chromium atom contributes ca. 1.00 Å to the length of a quadruple metal–metal bond. This estimate is in good agreement with the value of 1.98 Å "calculated" as the length of a Cr≣Cr bond on the basis of "maximum-valence radii" considerations.[25] Therefore, it is suggested that the metal–metal separation[4] in $[Cr_2(O_2CCH_3)_4 \cdot 2H_2O]$ should *not* be regarded as characteristic of a Cr–Cr quadruple bond.[26]

The average of the metal–oxygen bond lengths (Table IV) within the $[CrMo(O_2CCH_3)_4]$ molecule (2.07 (2) Å) is very close to the average of the corresponding values for $[Cr_2(O_2CCH_3)_4 \cdot 2H_2O]$ (2.018 (8) Å)[4] and $[Mo_2(O_2CCH_3)_4]$ (2.12 (1) Å).[7] The average bond lengths within the acetato groups (C–O = 1.27 (1); C–C = 1.51 (1) Å) agree well with the corresponding details for the $[Mo_2(O_2CCH_3)_4]$[7] and $[Cr_2(O_2CCH_3)_4 \cdot 2H_2O]$[4] structures. As expected in view of the metal–metal separations, the interbond angles, M′–M–O = 92.3 (1.7) and O–C–O = 121.1 (1.2)°, more closely resemble the values found for $[Mo_2(O_2CCH_3)_4]$ than for $[Cr_2(O_2CCH_3)_4 \cdot 2H_2O]$. The $[CrMo(O_2CCH_3)_4]$ molecules are linked together to form infinite chains in the manner described[7] for $[Mo_2(O_2CCH_3)_4]$. The oxygen atoms O(2) and O(2′) each make a contact that is approximately coaxial (O(2)–M–M′ = 161.2 (1)°) with a Cr–Mo bond to the closest metal atom of the adjacent molecule. The O···M distance of 2.548 (4) Å is ca. 0.1 Å shorter than the corresponding distance in $[Mo_2(O_2CCH_3)_4]$.

The anisotropic temperature factors for $[CrMo(O_2CCH_3)_4]$ (Table III) are slightly (~11%) larger than the corresponding[7] values for $[Mo_2(O_2CCH_3)_4]$. This difference probably arises, at least in part, from the metal atom disorder obtained in $[CrMo(O_2CCH_3)_4]$. It is of interest to note that the same general pattern in the relative magnitudes of these temperature factors is observed for these two crystal structure determinations.

The ready cleavage of this Cr≣Mo bond is disappointing. Although $[CrMo(O_2CCF_3)_4]$ has been partially characterized in this study, the number of derivatives containing a Cr≣Mo bond which may be readily obtained appears to be severely limited.

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Supplementary Material Available: A listing of structure factor amplitudes and phases (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Preliminary account of this work has been published; C. D. Garner and R. G. Senior, *J. Chem. Soc., Chem. Commun.*, 580 (1974). (b) Manchester University. (c) Nottingham University.
(2) L. Ocone and B. P. Block, *Inorg. Synth.*, **8**, 125 (1966), and references therein.
(3) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).
(4) F. A. Cotton, B. G. DeBoer, M. D. LaPrade, J. R. Pipal, and D. A. Ucko, *Acta Crystallogr., Sect. B*, **27**, 1664 (1971).
(5) T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).
(6) D. Lawton and R. Mason, *J. Am. Chem. Soc.*, **87**, 921 (1965).
(7) F. A. Cotton, Z. C. Mester, and T. R. Webb, *Acta Crystallogr., Sect. B*, **30**, 2678 (1974).
(8) M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *Inorg. Chem.*, **7**, 1570 (1968).
(9) M. A. Porai-Koshits and A. S. Antschishkina, *Dokl. Chem.*, **146**, 920 (1962).
(10) J. N. van Niekerk and F. R. L. Schoening, *Acta Crystallogr.*, **6**, 227 (1957).
(11) V. Katovic, J. L. Templeton, R. J. Hoxmeier, and R. E. McCarley, *J. Am. Chem. Soc.*, **97**, 5300 (1975).
(12) M. S. Matson and R. A. D. Wentworth, *J. Am. Chem. Soc.*, **96**, 7837 (1974).
(13) Prepared according to the method of M. Kranz and A. Witkowska, *Inorg. Synth.*, **6**, 144 (1960).
(14) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, 1965.
(15) The discrepancy indices used were $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$ where $w = 1/(1 + [F_o - P_2/P_1]^2)$ with $P_1 = 22.0$ and $P_2 = 23.0$.
(16) See paragraph at end of paper regarding supplementary material.
(17) R. D. Cannon and J. S. Lund, *J. Chem. Soc., Chem. Commun.*, 904 (1973).
(18) J. G. Dawber, *Chem. Ind. (London)*, 973 (1964).
(19) This work.
(20) F. A. Cotton and J. G. Norman, Jr., *J. Coord. Chem.*, **1**, 161 (1971).
(21) J. Krausse, G. Marx, and G. Schoedl, *J. Organomet. Chem.*, **21**, 159 (1970).
(22) J. Krausse and G. Schoedl, *J. Organomet. Chem.*, **27**, 59 (1971).
(23) T. Aoki, A. Furusaki, Y. Tomiie, K. Ono, and K. Tanaka, *Bull. Chem. Soc. Jpn.*, **42**, 545 (1969).
(24) Insufficient pure material was prepared to allow bulk magnetic susceptibility data to be obtained.
(25) L. Pauling, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 3799 (1975).
(26) It has been suggested that the metal–metal bond in $[Cr_2(O_2CCH_3)_4 \cdot 2H_2O]$ *does* involve a total of four (σ, 2π, and δ) components, these being relatively weak because the metal atoms achieve reasonably strong binding to the addended water molecules (F. A. Cotton, personal communication).

Direct Synthesis of Fluorinated Peroxides. 6. The Addition of Fluorinated Hydroperoxides to Perfluoro-2-azapropene and the Preparation of the First Perfluorooxazirine

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Abstract: The addition of CF_3OOH and SF_5OOH to $CF_3N{=}CF_2$ has been observed to result in the formation of $CF_3OOCF_2NHCF_3$ and $SF_5OOCF_2NHCF_3$. Physical and spectral data on the new peroxides are reported including an analysis of the AB_4 portion of the ^{19}F NMR spectrum of $SF_5OOCF_2NHCF_3$. The NaF induced HF elimination from $CF_3OOCF_2NHCF_3$ and $SF_5OOCF_2NHCF_3$ to produce COF_2, SOF_4, $NaF \cdot HF$, and $CF_3\overline{NCF_2O}$ is discussed.

Several methods for the introduction of the CF_3OO– and SF_5OO– groups into organic molecules have been reported. Both CF_3OOH and SF_5OOH have proven to be valuable in this respect in their reactions with acid halides to produce $RC(O)OOCF_3$ and $RC(O)OOSF_5$.[2,3] The addition of CF_3OOCl,[4] SF_5OOCl,[5] CF_3OOF,[6] and CF_3OOOCF_3[7] to alkenes has also resulted in the convenient direct synthesis of peroxides containing the CF_3OO– or the SF_5OO– groups. However, attempts to add CF_3OOH to a wide variety of alkenes were unsuccessful.[8]

The addition of HF, HCl, HBr, and H_2SO_4 to $CF_3N{=}CF_2$ to yield CF_3NHCF_2X (X = F, Cl, Br, OSO_3H) has been demonstrated.[9] Further reaction of CF_3NHCF_2Cl to produce $CF_3N{=}CCl_2$ and $(CF_3)_2NH$ has been noted.[10] Alcohols and thiols have been reported to form a variety of complex addition products with $CF_3N{=}CF_2$. These reactions apparently involve the initial addition of REX (E = O, S) followed by loss of HF and, in some cases, further reaction of the resultant imines depending on the alcohol or thiol.[11]

Based on the proceeding and the appreciable acidity of CF_3OOH and SF_5OOH, their reaction with $CF_3N{=}CF_2$ was investigated in anticipation of the formation of reasonably stable, simple addition products. The resultant products, $CF_3OOCF_2NHCF_3$ and $SF_5OOCF_2NHCF_3$, are the first examples of peroxides of this type and represent the second addition of fluorinated hydroperoxide to an unsaturated center (the first is the isolated reaction of CF_3OOH with SO_3 to produce $HOSO_2OOCF_3$).[12] The base promoted elimination of HF from $CF_3OOCF_2NHCF_3$ and $SF_5OOCF_2NHCF_3$ has resulted in the first example of a perfluorooxazirine.[13]

Experimental Section

General. Standard high vacuum techniques utilizing both glass and stainless steel systems were used throughout. Quantities of reactants and products were measured either by direct weighing or by the relationship, $n = PV/RT$ with pressure measured on a Wallace and Tiernan Model FA 145 differential pressure gauge. Molecular weights were obtained by the vapor density method. Vapor pressure curves were obtained by a static method and the data analyzed by a computer assisted least-squares fit to both linear and quadratic equations with the best result reported. Ir spectra were obtained on a Perkin-Elmer Model 180 spectrometer using a 10-cm gas cell fitted with AgCl windows. The ^1H NMR spectra were obtained using a Varian EM-360 spectrometer on 80 mol % $CFCl_3$ solutions with Me_4Si as an external standard. The ^{19}F NMR spectra were recorded on 80 mol % $CFCl_3$ solutions utilizing a Varian XL-100-15 spectrometer. The ^{19}F NMR data corresponding to the decoupled SF_5 portion of $SF_5OOCF_2NHCF_3$ was simulated with the aid of the LAOCOON 3 computer program.[14] Chromatography was carried out at 28° using a 1 ft × ⅜ in. or 10 ft × ⅜ in. ss column packed with 49% halocarbon 11-21 polymer oil on acid washed Chromosorb P. The GLC separation employed gas injection. The starting materials CF_3OOH,[2] SF_5OOH,[15] and $CF_3N{=}CF_2$[16] were prepared by literature methods. *Caution!* The peroxides described in this work are powerful oxidants and may be subject to explosive decomposition. Adequate safety precautions should be taken when handling these materials.

Preparation of $CF_3OOCF_2NHCF_3$. In a typical reaction 4.01 mmol of CF_3OOH was condensed at −196° onto 4.72 mmol of $CF_3N{=}CF_2$ in a 100-ml glass reaction bulb equipped with a glass-Teflon valve. The reaction system was allowed to warm slowly to 24° and stand with occasional refreezing and fast warming for 1.3 h. The reaction bulb was cooled to −196° and opened to a pressure gauge. No noncondensables were observed. The volatile products were distilled through traps held at −78 and −196°. The contents of the −196° trap were distilled again through a −78° trap and the contents of the two −78° traps combined. The −78° traps contained a total of 3.83 mmol of a clear liquid which was subsequently identified as $CF_3OOCF_2NHCF_3$ (ir). The multiple distillations were necessary to obtain maximum yield of $CF_3OOCF_2NHCF_3$ as this compound distills slowly through a −78° trap and any lower trap temperatures result in retention of CF_3OOH. The yield of $CF_3OOCF_2NHCF_3$ based upon the amount of CF_3OOH and a balanced equation was 95%. Reactions run under identical conditions on a smaller scale resulted in lower yields. For example, on a 1.5-mmol scale only a 50% yield was observed, and a 2.7-mmol scale resulted in a 63% yield of $CF_3OOCF_2NHCF_3$. Physical and spectral data for $CF_3OOCF_2NHCF_3$ are as follows: clear liquid at 23°; mol wt 231.5, calcd 235.0; mp −95.7°; bp 47.1°; log P (mm) = $11.065 - 3281.4/T + 21142/T^2$; ΔH_{vap} = 8.97 kcal/mol; ΔS_{vap} = 28.02 eu; ir 3468 (w), 1497 (m), 1340 (m), 1285 (s), 1260 (s), 1242 (s), 1222 (s), 1184 (s), 1022 (s), 970 (vw), 952 (w), 875 (w), 768 (w), 704 (w), 623 (w) cm^{-1}.

Preparation of $SF_5OOCF_2NHCF_3$. In a typical reaction 1.54 mmol of SF_5OOH and 1.58 mmol of $CF_3N{=}CF_2$ were combined in a similar manner as described for the preparation of $CF_3OOCF_2NHCF_3$. The reaction bulb was placed at −29° and allowed to warm to −20° over a period of 1.5 h at which point it was warmed quickly to 23° and allowed to stand for an additional hour. The reaction bulb was cooled to −196° and opened to a pressure gauge. No noncondensables were observed. The voltatile products were distilled through traps held at −111 and −196°. The −111° trap contained a mixture of SF_5OOH and $SF_5OOCF_2NHCF_3$. Attempted purification of $SF_5OOCF_2NHCF_3$ by trap to trap distillation proved ineffective in that complete separation of SF_5OOH and $SF_5OOCF_2NHCF_3$ was not obtainable without sacrifice of large amounts of $SF_5OOCF_2NHCF_3$. The contents of the −111° trap were separated by GLC using the 1-ft column. Two major components were collected. A 0.45-mmol sample of SF_5OOH(ir) was collected after 2.9 min. A 0.77-mmol sample of a clear liquid which was subsequently identified as $SF_5OOCF_2NHCF_3$ was collected after 12.2 min. The yield of $SF_5OOCF_2NHCF_3$ based on the amount of SF_5OOH employed was 50%. As in the case of CF_3OOH the yield can be increased employing a higher initial pressure of reactants. Physical and spectral data for $SF_5OOCF_2NHCF_3$ are as follows: clear liquid 23°; mol wt 291.3, calcd 293.1; mp −87.2°; vp data, t(mm), −12.7 (6.6), −8.6 (8.6), −4.3 (11.8), 0.0 (15.8), 19.5 (48.7), 26.2 (67.8); ir 3468 (m), 1495 (m), 1340 (s), 1246 (s) 1189 (s), 1027 (s), 935 (s), 874 (s), 790 (w), 735 (w), 706 (w), 612 (w), 608 (s), 593 (w) cm^{-1}.

Preparation of $CF_3\overline{NCF_2O}$. In a typical reaction, a 2.06-mmol sample of $CF_3OOCF_2NHCF_3$ was condensed at −196° onto 84.46 mmol of dry NaF in a 100-ml glass reaction bulb equipped with a Teflon valve. The reaction mixture was allowed to warm to 23° and stand for 4.5 h with occasional shaking by hand. The system was cooled to −196° and opened to a pressure gauge. No noncondensables were observed. Volatile products were removed from the reaction bulb by distillation into a trap held at −196°. Weighing the solids remaining in the reaction bulb indicated the take up of 2.07 mmol of HF by the NaF. The volatile products were distilled through traps held at −111 and −196°. The −111° trap contained a trace (<0.05 mmol) of unidentified material. The trap held at −196° contained 3.98 mmol of material which was subsequently determined to be a 1:1 mixture of COF_2 and $CF_3\overline{NCF_2O}$. The material in the −196° trap was separated by GLC using the 10 ft column. Two major fractions were collected, which corresponded to 1.90 mmol of COF_2 (retention time = 2.2 min) and 1.50 mmol of $CF_3\overline{NCF_2O}$ (retention time = 4.1 min). Small amounts (<2% total) of four additional components were observed in the GLC. Two of these components had retention times close to that of $CF_3\overline{NCF_2O}$ and necessitated sacrifice to some $CF_3\overline{NCF_2O}$ to obtain a completely pure material. Therefore, while the amount of volatile products and the amount of HF formed suggest a yield of $CF_3\overline{NCF_2O}$ based on amount of $CF_3OOCF_2NHCF_3$ used in excess of 95%, actual recoverable yield of the pure compound was 73%.

The reaction $SF_5OOCFNHCF_3$ (0.48 mmol) with NaF (~100 mmol) was carried out in a 75-ml ss vessel in a manner similar to that described for $CF_3OOCF_2NHCF_3$. After 5 h, there were no noncondensables at −196° and the total volatile material at 23° corresponded to 0.95 mmol. Ir analysis showed a mixture of OSF_4 and $CF_3\overline{NCF_2O}$. Separation of the mixture was not carried out as pure $CF_3\overline{NCF_2O}$ was available from the reaction of $CF_3OOCF_2NHCF_3$. Physical and spectral data for $CF_3\overline{NCF_2O}$ are as follows: clear liquid −160°, mol wt 148.7, calcd 149.03; mp forms a glass at −196°; bp −34.8°; log P (mm) = $7.8115 - 1175.3/T$ (−51 to −36°); ΔH_{vap} = 5.38 kcal/mol; ΔS_{vap} = 22.6 eu; ir 2304 (vw), 2269 (vw), 1458 (vs), 1411 (m), 1299 (vs), 1253 (s), 1223 (vs), 1158 (w), 1150 (w), 1079 (m), 961 (s), 956 (s), 951 (s), 830 (w), 692 (m), 687 (m), 681 (m) cm^{-1}.

Results and Discussion

The reactions of CF_3OOH and SF_5OOH with $CF_3N{=}CF_2$ have resulted in simple addition (1 and 2).

$$CF_3OOH + CF_3N{=}CF_2 \longrightarrow CF_3OOCF_2NHCF_3 \quad (1)$$

$$SF_5OOH + CF_3N{=}CF_2 \longrightarrow SF_5OOCF_2NHCF_3 \quad (2)$$

Yields of the new addition products are dependent on reaction scale. Reactions in which the reactants are at higher initial pressure proceed significantly further toward completion. Both

$CF_3OOCF_2NHCF_3$ and $SF_5OOCF_2NHCF_3$ are stable at 23° in glass but decompose suddenly on heating to ca. 75° with large increase in pressure. They are unstable in the presence of mercury decomposing rapidly to noncondensable gases (probably O_2), COF_2, and other products.

Hydrogen fluoride forms the stable adduct $(CF_3)_2NH$ with $CF_3N{=}CF_2$ which remains intact in the presence of NaF. However, the analogous product with HCl, CF_3NHCF_2Cl, can eliminate HF to form $CF_3N{=}CCl_2$ and $(CF_3)_2NH$.[10] Alcohols and thiols undergo similar HF elimination.[11] The low energy threshold toward HF elimination of compounds of the type CF_3NHCF_2X (X = Cl, OR, SR), suggested the formation of the first example of an unsaturated fluoroperoxide, $CF_3OOCF{=}NCF_3$, might be possible. The reaction of $CF_3OOCF_2NHCF_3$ with NaF (to stimulate HF elimination) was undertaken. Elimination of HF readily occurred and the high yield production of NaF HF, COF_2 and 2-trifluoromethyl-3,3-difluorooxaziridine ($CF_3\overline{NCF_2O}$) was observed (3).

$$CF_3NHCF_2OOCF_3 + NaF \longrightarrow CF_3\overline{NCF_2O} + COF_2 + NaF{\cdot}HF \quad (3)$$

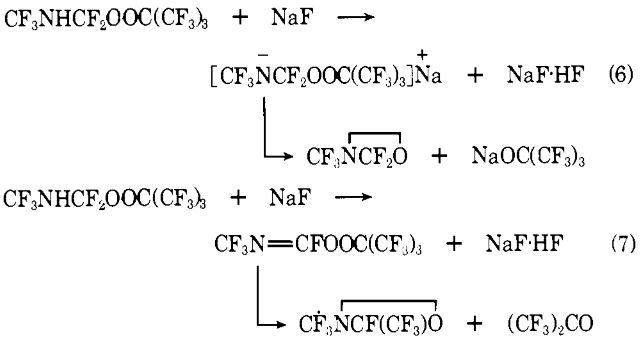
Similar results were observed with $SF_5OOCF_2NHCF_3$ forming SOF_4 instead of COF_2. These reactions indicate the anticipated unsaturated peroxide, if formed, is unstable. However, the reactions provide the first preparative route to a highly fluorinated oxazirine. The NaF induced elimination of HF from related compounds may provide a general route to new oxazirines with particular emphasis on highly fluorinated derivatives (4 and 5).

$$R_fNHCF_2OOCF_3 + NaF \longrightarrow R_f\overline{NCF_2O} + COF_2 + NaF{\cdot}HF \quad (4)$$

$$R_fNHCF(R_f')OOCF_3 + NaF \longrightarrow R_f\overline{NCF(R_f')O} + COF_2 + NaF{\cdot}HF \quad (5)$$

These conversions have not been demonstrated and will depend on the efficacy of the addition of CF_3OOH to substituted fluoroimines as well as on the actual mechanism of the HF elimination. The relative cleanness of reaction 3 suggests a nonfree radical mechanism. The base NaF may initiate the reaction by forming an unsaturated intermediate ($CF_3OOCF{=}NCF_3$) which would be expected to be unstable and could decompose to COF_2 and $CF_3\overline{NCF_2O}$. Alternately, it is conceivable that the first step in the reaction could be hydrogen abstraction by 2NaF to give NaF·HF and an unstable anion, $CF_3NCF_2OOCF_3$, which could decompose to $CF_3\overline{NCF_2O}$ and $NaOCF_3$. Sodium trifluoromethoxide is not stable and decomposes to NaF and COF_2.[17] Identical considerations apply to reaction of $SF_5OOCF_2NHCF_3$ with NaF.

A rather simple test of the above alternatives may be possible using the recently discovered hydroperoxide, $(CF_3)_3COOH$.[18] In our opinion, one of the following reactions will occur on reaction with NaF (providing $(CF_3)_3COOH$ will add to $CF_3N{=}CF_2$) (6 and 7). Unlike $NaOCF_3$, $NaOC(CF_3)_3$[19] is stable but we do not expect this fact to influence the course of the reaction to any extent. In eq 7, a different oxazirine will be formed. The latter can be envisioned as CF_3 radical transfer with the elimination of $(CF_3)_2CO$, analogous to the possible conversion of $CF_3N{=}CFOOCF_3$ to $CF_3\overline{NCF_2O}$ by fluorine transfer and elimination of COF_2. We hope to test these hypotheses in future work.



$$CF_3NHCF_2OOC(CF_3)_3 + NaF \longrightarrow [CF_3\overset{-}{N}CF_2OOC(CF_3)_3]\overset{+}{Na} + NaF{\cdot}HF \quad (6)$$
$$\longrightarrow CF_3\overline{NCF_2O} + NaOC(CF_3)_3$$

$$CF_3NHCF_2OOC(CF_3)_3 + NaF \longrightarrow CF_3N{=}CFOOC(CF_3)_3 + NaF{\cdot}HF \quad (7)$$
$$\longrightarrow CF_3\overline{NCF(CF_3)O} + (CF_3)_2CO$$

Characterization of $CF_3OOCF_2NHCF_3$. The composition of $CF_3OOCF_2NHCF_3$ is reflected by the experimental molecular weight value as well as the stoichiometric decomposition to COF_2, HF, and $CF_3\overline{NCF_2O}$. The ir spectrum displays absorption bands at 3468 cm^{-1} (νNH) and 1497 cm^{-1} (δNH) which strongly support the presence of an N—H bond in the molecule. Elimination of the C=N bond is confirmed by the lack of an absorption band in the region associated with νC=N in fluorocarbons (~1800 cm^{-1}). Bands attributable to the CF_3 and CF_2 groups are apparent in the region 1285–1184 cm^{-1}.

Unequivocal identification of $CF_3OOCF_2NHCF_3$ is given by the ^1H and ^{19}F NMR spectra. The notation used in the following data refer to $CF^a{}_3OOCF^b{}_2NHCF^c{}_3$. The ^1H NMR spectrum shows a broad symmetrical signal (44 Hz at half height) which reflects the proton attached to nitrogen. No coupling constants could be resolved presumably due to the quadrapolar broadening effect of the nitrogen as well as the expected large number of lines. The ^{19}F NMR spectrum consists of a triplet of relative area 3 centered at $\phi^*{}_a = +68.7$, $J_{F^aF^b} = 4.0$ Hz; a doublet of triplets of relative area 3 centered at $\phi^*{}_c = +55.9$, $J_{F^cF^b} = 8.5$ Hz, $J_{F^cH} = 4.25$ Hz; and a multiplet consisting of 11 lines 4.1 Hz apart (nine lines are clearly visible with the outermost lines fairly difficult to distinguish above background) centered at $\phi^*{}_b = +70.2$.[20] This multiplet arises from the NMR signal of the "b" fluorines being split into a quartet by the three "c" fluorine nuclei ($J_{F^cF^b} = 8.5$ Hz from "c" portion of spectrum). Each member of this quartet is further split into a quartet by the three "a" fluorines ($J_{F^aF^b} = 4.0$ Hz from "a" portion of spectrum); each member of which is split into a doublet by the proton attached to nitrogen. This coupling pattern produces the observed 11-line spectrum if it is assumed $J_{F^bH} \approx J_{F^aF^b} \approx 4.1$ Hz. This is a good approximation since the observed value for $J_{F^aF^b}$ is 4.0 Hz and that observed for J_{F^cH} is 4.25 Hz.

The peroxide linkage in $CF_3OOCF_2NHCF_3$ is indicated by the magnitude of both the chemical shift in the "a" fluorine NMR signal and the coupling constant between the "a" and "b" fluorine nuclei. All previous examples of compounds containing the CF_3OOCF_2 group have displayed chemical shifts for the methyl fluorines in the region of +69 and have shown values for the methyl–methylene fluorine coupling constants in the range of 4 Hz.[4,6,7] These compare favorably with the observed values for $CF_3OOCF_2NHCF_3$ of $\phi^*{}_a = +68.7$ and $J_{F^aF^b} = 4.0$ Hz. Analogous CF_3OCF_2 groups all show significantly different chemical shifts and F–F coupling of greater magnitude.

Characterization of $SF_5OOCF_2NHCF_3$. The experimental molecular weight and stoichiometry agrees with the formulation of $SF_5OOCF_2NHCF_3$. The reaction with NaF to produce OSF_4 and $CF_3\overline{NCF_2O}$ is also supportive. The ir spectrum strongly supports the presence of an N–H bond (νNH 3468, δNH 1495). The SFOO– group is reflected by bands at 934, 874, and 608 cm^{-1}.[21] Absorption bands in the appropriate range for CF_3 and CF_2 groups are also observed at 1246 and 1189 cm^{-1}.

The ^1H and ^{19}F NMR spectra provide unequivocal identification of $SF_5OOCF_2NHCF_3$. The ^1H NMR spectrum

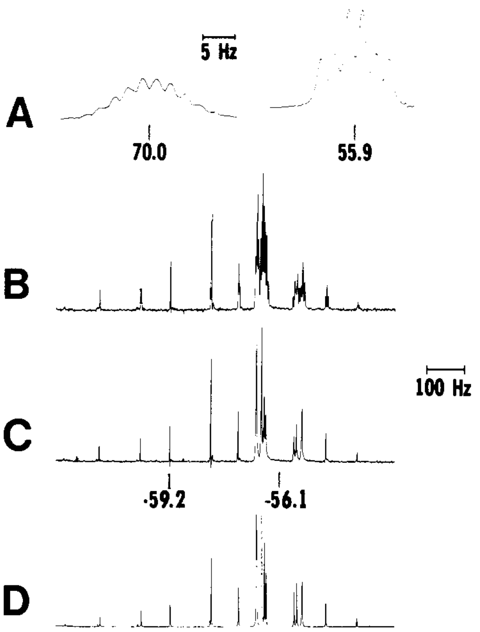
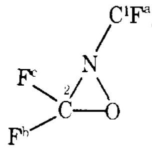


Figure 1. ^{19}F NMR spectrum of $SF_5OOCF_2NHCF_3$: (A) C-F region, (B) experimental SF_5- spectrum, (C) experimental SF_5- spectrum decoupled from $-CF_2-$, (D) simulation of decoupled (C) spectrum.

consists of a broad symmetrical signal (width at half height = 24 Hz) centered at δ 4.85 (Me_4Si) which reflects the proton attached to nitrogen. Quadrapolar broadening effects of nitrogen on the proton signal presumably prevented resolution of the expected large number of lines due to coupling between the proton and the fluorines in the molecule. The ^{19}F NMR spectrum of $F^aSF_4{}^bOOCF_2{}^cNHCF_3{}^d$ (Figure 1) consists of a doublet of triplets centered at $\phi^*_d = +55.9$ of relative area 3, $J_{F^dF^c} = 8.5$ Hz, $J_{F^dH} = 4.2$ Hz; a 12-line multiplet (ten of which are clearly obvious above the noise) separated by 4.2 Hz of relative area 2 centered at $\phi^*_c = +70.0$; and a complex pattern due to the SF_5 fluorines. The 12-line multiplet corresponding to the methylene fluorines arises in the following way. The NMR signal of these fluorines is split into a quartet by the methyl fluorine nuclei; each member of which is split into a quartet by the "b" fluorine nuclei, each member of which is split into a doublet by the proton nucleus attached to nitrogen. The observed 12-line pattern results if $\frac{1}{2}J_{F^dF^c} \approx J_{F^bF^c} \approx J_{F^bH}$. The coupling of the methylene fluorine nuclei to the "a" fluorine is small. This is reflected by a comparison of the experimental SF_5 portion of the spectrum (Figure 1B) with the experimental SF_5 spectrum decoupled from the methylene fluorine nuclei (Figure 1C) and conforms to an AB_4 pattern with $\phi^*_a = -59.2$, $\phi^*_b = -56.1$, and $J_{F^aF^b} = 154.5$ Hz. Attempted computer simulation of the nondecoupled experimental spectrum failed due to storage capacity overload of the LAOCOON 3 program.

Characterization of $CF_3\overline{NCF_2O}$. The molecular weight and stoichiometry agree with the formula C_2F_5NO. The infrared spectrum is consistent with the formulation of the compound as $CF_3\overline{NCF_2O}$. No bands consistent with $-N{=}O$, $-C{=}N$, or $C{=}O$ were present eliminating molecular structures such as C_2F_5NO, $CF_2{=}N(O)CF_3$, and $CF_3NFC(O)F$.

The ^{19}F NMR provides strong evidence for the ring structure I. The differentiation of the two methylene fluorines indicates the nitrogen inversion process to be slow on the NMR scale.



I

The magnitude of the observed $J_{F^{13}C}$ coupling constants indicates all fluorines to be attached to carbon.[22] Superscripts given in the following data refer to I. The observed spectrum shows a doublet of doublets of relative area 3 centered at $\phi^*_a = +67.9$; $J_{F^aF^c} = 15.8$ Hz, $J_{F^aF^b} = 3.1$ Hz and $J_{F^a{}^{13}C^1} = 293$ Hz; an unresolved signal (10.6 Hz wide at half height) of relative area 1 centered at $\phi^*_b = +91.8$; $J_{F^b{}^{13}C^2} = 295$ Hz; and a quartet of doublets of relative area 1 centered at $\phi^*_c = +108.1$, $J_{F^aF^c} = 15.8$ Hz, $J_{F^cF^b} = 1.8$ Hz, $J_{F^c{}^{13}C^2} = 280$ Hz.[23]

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References and Notes

(1) Alfred P. Sloan Fellow, 1975–1977.

(2) P. A. Bernstein, F. A. Hohorst, and D. D. DesMarteau, *J. Am. Chem. Soc.*, **93**, 3882 (1971).

(3) M. Hopkinson and D. D. DesMarteau, *J. Fluorine Chem.*, in press.

(4) N. Walker and D. D. DesMarteau, *J. Am. Chem. Soc.*, **97**, 13 (1975).

(5) M. Hopkinson, N. Walker, and D. D. DesMarteau, *J. Org. Chem.*, in press.

(6) F. A. Hohorst and D. D. DesMarteau, *J. Inorg. Nucl. Chem.*, **7**, 501 (1976).

(7) F. A. Hohorst, J. V. Paukstelis, and D. D. DesMarteau, *J. Org. Chem.*, **39**, 1298 (1974).

(8) E. R. Falardeau and D. D. DesMarteau, unpublished results.

(9) S. P. Makarov, M. A. Englin, V. A. Shpanskii, and I. V. Ermakova, *Zh. Obshch. Khim.*, **38**, 38 (1968).

(10) D. A. Barr, R. N. Haszeldine, and C. J. Willis, *J. Chem. Soc.*, 1351 (1961).

(11) S. P. Makarov, M. A. Englin, V. A. Shpanskii, and I. V. Ermakova, *Zh. Obshch. Khim.*, **39**, 199 (1969).

(12) R. A. DeMarco and J. M. Shreeve, *Adv. Inorg. Chem. Radiochem.*, **16**, 109 (1974).

(13) E. Schmitz, *Adv. Heterocycl. Chem.*, *2*, 85–103 (1963).

(14) A. A. Bothner-By and S. M. Castellano in "Computer Programs for Chemistry", Vol. 1, D. F. Detar, Ed., W.A. Benjamin, New York, N.Y., 1968, p 10.

(15) D. D. DesMarteau, *J. Am. Chem. Soc.*, **94**, 8933 (1972).

(16) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1881 (1955).

(17) M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **43**, 1893 (1965).

(18) D. D. DesMarteau, to be submitted for publication.

(19) R. E. A. Dear, W. B. Fox, R. J. Fredericks, E. E. Gilbert, and D. K. Huggins, *Inorg. Chem.*, **9**, 2590 (1970).

(20) The ^{19}F chemical shifts are given as ϕ^* values, which are experimental values in parts per million relative to $CFCl_3$ as an internal standard. G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

(21) D. D. DesMarteau and R. M. Hammaker, manuscript in preparation. A. A. Carter and J. M. Shreeve, *Spectrochim. Acta, Part A*, **29**, 1321 (1973).

(22) J. W. Emsley, J. Fenney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Pergamon Press, New York, N.Y., 1966, p 1022.

(23) It is impossible to distinguish which NMR signal of area 1 corresponds to the methylene fluorine cis to the CF_3 group and that which is trans to the CF_3 group. We have arbitrarily assigned the signal at ϕ^* 108.1 ppm to the cis fluorine by virtue of its larger interaction with the fluorines of the CF_3 group. This assumption has been made in the case of fluorinated oxazetidines. J. Lee and K. G. Orell, *Trans. Faraday Soc.*, **61**, 2342 (1965).