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Synthesis of 1,1-Difluoro-2-azaperhalo-1-butenes and Their Conversion to Oxaziridines[1]

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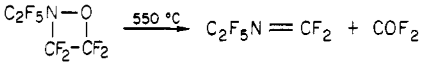
At elevated temperatures, *N*-chlorodifluoromethanimine ($CF_2{=}NCl$) adds to perhaloalkenes of the type $CF_2{=}CFX$, forming $CF_2{=}NCF_2CFXCl$ (X = F, Cl, Br) in good yields. Reaction of these butenes with trifluoromethyl hydroperoxide (CF_3OOH) gives $CF_3OOCF_2NHCF_2CFXCl$, and subsequent treatment with KHF_2 forms the corresponding oxaziridine, $\overline{OCF_2N}CF_2CFXCl$, in excellent yield. Eight new compounds, along with the previously reported $CF_2{=}NCF_2CF_2Cl$, were characterized by their IR, NMR, and mass spectra and physical properties.

The synthesis of 1,1-difluoro-2-azaperhalo-1-alkenes or *N*-(perhaloalkyl)difluoromethanimines of the type $CF_2{=}NR_x$ is very difficult, and only a few such compounds are known. Examples have, in general, been prepared by pyrolysis of perfluoro tertiary amines and by the pyrolysis of perfluoro-2-alkyl-1,2-oxazetidines or the corresponding copolymer formed from R_fNO and $CF_2{=}CF_2$[3] (eq 1–3). In the case of perfluoro-2-azapropene, more practical methods of synthesis have been developed by utilizing $(CF_3)_2NC(O)F$, available from electrochemical fluorination of $(CH_3)_2NC(O)F$,[4] or $Cl_3CN{=}CCl_2$ from high-temperature chlorination of $(CH_3)_2NC(O)Cl$[5] (eq 4–7).

$$(C_2F_5)_3N \xrightarrow{750\ °C} C_2F_5N{=}CF_2 + \text{fluorocarbons} \tag{1}$$



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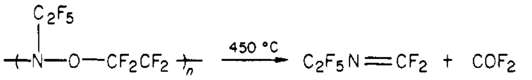


$$-\!\left[\overset{\overset{C_2F_5}{|}}{N}-O-CF_2CF_2\right]_n\!- \xrightarrow{450\ °C} C_2F_5N{=}CF_2 + COF_2 \tag{3}$$

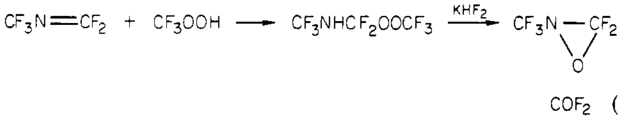
$$(CF_3)_2NC(O)F \xrightarrow{575\ °C} CF_3N{=}CF_2 + COF_2 \tag{4}$$

$$(CH_3)_2NC(O)Cl \xrightarrow[120 °C]{Cl_2,\ h\nu} \xrightarrow[200\ °C]{Cl_2,\ \text{carbon}} Cl_3CN{=}CCl_2 + COCl_2 + HCl \tag{5}$$

$$Cl_3CN{=}CCl_2 \xrightarrow[185\ °C]{HF} (CF_3)_2NH \xrightarrow{MF} CF_3N{=}CF_2 \tag{6}$$

$$Cl_3CN{=}CCl_2 \xrightarrow[150\ °C]{\text{NaF, sulfolane}} CF_3N{=}CF_2 \tag{7}$$

Our interest in perhalogenated azaalkenes relates in part to the fascinating chemistry of $CF_3\overline{NCF_2O}$,[6] which is prepared from $CF_3N{=}CF_2$[7] (eq 8). Extension of this reaction sequence to $SF_5N{=}CF_2$[8] suggested that a variety of $R_xN{=}CF_2$ azaalkenes might similarly lead to new oxaziridines. A patent on the use of $CF_2{=}NCl$ for the direct synthesis of $CF_2{=}NR_x$ compounds by thermal addition to olefins appeared to be a particularly promising route to new azaalkenes.[9] In this paper we present details for the synthesis of $CF_2{=}NCF_2CFXCl$ (X = F, Cl, Br) via the addition of $CF_2{=}NCl$ to $CF_2{=}CFX$. These azaalkenes are converted to the corresponding oxaziridines $ClXCFCF_2\overline{NCF_2O}$ in excellent yields via the intermediate amines $ClXCFCF_2NHCF_2OOCF_3$ formed by addition of CF_3OOH.



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Experimental Section

General Methods. All work was carried out in Pyrex or stainless steel (Types 304 and 316) vacuum systems equipped with glass–Teflon or stainless steel valves. Pressures were measured with a Wallace and Tiernan Series 1500 differential pressure gauge. Quantities of reactants and products were measured by direct weighing or by PVT measurements. Temperatures were measured by using a digital-indicating iron–constantan thermocouple.

Infrared spectra were taken on a Perkin-Elmer 337, 1330, 180, or 1430 spectrometer. A 10-cm glass cell fitted with AgCl or KCl windows was employed. NMR spectra were recorded on a Varian XL-100-15 spectrometer by using 80 mol % $CFCl_3$ as a solvent and an internal reference or on a JEOL FX-90Q spectrometer by using ~68 mol % CCl_4 as the solvent, ~30 mol % $CDCl_3$ as an internal lock, and ~1 mol % $CFCl_3$ as an internal reference. Proton chemical shifts were measured against external Me_4Si and are given in δ units (with the coupling constants given in hertz). Mass spectra were taken on Finnigan 4021-C or a Hewlett-Packard 5985B instrument at 70 eV for electron-impact (EI) and chemical-ionization [CI (CH_4)] spectra. Samples were introeduced by direct gas injection.

Melting points were determined by a modified Stock procedure. Vapor pressures as a function of temperature were determined by using a small isoteniscope.[10] Equations describing pressure as a function of temperature were obtained by a least-squares fit of the data to both linear and quadratic equations, and the best fit is reported.

For further purification of reaction products, GLC was carried out on a Victoreen Series 4000 gas chromatograph equipped for gas injection, TCD, and low-temperature collection. Columns of 10, 2, or 1 ft × 3/8 in. packed with 35% Halocarbon 11-21 polymer oil on acid-washed Chromosorb P were used.

Reagents. The olefins $CF_2{=}CFX$ (X = F, Cl, Br) were obtained from PCR, Inc., and Cl_2, F_2, KHF_2, and ClCN were obtained from commercial sources and appropriately purified before use. ClF was prepared by reaction of equimolar amounts of Cl_2 and F_2 in a Monel bomb at 250 °C. CF_3OOH was prepared by the litrature method.[11] $CF_2{=}NCl$ was prepared by a modification of the literature method.[12]

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To a 150-mL stainless steel reactor at −196 °C was added 30 mmol of $ClCN$ by vacuum transfer, followed by 60 mmol of ClF. The mixture was then allowed to warm slowly to 22 °C in a cold dewar container initially at −196 °C. After being allowed to stand at 22 °C for 20 h, the contents of the cylinder were separated through a −78 °C trap to collect $ClCF_2NCl_2$ (~85%). A 10-mmol sample of $ClCF_2NCl_2$ was then heated in a 100-mL Pyrex vessel for 5 h at 135 °C. The contents were then transferred onto 10 g of Hg and allowed to stand for 20 min at 22 °C. The volatiles were then separated through traps at −95, −125, and −196 °C. Pure $CF_2{=}NCl$ (85%) collected in the −125 °C trap.

Reactions of $CF_2{=}NCl$ with Olefins. Reactions were carried out in a 66-mL glass reaction vessel fitted with a glass–Teflon valve. In a typical reaction, $CF_2{=}NCl$ (8 mmol) and olefin (4–8 mmol) were condensed into the flask, and it was then heated for 8–12 h at 150–200 °C. The products were separated by pumping through traps held at appropriate temperatures. Pure samples of the perhalo-2-aza-1-butenes were obtained by reseparating the crude products by using trap-to-trap distillation or by GLC on a 10 ft × $^3/_8$ in. stainless steel column.

$CF_2{=}NCF_2CF_2Cl$: yield 40%; bp 31.9 °C; mol wt 198.0, calcd 199.5; $\log P$ (torr) = $7.489 - (1405.9/T)$; $\Delta H_{vap} = 6.43$ kcal/mol; $\Delta S_{vap} = 21.1$ eu; IR 1791 (s), 1740 (w), 1312 (s), 1288 (s), 1250 (s), 1204 (s), 1163 (s), 1113 (s), 999 (s), 916 (s), 819 (w), 779 (w), 714 (w) cm^{-1}; MS (CI, major), m/z 200/202 $[(MH)^+]$, 180/182 $[(M - F)^+]$: MS (EI), m/z 164 $[(M - Cl)^+]$, 114 $[(C_2F_4N)^+]$, 85/87 $[(CF_2Cl)^+]$; ^{19}F NMR ($F^AF^BC{=}NCF_2{}^CCF_2{}^DCl$) A = −45.3 (br d), B = −29.3 (br d), C = −95.0 (m), D = −73.9 (m), $J_{AB} = 83$, $J_{AC} = J_{BC} = 10.0$, $J_{AD} \simeq J_{BD} = 2.0$, $J_{CD} = 4.0$.

$CF_2{=}NCF_2CFCl_2$: yield, 48%; bp 64.9 °C; mol wt 214.0, calcd 215.95; $\log P$ (torr) = $7.828 - (1672.5/T)$; $\Delta H_{vap} = 7.65$ kcal/mol; $\Delta S_{vap} = 22.6$ eu; IR 1795 (s), 1741 (m), 1413 (w), 1312 (s), 1251 (s), 1204 (s), 1163 (s), 1107 (s), 1040 (m), 981 (m), 899 (s), 858 (s), 810 (s), 705 (w), 649 (w), 628 (w) cm^{-1}; MS (CI, major) m/z 216/218/220 $[(MH)^+]$, 196/198/200 $[(M - F)^+]$, 180/182 $[(M - Cl)^+]$; MS (EI), m/z 180/182 $[(M - Cl)^+]$, 151/153/155 $[(C_2F_3Cl_2)^+]$, 114 $[(C_2F_4N)^+]$, 101/103/105 $[(CFCl_2)^+]$; ^{19}F NMR ($F^AF^BC{=}NCF_2{}^CCF^DCl_2$) A = −45.5 (br d), B = −29.1 (br d), C = −92.3 (m), D = −75.7 (tt), $J_{AB} = 82$, $J_{CD} = 9.0$, J_{AC} or $J_{BC} = 11.5$, J_{AB} or $J_{BC} = 9.0$, $J_{AD} \simeq J_{BD} = 3.0$.

$CF_2{=}NCF_2CFBrCl$: yield 30%; bp 84.9 °C; mol wt 257.0, calcd 260.4; $\log P$ (torr) = $7.642 - (1704.8/T)$; $\Delta H_{vap} = 7.80$ kcal/mol; $\Delta S_{vap} = 21.8$ eu; IR 1785 (s), 1779 (s), 1573 (w), 1415 (w), 1305 (s), 1247 (s), 1199 (s), 1154 (s), 1100 (s), 1026 (m), 993 (m), 973 (m), 887 (s), 859 (s), 768 (s), 729 (m), 601 (w) cm^{-1}; MS (CI, major), m/z 260/262/264 $[(MH)^+]$, 240/242/244 $[(M - F)^+]$, 224/226 $[(M - Cl)^+]$, 195/197/199 $[(C_2F_3BrCl)^+]$, 116/118 $[(C_2F_3Cl)^+]$; MS (EI), m/z 180/182 $[(M - Br)^+]$, 114 $[(C_2F_4N)^+]$; ^{19}F NMR ($F^AF^BC{=}NCF_2{}^CCF^DBrCl$) A = −45.6 (br d), B = −31.1 (br d), C = −90.9 (m), D = −75.1 (tt), $J_{AB} = 89$, $J_{AC} = J_{BC} = J_{CD} = 11.0$, $J_{AD} = J_{BD} = 2.5$.

Reactions of $CF_2{=}NCF_2CFXCl$ with CF_3OOH. Reactions were carried out in a 100-mL glass bulb fitted with a glass–Teflon valve. In a typical reaction, the $CF_2{=}NCF_2CFXCl$ (3.0 mmol) and CF_3OOH (4.0 mmol) were condensed into the glass bulb at −196 °C. The vessel was then allowed to stand in an ice bath for 1 day. The reaction mixture was separated by pumping through traps at −50, −78, and −196 °C. Both the −78 and −196 °C traps contained some unreacted starting materials (CF_3OOH and $CF_2{=}NCF_2CFXCl$). Essentially pure $CF_3OOCF_2NHCF_2CFXCl$ was obtained by refractionation of the contents of the −50 °C trap by using the same procedure.

$CF_3OOCF_2NHCF_2CF_2Cl$: yield 76%; mol wt 300.1; calcd 301.5; IR 3455 (m), 1892 (w), 1774 (w), 1613 (w), 1510 (s), 1502 (s), 1424 (vw), 1327 (s), 1283 (s), 1095 (s), 1025 (vw), 972 (s), 875 (s), 837 (s), 793 (vw), 768 (vw), 740 (m), 718 (m), 669 (w), 646 (m), 633 (m) cm^{-1}; MS (CI, major), m/z 302/304 $[(MH)^+]$, 282/284 $[(M - F)^+]$, 266 $[(M - Cl)^+]$, 180/182 $[(C_3F_5NCl)^+]$, 160/162 $[(C_3F_4NCl)^+]$, 64 $[(CF_2N)^+]$; ^{19}F NMR ($CF_3{}^AOOCF_2{}^BN(H)\text{-}CF_2{}^CCF_2{}^DCl$) A = −68.6 (t), B = −68.0(m), C = −93.4 (qt), D = −73.6 (m), ^1H NMR $\delta_H = 5.0$ (br s), $J_{AB} = 4.0$, $J_{BH} = 4.0$, $J_{BC} = 9.4$, $J_{BD} = 1.4$, $J_{CH} = 9.4$, $J_{CD} = 3.0$, $J_{DH} \simeq 0$.

$CF_3OOCF_2NHCF_2CFCl_2$: yield 75%; mol wt 317.0, calcd 318.0; IR 3445 (m), 1493 (s), 1313 (s), 1273 (s), 1228 (s), 1208 (s), 1119 (s), 1095 (s), 904 (s), 815 (w), 710 (w), 610 (w) cm^{-1}; MS (CI, major), m/z 298/300/302 $[(M - F)^+]$, 216/218/220 $[(C_3F_5NCl_2H)^+]$, 196/198/200 $[(C_3F_4NCl_2)^+]$, 180/182 $[(C_3F_5NCl)^+]$, 136 $[(C_3F_4N)^+]$; ^{19}F NMR ($CF_3{}^AOOCF_2{}^BN(H)\text{-}CF_2{}^CCF^DCl_2$) A = −68.5 (t), B = −68.0 (m), C = −91.1 (m), D = −74.8 (t), ^1H NMR $\delta_H = 5.0$ (br s), $J_{AB} = J_{BH} = 3.7$, $J_{BC} = J_{CH} = 9.4$, $J_{CD} = 8.0$, $J_{DH} = J_{BD} = 1.0$.

$CF_3OOCF_2NHCF_2CFBrCl$: yield 86%; mol wt 368.8, calcd 362.4; IR 3441 (m), 1495 (s), 1418 (w), 1308 (s), 1278 (vs), 1235 (vs), 1206 (vs), 1122 (vs), 1114 (vs), 1014 (w), 861 (s), 808 (m), 772 (w), 731 (m), 615 (w) cm^{-1}; MS (CI, major), m/z 200–400, 362/364/366 $[(MH)^+]$, 342/344/346 $[(M - F)^+]$, 260/262/264 $[(C_3F_5NBrCl)^+]$, 240/242/244 $[(C_3F_4NBrCl)^+]$; ^{19}F NMR ($CF_3{}^AOOCF_2{}^BNHCF_2{}^CCF^DBrCl$) A = −68.5 (t), B = −68.0 (m), C = −90.0 (m), D = −74.1 (t), ^1H NMR $\delta_H = 5.0$ (br s), $J_{AB} \simeq J_{BH} = 4.3$, $J_{BC} = J_{CH} = J_{CD} = 10.3$, $J_{BH} \simeq J_{BD} \simeq 1.0$.

Reactions of $CF_3OOCF_2NHCF_2CFXCl$ with KHF_2. Reactions were carried out in a 75-mL stainless steel reactor. In a typical reaction, dried KHF_2 (~10 g) was placed in the reactor in a drybox. The vessel was then evacuated and cooled to −196 °C, and $CF_3OOCF_2NHCF_2CFXCl$ was added by vacuum transfer. The reactor was allowed to stand for 1 day at 22 °C, and the volatile products were then distilled through a series of cold traps, giving COF_2 and $ClXCFCF_2\overline{NCF_2O}$ as the major products. Pure samples of the oxaziridines were obtained by GLC.

$ClCF_2CF_2\overline{NCF_2O}$: yield 70%; bp 37.2 °C; mol wt 214.1, calcd 215.5; $\log P$ (torr) = $7.5081 - (1436.17/T)$; $\Delta H_{vap} = 6.57$ kcal/mol; $\Delta S_{vap} = 21.2$ eu; IR 1437 (s), 1316 (m), 1272 (s), 1249 (s), 1176 (s), 1118 (s), 1063 (m), 980 (s), 892 (m), 850 (m), 780 (m), 694 (w), 662 (w), 640 (w), 602 (m), 557 (w), 537 (w), 472 (w) cm^{-1}; MS (CI, major), m/z 150–300, 216/218 $[(MH)^+]$, 200/202 $[(MH - O)^+]$, 178/180 $[(C_3F_4ClNOH)^+]$, 180/182 $[(C_3F_5NCl)^+]$, 158/160 $[(C_3F_3ClNO)^+]$; 150/152 $[(C_2F_4ClNH)^+]$; ^{19}F NMR ($ClCF^AF^BCF^CF^D\overline{NCF^EF^FO}$; approximate values for C, D, and E taken from computer simulation; see discussion) A ≃ B = −71.8 (m), C = −109.4 (m), D = −104.1 (m), E = −105.2 (m), F = −89.5(m); $J_{AB} \simeq 1.0$, $J_{AC} \simeq J_{AD} \simeq 5.0$, $J_{AE} \simeq J_{AF} \simeq 0$, $J_{BC} = J_{BD} = 5.0$, $J_{BE} \simeq J_{BF} \simeq 0$, $J_{CD} = 190$, $J_{CE} = 40$, $J_{CF} \simeq J_{DF} \simeq 8.0$, $J_{DE} = 20$, $J_{EF} = 2.0$.

$Cl_2CFCF_2\overline{NCF_2O}$: yield 85%; bp 70.5 °C; mol wt 229.0, calcd 231.94; $\log P$ (torr) = $7.7775 - (1682.65/T)$; $\Delta H_{vap} = 7.69$ kcal/mol; $\Delta S_{vap} = 22.4$ eu; IR 1423(s), 1265 (s), 1159 (s), 1088 (s), 1061 (s), 1025 (m), 950 (m), 895 (s), 834 (s), 767 (s), 694 (m), 650 (m), 522 (w) cm^{-1}; MS, (CI, major), m/z 150–300, 232/234/236 $[(MH)^+]$, 216/218/220 $[(MH - O)^+]$, 212/214/216 (?), 196/198 $[(M - Cl)^+]$, 194/196/198 $[(MH - F_2)^+]$, 174/176/178 $[(C_3F_2Cl_2NO)^+]$, 178/180/182 $[(C_3F_3Cl_2NH)^+]$, 166/168/170 $[(C_2F_3Cl_2NH)^+]$, 158/160 $[(C_3F_3ClNO)^+]$, 150/152 $[(C_2F_4ClN)^+]$; ^{19}F NMR ($Cl_2CF^ACF^BF^C\overline{NCF^DF^EO}$; approximate values for B, C, and D taken from computer simulation) A = −89.2 (t), B = −106.6 (m), C = −100.3 (m), D = 104.7 (m), E = −74.2 (td), $J_{AB} = J_{AC} = 6.0$, $J_{AD} = J_{AE} \simeq 0$, $J_{BC} = 190$, $J_{BD} = 33$, $J_{BE} = J_{CE} = 8.0$, $J_{CD} = 22.0$, $J_{DE} = 3.0$.

$ClBrCFCF_2\overline{NCF_2O}$: yield 93%; bp 90.4 °C; mol wt 275.1, calcd 276.40; $\log P$ (torr) = $7.4681 - (1667.85/T)$; $\Delta H_{vap} = 7.63$ kcal/mol; $\Delta S_{vap} = 20.9$ eu; IR 1434 (s), 1271 (s), 1235 (m), 1193 (m), 1163 (m), 1096 (m), 1064 (m), 1024 (m), 948 (w), 864 (m), 834 (m), 812 (m), 764 (m), 693 (w), 646 (w) cm^{-1}; MS (CI, major), m/z 150–300, 276/278/280 $[(MH)^+$ weak], 260/262/264 $[(MH - O)^+]$, 238/240/242 $[(MH - F_2)^+]$, 218/220/222 $[(C_3F_2BrClNO)^+]$, 202/204 $[(C_3F_3BrNO)^+]$, 158/160 $[(C_3F_3ClNO)^+]$; ^{19}F NMR ($ClBrCF^ACF^BF^C\overline{NCF^DF^EO}$; mixture of diastereoisomers, approximate values of chemical shifts and coupling constants given by comparison with previous oxaziridine) A = −89 (m), B = −105 (m), C = −98 (m), D = −104 (m), E = −74 (m), $J_{BC} = 200$, $J_{BD} = 40$, $J_{CD} = 30$, and other coupling constants similar to $Cl_2CFCF_2\overline{NCF_2O}$ but not easily determined (see discussion).

Results and Discussion

2-Azaperhalo-1-butenes. The thermal addition of

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$CF_2{=}NCl$ to the olefins $CF_2{=}CFX$ (X = F, Cl, Br) proceeds readily in the temperature range 150–200 °C (eq 9).

$$CF_2{=}NCl + CF_2{=}CFX \rightarrow CF_2{=}NCF_2CFXCl \tag{9}$$

The yields of addition product depend on many factors including pressure, reaction time, temperature, stoichiometry, and the type of reaction vessel. The earlier report of a 75% yield for this reaction with $CF_2{=}CF_2$ in a 30-mL stainless steel vessel at 150 °C, employing a 1:1 stoichiometry, 4 h reaction time, and total initial pressure of ~11 atm,[9] gave only very low yields of the addition product in our hands. The major products were polymeric. We ultimately found that a Pyrex reaction vessel was more suitable. By trial and error, we found that a 2:1 ratio of imine to olefin, a temperature of 150 °C, an initial pressure of ~7 atm and a reaction time of 10 h gave acceptable yields with $CF_2{=}CFX$.

The conversion based on the amount of $CF_2{=}NCl$ consumed is 75–95%, but the yield of $CF_2{=}NCF_2CFXCl$ based on starting olefin is typically only 20–50%. The high recovery of unreacted $CF_2{=}NCl$ combined with the complete disappearance of the olefin, shows that a major side reaction involves the formation of oligomers, telomers, and higher molecular weight polymers of the olefin. These polymers have not been identified except for $CF_2{=}N(CF_2CFX)_2Cl$, which was identified by mass spectrometry. In all reactions, after removal of unreacted $CF_2{=}NCl$ and the adduct $CF_2{=}NCF_2CFXCl$, a low volatile residue remained in the reactor. This residue varied in appearance from a viscous oil to a gel, to a solid, or to a combination of these. In general, these residues were soluble in acetone.

Attempts to extend the reaction of $CF_2{=}NCl$ to hydrogen-containing olefins were not very successful. With $CF_2{=}CH_2$ and $CH_2{=}CH_2$, reaction under similar conditions gave a plethora of products including HCl and SiF_4 (from HF). Small amounts of $CF_2{=}NCF_2CH_2Cl$ were apparently formed with $CF_2{=}CH_2$, but no evidence for $CF_2{=}NCH_2CH_2Cl$ was found. In both cases the major products were polymeric, and these reactions were abandoned.

The addition of $CF_2{=}NCl$ to $CF_2{=}CFX$ is regiospecific and is probably a free-radical process as illustrated in Scheme I. The chain-transfer reaction leading to the 2-azaperhalo-1-butene clearly competes effectively with other processes. The polymers formed, while not characterized, are potentially very interesting because they could be readily converted to isocyanates and other products if they contain terminal $CF_2{=}N$ groups.

Scheme I

$$CF_2 = NCl \rightleftharpoons CF_2N\cdot + Cl\cdot$$

$$CF_2N\cdot + CF_2 = CFX \rightarrow CF_2{=}NCF_2CFX\cdot$$

$$CF_2{=}NCF_2CFX\cdot \xrightarrow{\text{olefin}} \text{polymer}$$

$$CF_2{=}NCF_2CFX\cdot + CF_2{=}NCl \rightarrow CF_2{=}NCF_2CFXCl + CF_2N\cdot$$

The identification of $CF_2{=}NCF_2CFXCl$ is straightforward based on the data given in the Experimental Section. Molecular ions are observed for each compound in the CI mass spectra, and each contains a strong absorption in the IR near 1800 cm^{-1} due to ν(C=N).[13] The ^{19}F NMR exhibit the expected AB pattern for the $CF_2{=}N$ group with J_{AB} near 85 Hz.[14] Assuming $^4J_{FF}$ to be larger than $^5J_{FF}$, the structural isomers are readily assigned for X = Cl and Br. Similar conclusions may be made from the chemical shift of the N–CF_2 group. For the alternative structural isomer $CF_2{=}NCFXCF_2Cl$, the chemical shift of the CF_2Cl group would be expected at considerably higher field than observed.[15]

Reaction of $CF_2{=}NCF_2CFXCl$ with CF_3OOH. The previously observed addition of CF_3OOH to $CF_2{=}NCF_3$[7] and $CF_2{=}NSF_5$[8] proceeds readily with $CF_2{=}NCF_2CFXCl$ under similar conditions (eq 10). The expected amines

$$CF_2{=}NCF_2CFXCl + CF_3OOH \rightarrow CF_3OOCF_2N(H)CF_2CFXCl \tag{10}$$

are isolated in very good yield. However, this is not a general reaction with all fluorinated imines; CF_3OOH will not add to $CF_2{=}NF$, $CF_2{=}NCl$, $NCCF{=}NF$, or $(CF_3)_2NCF{=}NCF_3$ under the same conditions. The addition of CF_3OOH to $CF_2{=}NCF_2CFXCl$ proceeds mainly in the condensed phase. It was previously found with $CF_2{=}NCF_3$ that the yields increased for a given reaction scale as the reactor volume decreased. In this work the rate of reaction of $CF_2{=}NCF_2CFXCl$ under identical conditions was the slowest for X = F. We attribute this to the lower boiling point of $CF_2{=}NCF_2CF_2Cl$, resulting in a larger fraction of the compound initially present in the gas phase. Consistent with this, the 0 °C reaction temperature also gave higher yields than reactions carried out at 22 °C. In addition, at 22 °C, some O_2 is formed from the decomposition of CF_3OOH.[16] This results in the formation of HF, which rapidly adds to $CF_2{=}NCF_2CFXCl$ to form CF_3NHCF_2CFXCl as a significant byproduct.[17]

The pure $CF_3OOCF_2NHCF_2CFXCl$ amines are apparently stable in glass at 22 °C. No detectable decomposition was observed in routine handling of the compounds in the vacuum system. The characterization of the compounds is given in the Experimental Section. Parent MH^+ molecular ions are observed in the CI mass spectrum for X = F and Br, and $(M - F)^+$ is observed for X = Cl. The IR and NMR spectra are consistent with that of $CF_3OOCF_2NHCF_3$,[7] and the extensive J_{F-F} and J_{H-F} couplings strongly support the structural formula indicated. Additional proof of the peroxide linkage is given by the fact that the compounds are strongly oxidizing toward aqueous KI.

Reaction of $CF_3OOCF_2NHCF_2CFXCl$ with KHF_2. The conversion of $CF_3OOCF_2NHCF_3$ to the novel oxaziridine $CF_3\overline{NCF_2O}$ was first accomplished by reaction of $CF_3OOCF_2NHCF_3$ with NaF.[7] Subsequently, a more detailed study of this reaction with a variety of metal fluorides indicated that the metal fluoride had to be effective in complexing HF and that the resultant oxaziridine was very easily isomerized by active fluorides to $CF_3NFC(O)F$.[18] For alkali metal fluorides which complex HF, the order of reactivity for ring opening and isomerization was NaF < KF < CsF. However, even NaF gave a significant yield of $CF_3NFC(O)F$ in the preparation of the oxaziridine. Potassium bifluoride, on the other hand, is effective in complexing HF but is of low fluoride ion ac-

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[13] In $CF_2{=}NX$ (X = Cl, F) ν (C=N) is at 1728 and 1740 cm^{-1}, respectively. Christen, D.; Oberhammer, H.; Hammaker, R. M.; Chang, S. C.; DesMarteau, D. D. *J. Am. Chem. Soc.* **1982**, *104*, 6186.

[14] These J_{AB} values in $CF_2{=}NX$ (X = Cl, F) are 69.0 and 52.6 Hz, respectively: Reference 12. Dybvig, D. H. *Inorg. Chem.* **1966**, *5*, 1795.

[15] This is based on a variety $R_fOCF_2CF_2Cl$, $R_fOCF_2CX_3$, and $R_fOCX_2CF_2Cl$ derivatives where R_f = CF_3O, CF_3SO_2, and $CF_3C(O)$. See for example: Johri, K. K.; DesMarteau, D. D. *J. Org. Chem.* **1983**, *48*, 242. Tari, I.; DesMarteau, D. D. *Ibid.* **1980**, *45*, 1214.

[16] CF_3OOH is stable in clean glass at 22 °C, but it is quite sensitive to the presence of certain impurities (see ref 11).

[17] Details on the preparation of these compounds will be reported separately.

[18] Sekiya, A.; DesMarteau, D. D. *Inorg. Chem.* **1979**, *18*, 919.

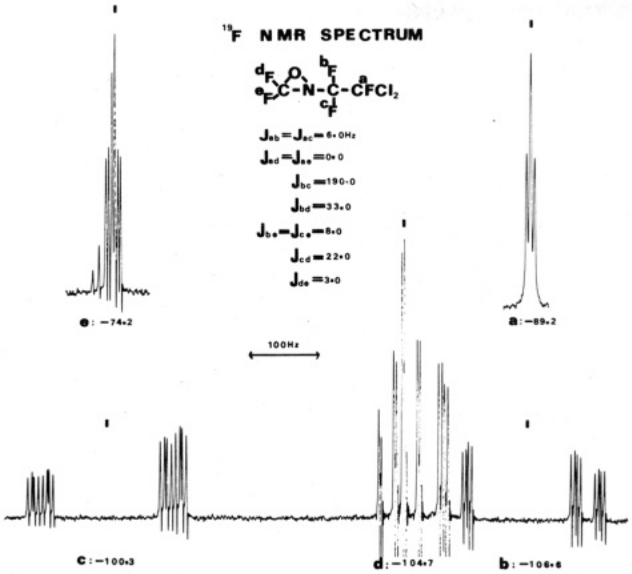
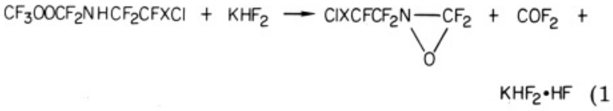


Figure 1. 94.1-MHz CW ^{19}F NMR (5 mm) of 15 mol % of $Cl_2CFCF_2\overline{NCF_2O}$ in $CFCl_3$.

tivity. Thus in the planned conversion of $CF_3OOCF_2NHCF_2CFXCl$ to the respective oxaziridines, KHF_2 was the reagent of choice.

The reaction of excess KHF_2 with $CF_3OOCF_2NHCF_2CFXCl$ at 22 °C gives excellent yields of the oxaziridines (eq 11). A minor byproduct in each



$$CF_3OOCF_2NHCF_2CFXCl + KHF_2 \rightarrow ClXCFCF_2\overline{NCF_2O} + COF_2 + KHF_2{\cdot}HF \quad (11)$$

case is $O{=}C{=}NCF_2CFXCl$, which presumably arises from hydrolysis of the oxaziridine by small amounts of H_2O in the KHF_2. The latter is difficult to dry thoroughly. The mechanism of this reaction remains obscure,[18] but the generality of the reaction is more clear with the five examples now demonstrated.

Like the previous examples of perhalogenated oxaziridines $CF_3\overline{NCF_2O}$[7] and $SF_5\overline{NCF_2O}$,[8] these new oxaziridines are thermally stable but highly reactive. Their characterization is given in the Experimental Section. Their IR spectra exhibit strong absorptions near 1430 cm^{-1}, as well as absorptions near 1060 and 950 cm^{-1}, which are characteristic of the oxaziridine ring.[8] The CI mass spectra exhibit parent $(MH)^+$ ions for each compound and a variety of other ions which are supportive of the parent compound. The ^{19}F NMR, while quite complex, provide the most definitive proof of structure.

The experimental spectrum for $Cl_2FCCF_2\overline{NCF_2O}$ is shown in Figure 1. The spectra are clearly of the type ABCMN, where the fluorines labeled b–d in Figure 1 constitute the ABC portion and fluorines a and e the MN portion. The high inversion barrier of the nitrogen is responsible for the magnetic nonequivalence of fluorines b,c and d,e. The large value of J_{bc} = 190 Hz is quite comparable to that found for acyclic nitrogen compounds of the type R_fCF_2NClF and R_fCF_2NBrF where R_f is a perfluoroalkyl group.[19] The very small value of J_{de} = 3.0 Hz is surprising but is similar to that in $CF_3\overline{NCF_2O}$, where the ring methylene fluorines exhibit an apparent simple first-order spectrum.[7] The spectrum with X = Cl in $\overline{OF_2CN}CF_2CFXCl$ could be readily simulated by application of LAOCOON 3,[20] and the stated coupling constants are taken from this simulation. For X = F and Br, the overall appearance of the spectra are similar to that for X = Cl, but they are more complex. In the case of X = F, a reasonable simulation could only be achieved by assuming the two CF_2Cl fluorines to be nonequivalent. For X = Br, the two chiral centers give rise to a mixture of diastereoisomers differing somewhat in the chemical shifts and J_{FF} values. For the latter two compounds, a detailed analysis of the spectra would require a major effort, and we did not attempt this.

Conclusion

The practical use of $CF_2{=}NCl$ to prepare a variety of 1,1-difluoro-2-azaperhalo-1-butenes by thermal addition to $CF_2{=}CFX$ (X = F, Cl, Br) olefins has been demonstrated. These azabutenes can be converted to novel oxaziridines by oxidation of the C=N double bond with CF_3OOH via the intermediate adducts $CF_3OOCF_2NHCF_2CFXCl$ followed by treatment with KHF_2. Both $CF_2{=}NCF_2CFXCl$ and $\overline{OF_2CN}CF_2CFXCl$ are useful reagents for the synthesis of a variety of novel fluorochemicals, and these results will be reported separately.

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Registry No. ClCN, 506-77-4; ClF, 7790-89-8; $ClCF_2NCl_2$, 28245-34-3; $CF_2{=}NCl$, 28245-33-2; $CF_2{=}NCF_2CF_2Cl$, 25688-36-2; $CF_2{=}NCF_2CFCl_2$, 87533-02-6; $CF_2{=}NCF_2CFBrCl$, 87533-03-7; CF_3OOH, 16156-36-8; $CF_3OOCF_2NHCF_2CF_2Cl$, 87533-04-8; $CF_3OOCF_2NHCF_2CFCl_2$, 87533-05-9; $CF_3OOCF_2NHCF_2CFBrCl$, 87533-06-0; KHF_2, 7789-29-9; $ClCF_2CF_2\overline{NCF_2O}$, 87533-07-1; $Cl_2CFCF_2\overline{NCF_2O}$, 87533-08-2; $ClBrCFCF_2\overline{NCF_2O}$ (isomer 1), 87533-09-3; $ClBrCFCF_2\overline{NCF_2O}$ (isomer 2), 87533-10-6; $CF_2{=}CF_2$, 116-14-3; $CF_2{=}CFCl$, 79-38-9; $CF_2{=}CFBr$, 598-73-2.

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(19) Chang, S. C.; DesMarteau, D. D. *Inorg. Chem.* **1983**, *22*, 805.

(20) Bothner-By, A. A.; Castellano, S. M. In "Computer Programs for Chemistry"; Detar, D. F., Ed., W. A. Benjamin: New York, 1968; Vol. 1, p 10.