Perfluorooxazetidines[1a]

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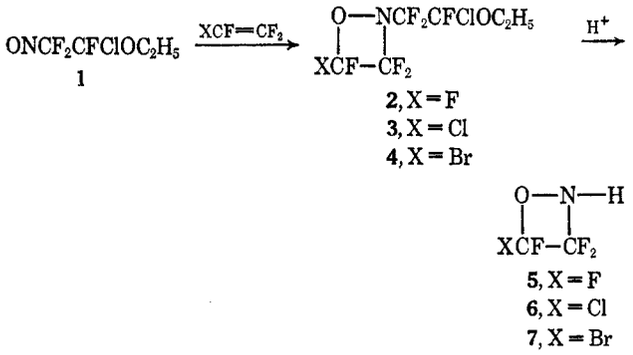
Several new functionally reactive fluorooxazetidines have been prepared. The parent amine, perfluoro-1,2-oxazetidine, can be obtained by the hydrolysis of 2-(2′-chloro-2′-ethoxy-1′,1′,2′-trifluoroethyl)perfluoro-1,2-oxazetidine. Similarly, the 4-chloro- and 4-bromoperfluoro-1,2-oxazetidines have been prepared from their respective ethers. Perfluoro-1,2-oxazetidine has been fluorinated, chlorinated, and acylated with carbonyl fluoride to give perfluoro-2-fluoro-1,2-oxazetidine, perfluoro-2-chloro-1,2-oxazetidine, and perfluoro-2-fluoroformyl-1,2-oxazetidine, respectively. Infrared, mass spectral, and ^1H and ^{19}F nmr data are reported for the above new compounds.

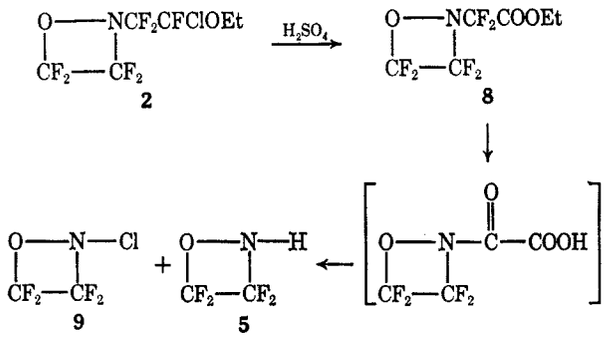
Numerous preparations of perfluoro-N-alkyloxazetidines have been described,[2-5] but no examples of the syntheses of perfluorooxazetidines are found in the literature. We wish to report the preparation of several new compounds of this type and to present some of the reactions which they undergo.

Perfluoro-1,2-oxazetidine (**5**), perfluoro-4-chloro-1,2-oxazetidine (**6**), and perfluoro-4-bromo-1,2-oxazetidine (**7**) were obtained by the sulfuric acid hydrolysis of oxazetidine ether adducts. The latter compounds were prepared by the reaction of ethyl 1-chloro-2-nitroso-1,2,2-trifluoroethyl ether (**1**) with the corresponding olefins to yield the oxazetidine ethers **2**, **3**, and **4**.[6]



Perfluoro-1,2-oxazetidine (**5**) is a pungent gas boiling at approximately 10°. It is stable for short periods of time in the gaseous state at 0°, but is unstable to prolonged standing in glass at room temperature. The 4-chlorooxazetidine **6** and the 4-bromooxazetidine **7** are also pungent materials with approximate boiling points of 45 and 70°, respectively. They likewise are very unstable in glass at room temperature. These compounds are examples of perfluorinated secondary amines of which only a few have been reported;[7] others are bistrifluoromethylamine,[8,9] perfluoropiperidine,[10,11] perfluoromorpholine,[11] and 2,2,3-trifluoro-3-trifluoromethylaziridine.[12,13]

Isolation of ethyl (2′-perfluoro-1′,2′-oxazetidinyl)difluoroacetate (**8**) suggests that the hydrolysis of **2** in concentrated sulfuric acid occurs in the following manner.



It is not unexpected that the initial hydrolysis of the α-chlorofluoromethylene group leads to ester/acid. This has frequently been observed and in fact forms the basis of the standard synthesis of ethyl chlorofluoroacetate from ethyl 1,1,2-trifluoro-2-chloroethyl ether.[14] Although the keto acid was not isolated, the further hydrolysis of the geminal difluoromethylene to a keto group has a number of direct analogies, wherein nucleophilic displacement is facilitated on a $-CF_2-$ group attached to an oxygen or nitrogen atom.[15,16] Decarboxylation and decarbonylation would then lead to the final amine product. Only a small quantity of perfluoro-2-chloro-1,2-oxazetidine (**9**) was formed.

The 2-chlorooxazetidine **9** was also prepared by direct chlorination of **5**, whereas fluorination of the same oxazetidine with fluorine over sodium fluoride yielded the related perfluoro-2-fluoro-1,2-oxazetidine (**10**). Attempts to prepare **10** by the reaction of

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(2) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1881 (1955); 3416 (1956); R. E. Banks, R. N. Haszeldine, H. Sutcliffe, and C. J. Willis, *ibid.*, 2506 (1965); R. E. Banks, M. G. Barlow, and R. N. Haszeldine, *ibid.*, 6149 (1965); C. E. Griffin and R. N. Haszeldine, *ibid.*, 1398 (1960); J. M. Birchall, A. J. Bloom, R. N. Haszeldine, and C. J. Willis, *ibid.*, 3021 (1962); S. Andreades, *Chem. Ind.* (London), 782 (1962); V. A. Ginsburg, S. S. Dubov, *et al.*, *Dokl. Akad. Nauk SSSR*, **152** (5), 1104 (1963); S. P. Makarob, *et al.*, *ibid.*, **142** (3), 596 (1962); Peninsular Chem Research, Inc., Contract NAS 8-5353, NASA SP-5901(01) (1968); W. S. Durrell, E. C. Stump Jr., G. Westmoreland, and C. D. Padgett, *J. Polym. Sci., Part A*, 4065(1965).

(3) S. Andreades, U. S. Patent 3,248,394 (1966); *J. Org. Chem.*, **27**, 4163 (1962).

(4) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1151 (1960).

(5) D. A. Barr, R. N. Haszeldine, and C. J. Willis, *ibid.*, 1351 (1961).

(6) Assignments are based on the nmr data and are consistent with the structure of the oxazetidine product obtained from the analogous addition of trifluoronitrosomethane to chlorotrifluoroethylene.[5]

(7) Compound **5** may also be structurally envisioned as a disubstituted alkylhydroxylamine, RNHOR. Trisubstituted fluoroalkylhydroxylamines have been reported: R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, *ibid.*, 7203 (1965).

(8) J. A. Young, *et al.*, *J. Amer. Chem. Soc.*, **80**, 3604 (1958).

(9) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 2532 (1955).

(10) R. E. Banks, W. M. Cheng, and R. N. Haszeldine, *ibid.*, 2485 (1964).

(11) R. E. Banks, R. N. Haszeldine, and R. Hatton, *ibid.*, 427 (1967).

(12) C. S. Cleaver and C. G. Krespan, *J. Amer. Chem. Soc.*, **87**, 3716 (1965).

(13) R. E. Banks and G. J. Moore, *J. Chem. Soc.*, 2304 (1966).

(14) N. Rabjohn, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 423.

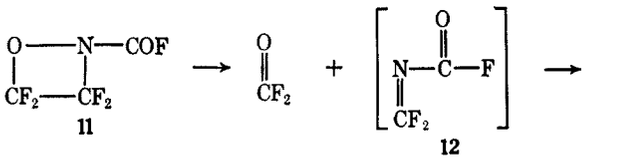
(15) I. L. Knunyants and A. V. Fokin, *Dokl. Akad. Nauk SSSR*, **112** (67) (1957).

(16) M. Hudlicky, "Chemistry of Organic Fluorine Compounds," The Macmillan Co., New York, N. Y., 1962, pp 203–205.

nitrosyl fluoride and tetrafluoroethylene were exhaustively pursued by others,[3,4] but only perfluoro(2-ethyl-1,2-oxazetidine) or perfluoro(2-methyl-1,2-oxazetidine) could be isolated. Similar attempts to obtain **9** from the reaction of nitrosyl chloride and tetrafluoroethylene gave 2-(2′-chlorotetrafluoroethyl)perfluoro-1,2-oxazetidine.[4]

The oxazetidine nitrogen of compound **5** retains some degree of nucleophilicity in contrast to the inertness of the previously reported secondary fluoroalkyl amines. This may be due to electron release from the adjacent oxygen. The oxazetidine **5** can be acylated with carbonyl fluoride to yield perfluoro-2-fluoroformyl-1,2-oxazetidine (**11**).

The pyrolyses of these novel perfluorooxazetidines would be expected to yield terminal azomethines, and the behavior of the 2-fluoroformyloxazetidine **11** was of particular interest. Pyrolysis of **11**, however, did not yield the anticipated perfluoro-2-azaacryloyl fluoride (**12**), but instead gave the rearrangement product, trifluoromethyl isocyanate (**13**).

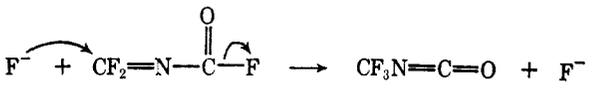


11 **12**

$CF_3-N=C=O$

13

This same isomerization was reported in a photolytic study by Ogden,[17] who postulated nucleophilic attack at the terminal azomethine group by traces of fluoride ion.



Experimental Section

Chromatographic preparative scale separations were performed on a Wilkens Autoprep Model A 700 utilizing either of two columns: column A—20% SF-96 on Chromosorb P[18] (20 ft × 3/8 in.), cooled externally; column B—30% SE-30 on Chromosorb W (20 ft × 3/8 in.).

The elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Infrared spectra were obtained with a Perkin-Elmer Model 137 double-beam spectrophotometer. Spectra of gaseous samples were obtained with a 7.5-cm gas cell equipped with silver chloride windows.

The ^{19}F nmr spectra were obtained with a Varian DP-60 spectrometer at 56.4 MHz. Spectra were calibrated by the sideband modulation technique using a Hewlett-Packard wide-range oscillator. All ^{19}F chemical shifts were obtained using $CFCl_3$ as an internal standard and are reported in ppm from this reference. The ^1H spectra were obtained with a Varian A-60A high-resolution spectrometer using tetramethylsilane as external standard.

A Bendix time-of-flight mass spectrometer (Model 12-101) with source elements S14-107 was employed to record the mass spectra at 70 eV.

Ethyl 1-chloro-2-nitroso-1,2,2-trifluoroethyl ether (**1**) is prepared by the addition of nitrosyl chloride to ethyl trifluorovinyl ether at −78°.[19] Ethyl trifluorovinyl ether was prepared from tetrafluoroethylene and sodium ethoxide in dioxane.[20]

(17) P. H. Ogden, *J. Org. Chem.*, **33**, 2518 (1968).

(18) A product of Wilkens Instrument and Research, Inc.

(19) B. L. Dyatkin, R. A. Bekker, Yu. S. Konstantinov, and I. L. Knunyants, *Dokl. Akad. Nauk SSSR*, **165** (6), 1305 (1965).

(20) S. Dixon, U. S. Patent 2,917,548 (1959).

2-(2′-Chloro-2′-ethoxy-1′,1′,2′-trifluoroethyl)perfluoro-1,2-oxazetidine (**2**).—A 2-l. bulb fitted with a freeze-out tip and vacuum stopcock was charged with **1** (9.6 g, 50 mmol), cooled at −196°, and evacuated. Tetrafluoroethylene (5.3 g, 53 mmol) was condensed into the bulb. The bulb was then transferred to a heating jacket and heated at 100–110° for 16 hr. After cooling to room temperature, the bulb was opened. The reaction mixture was then distilled under vacuum from the bulb into a trap at −196°, yielding crude **2** (8.9 g, 31 mmol, 62%). This product was distilled at atmospheric pressure, bp 110–115°, and was used for subsequent reactions without further purification. Preparative glpc at 90° using column B afforded pure **2**: ir 3.35 (w), 7.10 (s, oxazetidine ring vibration), 8.30 (vs), 9.30 (m), 10.7 (m), and 12.55 μ (s); ^{19}F nmr—CF_2O, 84.5 ppm (s); CF_2N (ring), 94.2, 96.6, 97.6, and 100.1 ppm AB q); CF_2N (side chain), 101.9, 105.6, 106.2, and 109.8 ppm (complex q); CFCl, 69.6 ppm (s); OCH_2, 4.41 ppm (q); CH_3, 1.58 ppm (t).

Anal. Calcd for $C_6H_5F_7ClNO_2$: C, 24.72; H, 1.73; F, 45.61; N, 4.80. Found: C, 24.88; H, 2.00; F, 45.34; N, 4.88.

2-(2′-Chloro-2′-ethoxy-1′,1′,2′-trifluoroethyl)perfluoro-4-chloro-1,2-oxazetidine (**3**).—Compound **3** was prepared by reaction of chlorotrifluoroethylene (41 mmol) and the nitroso ether **1** (41 mmol) using essentially the same method as utilized for the preparation of **2** above. The reaction was run at 115° for 16 hr. Distillation afforded **3** (30%), bp 70° (30 mm), with further purification by glpc at 140° using column B: ir 3.35 (w), 7.42 (s, oxazetidine ring), 8.30 (vs), 9.4 and 9.7 (s), and 12.7 and 12.8 μ (s); ^{19}F nmr—CFCl (ring), 65.7 ppm (s); CF_2N (ring), 86.5, 88.8, 90.6, 91.6, 93.8, and 96.1 ppm (m); CF_2N (side chain), 101.8, 105.7, 106.2, and 109.9 ppm (complex q); CFCl (side chain), 69.7, and 70.3 ppm (d); OCH_2, 4.47 ppm (q); CH_3, 1.68 ppm (t).

Anal. Calcd for $C_6H_5F_6Cl_2NO_2$: C, 23.40; H, 1.64; F, 37.00. Found: C, 23.42; H, 1.63; F, 36.71.

2-(2′-Chloro-2′-ethoxy-1′,1′,2′-trifluoroethyl)perfluoro-4-bromo-1,2-oxazetidine (**4**) was prepared by reaction of bromotrifluoroethylene (41 mmol) and the nitroso ether **1** (41 mmol) at 120° for 8 hr. Distillation afforded **4** (20%), bp 82° (30 mm). Further purification was obtained by glpc at 150° using column B: ir 3.35 (w), 7.3 (s, oxazetidine ring), 8.3 (vs), 8.95 (s), 9.4 (s), 9.8 (s), 10.7 (m), 12.8, and 12.9 μ (s); ^{19}F nmr—CFBr, 58.2 ppm (s); CF_2N (ring), 82.2, 84.2, 86.2, 91.0, 93.5, and 96.0 ppm (m); CF_2N (side chain), 101.9, 105.8, 106.3, and 110.0 ppm (complex q); CFCl, 69.6 and 70.2 ppm (d); OCH_2, 4.52 ppm (q); CH_3, 1.69 (t).

Anal. Calcd for $C_6H_5F_6ClBrNO_2$: C, 20.45; H, 1.43; F, 32.34. Found: C, 20.48; H, 1.50; F, 32.28.

Perfluoro-1,2-oxazetidine (**5**).—To a reaction flask equipped with a condenser vented to a U-tube immersed in Dry Ice–acetone was added crude **2** (23.4 g, 80 mmol) and 400 ml of 92% sulfuric acid. The mixture was stirred for 16 hr at room temperature and was then warmed and degassed. The gases were collected at −196°, combined with the contents of the U-tube, and freed of silicon tetrachloride by pumping at −78°. The residual material consisted of **5** (2.2 g, 16.8 mmol, 21%), bp *ca.* 10°. Final purification was accomplished by glpc at 20° using column A: ir 3.1 (w), 7.1 (s, oxazetidine ring), 7.5 (s), 7.95 (s), 8.2–8.5 (vs), 9.3 (s), and 10.2 μ (s); mass spectrum *m/e* (rel intensity, ion) 131 [7.8, $C_2F_4HNO^+$ (parent ion)], 100 (33.6, $C_2F_4^+$), 69 (2.4, CF_3^+), 67 (5.3, CF_2HO^+), 66 (13.2, CF_2O^+), 65 (50.8, CF_3NH^+), 51 (21.4, CF_2H^+), 50 (14.3, CF_2^+), 47 (88.6, CFO^+), 46 (100, $CFHN^+$), 43 (9.0, $CHNO^+$), 31 (75.9, CF^+), and 30 (23.0, NO^+); ^{19}F nmr—CF_2O, 81.4 ppm (broad s); CF_2N, 97.8 ppm (broad s); NH, 7.73 ppm (broad).

Anal. Calcd for C_2HF_4NO: C, 18,32; H, 0.77; N, 10.69. Found: C, 18.62; H, 1.00; N, 10.86.

Perfluoro-4-chloro-1,2-oxazetidine (**6**).—Hydrolysis of compound **3** by the method described above gave **6** (30%), bp *ca.* 45°. Final purification was obtained by glpc at 40° using column A: ir 3.1 (w), 7.32 (s, ring), 8.0 (m), 8.5–8.6 (vs), 9.7 (s), and 10.3 μ (m); mass spectrum *m/e* (rel intensity, ion) 149, 147 [0.72, 1.9, $C_2F_3ClHNO^+$ (parent ion)], 129, 127 (0.5, 1.4, $C_2F_2ClNO^+$), 118, 116 (3.4, 10.4, $C_2F_3Cl^+$), 112 (10.4, $C_2F_3NOH^+$), 102 (0.9, CF_2ClNH^+), 100 (2.9, $C_2F_4^+$), 82 (7.5, $C_2F_3H^+$), 69 (4.1, CF_3^+), 66 (1.0, CF_2O^+), 65 (38.9, CF_2NH^+), 51 (1.3, CF_2H^+), 50 (7.0, CF_2^+), 47 (100, COF^+), 46 (87, $CFNH^+$), 37, 35 (7.9, 27.6, Cl^+), 31 (40.6 CF^+), and 30 (10.3, NO^+); ^{19}F nmr—CFCl, 62.5 (s); CF_2N, 86.7, 89.1, 94.4, and 96.8 ppm (AB q).

Elemental analysis could not be obtained on compound **6** due to its instability.

Perfluoro-4-bromo-1,2-oxazetidine (7).—Hydrolysis of **4** as above gave **7** (20%), bp *ca.* 70°. Preparative glpc at 50° with column A afforded pure **7**: ir 3.1 (w), 7.4 (s, ring), 8.02 (m), 8.5–8.6 (s), 9.7 (s), 10.35 (m), and 13.7 μ (m); mass spectrum *m/e* (rel intensity, ion) 192 [trace, $C_2F_3BrHNO^+$ (parent ion)]; 172, 170 (1.4, 1.1, $C_2F_2BrNO^+$), 162, 160 (5.9, 11.0, $C_2F_3Br^+$), 147, 145 (trace, CF_2BrO^+), 112 (7.2, $C_2F_3NHO^+$), 69 (4.3, CF_3^+), 66 (5.3, CF_2O^+), 65 (13.6, CF_2NH^+), 51 (0.9, CF_2H^+), 50 (5.9, CF_2^+), 47 (100, COF^+), 46 (64.6, $CFNH^+$), 31 (32.3, CF^+), and 30 (17.7, NO^+); ^{19}F nmr—CFBr, 53.4 (s); CF_2N, 80.9, 83.2, 93.9, and 96.2 (AB q). Compound **7** is also very unstable and no elemental analysis could be obtained.

Ethyl 2-(2′-Perfluoro-1′,2′-oxazetidinyl)difluoroacetate (8).—Compound **2** (11.7 g, 40 mmol) was stirred with 50 ml of 92% sulfuric acid for 16 hr at room temperature. Vacuum distillation of the reaction mixture at 80° (1 mm) then afforded crude ester **8** (7.0 g, 27.6 mmol, 69%). This product was washed with water and dilute sodium bicarbonate and was dried over calcium sulfate. Glpc at 90° using column B yielded an analytically pure sample of **8**. Its infrared spectrum showed bands at 3.35 (w), 5.65 (s), 7.1 (s, ring), 7.5 (s), and 8.30 μ (vs); ^{19}F nmr—CF_2O, 83.1 ppm (s); CF_2N (ring), CF_2N (side chain), 97.3 ppm (broad s), resolved at low temperature into a quartet (ring CF_2N) and a singlet; OCH_2, 4.66 ppm (q); CH_3, 1.58 ppm (t).

Anal. Calcd for $C_6H_5F_5NO_3$: C, 28.47; H, 1.99; F, 45.04; N, 5.53. Found: C, 28.51; H, 2.10; F, 45.29; N, 5.30.

Perfluoro-2-chloro-1,2-oxazetidine (9) was obtained by reaction of perfluoro-1,2-oxazetidine (**5**) (2.3 g, 17.5 mmol) and chlorine (1.3 g, 18 mmol) at reduced pressure in a 2-l. flask for 16 hr. The product **9** (80%) was purified by preparative glpc using column A at 0°: ir 7.1 (s), 7.9 (s), 8.2 (s), 8.65 (s), 9.8 (m), and 12.8 μ (s); mass spectrum *m/e* (rel intensity, ion) 167 (trace, $C_2F_4ClNO^+$), 165 (0.3, $C_2F_4ClNO^+$), 100 (19.5, $C_2F_4^+$), 66 (1.0, CF_2O^+), 64 (1.9, C_2FN^+), 51 (6.8, ClN^+), 50 (12.9, CF_2^+), 49 (7.5 ClN^+ or FNO^+), 47 (23.4, CFO^+), 45 (2.3, CFN^+), 37 (3.0, Cl^+), 35 (11.0, Cl^+), 31 (31.6, CF^+), and 30 (100, NO^+); ^{19}F nmr[21]—CF_2O, 77.2, 78.8, 81.1, and 82.7 ppm (AB q); CF_2N, 94.2, 96.4, 99.3, and 101.5 ppm (AB q).

Anal. Calcd for C_2F_4ClNO: C, 14.52; H, 0.00; F, 45.92; N, 8.46. Found: C, 14.39; H, 0.00; F, 45.82; N, 8.79.

Perfluoro-2-fluoro-1,2-oxazetidine (10).—A 2-l. steel reactor (passivated with fluorine) was charged with sodium fluoride pellets (20 g), perfluoro-1,2-oxazetidine (**5**) (4.6 g, 35 mmol), and fluorine (1.5 g, 40 mmol) at −196°. The mixture was permitted to warm to room temperature slowly (12 hr) and the excess fluorine was pumped off at −196°. The crude product consisted essentially of perfluoro-2-fluoro-1,2-oxazetidine (**10**). Pure **10** was obtained by preparative glpc at −48° using column A: ir 7.03 (s, ring), 7.7 (s), 8.0–8.3 (vs), 8.65 (vs), 10.7 (s), and 12.0–12.4 μ (vs); mass spectrum *m/e* (rel intensity, ion) 119 (0.2, $C_2F_5^+$), 100 (20.0, $C_2F_4^+$), 83 (0.7, CF_3N^+), 69 (5.3, CF_3^+), 66 (0.2, CF_2O^+), 64 (2.0, CF_2N^+), 50 (11.0 CF_2^+), 47 (22.0, COF^+), 45 (1.4, CFN^+), 33 (3.0, NF^+), 31 (46.0, CF^+), and 30 (100, NO^+); ^{19}F nmr[21]—CF_2O, 77.2, 78.8, 79.5, and 81.1 (AB q); CF_2N, 103.2, 105.7 106.4, and 108.9 (AB q); NF, −25.3 (broad s).

Anal. Calcd for C_2F_5NO: C, 16.12; H, 0.00; F, 63.74; N, 9.40. Found: C, 16.30; H, 0.00; F, 64.00; N, 9.62.

Perfluoro-2-fluoroformyl-1,2-oxazetidine (11).—A 2-l. glass flask was charged with sodium fluoride pellets (20 g), perfluoro-1,2-oxazetidine (**5**) (4.6 g, 35 mmol), and carbonyl fluoride (3.4 g, 50 mmol). The flask was then heated in a water bath at 50° for 24 hr. The crude product consisted essentially of **11** and excess COF_2. Pure **11** was obtained by preparative glpc using column A at −33°: ir 5.3–5.4 (s), 7.1 (s, ring), 7.7–8.6 (vs, broad), 9.15–9.30 (m), 10.2 (vs), and 14.15 μ (m); mass spectrum *m/e* (rel intensity, ion) 177 [1.1, $C_3F_5NO_2^+$ (parent)]; 100 (2.9, $C_2F_4^+$), 78 (2.7, $C_2F_2O^+$), 69 (1.8, CF_3^+), 64 (1.6, CF_2N^+), 50 (4.7, CF_2^+), 47 (100, CFO^+), 45 (2.4, CFN^+), 42 (2.3, CNO^+), 31 (10.0 CF^+), and 30 (23.3, NO^+); ^{19}F nmr—CF_2O, 84.4 (s); CF_2N, 95.1 (s); COF, 5.8 (broad s).

Anal. Calcd for $C_3F_5NO_2$: C, 20.35; H, 0.00; F, 53.66; N, 7.91. Found: C, 19.90; H, 0.00; F, 53.69; N, 7.89.

Pyrolysis of Perfluoro-2-fluoroformyl-1,2-oxazetidine (11).—Compound **11** under vacuum was passed through a glass tube at 400° and the gaseous products were collected at −196°. The process was repeated several times to ensure complete pyrolysis. The crude product showed the presence of COF_2 and an additional material. Preparative glpc using column A at −30° allowed for a separation of the two products. Nmr and infrared analysis indicated that the second gaseous product was trifluoromethyl isocyanate (**13**). The ^{19}F nmr showed a singlet at ϕ 48.2. The ir spectrum of **13** showed bands at 4.4 (s), 6.89 (s), 8.3 (s), and 8.7 μ (s).

Registry No.—**2**, 21720-73-0; **3**, 21720-74-1; **4**, 21720-75-2; **5**, 21720-76-3; **6**, 21720-77-4; **7**, 21720-78-5; **8**, 21720-79-6; **9**, 21720-80-9; **10**, 21720-81-0; **11**, 21720-82-1; **13**, 460-49-1.

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(21) A more detailed explanation of these nmr results will be presented in a future publication.