bromo-1-methylcyclohexane, 931-77-1; 1-chloro-1-methylcyclohexane, 931-78-2; cyclohexane, 110-82-7; cyclopentane, 287-92-3; adamantane, 281-23-2; 2-methyldodecane, 1560-97-0; methylcyclohexane, 108-87-2; benzyl bromide, 100-39-0; benzyl chloride, 100-44-7; 3-bromocyclohexene, 1521-51-3; (*E*)-3-bromo-3-hexane, 42843-52-7; (*Z*)-3-bromo-3-hexene, 16645-01-5; 1-bromocyclohexene, 2044-08-8; 1-chlorocyclohexene, 930-66-5; 4-methyl-1-chlorocyclohexene, 31053-83-5; 1–bromocyclooctene, 4103-11-1; methylbenzene, 108-88-3; diphenylmethane, 101-81-5; cyclohexene, 110-83-8; (*Z*)-3-hexene, 7642-09-3; (*E*)-3-hexene, 13269-52-8; 4-methylcyclohexene, 591-47-9; cyclooctene, 931-88-4; 1-chloro-4-bromobutane, 6940-78-9; 4-bromooctane, 999-06-4; 4-chlorobenzyl chloride, 104-83-6; 2-bromochlorobenzene, 694-80-4; butyl chloride, 109-69-3; 4-chlorotoluene, 106-43-4; chlorobenzene, 108-90-7; 11-bromo-1-undecanol, 1611-56-9; *trans*-2-bromocyclohexanol, 2425-33-4; *trans*-2-[(2-bromocyclohexyl)oxy]tetrahydro-2*H*-pyran, 76402-84-1; *trans*-1-bromo-2-methoxycyclohexane, 5927-93-5; 6-bromo-1,4-dioxaspiro[4.5]decane, 1724-15-0; 6-chloro-1,4-dioxaspiro[4.5]decane, 6954-16-1; 2-(3-chloropropyl)-2-methyl-1,3-dioxolane, 5978-08-5; 2-chloro-1-phenylethanone, 532-27-4; 3-bromocamphor, 76-29-9; 2-bromocyclohexanone, 822-85-5; 2-chlorocyclohexanone, 822-87-7; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; ethyl 4-bromobutyrate, 5969-81-5; 4-(bromomethyl)benzonitrile, 17201-43-3; 2-bromoundecanoic acid, 2623-84-9; 11-bromoundecanoic acid, 2834-05-1; 2-chlorobutyric acid, 4170-24-5; 5-chloropentanoic acid, 1119-46-6; cyclohexene oxide, 286-20-4; 2-(cyclohexyloxy)tetrahydro-2*H*-pyran, 709-83-1; methoxycyclohexane, 931-56-6; 1,4-dioxaspiro[4.5]decane, 177-10-6; 2-methyl-2-propyl-1,3-dioxolane, 4352-98-1; 1-phenylethanone, 98-86-2; camphor, 76-22-2; ethyl butyrate, 105-54-4; 4-tolunitrile, 104-85-8; undecanoic acid, 112-37-8; butyric acid, 107-92-6; pentanoic acid, 109-52-4; $Cr(OAc)_3$, 1066-30-4; $Cu(OAc)_2$, 142-71-2.

Reaction of *N*-Chloro-*N*-fluoroperhaloalkylamines with Mercury. Facile Synthesis of *N*-Fluoro Imines and *N*-Fluoro Amines

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Received September 2, 1980

The reaction of *N*-chloro-*N*-fluoroalkylamines with mercury has been studied with $ClCF_2NClF$, CF_3NClF, CF_3CF_2NClF, $CF_3CF_2CF_2NClF$, and $(CF_2NClF)_2$. In the absence of solvents, all but CF_3NClF undergo dehalogenation to form the corresponding *N*-fluoro imines in good yield. Only the syn isomers of $CF_3CF{=}NF$, $CF_3CF_2CF{=}NF$, and $(CF{=}NF)_2$ are observed. With trifluoroacetic acid as a solvent, the reactions with mercury yield the corresponding *N*-fluoro amines $ClCF_2NHF$, CF_3NHF, CF_3CF_2NHF, and $CF_3CF_2CF_2NHF$ in excellent yields except with $(CF_2NClF)_2$. For the latter, the amine $(CF_2NHF)_2$ eliminates HF under the reaction conditions, and only $(CF{=}NF)_2$ is isolated. With trifluoroacetic anhydride as a solvent, $ClCF_2NClF$ is dehalogenated with mercury to give excellent yields of $CF_2{=}NF$ in the first practical synthesis of this simplest perfluoro imine. Details of these reactions and the characterization of the new compounds $ClCF_2NHF$, CF_3CF_2NHF, $CF_3CF_2CF_2NHF$, and $CF_3CF_2CF{=}NF$ are presented.

Highly fluorinated organonitrogen compounds encompass a broad range of materials, whose synthesis, properties, and chemical reactions are of continuing interest.[1] The variety and number of fluorinated compounds are far less than hydrocarbon analogues, due in part to the lack of suitable preparative methods for their synthesis. The latter consideration also limits the investigation of the chemistry of some known fluorinated compounds.

Two related classes of compounds illustrative of the above are the *N*-fluoro imines, $R_fCF{=}NF$, and *N*-fluoro amines, R_fNHF. Several imines are known[2] but not easily prepared, and only one example of an amine, CF_3NHF,[3] has been isolated. These two classes of compounds are, of course, related and in principle interconvertible by the addition or elimination of hydrogen fluoride (eq 1).

$$R_fCF{=}NF \underset{-HF}{\overset{HF}{\rightleftharpoons}} R_fCF_2NHF \tag{1}$$

Recently a general and preparatively useful method for the synthesis of *N*-chloro-*N*-fluoro amines has been found[4] (eq 2). This paper reports the conversion of these compounds to the corresponding *N*-fluoro imines and *N*-fluoro amines.[5]

$$R_fCN + F_2 + ClF \rightarrow R_fCF_2NClF \tag{2}$$

Experimental Section

General Methods. All compounds were handled in Pyrex or stainless-steel vacuum systems equipped with glass–Teflon valves or Teflon-packed, stainless-steel valves. Pressures were measured with a Wallace and Tiernan differential pressure gauge (Series

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Table I. Reaction of RCF_2NClX with Hg[a]

R/X	reaction conditions[b] temp, °C	time, h	volatile products (% yield[c])
Cl/F	20	0.5	CF_2=NF (64), CF_3Cl (16), $ClCF_2N$=NCF_2Cl (12)
F/F	20	1.0	CF_3NClF (80)
F/F	25	17.0	none[d]
CF_3/F	20	1.0	CF_3CF=NF (59), CF_3CF_2-N=NCF_2CF_3 (38), C_2F_6 (trace)
C_2F_5/F	20	1.0	CF_3CF_2CF=NF (54), $CF_3CF_2CF_2N$=NCF_2CF_2-CF_3 (26), C_3F_8 (30), N_2 (28)
CF_2NClF/F[e]	0	1.0	$(CF{=}NF)_2$ (65)
CF_3/Cl	20	4.0	$CF_3C{\equiv}N$ (67), CF_3CF=NCl (5), CF_3CF_2N=NCF_2CF_3 (26)

[a] 3.0 mmol of RCF_2NClX and 10 g of Hg. [b] Reaction rate depends on the rate of stirring. Similar conditions were used in each reaction. [c] Yield calculated on the basis of starting RCF_2NClX. For N_2 and RCF_2N=NCF_2R, the yield is based on 2 mol of RCF_2NClX to 1 mol of these materials. [d] See Experimental Section. [e] 20 g of Hg.

Table II. Reaction of RCF_2NClX with Hg in TFA or TFAA[a]

R/X/solvent	reaction conditions[b] temp, °C	time, h	volatile products (% yield[c])
Cl/F/TFA	20	5 × 0.17[b]	CF_2=NF (90), CF_3-C(O)F (trace)
Cl/F/TFA	0	4	CF_2=NF (~40), $ClCF_2NHF$ (~40), $CF_3C(O)F$ + other
Cl/F/TFAA	20	6	CF_2=NF (88), CF_3Cl (trace), $CF_3C(O)F$
F/F/TFA	20	5	CF_3NHF (92)
CF_3/F/TFA	20	5	CF_3CF_2NHF (92), CF_3CF=NF (4)
C_2F_5/F/TFA	20	5	$CF_3CF_2CF_2NHF$ (89), CF_3CF_2CF=NF (5)
CF_2NClF/F/TFA[d]	20	5	$(CF{=}NF)_2$ (84), SiF_4 (1.2 mmol)
CF_3/Cl/TFA	20	5	CF_3CF=NCl (38), CF_3CF_2N=NCF_2-CF_3 (14), SiF_4 (0.81 mmol), N_2

[a] 3.0 mmol of RCF_2NClX, 10 g of Hg, and 3.5 g of TFA or TFAA. [b] See Experimental Section. [c] Yield based on starting RCF_2NClX (see Table I, footnote *c*). [d] 20 g of Hg.

1500) in the glass system and with a precision Heise Bourdon tube gauge in the metal system. Amounts of volatile compounds were determined by PVT measurements with the assumption of ideal gas behavior. Molecular weights were determined by gas density measurements. Temperatures were measured with a digital, indicating, copper–constantan thermocouple.

Infrared spectra were recorded on a Perkin-Elmer 180 spectrometer using a 10-cm glass cell fitted with AgCl or KCl windows. NMR spectra were taken at 29 °C on a Varian XL-100-15 spectrometer by using ~15 mol % solutions of the compounds in $CFCl_3$. Chemical shifts for ^{19}F are given as ϕ^* values (δ relative to internal $CFCl_3$ not at infinite dilution) and for ^1H as δ relative to external Me_4Si.

Reagents. The reagents CF_3CO_2H(TFA) and Hg were from commercial sources and were purified by distillation. The anhydride $[CF_3C(O)]_2O$ (TFAA) was prepared by reaction of CF_3CO_2H with excess P_4O_{10}. The compounds RCF_2NClF (R = Cl,[4] F,[5] CF_3,[4] C_2F_5,[4] and CF_2NClF[4]) and $CF_3CF_2NCl_2$[6] were prepared by literature methods.

Reaction of RCF_2NClF with Hg. The RCF_2NClF (3.0 mmol) was condensed onto 10 g of Hg cooled to −195 °C in a 100-mL/glass reactor. After being warmed to 0 °C, the reaction mixture was stirred in a water bath under the conditions given in Table I. The reactions are initially quite exothermic, and the Hg is partially converted to a black powder. After the indicated reaction times, the reactor was cooled to −195 °C, and a small amount of a noncondensable gas, N_2, was measured and pumped out. The volatile products were then separated by GLC using a 10 ft × $^3/_8$ in. column with 40% Halocarbon 11-21 polymer oil on Chromosorb P. The results are summarized in Table I.

The reaction of $ClCF_2NClF$ with Hg produced CF_2=NF and CF_3Cl which were very difficult to separate. The mixture was identified by IR, ^{19}F NMR, and average molecular weight values. The ratio of the two materials was determined by integration of the ^{19}F NMR spectra of the mixture. In the case of CF_3NClF, the only reaction appeared to be a slow chemisorbtion of the amine to form some unknown mercury derivative. The known products CF_2=NF,[7] CF_3Cl, $ClCF_2N$=NCF_2Cl,[8] CF_3CF=NF,[9] CF_3CF_2-N=NCF_2CF_3,[10] CF_3CF=NCl,[11] C_2F_6, C_3F_6, $CF_3CF_2CF_2N$=$NCF_2CF_2CF_3$,[10] and $(CF{=}NF)_2$[12] were identified by their molecular weight, IR, and ^{19}F NMR values as compared with literature values or a known sample of the compound.

Reaction of RCF_2NClF with Hg in TFA or TFAA. A 100-mL glass reactor containing 10 g of Hg was evacuated, and 3.5 g of TFA was added by vacuum transfer. The mixture was warmed to 20 °C to cover the Hg with the TFA and then cooled again to −195 °C. The RCF_2NClF (3.0 mmol) was then condensed into the reactor. The vessel was placed in ice bath to warm to 0 °C, and stirring was begun as soon as the mixture liquified. The reactions were then continued at 20 °C as given in Table II. During the reactions, the Hg was converted to a fine white solid. The products were then pumped through traps at −70 and −195 °C. The −70 °C trap removed the TFA, and the contents of the −195 °C trap were further separated by GLC using a 10 ft × $^3/_8$ in. column packed with 40% Halocarbon 11-21 polymer oil on Chromosorb P. In the case of $ClCF_2NClF$, reaction in TFA at 20 °C yields mainly CF_2=NF and $CF_3C(O)F$ as volatile products, and the yield of CF_2=NF is only 30–50%. Using several short reaction times greatly improves the yield of CF_2=NF. Lowering the reaction temperature to 0 °C results in appreciable yields of both CF_2=NF and $ClCF_2NHF$. A superior route to CF_2=NF was found by substituting TFAA for TFA. This results in a high yield of the imine which is easily purified by collection in a −135 °C trap after being passed through a −111 °C trap.

For $(CF_2NClF)_2$, no evidence for the expected amine $(CF_2NHF)_2$ was found. However, in contrast to the other RCF_2NClF derivatives, large amounts of SiF_4 were observed, suggesting the formation of HF. Similar results were observed when $CF_3CF_2NCl_2$ was allowed to react with Hg in TFA. The products for all reactions are summarized in Table II. The known compounds CF_2=NF,[7] CF_3NHF,[3] CF_3CF=NF,[9] CF_3CF=NCl,[11] CF_3CF_2N=NCF_2CF_3,[10] $(CF{=}NF)_2$,[12] SiF_4, and $CF_3C(O)F$ were identified by molecular weight and comparison of their IR and ^{19}F NMR with literature values or a known sample of the compound. Characterization of new compounds follows.

$ClCF_2NHF$ (this material was not purified by GLC): IR 3310 (s), 1440 (s) cm^{-1}, other absorptions in 1300–600 cm^{-1} region uncertain due to impurities; NMR of $ClCF_2^ANH^BF^C$ ϕ^*_A 77.0 (dd),

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ϕ^*_C 127.7 (dt), δ_B 8.6 (dt); J_{AB} = 12.8, J_{AC} = 27, J_{BC} = 50 Hz.

CF_3CF_2NHF: bp 2.7 °C; glass at −195 °C; mol wt 155.0, calcd 153.03; log *P* (torr) = 7.0108 − 843.57/*T* − 81547/T^2; ΔH_{vap} = 6.57 kcal/mol; ΔS_{vap} = 23.8 eu; IR 3301 (m), 1423 (m), 1355 (s), 1275 (w), 1233 (vs), 1208 (vs), 1150 (m), 1080 (s), 1003 (s), 922 (vw), 898 (s), 727 (w) cm^{-1}; NMR of $CF_3^ACF_2^BNH^CF^D$ ϕ^*_A 83.7 (d), ϕ^*_B 111.2 (dd), ϕ^*_D 136.3 (dtq), δ_C 7.9 (brd); J_{AD} = 8.5, J_{BC} = 13.5, J_{BD} = 21.0, J_{CD} = 55.0 Hz.

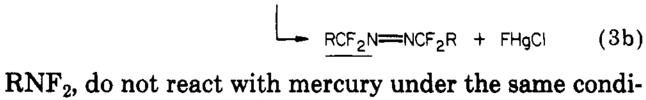
$CF_3CF_2CF_2NHF$: bp 31.3 °C; glass at −195 °C; mol wt 206.0, calcd 203.04; log *P* (torr) = 5.4770 − 101.05/*T* − 209870/T^2; ΔH_{vap} = 6.77 kcal/mol, ΔS_{vap} = 22.2 eu; IR 3303 (m), 1420 (s), 1343 (s), 1299 (w), 1260 (sh), 1230 (vs), 1180 (s), 1120 (vs), 1025 (m), 978 (vs), 911 (m), 886 (w), 863 (s), 796 (vw), 738 (m), 530 (vw) cm^{-1}; NMR $CF_3^ACF_2^BCF_2^CNH^DF^E$ ϕ^*_A 82.2 (tm), ϕ^*_B 128.4 (dm), ϕ^*_C 107.5 (ddq), ϕ^*_E 136.3 (brdt); δ_D 8.1 (brdt); J_{AC} = 8.0, J_{CD} = 13.0, J_{CE} = 17.0, J_{DE} = 55.0, J_{BE} = 6.5, $J_{AB} \leq 1.0$ Hz.

***syn*-$CF_3CF_2CF{=}NF$**: bp −6.9 °C; glass at −195 °C; mol wt 185.0, calcd 183.03; log *P* (torr) = 7.2631 − 1007.4/*T* − 42461/T^2; ΔH_{vap} = 6.21 kcal/mol; ΔS_{vap} = 22.8 eu; IR 1672 (m), 1348 (sh), 1324 (s), 1223 (vs), 1195 (sh), 1139 (s), 1020 (s), 836 (m), 743 (w), 739 (m), 734 (w) cm^{-1}; NMR for $CF_3^ACF_2^BCF^C{=}NF^D$ ϕ^*_A 83.9 (dt), ϕ^*_B 121.4 (ddq), ϕ^*_C 79.0 (dtq), ϕ^*_D 14.4 (br); J_{AB} = 2.0, J_{AC} = 4.0, J_{BC} = 13.5, J_{BD} = 2.0, J_{CD} = 39.0 Hz.

Results and Discussion

The reactions of *N*-chloro amines with mercury are summarized in Table I. The reactions proceed readily above the melting point of mercury to give good yields of the corresponding *N*-halo imines except in the case of CF_3NClF and $CF_3CF_2NCl_2$. For CF_3NClF, the compound is slowly absorbed by the mercury to form some unknown mercurial. Essentially no gaseous products are observed. With $CF_3CF_2NCl_2$, successive reductions occur to form the nitrile, CF_3CN, as the major product. Other volatile products observed in the reactions are N_2, the fluorinated alkyl group of RNClF, and the corresponding azoalkanes, RN=NR. The mercury is partially converted to a black powder, which is very similar in appearance to the black residue formed by the reaction of Hg_2Cl_2 with aqueous ammonia.[13] The composition of the black material has not been determined, but it probably contains some nitrogen in addition to the halogens, fluorine, and chlorine. The material balance for nitrogen in these reactions is normally low, especially in the case of $ClCF_2NClF$.

The mechansim for these reactions is unknown, but it is reasonable that the initial interaction involves an insertion of Hg into the N–Cl bond, followed by an elimination of mercury halide and/or additional reactions with the excess mercury (eq 3a,b). Analogous difluoroamines, RNF_2, do not react with mercury under the same conditions. The major products can be rationalized by 1,1- or 1,2-eliminations of ClF or Cl_2 from the starting amines.



$$RCF_2NClF + Hg \longrightarrow \text{“}RCF_2N(F)HgCl\text{”} \longrightarrow RCF{=}NF + FHgCl \qquad (3a)$$

$$\text{“}RCF_2N(F)HgCl\text{”} \longrightarrow \underline{RCF_2N}{=}NCF_2R + FHgCl \qquad (3b)$$

Previous studies have shown that a 1,2-elimination of Cl_2 by Hg is possible with FCl_2CNFCl and $F_2ClCNClF$,[14] and a 1,2-elimination of ClF is observed with Hg and $NCCCl_2NF_2$,[15] Cl_2FCNF_2, and Cl_3CNF_2.[14] Earlier investigations have also shown that 1,1-eliminations of Cl_2 from $RNCl_2$ take place either thermally or on photolysis to yield azoalkanes, RN=NR.[6,16] The 1,1- and 1,2-eliminations described in this work represent a new type of reaction for the synthesis of perfluoroimines and azoalkanes.[17] Because the RNClF derivatives can be readily prepared, this method is one of the more useful ones for the synthesis of perfluoro imines. The other generally useful method for the synthesis of perfluoro imines is by the reductive defluorination of perfluoro amines with ferrocene (eq 4).

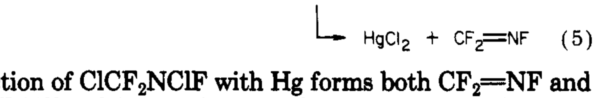
$$R_fCF_2NF_2 + 2Fe(C_5H_5)_2 \rightarrow R_fCF{=}NF + 2Fe(C_5H_5)_2F \qquad (4)$$

This reaction is relatively slow in solution and perfluoro amines of the type R_fNF_2 are probably not as readily available as R_fNClF. However, perfluoro amines containing an NF_2 group attached to a secondary carbon can be obtained by fluorination reactions and subsequently used to prepare cyclic and acyclic perfluoro imines containing the imine function on a secondary carbon atom. A similar transformation using *N*-chloro-*N*-fluoro amines is impractical because the only way to obtain the required NClF derivative at the present time is by addition of ClF to the imine.

One of the major goals of this work was to prepare $CF_2{=}NF$ in quantity by the dechlorination of $ClCF_2NClF$ with Hg, as previously reported by Shreeve.[14] Trifluoromethylenimine, the simplest member of this class of compounds, had previously been synthesized by a variety of routes.[3,7,10,14,18] However, the difficulty of these methods was evident by an almost complete lack of any reports of the chemistry of $CF_2{=}NF$. We found that the dechlorination of $ClCF_2NClF$ with Hg did not give $CF_2{=}NF$ as the only product, as previously reported. The significant amounts of CF_3Cl formed in the reaction were a problem in obtaining pure $CF_2{=}NF$ because the two compounds are very difficult to separate by distillation or GLC.

The mechanism for the formation of the CF_3Cl was unknown, but it seemed possible that it might be a consequence of the exothermicity of the reaction of $ClCF_2NClF$ with Hg. In an effort to moderate the reaction, various solvents were tried. Low polarity solvents such as $CFCl_3$ were ineffective and resulted in low yields of $CF_2{=}NF$ and large amounts of nitrogen. Polar solvents such as TFA and TFAA resulted in good yields of $CF_2{=}NF$ and no CF_3Cl. TFA, however, reacts with $CF_2{=}NF$, forming $CF_3C(O)F$ and other products. With TFAA as solvent, greater than 90% yields of easily purified $CF_2{=}NF$ were obtained. The Hg in the latter reaction is converted to a fine gray powder, similar in appearance to a fine mixture of Hg and $HgCl_2$. This is in contrast to the black powder observed in the absence of solvents or with $CFCl_3$ as solvent.

The effect of the polar solvent may be to enhance the formation of an intermediate anion $ClCF_2NF^-$, which then loses Cl^- to form the imine (eq 5). In TFA at 0 °C, the reaction of $ClCF_2NClF$ with Hg forms both $CF_2{=}NF$ and $ClCF_2NHF$. This can be viewed as a competition between the loss of Cl^- and the abstraction of a proton from the solvent by $ClCF_2NF^-$. The Hg under these conditions is converted to fine white powder, which is probably $ClHgOC(O)CF_3$.



$$ClCF_2NClF + Hg \xrightarrow[Hg]{TFAA} Hg_nCl^+ + ClCF_2NF^-$$

$$ClCF_2NF^- \longrightarrow HgCl_2 + CF_2{=}NF \qquad (5)$$

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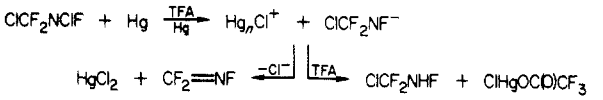
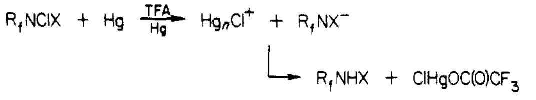


(6)

The above conclusions with $ClCF_2NClF$ are supported by the results found for the reactions of R_fNClF with Hg in TFA, summarized in Table II. In each case, the products result from abstraction of a proton from the TFA by the intermediate anion (eq 7). In the case of $CF_3CF_2NCl_2$



(7)

X = Cl, F

and $(CF_2NClF)_2$, the amine is unstable with respect to the loss of HF, and the observed products are the imines. This is evident by the formation of large amounts of HF, which is observed as SiF_4 in the glass apparatus. The exclusive formation of amines in TFA with R_fNClX, compared to $ClCF_2NClF$, can be rationalized on the basis that the loss of F^- from R_fNX^- is less favorable than the loss of Cl^- from $ClCF_2NF^-$. The predominant reaction is then the abstraction of a proton from the TFA by R_fNX^-.

The reaction of RCF_2NClF with Hg in TFA is the only general synthesis for *N*-fluorohaloalkylamines. Three new examples, $ClCF_2NHF$, CF_3CF_2NHF, and $CF_3CF_2CF_2NHF$, have been isolated, and the synthesis of CF_3NHF is far superior to earlier methods.[3] From the results with $(CF_2NClF)_2$ and $CF_3CF_2NCl_2$, it is obvious that not all amines of this type will be stable with respect to HF elimination. The four isolated amines show no tendency to lose HF in glass at 25 °C, and CF_3NHF is unaffected by NaF at 25 °C. With KF, however, reaction at 25 °C results in the rapid dehydrofluorination of CF_3NHF, CF_3CF_2NHF, and $CF_3CF_2CF_2NHF$ ($ClCF_2NHF$ was not tried) to the imines. Only the syn isomers of $CF_3CF{=}NF$ and $CF_3CF_2CF{=}NF$ are observed.

The reaction with $CF_3CF_2NCl_2$ in TFA is interesting in that a moderate yield of $CF_3CF{=}NCl$ is obtained. With only one example it is difficult to generalize, but this may represent a useful synthetic method for $R_fCF{=}NCl$. Only $(CF_3)_2C{=}NCl$[14,19] and $CF_2{=}NCl$[20] are readily available from $(CF_3)_2C{=}NH$ and ClCN. The general synthesis of $R_fCF{=}NCl$ from $R_fCN/Cl_2/AgF$ is expensive, and the yields are quite low.[11]

The characterization of the new imine, *syn*-$CF_3CF_2CF{=}NF$ is given in the Experimental Section. The syn configuration of $CF_3CF_2CF{=}NF$ is based on the small value of $^3J_{FF}$ (39 Hz) for the nitrogen fluorine. For the anti configuration, the coupling is expected to be ~200 Hz. It is interesting to note that in this and other work on the synthesis of imines of type $R_fCF{=}NF$, only the syn isomer appears to be formed.[22] This fact must relate to the greater thermodynamic stability of the syn vs. anti configuration and not to the method of preparation. For fluoroimines of other types, the syn and anti isomers are often observed. The eq 8 and 9 give examples of this by

$$NF_2CCl_2X \xrightarrow{Hg} syn\text{- and } anti\text{-}XClC{=}NF^{14,15} \qquad (8)$$

$$X = F, CN$$

$$RCH{=}CH_2 \xrightarrow{N_2F_4/NaF} syn\text{- and } anti\text{-}R(CN)C{=}NF^{22} \qquad (9)$$

$$R = F, N(C_2H_5)_2, CH_3, CH_2OC(O)CH_3, C_6H_5, OC(O)CH_3, SF_5$$

using related methods of synthesis which give only the syn isomer in the case of $R_fCF{=}NF$. Data given in the Experimental Section for the new amines $ClCF_2NHF$, CF_3CF_2NHF, and $CF_3CF_2CF_2NHF$ provide unambiguous proof of the structures for the compounds. The IR spectra contain sharp absorptions near 3300 and 1400 cm^{-1} which are readily assigned to ν(NH) and δ(NH), respectively. The large $^2J_{HF}$ (~50 Hz) coupling in the NMR is similar to $^2J_{HF}$ values found in some monofluorocarbamates[23] and in CF_3NHF.[3] The added J_{HF} couplings notwithstanding, the spectra of the alkyl groups in RCF_2NHF are considerably different from those in the parent RCF_2NClF amines. The latter compounds contain nonequivalent fluorine atoms in the α-methylene group, due to the asymmetric nitrogen and a slow inversion rate. In RCF_2NHF, the inversion is relatively faster, and the inherent nonequivalence of the α-methylene fluorine is not observed. This faster inversion rate may also be responsible for the much narrower line width observed for the N–F fluorine in RCF_2NHF compared to that for RCF_2NClF. On comparison of $ClCF_2NClF$ with $ClCF_2NHF$, the N–F resonance for the former is seen to be a rather broad singlet while the latter is a very sharp double of triplets. A final point of interest is the large difference in chemical shift between the N–F fluorine in RCF_2NClF and in RCF_2NHF. The change is ~130 ppm to higher field for the latter in each case.

Acknowledgment. The financial support of this work by the Army Research Office (Grants No. DAAG 29-77-G-0071 and DAAG 29-80-C-0102) is gratefully acknowledged. The Alexander Von Humboldt Stiftung is also acknowledged for a research fellowship to D.D.D.

Registry No. $ClCF_2NClF$, 33757-11-8; CF_3CF_2NClF, 72306-68-4; $CF_3CF_2CF_2NClF$, 72306-69-5; $(CF_2NClF)_2$, 75347-90-9; $CF_3CF_2NCl_2$, 677-66-7; Hg, 7439-97-6; $CF_2{=}NF$, 338-66-9; CF_3Cl, 75-72-9; $ClCF_2N{=}NCF_2Cl$, 660-79-7; CF_3NClF, 13880-72-3; $CF_3CF{=}NF$, 76514-97-1; $CF_3CF_2N{=}NCF_2CF_3$, 756-00-3; $CF_3CF_2CF{=}NF$, 76514-98-2; $CF_3CF_2CF_2N{=}NCF_2CF_2CF_3$, 755-50-0; C_3F_8, 76-19-7; $(CF{=}NF)_2$, 76514-99-3; CF_3CN, 353-85-5; $CF_3CF{=}NCl$, 650-50-0; $ClCF_2NHF$, 76515-00-9; CF_3NHF, 25590-25-4; CF_3CF_2NHF, 72306-70-8; $CF_3CF_2CF_2NHF$, 72306-71-9.

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