or $(CH_3)_4Si$ as reference. Reported integrations are those obtained after exchange with $D_2O$.

GC/MS were obtained by using a DB-5 column (60 m) in a Finnigan 4000 E instrument in the electron impact mode with an Incos 2300 data system. Mass spectra are reported in mass to charge units ($m/z$) with the relative intensities as percentages of the base peak given in parentheses.

Isomerization reactions were carried out in glassware flame-dried under vacuum, under a slight positive pressure of dry nitrogen.

**Preparation of 1,3-Diaminopropane-*N*,*N*,*N'*,*N'*-*d*$_4$.** Under an atmosphere of nitrogen, to 1,3-diaminopropane (200 mL, 2.38 mol) cooled in an icebath was added $D_2O$ (260 mL, 14.4 mol) and then benzene (dry, 550 mL). The mixture was heated to reflux and the water removed by means of a Dean–Stark trap. Most of the benzene was distilled, and then the solution was cooled in an ice bath and fresh additions of $D_2O$ followed by benzene were introduced. After a total of three such exchanges, the 1,3-diaminopropane was distilled stored over activated 4-Å sieves, yielding approximately 130 mL of dry 1,3-diaminopropane-*N*,*N*,*N'*,*N'*-*d*$_4$ (bp 138–140 °C; density 0.85 g/mL); $^1H$ NMR $\delta$ 2.7 (t, $J$ = 6 Hz, 4 H), 1.46 (q, $J$ = 6 Hz, 2 H), and no NH absorption.

**Isomerization of 2-Decyn-1-ol.** To lithium wire (63 mg, 9.0 mmol) was added $D_2N(CH_2)_3ND_2$ (8.5 mL). The lithium partially dissolved to give a blue mixture which was heated in an oil bath at 70 °C for 1.5 h. To the resultant white suspension, cooled to 20 °C, was added potassium *tert*-butoxide (660 mg, 6.0 mmol). A pale lemon yellow solution was obtained in about 3 min. A solution of 2-decyn-1-ol (156 mg, 1.0 mmol) in $D_2N(CH_2)_3ND_2$ (2.0 mL) was added. The orange solution was stirred at 20 °C for 1.0 h and then cooled in an ice bath, and $D_2O$ (20 mL) was added by syringe. The product was obtained by extraction of the reaction mixture with $CHCl_3$ 4 times. The combined organic phases were washed with water and saturated sodium chloride solution and then dried over sodium sulfate and filtered and the solvent was removed at reduced pressure. The crude product was purified by HPLC (Ultrasil-Si column, 10-$\mu$m silica, 10 × 25 cm, eluting with 2% isopropyl alcohol 98% hexane, at 5.0 mL/min, refractive index detector) affording-9-decyn-1-ol (80 mg, 48%): $^1H$ NMR $\delta$ 3.6 (s, 2.00 H), 2.2 (s, 0.67 H), 1.0 (s, 0.20 H), 1.2–1.6 (m, 0.87 H); mass spectrum of $(CH_3)_3Si$ ether, $m/z$ (relative intensity) 226 (2.8), 225 (2.9), 224 (1.4), 223 (.5), 76 (100).

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**Registry No.** $HOCH_2C{\equiv}C(CH_2)_6CH_3$, 4117-14-0; $HO(CH_2)_4C{\equiv}C(CH_2)_3CH_3$, 68274-97-5; $HOCH_2C{\equiv}C(CH_2)_{14}CH_3$, 2833-97-8; $CH_3CH_2CH(OH)C{\equiv}C(CH_2)_5CH_3$, 91295-77-1; $CH_3(CH_2)_{12}CH(OH)C{\equiv}C(CH_2)_5CH_3$, 91295-78-2; $HOCH_2C{\equiv}C[C(H/D)_2]_{12}H$, 91311-04-5; $HOCH_2(CD_2)_7C{\equiv}CD$, 91295-79-3; $HOCH_2(CD_2)_7C{\equiv}CH$, 91295-80-6; $HOCH_2(CD_2)_{15}C{\equiv}CH$, 91295-81-7; $CH_3CH_2CH(OH)(CD_2)_6C{\equiv}CD$, 91295-82-8; $CH_3(CH_2)_{12}CH(OH)(CD_2)_6C{\equiv}CD$, 91295-83-9; $HOCH_2(CD_2)_{12}C{\equiv}CD$, 91295-84-0; $NaND(CH_2)_3ND_2$, 91295-85-1; $LiND(CH_2)_3ND_2$, 91295-86-2; $KND(CH_2)_3ND_2$, 91295-87-3; KO-*t*-Bu, 865-47-4; $NH_2(CH_2)_3NH_2$, 109-76-2; $D_2N(CH_2)_3ND_2$, 91295-88-4; $HO(CH_2)_8C{\equiv}CH$, 17643-36-6.

**Supplementary Material Available:** NMR and mass spectra of 9-decyn-1-ol, from isomerization of 2-decyn-1-ol with $NaHN(CH_2)_3NH_2$ and with $LiDN(CH_2)_3ND_3$, and full experimental details of reactions listed in Tables I and II (10 pages). Ordering information is given on any current masthead page.

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# Some Novel Reactions of *N*-Chlorodifluoromethanimine

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Some reactions of *N*-chlorodifluoromethanimine, $CF_2{=}NCl$, have been studied and are compared to related reactions of perfluoromethanimine, $CF_2{=}NF$. Fluoride promoted reactions of $CF_2{=}NCl$ result in evidence for the $CF_3NCl^-$ anion, which is thermally less stable and less reactive than $CF_3NF^-$. Oxidation of $CF_3NCl^-$, formed in situ by reaction of $CF_2{=}NCl$ with KF or CsF, with $Cl_2$ forms $CF_3NCl_2$. With $Br_2$, $CF_3NBrCl$ is formed along with $CF_3NBr_2$. The latter arises from a novel fluoride-catalyzed conversion of $CF_3NBrCl$ to $CF_3NBr_2$ by $Br_2$, and the same products can be obtained starting with $CF_3NCl_2$, $Br_2$, and MF. Extension of this reaction to $C_2F_5NCl_2$ and $C_3F_7NCl_2$ is also discussed. Addition of $XOSO_2F$ (X = Cl, Br) to $CF_2{=}NCl$ forms the novel diazene $FSO_2OCF_2N{=}NCF_2OSO_2F$, presumably via the intermediate $FSO_2OCF_2NClX$ addition products. Competitive reaction of $CF_2{=}NF$ and $CF_2{=}NCl$ with fluoride ion results in the preferential formation of $CF_3NF^-$. Nucleophilic attack of the latter on $CF_2{=}NCl$ forms the novel diaziridine $CF_3\overline{NCF_2N}Cl$, which can be reduced by Hg in trifluoroacetic acid to $CF_3\overline{NCF_2N}H$. The mechanism for the formation of the diaziridines is discussed.

## Introduction

*N*-Chlorodifluoromethanimine, $CF_2{=}NCl$, was reported first in 1970.[2] However, there have been very few reports on the chemistry of this easily prepared imine.[3-5] Investigations of the chemistry of the related imine $CF_2{=}NF$[6,7] led us to undertake studies of the reaction chemistry of $CF_2{=}NCl$. As was found for $CF_2{=}NF$, $CF_2{=}NCl$ reacts readily with electrophilic halogen sources. Similarly, $CF_2{=}NCl$ reacts with fluoride ion from CsF and KF to form the anion $CF_3NCl^-$. However, the products of the reactions involving $CF_2{=}NCl$ are often different from those of $CF_2{=}NF$. These differences are easily explained by the photochemical and thermal instability of the

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products arising from $CF_2{=}NCl$, and by an apparent lower reactivity of $CF_3NCl^-$ as a nucleophile in comparison with $CF_3NF^-$.

In the course of this research, a novel catalytic conversion of N–Cl bonds to N–Br bonds by alkali metal fluorides and bromine was found.[8] Some details of this reaction are also presented. Two new compounds $CF_3CF_2NBrCl$ and $CF_3CF_2CF_2NBrCl$ obtained via this reaction provide an opportunity to compare the effects of halogen substitution on nitrogen inversion barriers.

## Experimental Section

**General Methods.** All manipulations of volatile compounds were carried out in Pyrex and stainless steel vacuum systems equipped with glass–Teflon and Teflon-packed stainless steel valves, respectively. Pressures were measured with a Wallace and Tiernan differential pressure gauge, Series 1500. Amounts of reactants and products were measured by PVT measurements or by direct weighing. Temperatures were measured using a digital-indicating iron-constant thermocouple.

IR spectra were recorded on Perkin-Elmer 1330 or 1430 Data Systems employing a 10-cm gas cell fitted with AgCl or KCl windows, at pressures from 5 to 100 torr. NMR spectra were taken on a Varian XL-100-15 spectrometer using 85 mol % $CFCl_3$ as a solvent and internal reference, or on a JEOL FX-90Q spectrometer using 1 mol % compound in $CCl_4$ solvent, containing 20 mol % $CDCl_3$ as an internal $^2H$ lock and 1 mol % $CFCl_3$ as an internal standard. $^{19}F$ chemical shifts at lower frequency than $CFCl_3$ are negative. Mass spectra were recorded on Finnigan 4021-C or Hewlett-Packard 5985-B spectrometers at 70 eV for both EI and CI ($CH_4$). Samples were introduced by direct gas injection.

Melting points were measured by a modified Stock technique. Molecular weights were determined by vapor density measurements using a calibrated 0.2-L Pyrex bulb fitted with a glass–Teflon valve. Vapor pressures as a function of temperature were determined by the method of Kellogg and Cady.[9] Data were analyzed by a least-squares fit to both linear and quadratic equations, and the best fit is reported.

GLC purification of selected compounds was carried out on a Victoreen 4000 gas chromatograph equipped with gas injection, low temperature sample collection, and thermal conductivity detection. Stainless steel columns ($^3/_8$ in. OD) of appropriate length, packed with 35% Halcarbon 11-21 polymer oil on Chromosorb P, were employed.

**Reagents.** The compounds $CF_2{=}NF$,[10] $CF_2{=}NCl$,[2,5] $C_2F_5NCl_2$, $C_3F_7NCl_2$,[12] $FSO_2OX$ (X = Cl, Br),[12,13] and $CF_3SO_2OCl$[14] were prepared by literature methods. Chlorine monofluoride was prepared by heating equimolar amounts of $Cl_2$ and $F_2$ in a Monel bomb for 18 h at 250 °C. Fluorine was obtained from Air Products and Chemicals, Inc. and was passed through a NaF scrubber before use. The metal fluorides KF and CsF were fused in a Pt crucible and then ground to a fine powder under very anhydrous conditions. All other reagents were readily available from commercial sources and were appropriately purified as needed before using.

*Caution! Many of the starting materials and products of the reactions described in this research are potentially hazardous. Nearly all the materials described are potent oxidizers and some may be explosive. We have not encountered any difficulties in the course of this research for the quantities indicated, but due caution must be exercised when working with these materials.*

**Reaction of $CF_2{=}NCl$ with $FSO_2OX$ (X = Cl, Br).** In a typical reaction, $CF_2{=}NCl$ (2.1 mmol) was added by vacuum transfer to a 100-mL glass reactor at −196 °C. An equimolar amount of $FSO_2OX$ was then similarly added, and the reactor was allowed to warm to 22 °C in the air and stand for 1 day. The reactor was then cooled to −196 °C and checked for volatiles at this temperature. Nitrogen, 0.24 mmol and 0.46 mmol, was formed with X = Cl and Br, respectively. The content of the reactor was then pumped on through traps at −40, −80 and −196 °C, as it warmed in the air to 22 °C. The −196 °C trap contained $Cl_2$ (X = Cl) and $Cl_2$, BrCl, $Br_2$ (X = Br), and other unidentified fluorocarbon containing materials. The −80 °C trap contained a small amount of $(FSO_2OCF_2N)_2$ and an unidentified fluorosulfate derivative. The −40 °C trap contained 0.61 mmol (X = Cl) and 0.40 mmol (X = Br) of nearly pure $(FSO_2OCF_2N)_2$: mp −65.5 to −64.5 °C; $M_r$ 326.0, calcd 326.15; IR 1925 (w), 1490 (s), 1250 (s), 1203 (s), 1116 (s), 1026 (m), 954 (s), 931 (s), 838 (s), 772 (m), 672 (vw), 599 (s), 551 (w), 473 (w) $cm^{-1}$; major $m/z$ [CI] 327 ($MH^+$), 227 ($M - SO_3F^+$), 164 ($FSO_3CF_2NH^+$), 114 ($CF_2SO_2^+$), 67 ($FSO^+$); [EI] 149 ($FSO_3CF_2^+$), 128 ($CF_2NNCF_2$), 114 ($CF_2SO_2^+$), 85 ($CF_2O^+$), 83 $(CFSO_2)^+$, 69 ($CF_3^+$), 66 ($CF_2O^+$), 50 ($CF_2^+$), 47 ($FCO^+$); NMR 49.6 (t, SF), −73.5 (d, $CF_2$, $^4J_{FF}$ = 7.5 Hz).

**Reactions of $CF_2{=}NCl$ in the Presence of Metal Fluorides.** Reactions were carried out in 100-mL glass flasks fitted with a glass–Teflon valve and containing a small Teflon-coated magnetic stirring bar. The appropriate amount of active metal fluoride was added to the reactor in the glovebox and the reactor was then evacuated. After cooling to −196 °C, the gaseous reactants were added by vacuum transfer and the reactor was then warmed to 22 °C and stirred for an appropriate time in the dark. Products were then separated by vacuum fractionation through low temperature traps and by GLC with the exclusion of light. In the case of reactions involving $Br_2$, excess $Br_2$ was removed by brief treatment of the $-NClBr$ and $-NBr_2$ fractions with $CH_2{=}CH_2$ at 22 °C, followed by reseparation from the $BrCH_2CH_2Br$ formed. Details of the reactions are summarized in Table I and II; characterization of new compounds follows.

$CF_3NClBr$: mp −62 °C; IR 1248 (s), 1218 (vs), 1178 (vs), 1116 (w), 1025 (vw), 893 (w), 787 (m), 688 (m) $cm^{-1}$; NMR −72.3 (s); major $m/z$ [CI] 202/200/198 ($MH^+$), 201/199/197 ($M^+$), 182/180/178 ($M - F^+$), 148/144 ($MH - Cl^+$), 121/119 ($MH - Br^+$), 102/100 ($CF_2NClH^+$), 69 ($CF_3^+$); [EI] 201/199/197 ($M^+$), 145/143 ($CF_2NBr^+$), 101/99 ($CF_2NCl^+$), 95/93 ($NBr^+$), 69 ($CF_3^+$).

$CF_3NBr_2$: mp −56 °C; IR 1240 (s), 1211 (vs), 1168 (vs), 1089 (w), 1028 (w), 969 (vw), 890 (vw), 758 (m), 675 (m) $cm^{-1}$; NMR −70.5 (s); major $m/z$ [CI] 246/244/242 ($MH^+$), 245/243/241 ($M^+$), 226/224/222 ($M - F^+$), 69 ($CF_3^+$); [EI] 245/243/241 ($M^+$), 145/143 ($CF_2NBr^+$), 95/93 ($NBr^+$), 69 ($CF_3^+$).

$C_2F_5NClBr$: IR 1336 (s), 1234 (vs), 1188 (vs), 1149 (vs), 1071 (vs), 970 (vw), 902 (vw), 839 (w), 753 (w), 718 (m), 694 (m), 653 (w), 601 (w), 532 (w) $cm^{-1}$; NMR −77.8 (t, $CF_3$), −96.3 (q, $CF_2$, $^3J_{FF}$ = 1.0 Hz); major $m/z$ [CI] 251/249/247 ($M^+$), 232/230/228 ($M - F^+$), 196/194 ($C_2F_4NBrH^+$), 152/150 ($C_2F_4NClH^+$), 69 ($CF_3^+$); [EI] 195/193 ($C_2F_4NBr^+$), 182/180/178 ($CF_2NBrCl^+$), 151/149 ($C_2F_4NCl^+$).

$C_3F_7NClBr$: IR 1342 (m), 1276 (m), 1242 (vs), 1230 (vs), 1200 (s), 1177 (m), 1132 (s), 1110 (s), 983 (s), 964 (s), 829 (w), 806 (w), 753 (m), 703 (w), 678 (w), 666 (w), 601 (w), 531 (w) $cm^{-1}$; NMR $CF_3{}^ACF_2{}^BCF_2{}^CNBrCl$ A −82.2 (t), B −119.7 (t), C −87.9 (q–t, $J_{AB}$ 1.0, $J_{AC}$ = 9.0, $J_{BC}$ = 2.0 Hz); major $m/z$ [CI] 301/299/297 ($M^+$), 282/280/278 ($M - F^+$), 182/180/178 ($CF_2NBrCl^+$), 119 ($C_2F_5^+$), 69 ($CF_3^+$); [EI, 17 eV] 301/299/297 ($M^+$), 245/243 ($M - FCl^+$), 201/199 ($M - BrF^+$), 182/180/178 ($CF_2NClBr^+$), 119 ($C_2F_5^+$).

$CF_3\overline{NCF_2N}Cl$: bp 15.3 °C; mp −120 °C; $M_r$ 182.0, calcd 182.48; $\log P\,(\text{torr}) = 7.7071 - 1392.05/T - (1432 \times 10^2/T^2)$; $\Delta H$ vap = 6.37 Kcal/mol; $\Delta S$ vap = 22.1 eu; IR 1411 (vs), 1295 (vs), 1211 (vs), 1133 (w), 1048 (s), 979 (s), 827 (w), 770 (m), 742 (w), 677 (s), 571 (w), 517 (w) $cm^{-1}$; NMR $CF_3{}^M\overline{NCF^AF^BN}Cl$ M −64.9 (d), A −112.4 (m), B −106.3 (m, $J_{AB}$ = 32.5, $J_{AM}$ 12.0 Hz); major $m/z$ [CI] 185/183 ($MH^+$), 147 $(M - Cl)^+$, 134 ($C_2F_5NH^+$), 91 ($C_2F_2N_2H^+$), 87/85 ($CF_2Cl^+$), 69 ($CF_3^+$); [EI] 114 ($C_2F_4N^+$), 87/85 ($CF_2Cl^+$), 69 ($CF_3^+$), 50 ($CF_2^+$), 51/49 ($NCl^+$).

**Synthesis of $CF_3\overline{NCF_2N}H$.** In a typical reaction, a 100-mL flask fitted with a glass–Teflon valve and containing 2.5 g of Hg and a small magnetic stirring bar was cooled to −196 °C and evacuated. Trifluoroacetic acid (6.5 mmol) was added by vacuum transfer, followed by $CF_3\overline{NCF_2N}Cl$ (1.0 mmol). The reactor was

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**Table I. Fluoride Promoted Reactions of $CF_2{=}NCl$[a]**

| $CF_2{=}NCl$ | reactant | MF | time, 22 °C[c] | products[b] |
|---|---|---|---|---|
| 2.0 | $Cl_2$ (5.0) | | 2 d | no reactn |
| 2.0 | $Br_2$ (5.0) | | 2 d | no reactn |
| 2.0 | BrCl (5.0) | | 2 d | no reactn |
| 13.0 | | CsF (13) | 1 d | $CF_3NCl_2$ (4.6) |
| 2.0 | $Cl_2$ (2.3) | CsF (10) | 2 d (55 °C) | $CF_3NCl_2$ (1.5) |
| 2.0 | BrCl (6.0) | CsF (10) | 1 d | $CF_3NCl_2$ (1.96) |
| 2.0 | $Br_2$ (4.0) | CsF (9.2) | 11 h | $CF_3NBrCl$ (0.68), $CF_3NBr_2$ (0.55), $CF_3NCl_2$ (0.18) |
| 1.0 | $Br_2$ (7.0) | CsF (7.0) | 12 h | $CF_3NBrCl$ (0.22), $CF_3NBr_2$ (0.30), $CF_3NCl_2$ (?) |
| 2.0 | $Br_2$ (1.7) | CsF (8.5) | 11 h | $CF_3NBrCl$ (0.43), $CF_3NCl_2$ + $CF_2{=}NCl$ (1.2) |
| 2.0 | $Br_2$ (2.0) | CsF (20) | 12 h | $CF_3NClBr$ (0.78), $CF_3NCl_2$ (0.45) |
| 4.2 | $Br_2$ (10) | CsF (10) | 3 d | $CF_2NClBr$ (.49), $CF_3NBr_2$ (2.2), $CF_3NCl_2$ (.31) |
| 4.5 | $Br_2$ (10) | KF (10) | 2 d | $CF_3NClBr$ (.78), $CF_3NBr_2$ (2.4), $CF_3NCl_2$ (0.4) |
| 3.0 | $Br_2$ (3.0) | NaF (10) | 2 d | no reactn |
| 2.8 | $CF_2{=}NF$ (3.6) | CsF (13) | 3.5 h | $CF_3\overline{NCF_2N}Cl$ (0.8), $CF_3NClF$, $CF_3NCl_2$, $CF_3\overline{NCF_2N}F$ |

[a] Amounts in mmol. Reactions carried out in the absence of light. [b] Some $CF_2{=}NCl$ absorbed by MF. [c] d = days

then held at 10 °C for 2 h with stirring. The reactor was then cooled to −196 °C and a small amount of $N_2$ was removed. The vessel was then pumped on through traps at −78, −110, and −196 °C as it warmed in the air. The −78 °C trap collected $CF_3CO_2H$, the −196 °C trap contained unreacted starting material, and the −110 °C trap contained a mixture of the N–Cl and N–H diaziridines. This was reseparated by passing it through −100 and −196 °C traps to yield 0.48 mmol of $CF_3\overline{NCF_2N}H$ in the −100 °C trap: IR 3319 (m), 1517 (w), 1452 (vs), 1371 (w), 1327 (vs), 1269 (vs), 1231 (vs), 1177 (s), 1086 (s), 1040 (s), 934 (s), 825 (w), 739 (w), 681 (m), 520 (w) $cm^{-1}$; NMR $CF_3^{M}NCF^{A}F^{B}N^{X}H$ M −65.5 (dd), A −119.2 (m), B −98.0 (m), X ($Me_4Si$), 4.2 (br s, $J_{AM} = 14.0$, $J_{BM} = 3.5$, $J_{AB} = 46.0$, $J_{AX} = 14$, $J_{MX} \simeq J_{BX} \simeq 0$ Hz); major $m/z$ [CI] 149 ($MH^+$), 129 ($M - F^+$); [EI] 128 ($M - HF^+$), 109 ($C_2F_3N_2^+$), 69 ($CF_3^+$).

## Results and Discussion

**Reaction of $CF_2{=}NCl$ with $FSO_2OX$ (X = Cl, Br).** The addition of electrophilic halogen compounds to halogenated substrates containing carbon–nitrogen multiple bonds is now a well established reaction. Most examples involve reaction of ClF, where the formal positive chlorine always adds to the nitrogen, e.g.,[15]

$$ClCN + 2ClF \rightarrow ClCF_2NCl_2$$

$$CF_3CN + 2ClF \rightarrow CF_3CF_2NCl_2$$

$$CF_2{=}NCl + ClF \rightarrow CF_3NCl_2$$

$$CF_2{=}NF + ClF \rightarrow CF_3NClF$$

With $CF_2{=}NF$, we found that $FSO_2OX$ (X = Cl, Br, $OSO_2F$) underwent a similar facile addition, and in the case of X = Br, gave the first example of an $-NBrF$ derivative in $FSO_2OCF_2NBrF$.[7] We therefore undertook a study of the reactions of $FSO_2OX$ (X = Cl, Br) with $CF_2{=}NCl$ in hope of isolating $FSO_2OCF_2NBrCl$, as the first example of an $-NBrCl$ derivative.

Both $FSO_2OCl$ and $FSO_2OBr$ react readily with $CF_2{=}NCl$ at 22 °C. Unlike $CF_2{=}NF$, however, the expected addition product is not isolated. Instead, both reactions give a moderate yield of the diazene $FSO_2OCF_2N{=}NCF_2OSO_2F$. Since both $-NCl_2$[11] and $-NClBr$[8] derivatives are known to decompose both thermally and photolytically to diazenes, these reactions can be rationalized as follows.

$$FSO_2OX + CF_2{=}NCl \rightarrow \text{“}FSO_2OCF_2NClX\text{”} \xrightarrow{-XCl} FSO_2OCF_2N{=}NCF_2OSO_2F$$

$$X = Cl, Br$$

However, it is surprising that an $-NCl_2$ derivative would undergo this reaction so readily, based on the usual properties of such compounds. Either the fluorosulfate group has a pronounced effect on the N–X bond, or the reaction path leading to the observed diazene does not involve the sample addition of $FSO_2OX$ to the C=N bond as indicated above.

Attempts to extend this reaction by the use of $CF_3SO_2OCl$ were unsuccessful. Instead of the anticipated addition product or the diazene $(CF_3SO_2OCF_2N{=})_2$, the slow reaction below 0 °C resulted in the formation of large amounts of $CF_3Cl$, $Cl_2$, and polymeric products. This result was unexpected because $FSO_2OCl$ and $CF_3SO_2OCl$ often lead to analogous products in addition to unsaturated compounds such as olefins and $SF_4$.[15,16] However, if a radical species containing the $CF_3SO_3$ group is formed in the initial reaction or in the subsequent decomposition of an intermediate, the rapid loss of $CF_3$ from this radical can be expected to lead to $CF_3Cl$ and other products. This presumption is based on the apparent general instability of free-radicals of the type $CF_3SO_2M$. This the photolysis or thermal decomposition of compounds such as $RSO_2OCl$, $(RSO_2)_2NCl$, $(RSO_2O)_2$, and $(RSO_2O)_2Xe$, where R = $CF_3$ or F, does not lead to analogous products. For example, photolysis of $(RSO_2)_2NCl$ gives $(FSO_2)_2N{-}N(SO_2F)_2$ and $Cl_2$ for R = F and $O_2SNSO_2CF_3$ and $CF_3Cl$ for R = $CF_3$.[17]

**Fluoride Promoted Reactions of $CF_2{=}NCl$.** Reactions of $CF_2{=}NCl$ in the presence of fluoride ion from KF or CsF provide ample evidence for the formation of the *N*-chlorotrifluoromethanamine ion, $CF_3NCl^-$. This anion is apparently less stable than $CF_3NF^-$, formed analogously from $CF_2{=}NF$.[6,7,18] As shown in Table I, the reaction of $CF_2{=}NCl$ with CsF alone leads to $CF_3NCl_2$[19] as the only volatile product. This clearly results from a decomposition of the anion forming either $Cl_2$ or ClF, which then reacts with $CF_3NCl^-$ or $CF_2{=}NCl$ to form the observed $CF_3NCl_2$.

$$CF_2{=}NCl + F^- \xrightarrow{CsF} CF_3NCl^- \rightarrow ? + Cl_2 \text{ or } ClF$$

$$CF_3NCl^- + Cl_2 \xrightarrow{CsF} CF_3NCl_2 + Cl^-$$

$$CF_3NCl^- + ClF \xrightarrow{CsF} CF_3NCl_2 + F^-$$

$$CF_2{=}NCl + ClF \rightarrow CF_3NCl_2$$

The decomposition product resulting in the $Cl_2$ and/or ClF has not been identified. On a larger scale the CsF becomes tacky, indicating the possible formation of a polymeric material.

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When a mixture of $CF_2{=}NCl$ and $Cl_2$ is allowed to react in the presence of CsF the intermediate $CF_3NCl^-$ anion is rapidly oxidized to give a much improved yield of $CF_3NCl_2$. At 55 °C the yield is improved to 75%, although it is now clear that this yield will depend on the amount of $Cl_2$ and CsF used. It was also found that BrCl was even more effective than $Cl_2$ in this oxidation. As shown in Table I, a nearly quantitative conversion was found.

$$CF_3NCl^- + BrCl \xrightarrow{CsF} CF_3NCl_2 + Br^-$$

It appears that this reaction actually proceeds via the initial formation of $CF_3NBrCl$ as shown in the following equation.

$$\begin{tikzcd} CF_3NCl^- + BrCl \arrow[r, "CsF"] & CF_3NBrCl + Cl^- \arrow[d, "BrCl"] \\ & CF_3NCl_2 + Br_2 \end{tikzcd}$$

This is based on the fact that the Br in BrCl should be the electrophile and that in separate reactions of $CF_3NBrCl$ with excess BrCl in the absence of CsF, $CF_3NCl_2$ is formed in quantitative yield (see next section).

The use of $Br_2$ to oxidize the $CF_3NCl^-$ anion leads to good yields of $CF_3NClBr$, along with the formation of $CF_3NCl_2$ and $CF_3NBr_2$. As shown in Table I, the relative yields depend strongly on the relative amounts of $Br_2$ and CsF employed. Sodium fluoride is ineffective in this reaction, because the NaF is too weak a fluoride base to generate the $CF_3NCl^-$ anion from $CF_2{=}NCl$. On the other hand, KF is as effective as CsF. The formation of both $CF_3NCl_2$ and $CF_3NBr_2$ depend on the formation of BrCl and on the fluoride catalyzed conversion of $CF_3NClBr$ to $CF_3NBr_2$ by $Br_2$ (see following section).

$$CF_3NCl^- + Br_2 \xrightarrow{CsF} CF_3NClBr + Br^-$$

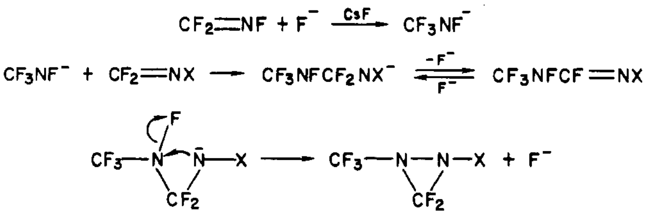
$$CF_3NClBr + Br_2 \xrightarrow{CsF} CF_3NBr_2 + BrCl$$

$$CF_3NBr_2 \xrightarrow{BrCl} CF_3BrCl \xrightarrow{BrCl} CF_3NCl_2$$

A large excess of $Br_2$ clearly increases the yield of $CF_3NBr_2$ and decreases the amount of $CF_3NClBr$ and $CF_3NCl_2$.

Attempts to use $CF_3NCl^-$ as a nucleophile in nucleophilic substitution reactions were unsuccessful. Reactions of $CF_2{=}NCl$ with $R_fC(O)F$ in the presence of CsF, which were successful with $CF_3NF^-$ anion,[6] led to the $CF_3NCl_2$ and unreacted $R_fC(O)F$. This may mean that $CF_3NCl^-$ is considerably less nucleophilic than $CF_3NF^-$, but it may also only serve to indicate that the rate of decomposition of $CF_3NCl^-$ is faster than the intended nucleophilic substitution on $R_fC(O)F$.

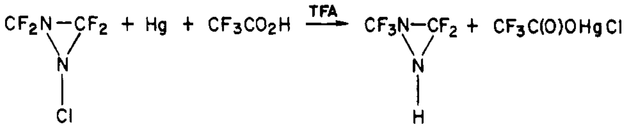
A competitive reaction involving $CF_2{=}NF$ and $CF_2{=}NCl$ indicates that $CF_3NF^-$ is formed preferentially to $CF_3NCl^-$, and the former is then sufficiently reactive to attack $CF_2{=}NCl$. The observed products are then easily explained based on the known chemistry of $CF_2{=}NF$.[6]



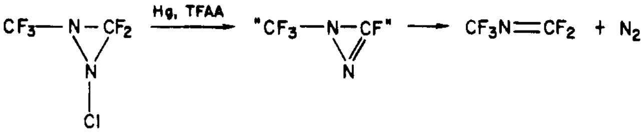
X = F, Cl

The intermediate formamidine $CF_3NFCF{=}NX$ was readily isolated in the case of X = F, but we could not isolate $CF_3NFCF{=}NCl$, presumably because of different reaction rates for the formation and cyclization of formamidine when X = F vs. X = Cl.

The conversion of 1-chloro-2-(trifluoromethyl)-3,3-difluorodiaziridine to the 1-hydro derivative was accomplished in low yield by reaction with Hg in trifluoroacetic acid (TFA).



This reaction is analogous to the conversion of $R_fNClF$ to $R_fNHF$ in the same manner.[10] In the latter reaction, substitution of trifluoroacetic anhydride (TFAA) for the acid gives excellent yields of the *N*-fluoroimines $R_f'CF{=}NF$. However, the same reaction with the 1-chlorodiaziridine gave $CF_3N{=}CF_2$ and $N_2$ as the major products, suggesting that the intermediate 2-diazirine, if formed, is unstable under the reaction conditions.



**Fluoride-Catalyzed Reactions of $R_fNClX$ (X = Cl, Br) with $Br_2$.** The formation of $CF_3NBr_2$ in the reaction $CF_2{=}NCl$ with $Br_2$ in the presence of CsF, indicated that an N–Cl bond in $CF_3NClBr$ was converted to an N–Br bond by an unknown reaction type. At first BrCl was assumed to be responsible, but as shown in the following equation this was clearly not the case.

$$CF_3NCl_2 + Br_2 \leftarrow CF_3NClBr + BrCl \nrightarrow CF_3NBr_2 + Cl_2$$

It was soon evident that the metal fluoride was directly involved in the reaction and surves as a catalyst for this conversion. The way in which the metal fluoride functions as a catalyst or promoter of this reaction is still unknown. The data in Table II clearly establish that alkali metal fluorides are effective and other materials such as $CaF_2$ and activated charcoal are not. As we have disucssed in a preliminary communication, a polyhalide anion may be involved.[8] The data in Table II may be summarized by the following reaction scheme.

$$CF_3NCl_2 \underset{BrCl}{\overset{Br_2,\ MF}{\rightleftharpoons}} CF_3NClBr \underset{BrCl}{\overset{Br_2,\ MF}{\rightleftharpoons}} CF_3NBr_2$$

Depending on the starting material, $CF_3NCl_2$ or $CF_3NBrCl$, the relative amount of BrCl is greater for $CF_3NCl_2$ and this decreases the amount of $CF_3NBr_2$ formed. Previously, we reported that only CsF leads to the formation of $CF_3NBr_2$.[8] This is clearly not the case if one starts with $CF_3NBrCl$, where both NaF and KF also yield $CF_3NBr_2$. The different results starting with $CF_3NCl_2$ can be explained by proposing that a larger amount of free BrCl is present in the case of KF or NaF. The very active CsF used in this work readily absorbs $Br_2$ and probably BrCl, whereas the absorption of $Br_2$ by KF is much less, and almost negligible by NaF.

The fluoride-promoted conversion of N–Cl bonds to N–Br bonds by $Br_2$ is a general reaction and has been extended to several other $NCl_2$ derivatives. Starting with $R_fCN$ and ClF, this method should allow the preparation of a variety of NClBr and $NBr_2$ derivatives.

$$R_fC{\equiv}N + 2ClF \rightarrow R_fCF_2NCl_2 \xrightarrow{MF,\ Br_2} R_fCF_2NBrCl \xrightarrow{MF,\ Br_2} R_fCF_2NBr_2$$

**Table II. Fluoride Promoted Reactions of $R_fNClX$ (X = Cl, Br)[a]**

| $R_fNClX$[a] | reactant | MF | time, 22 °C[a] | products |
|---|---|---|---|---|
| $CF_3NCl_2$ (0.5) | $Br_2$ (5.0) | | 2 d | no reactn[b] |
| $CF_3NCl_2$ (0.5) | BrCl (0.5) | | 2 d | no reactn[b] |
| $CF_3NClBr$ (0.7) | $Br_2$ (1.4) | | 12 h | no reactn[b] |
| $CF_3NClBr$ (0.7) | BrCl (2.8) | | 12 h | $CF_3NCl_2$ (0.7) |
| $CF_3NCl_2$ (1.0) | $Br_2$ (10) | CsF (10) | 42 h | $CF_3NClBr$ (0.2), $CF_3NBr_2$ (0.3)[b] |
| $CF_3NCl_2$ (1.0) | $Br_2$ (10) | CsF (20) | 40 h | $CF_3NClBr$ (0.3), $CF_3NBr_2$ (0.1)[b] |
| $CF_3NCl_2$ (1.0) | $Br_2$ (10) | KF (10) | 40 h | $CF_3NClBr$ (0.4), $CF_3NBr_2$ (trace)[b] |
| $CF_3NCl_2$ (1.0) | $Br_2$ (10) | NaF (10) | 40 h | $CF_3NClBr$ (0.5)[b] |
| $CF_3NCl_2$ (1.0) | $Br_2$ (10) | LiF (10) | 40 h | $CF_3NClBr$ (0.2)[b] |
| $CF_3NCl_2$ (1.0) | $Br_2$ (10) | $CaF_2$ (10) | 40 h | no reactn[b] |
| $CF_3NCl_2$ (1.1) | $Br_2$ (10) | Charcoal (0.5g) | 2 d | $CF_3NCl_2$, other |
| $CF_3NClBr$ (1.0) | $Br_2$ (10) | NaF (15) | 2 d | $CF_3NBrCl$ (0.28), $CF_3NBr_2$ (0.13), $CF_3NCl_2$ (0.15) |
| $CF_3NClBr$ (1.1) | $Br_2$ (10) | KF (10) | 2 d | $CF_3NBrCl$ (0.39), $CF_3NBr_2$ (0.35), $CF_3NCl_2$ (0.24) |
| $CF_3NClBr$ (0.6) | $Br_2$ (10) | CsF (10) | 12 h | $CF_3NBr_2$ (0.5), $CF_3NBrCl$, $CF_3NCl_2$ |
| $CF_3NClBr$ (0.5) | $Br_2$ (1.0) | CsF (20) | 12 h | $CF_3NBr_2$ (0.1), $CF_3NClBr$ (0.3), $CF_3NCl_2$ (0.1) |
| $C_2F_5NCl_2$ (1.0) | $Br_2$ (10) | CsF (10) | 40 h | $C_2F_5NClBr$ (0.4), $C_2F_5NBr_2$ (0.2)[b,c] |
| $C_3F_7NCl_2$ (1.7) | $Br_2$ (11) | CsF (10) | 40 h | $C_3F_7NBrCl$ + $C_3F_7NBr_2$ (0.7)[b,d] |

[a] Amounts in mmol. All reactions carried out in the absence of light. d = days. [b] Recovered starting $-NCl_2$. [c] $C_2F_5NBr_2$ identified by $^{19}F$ NMR and mass spectrum. See ref 20. [d] $C_3F_7NBr_2$ identified only by mass spectrum with intense $M^+$ in both EI and CI. See discussion.

Table II shows data for $CF_3CF_2NCl_2$ and $CF_3CF_2CF_2NCl_2$. In both cases, some of the respective $NBr_2$ derivatives were also formed, but the latter could not be readily isolated as pure compounds from the $BrCH_2CH_2Br$ formed on removal of excess $Br_2$ by treatment with ethylene. *N,N*-dibromoperfluoropropanamine was identified only by its mass spectrum and $CF_3CF_2NBr_2$ by its mass spectrum and $^{19}F$ NMR. The latter agreed with a published NMR spectrum.[20]

**Characterization of New Compounds.** The data given in the experimental section provides excellent support for the indicated structures. No direct spectroscopic evidence for the N–N double bond in $FSO_2OCF_2N{=}NCF_2OSO_2F$ is given, but the mass spectrum clearly identifies the presence of two nitrogens in the molecule. For $CF_3\overline{NCF_2N}X_2$ (X = Cl, H), the ring structure is clearly evident by comparison of the IR and NMR with $CF_3\overline{NCF_2N}F$.[6] Both diaziridines appear to be present in only one isomeric form as an enantiomeric pair of either the cis or trans diastereomers. On steric grounds the favored isomer should be trans, but our data do not allow an assignment to be made. However, the isomers are probably the same as $CF_3\overline{NCF_2N}F$, which can be reasonably assigned as trans based on the magnitudes of the $CF_3$–NF $^4J_{FF}$ coupling.[6] The syntheses of $CF_3NBrCl$ and $CF_3NBr_2$ complete the series $CF_3NXX'$ (X, X′ = F, Cl, Br). No *N*-iodo derivatives have been reported and we have thus far been unable to extend our reactions to iodine. The new compounds exhibit surprisingly high thermal stability, with $CF_3NBr_2$ (g, 100 torr) stable to at least 100 °C in glass. At near 140 °C, $CF_3NBr_2$ undergoes extensive decompostion to $CF_3N{=}NCF_3$ and $Br_2$. On the other hand, pure $CF_3NBrCl$ (g, 100 torr) was stable to 160 °C, but suddenly decomposed to $CF_3N{=}NCF_3$ and other products at ~175 °C. The stability of $CF_3NBrCl$ is strongly influenced by impurities (presumably $Br_2$) and impure samples were observed to slowly form $CF_3NBr_2$ and $CF_3NCl_2$ at 50 °C.

Both $CF_3NBrCl$ and $CF_3NBr_2$ are yellow gases and are very sensitive to Pyrex filtered sunlight, forming the diazene $CF_3N{=}NCF_3$[21] in high yield.

$$2CF_3NBrX \xrightarrow{h\nu} CF_3N{=}NCF_3 + 2XBr$$
$$X = Cl, Br$$

**Table III. Some Properties of $CF_3NXX'$**

| $CF_3NX_2$ | $\delta$ $CF_3$ ($CFCl_3$) | NX, $cm^{-1}$ |
|---|---|---|
| $CF_3NF_2$[22] | -84.1 | 1018, 951[a] |
| $CF_3NFCl$[19] | -79.3[b] | 951, 752[a] |
| $CF_3NFBr$[7] | -77.6 | 934, 731[b] |
| $CF_3NCl_2$[11] | -74.1[b] | 812, 708[b] |
| $CF_3NClBr$ | -72.3[b] | 787, 688[b] |
| $CF_3NBr_2$ | -70.5[b] | 758, 675[b] |

[a] Assignments taken from Schack, C. J.; Christe, K. O. *Inorg. Chem.* **1983**, *22*, 22. [b] This work.

This is in contrast to all other members of the $CF_3NXX'$ series, which are essentially stable to photolysis under the same conditions. In Table III, some comparative data for $CF_3NXX'$ are shown. The trends in Table III are remarkably regular. A simple plot of the $CF_3$ chemical shift vs. the sum of the Pauling electronegativities of X is essentially linear. In $CF_3NClBr$, the two N–X stretches must be strongly coupled, otherwise it is hard to understand why the $\nu$ (NCl) stretch would be higher than the average of the symmetric and assymmetric $\nu$ (NCl) stretches in $CF_3NCl_2$, and $\nu$ (NBr) lower than the same average in $CF_3NBr_2$.

Finally, the NMR for $CF_3CF_2NClBr$ and $CF_3CF_2CF_2NClBr$ are rather surprising. All known perhalogenated derivatives of the type $RCF_2NFX$ (X = Cl, Br, $FSO_3$ and R = $R_x$, Cl, $FSO_3$) exhibit pronounced second-order AB spectra for the methylene fluorines,[4,6,23] due to the high inversion barrier and resultant chiral nitrogen. In contrast, $CF_3CF_2NBrCl$ and $CF_3CF_2CF_2NBrCl$ exhibit apparent first-order NMR spectra. These observations leave only two possibilities concerning the inversion at nitrogen; the substitution of a fluorine atom on nitrogen by either chlorine or bromine lowers the inversion varrier, so that inversion is rapid on the NMR time scale at 22 °C, or the inversion is slow on the NMR time scale, but the diastereotopic $\alpha$-methylene fluorine atoms have identical or nearly identical chemical shifts leading to a very large $J/\Delta$ and the apparent first-order spectra.[24]

Recent work on inversion barriers of acylic nitrogen compounds indicates that two electronegative substituents on nitrogen are required to have an inversion barrier of

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(24) See: Corio, P. L. "Structure of High-Resolution NMR Spectra"; Academic Press: New York, 1966.

~23 kcal/mol and thus configuration stability at 22 °C.[25] These authors claim a lower limit of ~7.1 for the sum of the electronegativities of $CH_3O$ and X in $MeCO_2CH_2(CH_3)_2CN(X)OMe$. The related series, $CF_3N(F)CF_2CF_3$,[22] $ClCF_2CF_2N(Cl)CF_3$,[26] $CF_3CF_2NFCl$,[23] $CF_3CF_2NFBr$,[7] and $FSO_2OCF_2N(F)OSO_2F$,[7] provides an interesting comparison in this regard. If the contribution of the alkyl groups $C_2F_5$, $ClCF_2CF_2$, and $FSO_2OCF_2$ are all similar, the sum of the electronegativities of the other two substituents on nitrogen can be compared. Since the electronegativity of the $CF_3$ group is near 3.3 on the Pauling scale,[27] and that of $FSO_2O$ is close to 3.8,[16c] the sums for the aforementioned five compounds are 7.3, 6.5, 7.2, 7.0, and 7.8, respectively, but only the last three compounds exhibit configuration stability at 22 °C. Clearly, the prediction of inversion barriers on the basis of the electronegativities of the substituents on nitrogen is only a very approximate guide.

In the near future, we hope to prepare $ClCF_2CF_2N(X)OCF_3$ (X = F, Cl). These two compounds would provide interesting insight into the effect of electronegativities on inversion barriers in acyclic nitrogen compounds. The $CF_3O$ group has a value of at least 3.8.[28]

**Acknowledgment.** The financial support of this research by the U.S. Army Research Office (Contract No. DAAG29-82-K-0188 and DAAG29-83-K6173) and the National Science Foundation (CHE-8217217) is gratefully acknowledged.

**Registry No.** $CF_2{=}NCl$, 28245-33-2; $CF_3NCl_2$, 13880-73-4; $CF_3NClBr$, 88453-17-2; $C_2F_5NCl_2$, 677-66-7; $C_3F_7NCl_2$, 662-54-4; $FSO_2OCl$, 13997-90-5; $FSO_2OBr$, 13997-93-8; $Cl_2$, 7782-50-5; $Br_2$, 7726-95-6; BrCl, 13863-41-7; $CF_2{=}NF$, 338-66-9; CsF, 13400-13-0; KF, 7789-23-3; NaF, 7681-49-4; LiF, 7789-24-4; $C_3F_7NBrCl$, 91523-61-4; $C_2F_5NBr_2$, 83696-32-6; $C_2F_5NClBr$, 91523-62-5; $CF_3NBr_2$, 88453-18-3; $CF_3\overline{NCF_2N}Cl$, 91523-63-6; $CF_3\overline{NCF_2N}H$, 91523-64-7.

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# Synthesis and Highly Regioselective Diels–Alder Reaction of Functionalized Isoprenes Involving a Terminal Alkoxy Group and Chemical Modification of the Resulting Adducts

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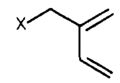
A variety of functionalized isoprenes involving a terminal alkoxy group (**2** and **3**) were newly synthesized according to eq 1, 2, and 3. These compounds proved to undergo a cycloaddition with various unsymmetric dienophiles highly regioselectively without a Lewis acid catalyst. Moreover, the resulting adducts **11** were transformed to cyclohexadienes **12** through elimination of an alcohol.

The Diels–Alder reaction provides powerful synthetic tools for constructing six-membered rings. It should be noticed, however, that the reaction must proceed regioselectively when unsymmetric dienes and dienophiles are employed. As for butadiene derivatives, this restriction seems to be almost removed through the extensive studies by both Danishefsky[1] and Overman.[2] On the other hand, there still remains the problem of regioselectivity unresolved in the case of isoprene derivatives, whose Diels–Alder reaction with various dienophiles should afford the most promising synthetic method for cyclic terpenoids.[3] For the synthetic purpose, appropriate functionalization of the isoprene unit is also desirable. Accordingly, it seems of great interest to develop a new method for functionalized isoprenes suitable for the regioselective Diels–Alder reaction.



**1a**, X = Cl
**b**, X = Br
**c**, X = OH
**d**, X = $Me_3Si$
**e**, X = $Me_3Sn$

So far, only a few studies have been made on the preparation of functionalized isoprenes. For example, 2-(halomethyl)-1,3-butadienes, **1a** and **1b**, have been obtained in ca. 10% yield by thermolysis of halides of the isoprene/$SO_2$ adduct[4,5] and the bromomethyl compound has been converted into the hydroxymethyl derivative **1c**.[6] We have developed a new method for compounds **1a** and **1c** employing 2-(hydroxymethyl)-4-(phenythio)-1-butene.[7] More recently, the trimethylsilyl and trimethylstannyl derivatives **1d** and **1e** have been reported.[8] However, the Diels–Alder reaction of these dienes with unsymmetric dienophiles, in general, resulted in unsatisfactory regioselectivity, though **1d** and **1e** gave rise to improvement of

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