(*E*)-**11**, 85233-47-2; (*Z*)-**11**, 85233-46-1; *cis*-**12**, 104693-07-4; *trans*-**12**, 104693-08-5; **13**, 85233-48-3; **17**, 104693-22-3; (*E*)-**19**, 104693-09-6; (*Z*)-**19**, 104693-10-9; (*E*)-**20**, 104693-11-0; (*Z*)-**20**, 104693-12-1; (*E*)-**21**, 104693-13-2; (*Z*)-**21**, 104693-14-3; (*E*)-**22**, 104693-15-4; (*Z*)-**22**, 104693-16-5; (*E*)-**23**, 104693-17-6; (*Z*)-**23**, 104693-18-7; **24**, 104693-19-8; **25**, 104693-20-1; **26**, 104693-21-2; SO_3, 7446-11-9; $CF_2{=}CFCF_3$, 116-15-4; BF_3, 7637-07-2; $FSO_2OSO_2OSO_2F$, 13709-33-6; $C_4F_9CF_2CF{=}CF_2$, 355-63-5; $C_4F_9CF_2\overline{CFCF_2OS}(O)_2$, 85211-95-6; $CF_3CF{=}CFCF_3$, 360-89-4; FSO_2OSO_2F, 13036-75-4; $CF_3CCl{=}CClCF_3$, 303-04-8; $CF_3C{\equiv}CCF_3$, 692-50-2; trimethyl borate, 121-43-7.

Cycloaddition and Oxygen-Transfer Reactions of 2-(Trifluoromethyl)-3,3-difluorooxaziridine[1]

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The oxaziridine $CF_3\overline{NCF_2O}$ (**1**) cycloadds to various 1,1-difluoroolefins under mild conditions, forming perhalo-1,3-oxazolidines, and to dialkyl ketones, forming the corresponding 1,3,4-dioxazolidines. Reaction of **1** with trimethylsilyl cyanide results in the formation of $(CH_3)_3SiN{=}C{=}NCF_3$ and COF_2, but **1** is unreactive with other alkyl nitriles and isocyanides. With 2,5-dimethylfuran and 2,3-dimethylbutene, **1** reacts rapidly and under mild conditions (~−50 °C) to yield $CF_3N{=}CF_2$ and organic products derived from the transfer of a single oxygen atom.

Our studies of the unusual oxaziridine pentafluoroazapropene oxide (PFAPO), $CF_3\overline{NCF_2O}$ (**1**), have shown thus far that its reaction chemistry is similar in some ways to that of hexafluoropropene oxide (HFPO), $CF_3\overline{CFCF_2O}$.[2,3] Both compounds readily undergo ring opening by nucleophiles, with attack exclusively at the central nitrogen or carbon, respectively. Hexafluoropropene oxide is, however, generally unreactive toward unsaturated systems; cycloaddition reactions of this epoxide with olefins have not been reported and only a single cycloadduct with acetone has been reported.[4,5] Pentafluoroazapropene oxide in contrast, readily reacts with a number of 1,1-difluoroolefins to form 3-(trifluoromethyl)perhalo-1,3-oxazolidines and reacts readily with certain ketones to form 2,2-disubstituted 5,5-difluoro-4-(trifluoromethyl)-1,3,4-dioxazolidines.

Additional differences in reactivity between HFPO and PFAPO are indicated by the isomerization of HFPO to hexafluoroacetone with SbF_5,[3] whereas PFAPO forms a high percentage of a dimer along with small amounts of higher oligomers.[2b] Finally, in this work we report the facile oxygen atom-transfer reaction of PFAPO with electron-rich alkenes, a reaction not observed with HFPO.

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 recorded with a Perkin-Elmer 337, 1330, 180, or 1430 spectrometer using a 10-cm glass cell fitted with AgCl or KCl windows. NMR spectra were recorded with a Varian XL-100-15 spectrometer by using ~80 mol % $CFCl_3$ as a solvent and an internal reference or with a JEOL FX-90Q spectrometer by using various deuterated media as both solvent and internal lock and ~1% $CFCl_3$ as the internal reference. Hydrogen chemical shifts are reported relative to internal $(CH_3)_4Si$.

Mass spectra were recorded with either a 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 introduced 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.[6] 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 with 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 were commercially available and were used as received. Other organic reactants were purified by distillation under vacuum. Oxaziridine **1** was prepared as described previously.[7]

General Procedure for Reaction of Oxaziridine 1 with Olefins. To a ~100-mL Pyrex vessel fitted with a glass-Teflon valve were added **1** (1–3 mmol) and an equamolar amount of olefin by vacuum transfer. The mixture was then heated at 55–100 °C for ~18 h, unless otherwise noted. The products were separated by vacuum fractionation through a series of cold traps, followed by GLC as needed.

(a) With $CF_2{=}CF_2$. Perfluoro-3-methyloxazolidine (**2a**) was obtained in 60% yield; bp 21 °C; $\log P\,(\text{torr}) = 6.969 - (949.14/T) - (74200/T^2)$; $\Delta H_{\text{vap}} = 6.65$ kcal/mol; $\Delta S_{\text{vap}} = 22.6$ eu; IR (gas) 1415 (m), 1360 (s), 1325 (vs), 1245 (vs), 1165 (m), 1080 (m), 1010 (m), 960 (vw), 910 (m), 745 (w), 700 (w), 680 (w), 580 (w) cm^{-1}; MS (CI, major), *m/z* 250 [$(M + 1)^+$], 230 [$(M + 1 - HF)^+$], 200 [$(M + 1 - CF_2)^+$], 183 ($C_3F_7N^+$), 154, 152, 134 ($C_2HF_5N^+$), 114; MS (EI, major), *m/z* (relative intensity) 249 (M^+), 230 [$(M - F)^+$, 100], 199 [$(M - CF_2)^+$], 183 [$(M - COF_2)^+$], 180, 164 ($C_3F_6N^+$),

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153, 142 ($C_3F_4NO^+$), 134, 133, 131, 130, 119, 116 ($C_2F_4NO^+$, 100), 114 ($C_2F_4N^+$), 100, 99, 97, 95, 92, 69 (CF_3^+), 65, 50 (CF_2^+), 47, 44; ^{19}F NMR ($CF_3^A\overline{NCF_2^BOCF_2^CC}F_2^D$) ($CFCl_3$) δ A −57.5, B −58.2, C −86.5, D −93.3 ($J_{AB} = 6.8$, $J_{BC} = 3.4$, $J_{AC} \simeq 1.5$, $J_{AD} = 6.8$, $J_{BD} = 6.8$ Hz).

(b) With $CF_2{=}CFCl$. 4-Chloro-3-(trifluoromethyl)perfluorooxazolidine (**2b**) was obtained in 78% yield: bp 51 °C; log P (torr) = 6.230 − (717.6/T) − (119500/T^2); $\Delta H_{vap} = 6.66$ kcal/mol; $\Delta S_{vap} = 20.5$ eu; IR (gas) 1430 (vw), 1370 (m), 1315 (vs), 1245 (vs), 1185 (m), 1145 (m), 1095 (m), 1075 (m), 1025 (m), 945 (m), 870 (m), 785 (vw), 740 (m), 695 (vw), 620 (vw) cm^{-1}; MS (CI, major) m/z (relative intensity) 266 [$(M + 1)^+$, weak], 248/246 [$(M + 1 - HF)^+$, 100], 230 [$(M + 1 - HCl)^+$], 134 ($C_2HF_5N^+$); MS (EI, major), m/z (relative intensity) 230 [$(M - Cl^+)$], 182/180 [$(M - CF_3O)^+$], 164 ($C_3F_6N^+$), 132/130 ($C_2ClF_3N^+$), 116 ($C_2F_4O^+$), 114 ($C_2F_4N^+$), 113, 95, 87, 85, 76, 69 (CF_3^+, 100), 66, 50 (CF_2^+), 47; ^{19}F NMR ($CF_3^A\overline{NCF^BF^COCF^DF^EC}F^FCl$) ($CFCl_3$) δ A −56.5, B −57.4, C −60.9, D −76.7, E −88.0, F −76.1 ($J_{AB} = J_{AC} = J_{AF} = 7$, $J_{BC} = 93$, $J_{DE} = 111$, $J_{BD\text{ or }BE} = J_{CE\text{ or }CD} = 6.5$, $J_{EF} \approx 5.5$, $J_{BF} \approx 5.5$ Hz).

(c) With $CF_2{=}CFBr$. 4-Bromo-3-(trifluoromethyl)perfluorooxazolidine (**2c**) was obtained in 85% yield: bp 65 °C; log P (torr) = 7.622 − (1604.8/T); $\Delta H_{vap} = 7.34$ kcal/mol; $\Delta S_{vap} = 21.7$ eu; IR (gas) 1420 (vw), 1400 (w), 1365 (vs), 1290 (vs), 1210 (vs), 1185 (m), 1145 (m), 1115 (w), 1090 (m), 1065 (m), 1020 (m), 920 (m), 855 (m), 740 (m), 695 (vw), 620 (vw); MS (CI, major), m/z (relative intensity) 292/290 [$(M + 1 - HF)^+$, 100], 230 [$(M + 1 - HBr)^+$], 211 ($C_4F_7NO^+$), 134 ($C_2HF_5N^+$); MS (EI, major), m/z (relative intensity) 230 [$(M - Br)^+$], 226, 224, 174, 164 ($C_3F_6N^+$), 160, 159, 131/129 ($CBrF_2^+$), 113 ($C_2F_4N^+$), 94, 91, 81/79 (Br^+), 76, 69 (CF_3^+, 100), 50 (CF_2^+), 47; ^{19}F NMR ($CF_3^A\overline{NCF^BF^COCF^DF^EC}F^FBr$) ($CFCl_3$) δ A −56.4, B −56.1, C −59.6, D −71.6, E −87.9, F −71.5 ($J_{AB} = J_{AC} = J_{AF} \approx 7.8$, $J_{BC} = 96$, $J_{DE} = 125$, $J_{BD} \approx 5$, $J_{CD} \approx 4.5$ Hz).

(d) With $CF_2{=}CCl_2$. 4,4-Dichloro-3-(trifluoromethyl)perfluorooxazolidine (**2d**) was obtained in 81% yield: vapor pressure [torr (°C)] 46.2 (9.8), 99.9 (26.2), 124.7 (31.8); IR (gas) 1410 (vw), 1390 (w), 1350 (s), 1295 (vs), 1255 (s), 1205 (vs), 1165 (m), 1130 (m), 1020 (m), 930 (w), 865 (m), 830 (m), 765 (vw), 730 (m), 605 (vw), 585 (vw), 540 (vw) cm^{-1}; MS (CI, major), m/z (relative intensity) 284/282 [$(M + 1)^+$, weak], 266/264/262 [$(M + 1 - HF)^+$], 248/246 [$(M + 1 - HCl)^+$, 100], 229, 228, 227, 149 ($C_2F_5NO^+$); MS (EI, major), m/z (relative intensity) 248/246 [$(M - Cl)^+$], 198, 196, 182/180 ($C_3ClF_5N^+$), 148, 146, 145, 134, 132, 130, 114, 113, 111, 103, 100, 87/85 (CF_2Cl^+), 82, 76, 69 (CF_3^+, 100), 66, 50(CF_2^+), 47; ^{19}F NMR ($CF_3^A\overline{NCF_2^BOCF_2^CC}Cl_2$) ($CFCl_3$) δ A −56.1, B −58.1, C −79.6 ($J_{AB} = 7.7$, $J_{BC} = 3$ Hz).

(e) With $CF_2{=}CFCF{=}CF_2$. 3-(Trifluoromethyl)-4-(trifluorovinyl)perfluoro-1,3-oxazolidine (**2e**) was obtained in 71% yield: glass, flows ∼−105 °C; IR (gas) 1785 (s, $CF{=}CF_2$), 1370 (vs), 1345 (vs), 1300 (vs), 1265 (vs), 1220 (vs), 1165 (vs), 1125 (m), 1080 (s), 1020 (s), 935 (s), 885 (w), 870 (s), 800 (w), 745 (s), 700 (w), 665 (w), 625 (w), 585 (w), 555 (w), 495 (w) cm^{-1}; MS (CI, major), m/z (relative intensity) 312 (MH^+, weak), 311 (M^+), 293 [$(M + 1 - HF)^+$, 100], 292, 226, 176 ($C_4F_6N^+$), 157 ($C_4F_5N^+$), 69 (CF_3^+); MS (EI, major) m/z (relative intensity) 311 (M^+), 245 [$(M - COF_2)^+$], 226, 195, 181, 178 ($C_4F_6O^+$), 177, 176 ($C_4F_6N^+$, 100), 159 ($C_4F_5N^+$), 131, 116, 114, 112, 109, 69 (CF_3^+); ^{19}F NMR (380 MHz) [$CF_3^A\overline{NCF^BF^{B'}OCF^CF^{C'}C}F^D(CF^E{=}CF^FF^G)$] (20:80 $CDCl_3/CCl_4$) δ A −57.04, B −57.40, B′ −57.88, C −77.69, C′ −88.87, D −134, E −182, F −87.04, G (trans to E) −105 ($J_{BB'} = 93$, $J_{CC'} = 134$, $J_{DF} = 42$, $J_{EG} = 115$, $J_{FG} = 55$ Hz, others not readily determined).

(f) With $CF_2{=}CHF$. 2,2,4,4,5-Pentafluoro-3-(trifluoromethyl)-1,3-oxazolidine and 2,2,4,5,5-pentafluoro-3-(trifluoromethyl)-1,3-oxazolidine (**3a** and **3b**) were formed in a ca. 40:60 ratio, in 33% yield: IR (gas) 3335 (w), 3025 (w), 1770 (w), 1410 (m), 1345 (vs), 1285 (s), 1215 (vs), 1140 (s), 1110 (s), 1075 (m), 1010 (s), 985 (m), 905 (m), 825 (m), 790 (m), 685 (w), 620 (w), 575 (w), 475 (w) cm^{-1}; M_r calcd 231, found 222; ^{19}F NMR $CF_3^A\overline{NCF^BF^COCH^XF^MC}F^DF^E$ (major isomer, C_6D_6) δ A −57.2, B, C −51.3, −60.8, D, E −84.2, −100.4, M −132.2, X 5.02 (overlaps X of minor isomer) ($J_{BC} = 98$, $J_{DE} = 180$, $J_{MX} = 60$ Hz); ^{19}F NMR $CF_3^A\overline{NCF^BF^COCF^DF^EC}H^XF^M$ (minor isomer) δ A −57.8, B, C ∼−55.6, ∼−57 (overlaps F^A of major isomer), D, E −75.8, −92.4, M −144.8, X 4.92 ($J_{BC} = 62$, $J_{DE} = 140$, $J_{MX} = 68$ Hz).

(g) With $CF_2{=}CBr_2$. 4,4-Dibromo-3-(trifluoromethyl)perfluoro-1,3-oxazolidine (**2f**) was obtained in 25% yield: IR (gas) 1415 (vw), 1385 (vw), 1350 (s), 1295 (vs), 1250 (s), 1210 (vs), 1190 (s), 1160 (m), 1120 (m), 1090 (vw), 1020 (m), 905 (w), 835 (m), 790 (m), 755 (w), 725 (m), 655 (vw) 605 (vw), 580 (vw), 525 (vw) cm^{-1}; MS (CI, major), m/z (relative intensity) 353/351/347 [$(M + 1 - HF)^+$], 292/290 [$(M - Br)^+$, 100], 286, 241, 239, 226, 224, 134; MS (EI, major), m/z (relative intensity) 291/289 [$(M - Br)^+$], 226, 223, 190, 159/157 ($C_2BrF_2O^+$), 145, 131/129 ($CBrF_2^+$), 115, 113, 111, 109, 91, 85, 76, 69 (CF_3^+, 100); ^{19}F NMR ($CF_3^A\overline{NCF_2^BOCF_2^CC}Br_2$) ($CFCl_3$) δ A −56.2, B −58.1, C −75.8 ($J_{AB} = 8$, $J_{BC} = 2.8$ Hz). Dibromofluoroacetyl fluoride was isolated in ∼70% yield: IR (gas) 1875 (s), 1210 (s), 1120 (s), 1025 (m), 930 (w), 915 (m), 820 (m), 685 (w), 640 (w), 625 (w) cm^{-1}; MS (EI, major) m/z (relative intensity) 240/238/236 (M^+), 193/191/189 (CBr_2F^+), 159/157 [$(M - Br)^+$, 100], 131/129 ($CBrF_2^+$); ^{19}F NMR ($CBr_2F^ACOF^X$) ($CFCl_3$) δ A −66.6, X 7.40 ($J_{AX} = 18$ Hz). When **1** and $CF_2{=}CBr_2$ were allowed to react at ∼23 °C for 18 h, only CBr_2FCOF and $CF_3N{=}CF_2$ were isolated.

(h) With $CF_2{=}CH_2$. A clear, nonvolatile oil was obtained: MS (EI, major) m/z 570, 429, 407, 357, 341, 321, 291; ^{19}F NMR (acetone/$CFCl_3$) δ −56.3 (br m, 5 F, CF_3NCF_2), −77.0 (br, 2 F, CF_2CH_2); ^{1}H NMR (acetic acid-d_6/acetone) δ 4.0 (br t, CF_2CH_2, $J_{HF} = 9$ Hz).

(i) With $CF_3CF{=}CF_2$. The reaction mixture was heated at 150 °C for 18 h. A clear, nonvolatile oil and a trace of volatile oxazolidine were obtained: IR (gas) 1380 (s), 1295 (vs), 1220 (vs), 1175 (s), 1140 (m), 1120 (m), 1095 (w), 1030 (m), 1005 (w), 970 (m), 895 (m), 870 (w), 755 (vw), 730 (m), 625 (vw), 580 (vw); MS (CI, major), m/z (relative intensity) 300 [$(M + 1)^+$], 281 [$(MH - F)^+$], 280 [$(M - F)^+$, 100], 230 [$(M - CF_3)^+$], 214 ($C_4F_8N^+$), 164 ($C_3F_6N^+$), 114 ($C_2F_4N^+$), 100, 95, 76, 69 (CF_3^+, 100), 50 (CF_2^+), 47; ^{19}F NMR, ($CF_3^A\overline{NCF^BF^{B'}OCF^CF^{C'}C}F^DCF_3^E$) ($CFCl_3$) δ A −56.1, B and B′ −57.5, C −79.3, C′ −86.8, D −139.9, E −76.9 ($J_{AB} \approx J_{AB'} \approx J_{AD} \approx J_{AE} \approx 8$, $J_{CC'} = 135$ Hz, other values not readily determined).

Reactions of 1 with Ketones. In a typical preparation, 1.0 mmol each of **1** and the ketone was condensed into a ∼140-mL Pyrex vessel and left at ∼23 °C for 18 h. Trap-to-trap fractionation, followed by GLC purification, afforded the 2,2-disubstituted 5,5-difluoro-4-(trifluoromethyl)dioxazolidine.

(a) With Acetone. 5,5-Difluoro-2,2-dimethyl-4-(trifluoromethyl)-1,3,4-dioxazolidine (**4a**) was obtained in 75% yield: IR (gas) 3010 (m), 2950 (w), 1865 (impurity, m), 1460 (w), 1385 (m), 1290 (vs), 1210 (vs), 1150 (m), 1110 (m), 1030 (s), 1005 (m), 975 (m), 905 (m), 875 (w), 830 (w), 760 (w), 690 (w), 640 (w), 550 (w), 525 (w) cm^{-1}; MS (CI, major), m/z (relative intensity) 208 (MH^+), 207, 189, 188 [$(M + 1 - HF)^+$, 100], 182, 178, 170, 150 ($C_2HF_5NO^+$), 143, 142 [$(M + 1 - COF_2)^+$], 141, 124, 123, 122 ($C_4H_6F_2NO^+$), 112; MS (EI, major), m/z (relative intensity) 207 (M^+), 192 [$(M - CH_3)^+$], 188 [$(M - HF)^+$], 150 ($C_2HF_5NO^+$), 149, 142, 141 [$(M - COF_2)^+$], 122 ($C_4H_6FNO^+$), 85, 69 (CF_3^+), 61, 58, 57, 47, 43 (100), 42, 41, 40, 39; ^{19}F and ^{1}H NMR see ref 2b.

(b) With 2-Butanone. 5,5-Difluoro-2-methyl-2-ethyl-4-(trifluoromethyl)-1,3,4-dioxazolidine (**4b**) was obtained in 35% yield: mp −108 to −107 °C; IR (gas) 2990 (m), 2955 (w), 2900 (w), 2430 (w), 1465 (w), 1390 (w), 1310 (vs), 1285 (vs), 1215 (vs), 1180 (m), 1150 (m), 1120 (m), 1040 (s), 995 (m), 945 (m), 915 (m), 820 (w), 770 (w), 720 (w), 690 (w), 645 (w) cm^{-1}; MS (CI, major), m/z (relative intensity) 222 [$(M + 1)^+$], 221, 203, 202 [$(M + 1 - HF)$, 100], 192, 178, 156 [$(M + 1 - COF_2)^+$], 155, 150 ($C_2HF_5NO^+$), 137, 136 ($C_2HF_5O^+$), 137, 136 ($C_2HF_5O^+$), 112, 73 ($C_4H_9O^+$), 72, 69 (CF_3^+), 57, 55; MS (EI, major), m/z (relative intensity) 221 (M^+), 206 [$(M - CH_3)^+$], 192 [$(M - C_2H_5)^+$], 172, 155, 150 ($C_2HF_5NO^+$, 100), 149, 72, 69, 57, 55; ^{19}F NMR [$CF_3^A\overline{NCF_2^BOC(CH_3)(C_2H_5)O}$] (acetone-$d_6$) δ A −68.14, B −67.35 ($J_{AB} \approx 7$ Hz); ^{1}H NMR [$CF_3\overline{NCF_2OC(CH_3^A)(CH_2^BCH_3^C)O}$] (acetone-$d_6$) δ A 1.71, B 2.03, C 1.02 ($J_{BC} = 15$ Hz).

(c) With 3,3-Dimethyl-2-butanone. 5,5-Difluoro-2-methyl-2-*tert*-butyl-4-(trifluoromethyl)-1,3,4-dioxazolidine (**4c**) was obtained in 40% yield: mp −94 °C; IR (gas) 3010 (w), 2980 (m), 2925 (w), 2890 (w), 1485 (w), 1385 (m), 1310 (vs), 1280 (s), 1250 (s), 1225 (s), 1205 (s), 1160 (s), 1145 (s), 1080 (m), 1035 (m), 995 (m), 950 (m), 920 (w), 845 (w), 690 (w), 670 (w) cm^{-1}; MS (CI, major), *m/z* (relative intensity) 250 $[(M + 1)^+]$, 231, 230 $[(M + 1 - HF)^+]$, 202, 192 $[(M - C_4H_9)^+]$, 184 $[(M + 1 - COF_2)^+]$, 165, 164 $(C_7H_{12}F_2NO^+)$, 150, 136, 103, 102, 101 $(C_6H_{13}O^+)$, 100, 84 $(CF_3N^+$, 100), 83, 69 (CF_3^+), 57; MS (EI, major), *m/z* (relative intensity) 249 (M^+, weak) 193 $[(M - C_4H_8)^+]$, 172, 150 $(C_2HF_5NO^+)$, 100, 85, 84, 83 (CF_3N^+), 69 (CF_3^+), 58, 57, $(C_4H_9^+$, 100), 55; ^{19}F NMR $(CF_3{}^ANCF_2{}^BOC[CH_3][C(CH_3)_3]O)$ (benzene-d_6) complex A_3B_2 pattern, most intense peak δ −68.31; ^1H NMR $(CF_3NCF_2OC[CH_3{}^A][C(CH_3)_3{}^B]O)$ (benzene-d_6) δ A 1.26, B 0.77.

(d) With 3-Buten-2-one. 5,5-Difluoro-2-methyl-2-vinyl-4-(trifluoromethyl)-1,3,4-dioxazolidine (**4d**) was obtained in 52% yield: bp (extrapolated, ~60 °C dec) 95 °C; log P (torr) = 6.7997 − (1078.1/T) − (135017/T^2); ΔH_{vap} = 82.85 kcal/mol; ΔS_{vap} = 22.5 eu; IR (gas) 3110 (w), 3040 (w), 3010 (w), 2950 (w), 1450 (m), 1420 (m), 1385 (m), 1295 (vs), 1220 (vs), 1150 (vs), 1100 (m), 1030 (s), 995 (s), 950 (s), 920 (m), 825 (w), 775 (w), 700 (w), 660 (w), 630 (w) cm^{-1}; MS (CI, major), *m/z* (relative intensity) 220 $[(M + 1)^+]$, 201 $[(M - F)^+]$, 200 $[(M + 1 - HF)^+$, 100], 178, 154 $[(M + 1 - COF_2)]$, 153, 152, 150, 134 $(C_5H_6F_2NO^+)$, 71 $(C_4H_7O^+)$; MS (EI, major), *m/z* (relative intensity) 219 (M^+), 204 $[(M - CH_3)^+]$, 192 $[(M - C_2H_3)^+]$, 153, 152 (100), 150, 149, 70, 69 (CF_3^+), 55, 54, 53; ^{19}F NMR $[CF_3{}^ANCF_2{}^BO(CH_3)(CH{=}CH_2)O]$ (20:80 $CDCl_3/CCl_4$) complex A_3B_2 pattern, most intense peak δ −68.98; ^1H NMR $[CF_3NCF_2OC(CH_3{}^A)(CH^L{=}CH^MH^N)O]$ (20:80 $CDCl_3/CCl_4$) δ A 1.76, L (trans to N) 5.78, M 5.46, N ~6.0 ($J_{LM} \approx 1.5$, $J_{LN} \approx J_{MN} \approx 10$ Hz).

Reactions of 1 with 2,5-Dimethylfuran and 2,3-Dimethylbutene. In each case, 1.0 mmol each of **1** and the organic coreactant was condensed (−196 °C) into a ~140-mL Pyrex vessel having a 10-mm NMR tube attached to its neck. The region of the vessel containing the reactants was then immersed in an ethanol bath held at ~−50 to −40 °C. At the end of the reaction period (~15 min for 2,5-dimethylfuran, ~1 h for 2,3-dimethylbutene) volatile materials were pumped out (at −40 °C for 2,5-dimethylfuran, −100 °C for 2,3-dimethylbutene) into a −196 °C trap. The volatile materials were shown by IR to consist primarily of $CF_3N{=}CF_2$, traces of unreactive impurities from preparation of **1**, and a small amount of unreacted **1**. The reactor was then cooled to −196 °C, and sufficient C_6D_6 to make a ~1 M NMR sample was condensed in, along with $(CH_3)_4Si$ as an internal standard. The sample was rapidly melted and poured into the attached NMR tube, which was then cooled to −196 °C and sealed under vacuum. The samples were stored at −196 °C until immediately before acquiring the NMR spectra.

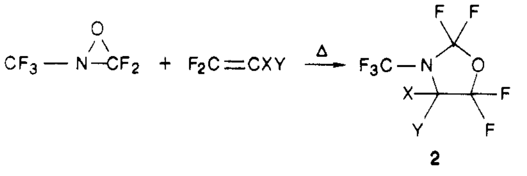
NMR of materials from oxidation of 2,3-dimethylbutene: ^1H (C_6D_6) δ 1.11 (s, tetramethyloxirane); ^{13}C δ 21.15, 61.46 (tetramethyloxirane) [lit.[8] δ 21.2, 61.7 (61.2)]. No absorptions attributable to 2,3-dimethylbutene were seen.

NMR of materials from oxidation of 2,5-dimethylfuran: ^1H (C_6D_6) δ 5.70, 1.87 (large s, *cis*-3-hexene-2,5-dione), δ 5.77, 2.06 (small s, 2,5-dimethylfuran), 1.42, 1.33; ^{13}C (C_6D_6) δ 199.8 (carbonyl), 29.25 (methyl), 135.5 (olefin) [attributable to *cis*-3-hexene-2,5-dione], 13.44, 106.5, 150.3 [attributable to 2,5-dimethylfuran]. No other ^{13}C signals were observed initially. An overnight run, however, led to extensive decomposition as seen both by spectral changes and darkening of the sample.

In a separate experiment, 1.0 mmol each of **1** and 2,5-dimethylfuran was condensed into a ~140-mL Pyrex vessel and allowed to react as described above. After pumping off the $CF_3N{=}CF_2$, the yellowish/greenish/white largely crystalline material remaining in the flask was allowed to warm to room temperature. It turned red immediately upon melting. The infrared spectrum (liquid film) indicated that the oxidation product was *cis*-3-hexene-2,5-dione: 1685 (s, C=O), 1613 (s, *cis*-alkene) cm^{-1} [lit.[9] 1689, 1613 cm^{-1}]. A broad hydroxyl absorption was also seen. We attribute this to water, as the dione is known to be highly hygroscopic.[9] The material remaining in the flask decomposed to a black sludge overnight.

Results and Discussion

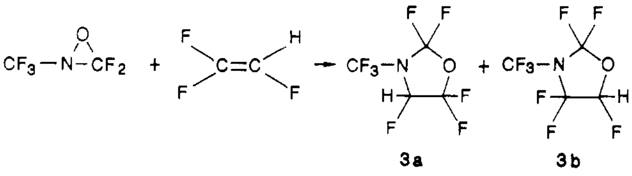
Cycloadditions with Olefins. Oxaziridine **1** reacts readily and regiospecifically with a number of simple 1,1-difluoroolefins under mild conditions (50–100 °C) to afford good yields of the corresponding 3-(trifluoromethyl)perhalo-1,3-oxazolidines **2** (eq 1).



(1)

2a, X = Y = F; **b**, X = F, Y = Cl; **c**, X = F, Y = Br; **d**, X = Y = Cl; **e**, X = F, Y = $CFCF_2$; **f**, X = Y = Br

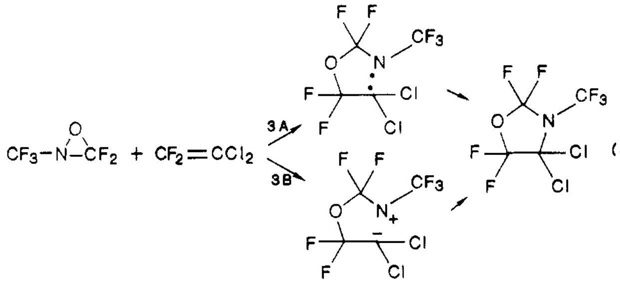
The nature of the reactivity of olefins with **1** begins to change when the olefin is substituted with hydrogen or trifluoromethyl. While **1** cycloadds readily to $CF_2{=}CHF$, the yield is poor, and much less regioselectivity is seen: a 40:60 mixture of **3a** and **3b** is obtained (eq 2). Reactions of **1** with $CF_2{=}CH_2$, CFH=CFH (mixtures of cis and trans isomers), and $CF_3CF{=}CF_2$ afforded nonvolatile oils which may be copolymers of the olefins and the oxaziridine, since both of the starting materials are consumed. [In the reaction with $CF_3CF{=}CF_2$, a trace of oxazolidine (reaction 1, X = F, Y = CF_3) was obtained.]



(2)

Attempts to carry out the cycloaddition of **1** with C_2H_4, CFCl=CFCl, perfluorocyclopentene, perfluoro-2-butyne, acrylonitrile, and acetylene (with which no reaction was observed even at 150 °C) failed; the starting materials were recovered in each case.

To account for the reactivity of **1** with the above olefins, we propose that the [2 + 3] cycloadditions, involving ring opening via the nitrogen–oxygen bond, could occur in two ways: a biradical mechanism in which the products are determined by the relative stabilities of the intermediate radicals or by formation of a 1,3-dipolar species CF_3N^+-CF_2O^-, where the products are controlled by the nucleophilic attack of the oxygen of the 1,3-dipolar species on the alkene. Either route can serve to explain the observed regiospecificity of the additions and both are consistent with the relative reactivity of the olefins. These proposals are illustrated in eq 3 for $CF_2{=}CCl_2$.



(3)

Reaction path 3A is supported, in part, by analogy to the well-known [2 + 2] thermal cycloadditions of 1,1-difluoroolefins which are generally accepted as proceeding

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[8] (a) Paulson, D. R.; Tang, F. Y. N.; Moran, G. F.; Murray, A. S.; Pelka, B. P.; Vasquez, E. M. *J. Org. Chem.* **1975**, *40*, 184. (b) Davies, S. G.; Whitman, G. H. *J. Chem. Soc., Perkin Trans. 2* **1975**, 861.

[9] Levisalles, J. *Bull. Soc. Chim. Fr.* **1957**, 997.

via a biradical transition state.[10] In this case, the more nucleophilic and less hindered oxygen of 1 attacks the 1,1-difluoromethylene carbon of the olefin to give the most stable intermediate biradical. The similarity of this process to that of the [2 + 2] cycloadditions of fluoroolefins is reinforced by the fact that a 1,1-difluoroolefin reactant is rigorously required in both cases. Reaction path 3B, while consistent with the expected nucleophilic attack on $CF_2{=}CCl_2$, is disfavored by the fact that examples of 1,3-dipolar additions to fluoroolefins leading to five-membered rings are rare. A more definitive resolution of this interesting mechanistic question must await further work.

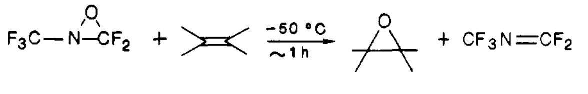
The perhalooxazolidines **2** are stable compounds of low reactivity (with the exception of **2e**, which contains a reactive trifluorovinyl group). No decomposition of compounds **2a–f** was noted during handling in glass or stainless steel vacuum systems or in contact with mercury at room temperature. The low reactivity of **2a**, prepared by another method, has been reported previously.[11] In addition to the reagents reported in ref 11, we have found **2a** to be unreactive with CsF, chromic acid, and $KMnO_4$ in water/*tert*-butyl alcohol. Compound **2a** was recovered unchanged upon heating alone at 110 °C or with CsF at 60 °C.

The assigned structures of the oxazolidines were strongly supported by their ^{19}F NMR spectra. The two doublets of a typical AB pattern arising from the methylene fluorines at both C-2 and C-5 of oxazolidines **2b** and **2c** clearly demonstrate the magnetic nonequivalence of each member of each of the pairs; this nonequivalence is induced by the chiral center at C-4 in **2b** and **2c**. Similarly, the spectra of **3a** and **3b** are complicated by the chiral center at C-4 and C-5, respectively. The ^{19}F spectrum of **2a** agrees with that reported earlier.[11]

Oxazolidine **2e** gave rise to a highly complex 90-MHz ^{19}F NMR spectrum, as all eight of the ring and olefinic fluorines are magnetically nonequivalent, and extensive coupling of the ring fluorines both with each other and with the olefinic fluorines was observed. The spectrum was simplified considerably when obtained at 380 MHz.[12]

Oxygen Atom Transfer. The reaction of 1 with hydrocarbon olefins other than ethylene reveals a striking new reaction path: instead of forming a cycloadduct, 1 transfers its oxygen atom to the olefin, forming $CF_3N{=}CF_2$.

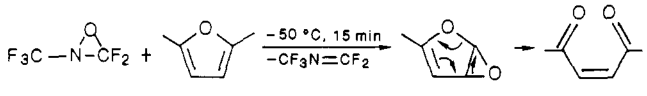
This process is illustrated in eq 4 for 2,3-dimethylbutene, which gives tetramethyloxirane as the sole oxidation product.



(4)

Similar reactions have been observed by others,[14] using 2-(phenylsulfonyl)-3-aryloxaziridines as the oxygen-transfer agents. Our results contrast with these in that 1 effects the oxidation rapidly and under extremely mild conditions (−50 °C, ~1 h), whereas the analogous reactions with the 2-(phenylsulfonyl)-3-aryloxaziridines require comparatively harsh conditions (60 °C, 3 h).

Oxaziridine 1 oxidizes 2,5-dimethylfuran even more readily than it oxidizes 2,3-dimethyl-2-butene. In this case the final product is *cis*-3-hexene-2,5-dione. This product possibly arises from rearrangement of an intermediate epoxide, as illustrated in eq 5. The dione is not particularly stable,[9] but we believe that our spectral data confirm it as the oxidation product. The infrared spectrum agrees with that reported in the literature[9] [strong bands for carbonyl (1685 cm^{-1}) and *cis*-alkene (1613 cm^{-1})], and a ^{13}C NMR spectrum reveals only signals attributable to unreacted 2,5-dimethylfuran and the dione (see Experimental Section). We attribute the red or orange color of the product mixture to condensation products of the dione.

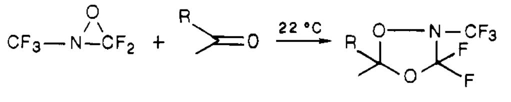


(5)

Reaction of 1 with propene, cyclohexene, cyclopentadiene, and furan also proceeded readily to give $CF_3N{=}CF_2$ as the major fluorine-containing product. In these cases, however, the hydrocarbons were mainly converted to polymeric materials which, depending on condition and the scale of the reaction, were often a clear glasslike material. A reaction with propene carried out in $CDCl_3$ in an NMR tube while the ^1H and ^{19}F NMR were monitored clearly showed the rapid formation of $CF_3N{=}CF_2$, complete consumption of the propene, a small amount of propylene oxide [δ 1.32 (d), 2.4 (m), 2.8 (m)] and two major broad resonances (δ 1.1, 3.5). We conclude that these reactions are also examples of oxygen atom transfer but the oxidized products polymerize under the reaction conditions.

Finally, the reaction of 1 with $CF_2{=}CBr_2$ may indicate that oxygen atom transfer is not limited to hydrocarbon olefins. This reaction forms only a 25% yield of the cycloadduct **2f**; the major products were $CF_3N{=}CF_2$ and $CFBr_2C(O)F$. These products do not arise from **2f**, which has high thermal stability. Quite probably, these products arise from the formation of the intermediate epoxide, $\overline{CF_2CBr_2O}$, formed by oxygen atom transfer and subsequent rearrangement of the epoxide to $CFBr_2C(O)F$. The epoxide $\overline{CF_2CBr_2O}$ does not appear to be a known species, but our proposal is supported by the photochemical oxidation of $CF_2{=}CFCl$ with oxygen. This produces only a small yield of epoxide, with $CF_2ClC(O)F$ as a major product.[15]

Cycloadditions with Ketones. Oxaziridine 1 adds readily to hydrocarbon ketones (no reaction occurred with hexafluoroacetone) to afford 1,3,4-dioxazolidines (eq 6).



(6)

4a, R=CH_3; **4b**, R=C_2H_5; **4c**, *t*-Bu; **4d**, R=$CH{=}CH_2$

These compounds are stable, colorless liquids at room temperature and were readily characterized by their mass (all show an intense M + 1 peak in their CI spectra), ^{19}F and ^1H NMR, and IR spectra. All exhibit a characteristic A_3B_2 pattern in the ^{19}F NMR.

These [2 + 3] cycloadditions may be explained as either an attack of the 1,3-dipolar species of 1 on the ketone, or as a nucleophilic attack of the ketone on the nitrogen of

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(10) Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley-Interscience: New York, 1973; pp 179–189. Sharkey, W. H. *Fluorine Chem. Rev.* **1968**, *2*, 1.

(11) Banks, R. E.; Burling, E. D. *J. Chem. Soc.* **1965**, 6077.

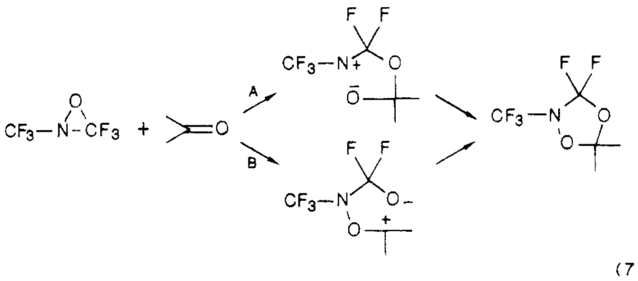
(12) Spectrum obtained at the Southeastern Regional Instrumentation Center, Columbia, S.C.

(13) For structurally related compounds, see: Dungan, C. H.; Van Wazer, J. R. *Compilation of Reported ^{19}F Chemical Shifts 1951 to mid 1967*; Wiley-Interscience: New York, 1970.

(14) Davis, F. A.; Abdul-Malik, N. F.; Curad, S. B.; Harakal, M. E. *Tetrahedron Lett.* **1981**, *22*, 917.

(15) Chow, D.; Johns, M. H.; Thorne, M. P.; Wong, E. C. *Can. J. Chem.* **1969**, *47*, 2591.

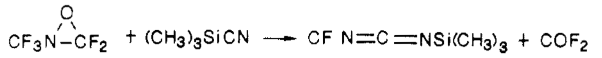
1. This is shown in eq 7 for acetone.



(7)

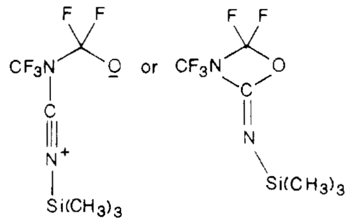
Reaction path 7B is very plausible on the basis of the ease with which oxaziridine 1 has been shown to undergo ring opening by a variety of nucleophiles.[16] This pathway also seems more consistent with the mild reaction conditions.

Reaction with $(CH_3)_3SiCN$. One additional reaction type that is of interest in demonstrating the varied reactivity of 1 is the reaction with $(CH_3)_3SiCN$. As reported earlier, this leads to 1-(trifluoromethyl)-3-(trimethylsilyl)carbodiimide and carbonyl fluoride (eq 8). When carried out by warming the reactants slowly from −196 to 22 °C, the reaction is quantitative. Attempts to extend this reaction to CF_3CN or CH_3CN resulted in recovery of starting materials. Since $(CH_3)_3SiCN$ has been shown to be in equilibrium with the isocyanide,[16] a reaction of *tert*-butyl isocyanide was carried out, but the latter also showed no reaction at 22 °C. Finally, in hopes of providing some insight into the mechanism of the reaction of 1, the reaction of HFPO with $(CH_3)_3SiCN$ was investigated. Surprisingly, no reaction was observed even at 150 °C.



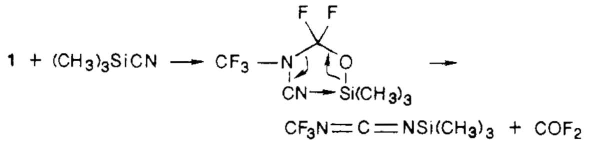
$$CF_3N\overset{O}{-}CF_2 + (CH_3)_3SiCN \longrightarrow CF\ N{=}C{=}NSi(CH_3)_3 + COF_2 \quad (8)$$

These observations make it difficult to rationalize the observed reaction of 1 with $(CH_3)_3SiCN$. An attractive proposal involving a reaction of 1 with the isonitrile form of $(CH_3)_3SiCN$, leading to the intermediate



followed by elimination of COF_2, seems to be precluded by the failure of 1 to react with *tert*-butyl isocyanide. Similarly, a reaction involving an intermediate [2 + 3] cycloadduct of 1 to the carbon–nitrogen triple bond in either $(CH_3)_3SiCN$ or $(CH_3)_3SiNC$ suffers from a lack of precedent for such reactions.

We propose the reaction scheme in eq 9 as one consistent with the established reactivity of $(CH_3)_3SiCN$.[17] An obvious criticism of this proposal is that the intermediate might be expected to eliminate $(CH_3)_3SiF$ instead of COF_2, leading to the known compound $CF_3N(CN)COF$.[18]



(9)

Conclusion

PFAPO has now been shown to undergo a variety of reactions involving the nitrogen–oxygen bond. The three main reaction types demonstrated are (1) ring opening by nucleophiles, (2) cycloadditions with halogenated olefins and dialkyl ketones, and (3) oxygen atom transfer with electron-rich olefins. Reaction type 1 is closely analogous to that of the commercial monomer hexafluoropropene oxide (HFPO), whereas types 2 and 3 are not readily observed for HFPO. Apart from the obvious utility of PFAPO in the synthesis of novel compounds, reactions 2 (except dialkyl ketone) and 3 represent unusual reaction types for small-ring heterocycles with little or no precedent.

Acknowledgment. The financial support of this research by the U.S. Army Research Office (Contracts DAAG29-82-K-0188 and DAAG29-83-K6173) and the National Science Foundation is gratefully acknowledged.

Registry No. 1, 60247-20-3; **2a**, 359-68-2; **2b**, 82135-35-1; **2c**, 104550-50-7; **2d**, 104550-51-8; **2e**, 104550-52-9; **2f**, 104550-55-2; **3a**, 104550-53-0; **3b**, 104550-54-1; **4a**, 82135-36-2; **4b**, 104550-56-3; **4c**, 104550-57-4; **4d**, 104550-58-5; $CF_2{=}CF_2$, 116-14-3; $CF{=}CFCl$, 79-38-9; $CF_2{=}CFBr$, 598-73-2; $CF_2{=}CCl_2$, 79-35-6; $CF_2{=}CFCF{=}CF_2$, 685-63-2; $CF_2{=}CHF$, 359-11-5; $CF_2{=}CBr_2$, 430-85-3; $CF_2{=}CH_2$, 75-38-7; $CF_3CF{=}CF_2$, 116-15-4; MeCOMe, 67-64-1; $CH_3COCH_2CH_3$, 78-93-3; AcBu-*t*, 75-97-8; $MeCOCH{=}CH_2$, 78-94-4; $CF_3N{=}CF_2$, 371-71-1; (*Z*)-$CH_3COCH{=}CHCOCH_3$, 17559-81-8; 2,5-dimethylfuran, 625-86-5; 2,3-dimethyl-2-butene, 563-79-1.

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(16) Seckar, J.; Thayer, J. S. *Inorg. Chem.* **1976**, *15*, 1976.

(17) Groutas, W. C.; Felker, D. *Synthesis* **1980**, 861.

(18) Sekiya, A.; DesMarteau, D. D. *J. Fluorine Chem.* **1979**, *14*, 289.