forms of aquo Mo(III) remain to be established.

Acknowledgment. This work was supported by the National Science Foundation. Helpful discussions with Dr. Daniel Polcyn and Professor Dennis Evans are gratefully acknowledged.

Registry No. $Cs_2Mo_3O_4(C_2O_4)_3(H_2O)_3$, 85165-04-4; $Mo_3O_4(C_2O_4)_3^{2-}$, 85165-05-5; $Mo_3O_4^{4+}$, 74353-85-8; $Mo_3(OH)_4(C_2O_4)_3^-$, 85096-90-8; $Mo_3(OH)_4(C_2O_4)_3$, 85096-91-9; HPTS, 104-15-4; HTFMS, 1493-13-6.

Contribution from Rocketdyne,
A Division of Rockwell International Corporation, Canoga Park, California 91304

Synthesis of *N*,*N*-Difluoro-*O*-perhaloalkylhydroxylamines. 2. Lewis Acid Catalyzed Addition of NF_3O to Olefins

RICHARD D. WILSON, WALTER MAYA,[1a] DONALD PILIPOVICH,[1b] and KARL O. CHRISTE*

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N,*N*-Difluoro-*O*-perhaloalkylhydroxylamines, R_fONF_2, were successfully prepared by the Lewis acid catalyzed addition of NF_3O to olefins. The new compounds $XC_2F_4ONF_2$ (X = F, Cl, Br) were obtained and characterized. The unexpected direction of the NF_3O addition, resulting exclusively in the anti-Markownikoff-type isomer $XCF_2CF_2ONF_2$, was elucidated by model reactions involving the stepwise addition of BF_3 and NF_3O to $CF_2{=}C{=}CF_2$. It is shown that all reactions can be rationalized in terms of an R_fBF_2 intermediate produced by the normal polar addition of BF_3 to the olefin. In the case of $CF_2{=}C{=}CF_2$, the new vinyldifluoroborane $CF_2{=}C(BF_2)CF_3$ was isolated and characterized. Attempts to isolate $-ONF_2$-substituted vinyl compounds by reaction of NF_3O with vinyldifluoroboranes led to difluoramino ketones formed via a keto–enol-type tautomerism.

Introduction

Following the discosvery of NF_3O in 1961 by Rocketdyne[2] and Allied Chemical,[3] studies were carried out in these two laboratories to add NF_3O to olefinic double bonds. Except for an incomplete description of some of the Rocketdyne results in a patent[4] and a one-sentence statement in a paper on NF_3O by the Allied group,[3] these data have not been published, partially due to their incompleteness and the lack of a plausible mechanism to explain the observed direction of the NF_3O addition. The previous Rocketdyne studies have now been complemented and are summarized in this paper.

Experimental Section

Caution! The addition reactions of NF_3O to olefins, particularly hydrogen-containing compounds, can proceed explosively. Appropritate safety precautions must be taken when these reactions are carried out.

Materials and Apparatus. The apparatus, handling techniques, and instrumental conditions used in this study have been described in part 1 of this series.[5] Literature methods were used for the syntheses of NF_3O,[6] $CF_2{=}C{=}CF_2$,[7] and $CF_2{=}CFBF_2$.[8] Monomeric $CF_2{=}CF_2$ was prepared by vacuum pyrolysis of poly(tetrafluoroethylene); C_2F_3Cl and BF_3 (The Matheson Co.) and C_2F_3Br (Ozark Mahoning Co.) were purified by fractional condensation prior to their use.

Syntheses of $XCF_2CF_2ONF_2$. Most reactions of NF_3O in the presence of BF_3 with C_2F_4, C_2F_3Cl, or C_2F_3Br were carried out according to the following general procedure. Equimolar amounts (3 mmol each) of C_2F_3X (X = F, Cl, Br) and BF_3 were condensed at −196 °C into the tip of a 250-mL Pyrex reactor. The mixture was warmed for 2 h to −78 °C and then recooled to −196 °C. An equimolar amount of NF_3O (3 mmol) was condensed at −196 °C above the C_2F_3X–BF_3 mixture. The reactor was allowed to warm slowly to −78 °C and was kept at this temperature for several hours before being allowed to warm to ambient temperature. The volatile materials were separated by fractional condensation through a series of traps at −78 °C, at −95 °C (for C_2F_3Br reaction), or −112 °C (for C_2F_3Cl reaction), or −142 °C (for C_2F_4 reaction), and at −196 °C. The −78 °C trap contained small amounts of unidentified material. The −196 °C trap contained mainly unreacted BF_3, C_2F_3X, C_2F_5X, and sometimes small amounts of NF_3O. The −95, −112, or 142 °C trap contained the desired $XC_2F_4ONF_2$ product. The reactor generally contained some white solid residue, which according to its spectra consisted of $NOBF_4$. The yields of $C_2F_5ONF_2$, $CF_2ClCF_2ONF_2$, and $CF_2BrCF_2ONF_2$ were about 60, 18, and 10%, respectively. Whereas $C_2F_5ONF_2$ could be obtained in high purity by the above described simple fractionation, $ClC_2F_4ONF_2$ and $BrC_2F_4ONF_2$ contained about 10% of an unidentified halocarbon impurity whose removal required either repeated careful fractionations or gas chromatographic techniques.

$CF_3{}^ACF_2{}^BONF_2{}^C$: bp −24.9 °C; mp −146.5 °C; mol wt found 185; mol wt calcd 187; log [*P* (mm)] = 8.0222 − 1271/[*T* (K)]; ΔH_{vap} = 5.8 kcal/mol; Trouton constant 23.5; mass spectrum (70 eV) [*m*/*e* (intensity) ion], 119 (69) $C_2F_5^+$, 100 (3.4) $C_2F_4^+$, 69 (100) CF_3^+, 66 (2.1) CF_2O^+, 52 (29) NF_2^+, 50 (10) CF_2^+, 47 (7.1) CFO^+, 33 (7.7) NF^+, 31 (12) CF^+, 30 (24) NO^+, 19 (1.1) F^+, 16 (0.3) O^+; ^{19}F NMR (positive shifts are low field from $CFCl_3$) neat ϕ_A (tr tr = sept) −89.0, Φ_B (quart tr) −95.9, ϕ_C (br tr) 124.9, $CFCl_3$ solvent ϕ_A −85.9, ϕ_B −93.0, ϕ_{C3} 128.1 (J_{AB} = 2.02, J_{AC} = 1.01, J_{BC} = 3.0, J_{NC} = 110 Hz); IR 2640 (vw), 2600 (vvw), 2478 (vw), 2408 (vw), 2350 (vvw), 2317 sh, 2235 (vw), 2090 (vvw), 2050 (vw), 1984 (vw), 1931 (vw), 1867 (vw), 1815 sh, 1791 (vw), 1775 sh, 1679 (vw), 1594 (vw), 1510 (vw), 1471 (vvw), 1401 (mw), 1300 sh, 1247 (vs), 1206 (vs), 1114 (vw), 1028 (vs), 903 (s), 850 (vs), 741 (m, PQR), 730 sh, 660 (w), 621 (vw), 569 (vw),531 (mw), 474 (vvw), 462 (vvw), 444 (vvw) cm^{-1}; Raman (liquid −90 °C) 1402 (0.7), 1240 (0.1), 1205 (0.1), 1111 (1.2) p, 1025 (6.6) p, 903 (0.7) dp, 849 (2.4) p, 835 (1.2) p, 741 (10) p, 659 (2.8) p, 619 (0.7) dp, 570 (3.1) p, 559 (0.2) dp, 529 (0.2) dp, 466 (0.2) dp, 442 (0.1) dp, 358 (1.7) p, 342 (1.9) dp, 303 (6.2) p, 244 (4.1) p, 121 (0.6) dp cm^{-1}. Anal. Calcd for C_2F_7NO: N, 7.48. Found: N, 7.21 (N_2 by evolution by Na reduction).

$ClCF_2{}^ACF_2{}^BONF_2{}^C$: bp 13.8 °C; mol wt found 204.6; mol wt calcd 203.5; log [*P* (mm)] = 7.6002 − 1355/[*T* (K)]; Δ_{vap} = 6.2 kcal/mol; Trouton constant 21.6; mass spectrum (70 eV) [*m*/*e* (intensity) ion] 137 (16.2) $C_2F_4{}^{37}Cl^+$, 135 (52.3) $C_2F_4{}^{35}Cl^+$, 119 (20.7) $C_2F_5^+$, 118 (0.6) $C_2F_3{}^{37}Cl^+$, 116 (1.9) $C_2F_3{}^{35}Cl^+$, 100 (9) $C_2F_4^+$, 87 (32) $CF_2{}^{37}Cl^+$,

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(1) Present addresses: (a) Department of Chemistry, California State University, Pomona, CA 91768; (b) MVT, Microcomputer Systems Inc., Westlake Village, CA 91361.

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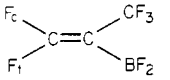
85 (100) $CF_2{}^{35}Cl^+$, 69 (20) $CF_3{}^+$, 68 (2.4) $CF^{37}Cl^+$, 66 (5.3) $CF^{35}Cl^+$, 52 (28) $NF_2{}^+$, 50 (23) $CF_2{}^+$, 49 (1.3) CCl^{37+}, 47 (4.2) CCl^{35+}, 47 (8.9) CFO^+, 37 (1.1) $^{37}Cl^+$, 35 (3.4) $^{35}Cl^+$, 33 (7.7) NF^+, 31 (21.2) CF^+, 30 (23) NO^+, 19 (1.2) F^+, 16 (0.5) O^+; ^{19}F NMR (neat) (liquid 29 °C) ϕ_A (tr tr) −75.2, ϕB (tr tr) −93.7, ϕ_C (br tr) 126.0 (J_{AB} = 2.3, J_{AC} = 0.95, J_{BC} 3.15, $J_{NC} \sim 100$ Hz); IR 1339 (m), 1286 (vw), 1241 (m), 1200 (vs), 1185 (vs), 1129 (s), 1100 sh, 1058 (vw), 1033 (m), 975 (vs), 909 (m), 898 sh, 845 (vs), 802 (w), 784 (vw), 768 (vw), 720 (vw), 702 (vw), 680 (vw), 656 (w), 615 (vw), 558 (vw), 480 (vvw) cm^{-1}.

$BrCF_2{}^ACF_2{}^BONF_2{}^C$: mol wt found 245; mol wt calcd 248; mass spectrum (70 eV) [*m*/*e* (intens) ion] 197 (4.6) $C_2F_4{}^{81}BrO^+$, 195 (4.6) $C_2F_4{}^{79}BrO^+$, 181 (66) $C_2F_4{}^{81}Br^+$, 179 (66) $C_2F_4{}^{79}Br^+$, 162 (2.4) $C_2F_3{}^{81}Br^+$, 160 (2.4) $C_2F_3{}^{79}Br^+$, 131 (100) $CF_2{}^{81}Br^+$, 129 (100) $CF_2{}^{79}Br^+$, 119 (83) $C_2F_5{}^+$, 112 (7.8) $CF^{81}Br^+$, 110 (7.8) $CF^{79}Br^+$, 100 (28) $C_2F_4{}^+$, 93 (4.2) $C^{81}Br^+$, 91 (4.2) $C^{79}Br^+$, 81 (38) $^{81}Br^+$, 79 (38) $^{79}Br^+$, 69 (59) $CF_3{}^+$, 66 (1.5) CF_2O^+, 52 (25) $NF_2{}^+$, 50 (46) $CF_2{}^+$, 47 (18) CFO^+, 33 (10) NF^+, 31 (60) CF^+, 30 (47) NO^+, 19 (2.4) F^+, 16 (8.0) O^+; ^{19}F NMR (neat liquid, −20 °C, trans rotamer) ϕ_A (tr tr) −70.5, ϕ_B (quint) −91.9, ϕ_C (br tr) 126 (J_{AB} = 3.2, J_{AC} = 1.0, J_{BC} = 3.2 Hz); IR 1330 (m), 1249 (m), 1208 (vs), 1183 (vs), 1126 (s), 1032 (m), 948 (vs), 908 (mw), 882 (w), 848 (s), 825 (sh), 782 (mw), 777 (mw), 751 (w), 672 (w), 650 (w), 635 (vw), 602 (vw), 550 (vw), 477 (vvw) cm^{-1}.

Synthesis of $CF_2{=}C(BF_2)CF_3$. Tetrafluoroallene (5.1 mmol) and BF_3 (5.1 mmol) were combined at −196 °C in a Pyrex ampule. The mixture was allowed to warm slowly to ambient temperature, then cooled again to −196 °C, and warmed as before. The volatile products were separated by fractional condensation with $CF_2{=}C(BF_2)CF_3$ (3.6 mmol) stopping in a −112 °C trap. The other reaction products were a trace of SiF_4, oily tetrafluoroallene polymer, and unreacted BF_3.

$CF_2{=}C(BF_2)CF_3$: colorless liquid and gas; mol wt found 179; mol wt calcd 179.8; approximate bp 12 °C; ^{19}F NMR (neat liquid, 25 °C) $\phi(CF_c)$ (broad unresolved multiplet) −47.6, $\phi(CF_t)$ (d quart)



−57.3, $\phi(CF_3)$ (d d)−59.9, $\phi(BF_2)$ (br s) −82.2; area ratios 1:1:3:2 ($J_{CF_cCF_3}$ = 22.6, $J_{CF_tCF_3}$ = 12.0, $J_{CF_cCF_t}$ = 39.0 Hz). Vibration spectra: IR (gas) 1769 (mw), 1714 (vs), 1689 (sh), 1469 (m), 1426 (vs), 1392 (vs), 1323 (m), 1290 (mw), 1260 (sh) 1170 (vs), 1129 (mw), 1081 (vw), 1043 (s), 998 (ms), 969 (mw), 875 (vw), 744 (mw), 736 (m), 708 (vw), 650 (vw), 642 (mw), 608 (m), 581 (w), 539 (mw), 434 (w), 392 (w) cm^{-1}; Raman (liquid, −80 °C) 1770 (0.3) p, 1713 (1.6) p, 1689 (sh), 1465 (0+), 1415 (0.1), 1382 (0.1), 1323 (0.7) p, 1298 (0.4), 1175 (0.1), 1135 (0.1), 992 (0.3) p, 964 (0.2) p, 873 (1.5) p, 742 (10) p, 730 (1.8) dp, 708 (0.5) p, 650 (2.4) p, 637 (1.7) dp, 608 (0.8) p, 580 (0.2) dp, 538 (0.6) p, 434 (0.2) dp, 399 (2.1), 376 (4.5) p, 331 (1.4) p, 193 (0.2) dp, 169 (1.5) dp, 150 (0.2) dp, 129 (0.2) cm^{-1}. The mass spectrum showed parent at *m*/*e* 180 ($C_2{}^{11}BF_7{}^+$) and 179 ($C_2{}^{10}BF_7{}^+$) and parent minus F at *m*/*e* 161 and 160. Hydrolysis of $CF_2{=}C(BF_2)CF_3$ gave $CF_2{=}CHCF_3$ + ($HOBF_2$).

Reaction of $CF_2{=}C(BF_2)CF_3$ with NF_3O. Trifluoramine oxide (1.8 mmol) and $CF_2{=}C(BF_2)CF_3$ (0.45 mmol) were combined at −196 °C in a Pyrex reactor and allowed to warm slowly to room temp. This cooling–warming was repeated several times. The volatile materials were separated by fractional condensation and consisted of BF_3 (0.45 mmol), unreacted NF_3O (1.3 mmol), and $CF_3COCF_2NF_2$ (0.45 mmol). This ketone stopped in a −112 °C trap and was identified by its infrared, mass, and ^{19}F NMR spectra,[9] molecular weight, and its hydrolysis reaction, which yielded the hydrate $CF_3C(OH)_2CF_2NF_2$.

The compound $CF_3COCF_2NF_2$ was also directly obtained by cocondensing equimolar amounts of NF_3O, BF_3, and $CF_2{=}C{=}CF_2$ at −196 °C in a Pyrex ampule and allowing the mixture to warm up slowly to ambient temperature. This warm-up procedure was repeated twice to ensure complete reaction. The reaction products were separated by fractional condensation with the −112 °C trap containing $CF_3COCF_2NF_2$ in 25% yield. $CF_3{}^ACOCF_2{}^BNF_2{}^C$: ^{19}F NMR ($CFCl_3$ −55 °C) ϕ_A (tr tr) −76.2, ϕ_B (quart tr) −109.9, ϕ_C (br s) 18.0 (J_{AB} = 6.4, J_{AC} = 2.0, J_{BC} = 3.1 Hz), area ratios A:B:C = 3:2:2.

Results and Discussion

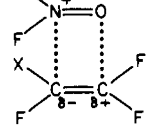
Syntheses of $-ONF_2$-Substituted Perhalocarbons and Mechanism of the NF_3O Addition. Shortly after the discovery of NF_3O in 1961,[2,3] studies were begun at Rocketdyne to add NF_3O across olefinic double bonds. At ambient temperature neat NF_3O was unreactive toward olefins such as $CF_2{=}CF_2$ or $CH_2{=}CH_2$. Furthermore, UV irradiation of mixtures of NF_3O with either $CF_2{=}CF_2$ or $CF_2{=}CFCl$ in Pyrex did not result in any appreciable reaction. Although heating of NF_3O with C_2F_4 or C_2F_3Cl to 150 °C resulted in reaction, the principal products (C_2F_6, C_4F_{10}, CF_3COF, C_2F_5Cl, etc.) arose from fluorination of the olefins and were not the desired $RONF_2$ addition compounds. However, Lewis acids catalyzed the addition of NF_3O to olefinic double bonds. The most effective Lewis acid was BF_3, but the reaction was generally limited to perhalogenated olefins. Low temperatures were necessary with NF_3O being added at −196 °C to a mixture of BF_3 and the olefin, which had been premixed at −78 °C. The ternary mixture was allowed to warm slowly from −196 to −78 °C and sometimes to ambient temperature. Although other Lewis acids such as PF_5, AsF_5, or SbF_5 in the presence or absence of solvents such as anhydrous HF or CF_3COCF_3 were also used, the above described low-temperature BF_3-catalyzed reaction gave generally the best and most reproducible results. With use of this method, the following reactions were carried out and their reaction products well characterized.

$$XC^{\delta+}F{=}C^{\delta-}F_2 + NF_3O \xrightarrow{BF_3} XCF_2CF_2ONF_2 \qquad (1)$$
$$X = F, Cl, Br$$

For X = F the yields of the $-ONF_2$ adduct were as high as 70% but decreased with increasing atomic weight of X, with the competitive fluorination reaction to C_2F_5X becoming dominant. For X being iodine, the yield of $ICF_2CF_2ONF_2$ became almost zero.

Only one isomer was obtained for all reactions and, surprisingly, corresponded to an anti-Markownikoff-type addition; i.e., the ONF_2 group was added to the positively polarized carbon atom of the substrate. The observation of only one isomer and the fact that free-radical conditions such as UV irradiation and heat did not produce significant amounts of $RONF_2$ adducts suggest a polar mechanism.

Since NF_3O is known[10] to form with Lewis acids such as BF_3 ionic adducts containing the NF_2O^+ cation and since the positive charge in NF_2O^+ resides on the nitrogen atom, the simplest polar mechanism would involve a π–π bond interaction between the N═O bond of NF_2O^+ and the C═C bond of the olefin:



Although such an intermediate could conveniently account for an attack of the positively polarized carbon by oxygen, the following arguments can be raised against this mechanism: (i) the above π–π mechanism is analogous to the reaction of two ground-state ethylene molecules to ground-state cyclobutane, which is symmetry forbidden;[11] (ii) also, the π–π mechanism cannot account for the products observed in the reaction of $CF_2{=}C(BF_2)CF_3$ with NF_3O (see below); (iii) the Lewis acid catalyzed addition of NF_3O to the olefin appears to require reaction temperatures at which the NF_2O^+ salt has some, albeit small, dissociation pressure. If a preformed stable NF_2O^+ salt is used, fluorination is obtained instead of sub-

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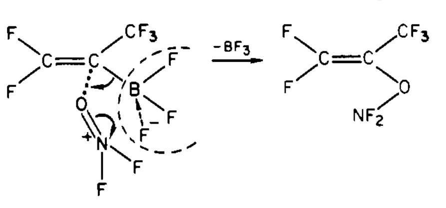
stitution; (iv) premixing of the Lewis acid with the olefin enhances the yield of $RONF_2$. Most of these arguments suggest that the first step in the NF_3O addition to olefins is the interaction of the olefin with the Lewis acid. Examination of the BF_3-C_2F_4 system at −112 °C showed a positive interaction between the two compounds; i.e., the vapor pressure was significantly lower than that expected from Raoult's law, but no stable adduct was formed. The lack of a stable $C_2F_4{\cdot}BF_3$ adduct is not surprising since $-BF_2$-substituted saturated fluorocarbons are very unstable due to the great facility for intramolecular migration of a fluorine atom from an α- or β-carbon atom to boron followed by BF_3 elimination.[12] This facility of BF_3 elimination can be strongly decreased by incorporation of an α-perfluorovinyl group. Thus $CF_2{=}CFBF_2$ is known[8] to be stable, and another stable compound $CF_2{=}C(BF_2)CF_3$ was prepared for the first time during this study from tetrafluoroallene and BF_3 (eq 2). The direction of this

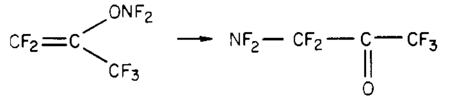
$$C^{\delta+}F_2{=}C^{\delta-}{=}C^{\delta+}F_2 + F^{\delta-}{-}B^{\delta+}F_2 \rightarrow CF_2{=}C(BF_2)CF_3 \qquad (2)$$

addition agrees with that expected from the known[13] polarity of the bonds in tetrafluoroallene and a normal polar addition of BF_3. The observation of only the BF_3 monoadduct is not surprising, since the addition of a second BF_3 molecule would result in a saturated $-BF_2$-substituted fluorocarbon, which would be prone to undergo the above mentioned BF_3 elimination[12] with re-formation of $CF_2{=}C(BF_2)CF_3$.

The availability of $CF_2{=}C{=}CF_2$ and of its BF_3 adduct allowed us to test the hypothesis that a BF_3 adduct is an intermediate in the BF_3-catalyzed addition of NF_3O to perhaloolefins. If in the BF_3-catalyzed addition reaction of NF_3O to $CF_2{=}C{=}CF_2$ the intermediate is $CF_2{=}C(BF_2)CF_3$, then the reaction of $CF_2{=}C(BF_2)CF_3$ with NF_3O should result in the same final product. Indeed this was found to be the case. In both reactions, $CF_3COCF_2NF_2$ was the only $-NF_2$-containing product. For the $CF_2{=}C{=}CF_2 + BF_3 + NF_3O$ reaction its yield was 25%, whereas for the $CF_2{=}C(BF_2)CF_3 + NF_3O$ reaction its yield was essentially quantitative. The fact that $CF_3COCF_2NF_2$ was the only product and that no evidence for an $-ONF_2$-substituted compound was observed can be readily rationalized by the following sequence. Reaction 2 is followed by a Lewis acid–Lewis base interaction between $CF_2{=}C(BF_2)CF_3$ and NF_3O. The formed adduct can then undergo BF_3 elimination (eq 3) to form the vinyl-ONF_2 compound, followed by a quasi keto–enol tautomeric rearrangement (eq 4) to give the observed final product, a difluoroamino ketone. The fact that in the BF_3-catalyzed addition of NF_3O to $CF_2{=}C{=}CF_2$ the yield of $NF_2CF_2C(O)CF_3$ was only 25% compared to 100% for the $CF_2{=}C(BF_2)CF_3 + NF_3O$ reaction can be ascribed to the low (60%) yield observed for reaction 2 and the ease of polymerization of tetrafluoroallene.[7]

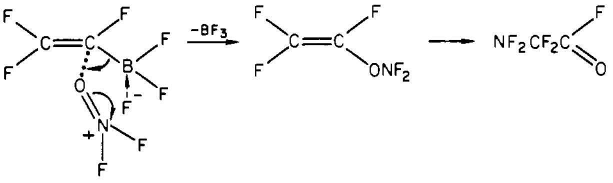


(3)



$$CF_2{=}C(ONF_2)CF_3 \longrightarrow NF_2{-}CF_2{-}C(O){-}CF_3 \qquad (4)$$

The above reactions of tetrafluoroallene lead to a better understanding of the observed reactions between $CF_2{=}CFBF_2$ and NF_3O. Two–NF_2-containing products, $CF_3CF_2ONF_2$ and $NF_2CF_2CF(O)$, were observed for this reaction. The formation of the latter compound is analogous to the tetrafluoroallene reactions

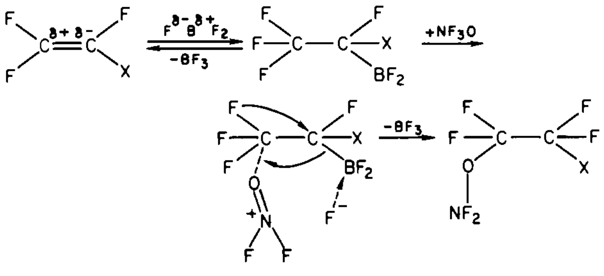


(5)

The formation of $CF_3CF_2ONF_2$ is ascribed to the competitive fluorination reaction (6), followed by reaction 1, the BF_3-catalyzed addition of NF_3O to CF_2CF_2.

$$CF_2{=}CF(BF_2) + NF_2O^+BF_4^- \rightarrow CF_2{=}CF_2 + NO^+BF_4^- + BF_3 \qquad (6)$$

The formation of an intermediate perhalo difluoroborane can also explain the unexpected "anti-Markownikoff-type" addition of NF_3O to the unsymmetric perhalogenated ethylene (eq 1). The observed reaction products can be rationalized by a mechanism assuming the normal polar addition of BF_3 to the double bond, followed by the interaction of the Lewis base NF_3O with the Lewis acid $R{-}BF_2$, followed by BF_3 elimination, a fluoride migration from the β- to the α-carbon atom, and formation of the $C{-}ONF_2$ bond (eq 7). This mechanism is analogous to that (eq 3 and 5) outlined for the perfluorovinylboranes, except for the $-ONF_2$ substitution occurring on the β-carbon due to the facile migration of fluorine from the β-carbon to the α-carbon in these saturated fluoroalkylboranes. The $-ONF_2$ substitution on the β-carbon in saturated fluoroalkylboranes vs. α-carbon substitution in vinylboranes may also be favored by the decrease in the C–C–B bond angle upon going from an sp^2-hybridized vinylborane to an sp^3-hybridized alkylborane.



(7)

Attempts to extend the BF_3-catalyzed NF_3O addition to hydrogen-containing olefins such as $CH{=}CH_2$, $CF_2{=}CH_2$, and $CF_2{=}CFH$ were unsuccessful due to both fluorination and polymerization of the substrate. Fluorination of the double bond was also the only reaction observed for $CFCl{=}CFCl$ and $CF_2{=}CClCF_2Cl$. Similarly, attempts to replace the BF_2 group in CH_2FBF_2 by an ONF_2 group by low-temperature treatment with NF_3O were unsuccessful, resulting in the quantitative fluorination (8).

$$CH_2FBF_2 + NF_3O \rightarrow CH_2F_2 + NO^+BF_4^- \qquad (8)$$

The low-temperature BF_3-catalyzed addition of NF_3O to the perfluorinated acetylene $CF_3C{\equiv}CCF_3$ was also studied, but no reaction was observed under the given conditions. With perfluorobutadiene a smooth reaction occurred, but resulted only in fluorination to perfluorobutene-2.

Attempts were unsuccessful to verify the intermediates postulated in eq 3–5 and 7 by low-temperature ^{19}F NMR spectroscopy. For the $CF_2{=}C(BF_2)CF_3$–NF_3O system, when kept at −80 °C or below, only the final products NF_2CF_2C-

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[12] Lappert, M. F. In "The Chemistry of Boron and its Compounds"; Muetterties, E. L., Ed.; Wiley: New York, 1967; p 461.

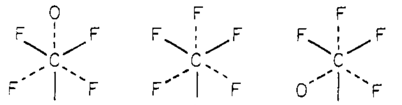
[13] Banks, R. E.; Hazeldine, R. N.; Taylor, D. R. *Proc. Chem. Soc., London* **1964**, 121.

(O)CF_3 and BF_3 were observed. For $CF_2{=}CF_2$ and BF_3 in $CFCl_3$ solution, no interaction was observable at temperatures as low as −120 °C.

Properties of the *N*,*N*-Difluoro-*O*-perhaloalkylhydroxylamines. All the $XCF_2CF_2ONF_2$-type (X = F, Cl, Br) compounds prepared in this study are colorless gases or liquids, which are stable at ambient temperature. The thermal stability of the compounds is surprisingly high. For example, $C_2F_5ONF_2$, when heated over CsF in a Pyrex ampule to 93 °C for 17 h, showed no decomposition. In stainless steel, heating to 325 °C for several hours was required to observe degradation to C_2F_6 and NO. In their chemical properties these R–ONF_2 compounds are similar to NF_3. Thus, $C_2F_5ONF_2$ is not reduced by HI and is not hydrolyzed by concentrated aqueous alkali solutions at 50 °C. Fluorination of $C_2F_5ONF_2$ with F_2 at 150 °C produced C_2F_6, but no evidence for NF_3O or the unknown and probably unstable $FONF_2$ was obtained.

The lack of NF_3O formation in this fluorination reaction supports the spectroscopic evidence that the ONF_2 group in these $RONF_2$ compounds is bonded to the carbon atom through an oxygen and not a nitrogen atom.

The new $RONF_2$ compounds prepared in this study were thoroughly characterized by spectroscopic techniques, and the observed data are listed in the Experimental Section. ^{19}F NMR data were particularly useful to demonstrate the presence of the $-ONF_2$ group and to show that, for the unsymmetric perhaloethylenes, $XCF_2CF_2ONF_2$ was the only isomer formed. It should be mentioned that for $BrCF_2CF_2ONF_2$ the ^{19}F NMR spectra were strongly temperature dependent, indicating the presence of different rotamers due to hindered rotation caused by the bulky bromine ligand. The $BrCF_2CF_2ONF_2$ molecule is expected to exist as three different rotamers, one trans and two equally probable gauche forms, which could be sterically less favored.



trans (A_2B_2) gauche (AA′BB′)

At 30 °C, the two CF_2 group signals consisted of broad (~15-Hz half-width) unresolved lines. At 20 °C, the two lines separated into two signals each, a resolved lower field signal for the trans isomer and a poorly resolved signal of similar intensity at slightly higher field attributed to the two gauche isomers. At −20 °C the relative intensity and resolution of the trans signals were significantly increased. At −50 °C, the resolution of the trans signal decreased again and the frequency separation between the trans and the gauche signals increased.

Although only the $XCF_2CF_2ONF_2$ isomers were present, the mass spectra generally exhibited CF_3^+ ions of medium intensity. This is not unusual for compounds of this type and is readily explainable by ion recombination in the mass spectrometer.

The vibrational spectra are listed in the Experimental Section. The assignments for the $CONF_2$ group are straightforward and can be made by comparison with those previously discussed for CF_3ONF_2.[5] In addition to the characteristic[5] $CONF_2$ stretching modes in the 1050–850-cm^{-1} region and the CF_2 stretching modes in the 1300–1100-cm^{-1} region, the spectra exhibit a medium intense infrared and weak Raman band at about 1400 cm^{-1}, characteristic for the C–C stretching mode.

Properties of $CF_2{=}C(BF_2)CF_3$. This new vinyldifluoroborane is a colorless liquid and gas and is stable at ambient temperature. In addition to its spectroscopic identification (see Experimental Section), the compound was identified by its hydrolysis reaction (9), yielding $CF_2{=}CHCF_3$.[14] The vibrational spectra of $CF_2{=}C(BF_2)CF_3$ show bands in the regions expected for the stretching modes of the C=C (~1710 cm^{-1}), BF_2, (~1450 and 1290 cm^{-1}),[15] and $F_2C{=}CF$ (~1390, 1177, and 1040 cm^{-1})[16] groups. However, these assignments are tentative, and a definitive assignment will require a more detailed study.

$$CF_2{=}CF(BF_2)CF_3 + H_2O \rightarrow CF_2{=}CHCF_3 + (HOBF_2) \quad (9)$$

Conclusion. The Lewis acid catalyzed addition of NF_3O to olefins provides a useful method for the synthesis of $-ONF_2$-substituted halocarbons, provided the substrates do not contain hydrogen and are highly fluorinated. Heavy halogens such as iodine or bromine also appear to be detrimental to the yield of R_fONF_2. The only isomer observed for the addition of NF_3O to $XCF{=}CF_2$ is $XCF_2CF_2ONF_2$. This apparent anti-Markownikoff-type addition is explainable by the normal polar addition of the Lewis acid to the olefins followed by appropriate substitution and elimination reactions. The intermediate formation of the Lewis acid–olefin adduct was demonstrated for $CF_2{=}C{=}CF_2$. The reactions of NF_3O with vinyldifluoroboranes such as $CF_2{=}CFBF_2$ and $CF_2{=}C(BF_2)CF_3$ indicate that $-ONF_2$-substituted vinyl compounds are unstable and easily undergo a keto–enol-type tautomeric rearrangement to the corresponding difluoramino ketones.

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Registry No. NF_3O, 13847-65-9; C_2F_4, 116-14-3; C_2F_3Cl, 79-38-9; C_2F_3Br, 598-73-2; $CF_3CF_2ONF_2$, 24687-10-3; $ClCF_2CF_2ONF_2$, 24684-27-3; $BrCF_2CF_2ONF_2$, 24684-28-4; $CF_2{=}C(BF_2)CF_3$, 84238-04-0; $CF_3COCF_2NF_2$, 4188-38-9; $CF_3C(OH)_2CF_2NF_2$, 84238-05-1; BF_3, 7637-07-2; tetrafluoroallene, 461-68-7.

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(15) Parsons, T. D.; Self, J. M.; Schaad, L. H. *J. Am. Chem. Soc.* **1967**, *89*, 3446.

(16) Shimanouchi, T. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1972**, *NSRDS-NBS 39*, 75–83.