methyl-4-phenyl-2(5*H*)-furanone (**7b**) in 78% and 15% yields, respectively.

6b: colorless oil; MS *m/e* 218; IR (neat) 1765 cm^{-1} (C=O). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.50; H, 6.44.

Hydrogenation of 6a. Into a solution of **6a** (408 mg, 2.0 mmol) in methanol (20 mL) was added Pd/C (5%, 100 mg), and the mixture was stirred for 18 h at room temperature under a hydrogen atmosphere. The catalyst was removed by filtration, and the filtrate was evaporated to give a mixture of diastereomers of 3,4-dihydro-5-methoxy-4-methyl-3-phenyl-2(5*H*)-furanone (**8a**): 406 mg; a colorless oil; IR (neat) 1775 cm^{-1} (C=O). The 400-MHz ^{1}H NMR spectrum showed four sets of signals: δ 0.69, 0.72, 1.05, and 1.15 for methyl protons and δ 3.52, 3.49, 3.48, and 3.56 for methoxy protons. The isomer ratio (8:2:1:1) was determined from the peak areas of the methoxy protons. The resonances for major component are as follows: δ 0.69 (d, 3 H, Me, *J* = 7.3 Hz), 2.85 (dqd, 1 H, CHMe, *J* = 9.8, 7.3, and 5.4 Hz), 3.52 (s, 3 H, OMe), 3.87 (d, 1 H, CHPh, *J* = 9.8 Hz), 5.37 (d, 1 H, OCHO, *J* = 5.4 Hz), 7.18–7.33 (m, 5 H, Ph).

Carbonylation of 1a in Ethanol in the Presence of $Rh_4(CO)_{12}$ and Various Bases (Table I). Into a 30-mL glass tube containing a Teflon-coated magnetic stirring bar were added **1a** (0.18 g, 1.0 mmol), $Rh_4(CO)_{12}$ (19 mg, 0.025 mmol), a base (1.0 mmol), and ethanol (15 mL), and the tube was placed into a 50-mL stainless-steel autoclave. The autoclave was sealed, flushed twice with carbon monoxide, pressurized to 40 kg/cm^2, and heated with stirring at 125 °C for 6 h. The reaction mixture was analyzed by GC. The results are shown in Table I.

Alcoholysis of 3b. A mixture of compound **3b** (100 mg, 0.36 mmol) and Na_2CO_3 (106 mg, 1.0 mmol) in ethanol (15 mL) was stirred at 150 °C for 6 h under 50 kg/cm^2 of carbon monoxide in the same way described above. GC analysis of the reaction mixture indicated the presence of **5** (81 mg) and **3b** (14 mg).

Registry No. **1a**, 501-65-5; **1b**, 503-17-3; **1c**, 928-49-4; **1d**, 673-32-5; **3a**, 42367-25-9; **3b**, 79379-66-1; **3c**, 79379-68-3; **3d**, 79379-69-4; **3e**, 79379-70-7; **3f**, 79379-71-8; **3g**, 83917-79-7; **4**, 79379-67-2; *meso*-**5**, 13638-89-6; *dl*-**5**, 24097-93-6; **6a**, 83917-80-0; **6b**, 79379-73-0; **7a**, 83917-81-1; **7b**, 79379-72-9; **8a** (isomer 1), 83917-82-2; **8a** (isomer 2), 83946-18-3; **8a** (isomer 3), 83946-19-4; **8a** (isomer 4), 83946-20-7; NaOEt, 141-52-6; NaOH, 1310-73-2; $NaHCO_3$, 144-55-8; Na_2CO_3, 497-19-8; NaOAc, 127-09-3; Li_2CO_3, 554-13-2; K_2CO_3, 584-08-7; Rb_2CO_3, 584-09-8; Cs_2CO_3, 534-17-8; $CaCO_3$, 471-34-1; $BaCO_3$, 513-77-9; LiOAc, 546-89-4; KOAc, 127-08-2; RbOAc, 563-67-7; CsOAc, 3396-11-0; $Rh_4(CO)_{12}$, 19584-30-6; $RhCl_3$, 10049-07-7; Rh_2O_3, 12036-35-0; $RhCl(PPh_3)_3$, 14694-95-2; 5-ethyl-4-methyl-3-phenyl-2(5*H*)-furanone, 79379-62-7; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 2-propanol, 67-63-0; 1-octanol, 111-87-5.

Comparison of the Reactivity of CF_3OX (X = Cl, F) with Some Simple Alkenes

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Reactions of CF_3OX (X = Cl, F) with a variety of simple alkenes were carried out to compare the regio- and stereoselectivity of the additions to carbon–carbon double bonds. The observed addition products with CF_3OCl are consistent with an electrophilic syn addition. With CF_3OF the observed products indicate a different regioselectivity and low stereoselectivity, consistent with a free-radical addition.

Introduction

Fluoroxytrifluoromethane, CF_3OF, was the first carbon compound to contain an OF group bonded to carbon. The compound is easily prepared in high purity by several different methods, and its high thermal stability renders it the most useful derivative for exploring the chemistry of the very reactive O–F bond.[2,3] Trifluoromethyl hypochlorite, CF_3OCl, is a related compound that is also readily obtained.[2,4,5] Its properties are similar to those of CF_3OF as the most suitable perfluoroalkyl hypochlorite for investigative purposes.

Superficially, CF_3OF and CF_3OCl appear to be closely related, and one might expect their reaction chemistry to be very similar. Indeed, both serve as sources of the $CF_3O\cdot$ radical in photochemical reactions.[4b,6,7] However, their reactivity must show substantial differences based on the electronegativity of Cl vs. F.

The chemistry of CF_3OF has been widely investigated, with the greatest interest centered on the ability of CF_3OF to serve as a selective fluorination reagent.[2,8–12] A variety of reactions with both aliphatic and aromatic compounds have been examined. Other fluoroxy reagents have also been examined in less detail and found to undergo analogous reactions.[13,14] In many of the reported reactions of CF_3OF, it has been proposed that the reactions proceed by an electrophilic mechanism involving the concept of

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fluorine bound to oxygen being attacked by a nucleophile, followed by the loss of CF_3O^- to generate a carbocation intermediate. For an ethylenic substrate, the nucleophile is the π-electron system, and the carbocation is a highly reactive α-fluorinated species.

The chemistry of CF_3OCl has received much less attention, but a variety of reactions clearly show the positive halogen character of the chlorine.[3,15,16] Additions of CF_3OCl to ethylenic systems show a high specificity, and the observed products are consistent with a polar mechanism where the positive chlorine attaches to the most electron-rich carbon.[17-19] It has been suggested, however, that the observed reactions of CF_3OCl are consistent with a radical ion reaction mechanism in which polar effects play a leading role.[2]

Nearly all mechanistic inferences with CF_3OF are based on studies of rather complex molecules. With simple olefins, essentially no studies had been made under conditions where a non-free-radical process might be favored and where the simple addition product could be observed. Similarly, reactions with CF_3OCl had not been carried out to allow elucidation of the stereochemistry of the addition to ethylenic substrates. This work was carried out to compare the reactivity of CF_3OF and CF_3OCl with some identical or closely related alkenes, with the goal of elucidating the stereochemistry of the addition to the carbon–carbon double bonds. It was anticipated a priori that similar results would be found for both compounds. However, our studies show the compounds to be quite different.

Experimental Section

General Methods. Volatile compounds were handled in a glass or stainless steel vacuum system equipped with glass–Teflon or stainless steel valves. Pressures were measured with a Wallace and Tiernan differential pressure gauge, series 1500. All reactions were carried out in 100-mL glass bulbs fitted with glass–Teflon valves. Separation of volatile products was done by trap to trap distillation. Further purification, if needed, was done by GLC with columns packed with 40% Halocarbon 11-21 polymer oil on Chromosorb P.

Infrared spectra were recorded on Perkin-Elmer 337, 180, and 1330 spectrometers with 10-cm cells fitted with AgCl or KCl windows. NMR spectra were recorded on Varian T-60 (proton) and XL-100-15 (fluorine and proton) spectrometers with ~20 mol % solutions in $CFCl_3$. ^{19}F chemical shifts are reported as ϕ^* values (δ relative to $CFCl_3$ as solvent, not at infinite dilution. A negative chemical shift is to higher field of $CFCl_3$ and vice versa). Me_4Si was used as an external standard for ^1H NMR. Mass spectra were recorded at 70 EV on a Finnigan 4021C system equipped with both electron impact and chemical ionization modes. EI spectra were taken at 70 EV. CI spectra were taken at 70 EV with methane as the ionizing gas.

Reagents. Carbonyl fluoride was prepared by reacting $COCl_2$ with NaF in CH_3CN at 40 °C for several days. Chlorine monofluoride was prepared by heating equimolar amounts of Cl_2 and F_2 at 230 °C in a Monel bomb. Fluorine was obtained from Air Products and was passed through a sodium fluoride scrubber before use. Cesium fluoride was activated by placing the powdered solid in a fluorinated metal reactor containing several stainless steel balls. It was pumped under dynamic vacuum for several hours at 22 °C and then treated with 2 atm of F_2 for several hours. The vessel was violently agitated in a paint shaker several times during treatment with F_2. Fluoroxytrifluoromethane[20] and CF_3OCl[4] were prepared according to the standard literature methods. Olefins and other chemicals were obtained from commercial sources and were appropriately purified as needed.

Reactions of CF_3OX (X = Cl, F) with Olefins. The reactions were carried out under the mildest conditions possible. Freon-11 or Freon-12 or a mixture of the two was usually used as the solvent. A typical reaction was performed with 2–3 mmol of the olefins. The olefin was first condensed into the reactor, and approximately 20 mmol of solvent was then condensed onto it at −195 °C. The contents were then warmed to 22 °C to form a homogeneous solution of the olefin in the solvent. The reactor was then cooled to −195 °C, and a stoichiometric amount of the hypohalite was condensed into the reactor. The reactor was then placed in a cold bath and allowed to warm up slowly to 22 °C. Several of the reactions were tried under a variety of experimental conditions to determine the effect of temperature, diluents, method of addition of CF_3OF and CF_3OCl, and other variations on the observed products. Some of these are presented in the following description of the reactions and the results section. All reactions are summarized in Tables I and II, and the characterization of the addition products follows.

Reactions of CF_3OF. *trans*-$CHCl{=}CHCl$. The reaction was tried under a variety of conditions to see if CF_3OF could be added stereospecifically across the carbon–carbon double bond. The reaction mixture was analyzed after separating through traps cooled to −35, −65, and −195 °C. The addition product collected in the −65 °C trap. Further purification was tried by using GLC, but the erythro and threo isomers could not be separated. *erythro*- and *threo*-$CF_3OCHClCHClF$: colorless liquid; mol wt 197.5 (calcd 201.0); IR 2960 (w), 1350 (vs), 1285 (sh, s), 1225 (vs), 1205 (sh, s), 1105 (s), 1055 (s), 1005 (w), 973 (vw), 950 (w), 882 (m), 810 (s), 765 (s), 743 (sh, m), 650 (m, br), 630 (m), 565 (m), 488 (w) cm^{-1}; ^{19}F NMR (*erythro*-$CF_3{}^AOCHClCHClF^B$) ϕ_A^* −60.6 (d), ϕ_B^* −143.6 (q, d, d), $J_{AB} = 2.0$, $^2J_{HF} = 49.5$, $^3J_{HF} = 4.5$ Hz; (*threo*-$CF_3{}^AOCHClCHClF^B$) ϕ_A^* 60.4 (d), ϕ_B^* −144.8 (q, d, d), $J_{AB} = 1.0$, $^2J_{HF} = 50.0$, $^3J_{HF} = 6.0$ Hz.

$CH_2{=}CCl_2$. This reaction was tried under a variety of conditions to see if the orientation of addition could be influenced. The products of the reaction were separated by distilling through traps cooled to −30, −75, and −195 °C. The addition product collected in the −75 °C trap. $CF_3OCH_2CCl_2F$: colorless liquid; mol wt 202.7 (calcd 201.0); IR 2950 (w), 1350–1220 (vs), 1150 (m), 1105 (vs), 1024 (w), 988 (sh, m), 945 (vs), 920 (vs), 895 (sh, s), 793 (m), 769 (w), 728 (m), 665 (m), 605 (w), 582 (w), 552 (w), 500 (w) cm^{-1}; ^{19}F NMR ($CF_3{}^AOCH_2CCl_2F^B$) ϕ_A^* −61.9 (d), ϕ_B^* −65.2 (q, t), $J_{AB} = 2.5$, $^3J_{HF} = 12.5$ Hz.

$CH_2{=}CF_2$. The products were separated through traps cooled to −78, −111, and −195 °C. The addition products collected in the −111 °C trap. ^{19}F NMR of the products indicated the presence of both regioisomers, which could not be separated by GLC. $CF_3OCH_2CF_3$ and $CF_3OCF_2CH_2F$: colorless liquid; mol wt 168.2 (calcd 168.0); IR 2975 (sh, w), 2955 (m), 1408 (s), 1300–1130 (vs), 1048 (w), 970 (s), 900 (sh, m), 875 (sh, m), 850 (s), 755 (w), 685 (br, m), 618 (s), 575 (sh, w), 530 (w) cm^{-1}; ^{19}F NMR ($CF_3{}^AOCH_2CF_3{}^B$) ϕ_A^* −63.1 (q), ϕ_B^* −75.2 (q, t), $J_{AB} = 1.7$, $^3J_{HF} = 8.0$ Hz; ($CF_3{}^AOCF_2{}^BCH_2F^C$) ϕ_A^* −56.1 (d, t), ϕ_B^* −83.8, ϕ_C^* very high field, $J_{AB} = 9.5$, $J_{BC} = 16.0$, $^3J_{HF^B} = 9.0$, $J_{AC} = 0.8$ Hz; ($CF_3{}^ACH_2F^B$) ϕ_A^* −78.7 (m), ϕ_B^* very high field, $J_{AB} = 15.5$, $^3J_{HF} = 8.2$ Hz.

$CF_2{=}CCl_2$. The reaction mixture was separated through traps cooled to −78, −111, and −195 °C. The addition products collected in the −111 °C trap. ^{19}F NMR indicated the presence of three compounds, $CF_3OCF_2CCl_2F$, $CF_3OCCl_2CF_3$, and CF_3CCl_2F. All compounds were colorless liquids: IR 1295 (sh, s), 1215 (vs), 1245 (vs), 1195 (vs), 1160 (vs), 1118 (vs), 955 (sh, m), 918 (vs), 880 (s), 848 (s), 813 (s), 735 (w), 688 (sh, m), 660 (s), 558 (w), 510 (br, w) cm^{-1}; ^{19}F NMR ($CF_3{}^AOCF_2{}^BCCl_2F^C$) ϕ_A^* −56.3 (t), ϕ_B^* −87.3 (q, d), ϕ_C^* −76.4 (t), $J_{AB} = 9.3$, $J_{AC} = <1.0$ Hz, $J_{BC} = 6.7$ Hz; ($CF_3{}^AOCCl_2CF_3{}^B$) ϕ_A^* −54.8 (s), ϕ_B^* −84.3 (s); ($CF_3{}^ACCl_2F^B$) ϕ_A^* −84.4 (d), ϕ_B^* −76.7 (q), $J_{AB} = 5.5$ Hz.

$CF_2{=}CBr_2$. The products were separated after distilling through −20, 78, and −195 °C traps. The addition products

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Table I. Reactions of CF_3OF with Some Alkenes

olefin	solvent	temp, °C (time, h)	products[a] [%][b]
trans-$CHCl{=}CHCl$	$CFCl_3$	−50 (24) −50 to 22 (20)	*threo*-$CF_3OCHClCHClF$ (50) [72] *erythro*-$CF_3OCHClCHClF$ (50)
$CH_2{=}CCl_2$	$CFCl_3$	−150 to 22 (20)	$CF_3OCH_2CCl_2F$ (100) [75]
$CH_2{=}CF_2$	$CFCl_3$	−160 to 22 (20)	$CF_3OCH_2CF_3$ (97.5), $CF_3OCF_2CH_2F$ (2), CF_3CH_2F (trace) [76]
$CF_2{=}CCl_2$	none	−150 to 22 (20)	$CF_3OCF_2CCl_2F$ (63), CF_3CCl_2F (25), $CF_3OCCl_2CF_3$ (12)
$CF_2{=}CBr_2$	none	−160 to 22 (20)	$CF_3OCBr_2CF_3$ (20), CF_3CBr_2F (50), $CF_3OCF_2CBr_2F$ (21)
$CF_2{=}CHBr$	none	−140 to 22 (20)	CF_3OCF_2CHBrF (70), $CF_3OCHBrCF_3$ (24)
$CF_2{=}CFBr$	none	−150 to 22 (20)	$CF_3OCF_2CF_2Br$ (80), $CF_3OCFBrCF_3$ (20)
cis-$CHF{=}CHF$	none	−150 to 22 (20)	$CF_3OCHFCHF_2$ (100)
$CH_2{=}CHCH_3$	CF_2Cl_2	−155 to −30 (24) −30 to 22 (0.2)	$CF_3OCH_2CHFCH_3$ (80), $CF_3OCH(CH_3)CH_2F$ (20)
$CH_2{=}CHCH_2Cl$	CF_2Cl_2 + $CFCl_3$	−165 to −30 (20)	$CF_3OCH_2CHFCH_2Cl$ (84), $CF_3OCH(CH_2Cl)CH_2F$ (16) [50]
cis-$ClCH_2CH{=}CHCH_2Cl$	$CFCl_3$	−155 to −30 (24) −30 to 22 (0.2)	*threo*-$CF_3OCH(CH_2Cl)CHFCH_2Cl$ (35), *erythro*-$CF_3OCH(CH_2Cl)CHFCH_2Cl$ (65) [90]
$CH_2{=}CHOCOCF_3$	CF_2Cl_2 + $CFCl_3$	−155 to −40 (20) −40 to 22 (0.5)	$CF_3OCH_2CHFOCOCF_3$ (77), $CF_3OCH(OCOCF_3)CH_2F$ (23) [83]
$CH_2{=}CHF$	CF_2Cl_2	−155 to 22 (24)	$CF_3OCH_2CHF_2$ (87), $CF_3OCHFCH_2F$ (13)
$CH_2{=}CHBr$	$CFCl_3$	−140 to −30 (16) −30 to 22 (0.5)	CF_3OCH_2CHBrF (100) [43]
$CH_2{=}CHOCOCH_3$	$CFCl_3$, CF_2Cl_2	−155 to 22 (20)	$CF_3OCH_2CHFOCOCH_3$ (61), $CF_3OCH(OCOCH_3)CH_2F$ (39), $CH_3COOCHFCH_2F$ (trace) [33]
$CF_3CF{=}CF_2$	none	−155 to 22 (20)	$CF_3OCF_2CF_2CF_3$ (67), $CF_3OCF(CF_3)_2$ (33) [34]
norbornylene	$CFCl_3$	−160 to 22 (20)	charring
cyclohexene	$CFCl_3$	−160 to 22 (24)	charring
cis- or *trans*-2-butene	$CFCl_3$ or CF_2Cl_2	−155 to 22 (20)	charring + oligomers (?)

[a] Relative amounts in parentheses as determined by ^{19}F NMR. [b] Total yield of products listed based on starting alkene.

Table II. Reactions of CF_3OCl with Some Alkenes

olefin	solvent	temp, °C (time, h)	products[a] [%][b]
trans-$CHCl{=}CHCl$	$CFCl_3$	−111 to 22 (20)	$CF_3OCHClCHCl_2$ (93.4), $FCHClCCl_2H$ (2.6) [75]
$CH_2{=}CCl_2$	$CFCl_3$	−111 to 22 (20)	$CF_3OCCl_2CH_2Cl$ (100)
$CH_2{=}CF_2$	$CFCl_3$	−111 to 22 (20)	$CF_3OCF_2CH_2Cl$ (50), CF_3CH_2Cl (50) [76]
$CF_3{=}CCl_2$	none	−150 to −30 (24) −30 to 22 (0.5)	$CF_3OCCl_2CF_2Cl$ (86), $CF_3OCF_2CCl_3$ (14) [90]
$CF_2{=}CBr_2$	none	−150 to −30 (20) −30 to 22 (0.5)	$CF_3OCBr_2CF_2Cl$ (56.5), $CF_3OCF_2CBr_2Cl$ (43.5)
$CF_2{=}CHBr$	none	−140 to 22 (20)	$CF_3OCF_2CHBrCl$ (54), $CF_3CHBrCl$ (46)
$CF_2{=}CFBr$	none	−140 to 22 (20)	$CF_3OCFBrCF_2Cl$ (71), $CF_3OCF_2CFBrCl$ (29)
cis-$CHF{=}CHF$	none	−150 to 22 (20)	*erythro*-$CF_3OCHFCHFCl$ (100) [86]
trans-$CHF{=}CHF$	none	−150 to 22 (20)	*threo*-$CF_3OCHFCHFCl$ (100) [88]
cis- and *trans*-$CHF{=}CHF$ (8:5)	none	−150 to 22 (20)	*erythro*- and *threo*-$CF_3OCHFCHFCl$ (8:5)
$CH_2{=}CHCH_3$	$CFCl_3$ + CF_2Cl_2	−150 to −30 (20) −30 to 22 (0.2)	$CF_3OCH(CH_3)CH_2Cl$ (78), $CF_3OCH_2CHClCH_3$ (22) [57]
$CH_2{=}CHCH_2Cl$	CF_2Cl_2 + $CFCl_3$	−150 to −30 (36) −30 to 22 (0.5)	$CF_3OCH(CH_2Cl)CH_2Cl$ (78), $CF_3OCH_2CHClCH_2Cl$ (22) [95]
cis-$ClCH_2CH{=}CHCH_2Cl$	$CFCl_3$	−111 to 22 (20)	*erythro*-$CF_3OCH(CH_2Cl)CHClCH_2Cl$ [92]
$CH_2{=}CHOCOCF_3$	CF_2Cl_2 + $CFCl_3$	−111 to −30 (20) −30 to 22 (0.5)	$CF_3OCH(OCOCF_3)CH_2Cl$ (84.5), $FCH(OCOCF_3)CH_2Cl$ (15.5)
$CH_2{=}CHF$	CF_2Cl_2	−150 to −30 (24) −30 to 22 (0.2)	$CF_3OCHFCH_2Cl$ (66), F_2CHCH_2Cl (33) [83]
$CH_2{=}CHBr$	$CFCl_3$	−135 to −40 (24) −40 to 22 (0.2)	$CF_3OCHBrCH_2Cl$ (100) [83]
cis-$CH_3CH{=}CHCH_3$	$CFCl_3$	−150 to 22 (20)	*erythro*-$CF_3OCH(CH_3)CHClCH_3$ (100)
trans-$CH_3CH{=}CHCH_2$	CF_2Cl_2 + $CFCl_3$	−140 to −30 (24) −30 to 22 (0.2)	*threo*-$CF_3OCH(CH_3)CHClCH_3$ (100)
cis- and *trans*-$CH_3CH{=}CHCH_3$ (1:2)	CF_2Cl_2 + $CFCl_3$	−140 to −30 (20) −30 to 22 (0.2)	*erythro*- and *threo*-$CF_3OCH(CH_3)CHClCH_3$ (1:2)
cyclohexene	none	−160 to 22 (20)	*cis*-1-chloro-2-(trifluoromethoxy)cyclohexane (100)
$CH_2{=}CHOCOCH_3$	none	−155 to 22 (20)	$CF_3OCH(OCOCH_3)CH_2Cl$ (100)
$CF_3CF{=}CF_2$	none	−155 to 22 (20)	$CF_3OCF_2CFClCF_3$ (71.5), $CF_3OCF(CF_3)CF_2Cl$ (28.5) [66]
norbornylene	none	−160 to 22 (20)	*cis*-2-chloro-3-(trifluoromethoxy)norbornane (100)

[a] Relative amounts in parentheses as determined by ^{19}F NMR. [b] Total yield of products listed based on starting alkene.

collected in the −78 °C trap. ^{19}F NMR and GLC purification indicated the presence of $CF_3OCF_2CBr_2F$, $CF_3OCBr_2CF_3$, and CF_3CBr_2F. The two regioisomers could not be separated by GLC. CF_3CBr_2F: colorless liquid; mol wt 261.2 (calcd 260.0); IR 1285 (sh, s), 1270 (vs), 1245 (vs), 1228 (vs), 1215 (vs), 1167 (s), 1142 (s), 1102 (vs), 960 (w), 908 (vs), 871 (w), 832 (vs), 718 (vs), 568 (w), 545 (w) cm^{-1}; ^{19}F NMR ($CF_3{}^ACBr_2F^B$) $\phi_A{}^*$ −85.5, $\phi_B{}^*$ −77.8, J_{AB} = 9.5 Hz. $CF_3OCBr_2CF_3$ and $CF_3OCF_2CBr_2F$: colorless liquid; mol wt 321.0 (calcd 326.0); IR 1250 (vs), 1190 (vs), 1145 (vs), 1105 (vs), 930 (sh, m), 915 (s), 875 (s), 835 (s), 800 (s), 760 (sh, w), 723 (s), 683 (w), 650 (m), 580 (w), 550 (m), cm^{-1}; ^{19}F NMR ($CF_3{}^AOCBr_2CF_3{}^B$) $\phi_A{}^*$ −55.1 (br, s), $\phi_B{}^*$ −81.8 (br, s), J_{AB} = <1.0 Hz; ($CF_3{}^AOCF_2{}^BCBr_2F^C$) $\phi_A{}^*$ −56.2 (t), $\phi_B{}^*$ −85.5 (m), $\phi_C{}^*$ −77.2 (t), J_{AB} = 9.0, J_{BC} = 11.0 Hz.

$CF_2{=}CHBr$. The products were separated through traps cooled to −30, −111, and −195 °C. The addition product collected in the −111 °C trap. ^{19}F NMR showed the presence of both regioisomers CF_3OCF_2CHBrF and $CF_3CHBrOCF_3$. These isomers were not readily separable by GLC. CF_3OCF_2CHBrF and $CF_3OCHBrCF_3$: colorless liquids; mol wt 245.3 (calcd 247.0); IR 2990 (w), 1352 (s), 1305 (vs), 1260 (vs), 1240 (vs), 1215 (vs), 1160 (vs), 1135 (vs), 1102 (s), 1075 (m), 1032 (vw), 962 (m), 910 (w), 835 (w), 808 (vw), 772 (s), 750 (sh, m), 710 (vw), 690 (w), 640 (m), 610 (sh, w), 572 (w) cm^{-1}; ^{19}F NMR ($CF_3{}^AOCF_2{}^BCHBrF^C$) $\phi_A{}^*$ −56.2 (d, t), $\phi_B{}^*$ −85.4 (m), $\phi_C{}^*$ −159.7 (q, t, d), J_{AB} = 9.3, J_{BC} = 14.0, J_{AC} = 0.7, $^2J_{HF}$ = 47.5 Hz; ($CF_3{}^AOCHBrCF_3{}^B$) $\phi_A{}^*$ −62.0 (q), $\phi_B{}^*$ −79.3 (q, d), J_{AB} = 0.8, $^3J_{HF}$ = 4.5 Hz.

$CF_2{=}CFBr$. The reaction products were analyzed after separating through traps cooled to −70, −111, and −195 °C. The addition product collected in the −111 °C trap. ^{19}F NMR indicated the presence of both regioisomers. $CF_3OCF_2CF_2Br$ and $CF_3OCFBrCF_3$: colorless liquids; mol wt 262.3 (calcd 265.0); IR 1352 (s), 1280 (vs), 1250 (vs), 1190 (vs), 1155 (vs), 1115 (vs), 990 (m), 960 (s), 940 (sh, m), 882 (s), 842 (s), 815 (s), 738 (br, w), 680 (w), 655 (m), 640 (sh, m), 630 (sh, w), 600 (w), 525 (br, w) cm^{-1}; ^{19}F NMR ($CF_3{}^AOCF_2{}^BCF_2{}^CBr$) $\phi_A{}^*$ −56.2 (t), $\phi_B{}^*$ −88.7 (t, q), $\phi_C{}^*$ −69.8 (t), J_{AB} = 9.7, J_{BC} = 3.5 Hz; ($CF_3{}^AOCF^BBrCF_3{}^C$) $\phi_A{}^*$ −55.5 (d), $\phi_B{}^*$ −77.9 (q, q), $\phi_C{}^*$ −85.3 (d), J_{AB} = 11.5, J_{BC} = 4.3 Hz.

***cis*-$CHF{=}CHF$.** The products were distilled through traps cooled to −78, −111, and −195 °C. The addition product collected in the −111 °C trap. $CF_3OCHFCHF_2$: colorless liquid; mol wt 167.7 (calcd 168.0); IR 2960 (vw), 1420 (m), 1352 (vs), 1282 (sh, s), 1245 (vs), 1205 (sh, s), 1162 (s), 1115 (vs), 1078 (vs), 1052 (sh, s), 1018 (sh, m), 955 (m), 902 (m), 878 (m), 840 (s), 778 (m), 708 (sh, w), 700 (m), 682 (m), 615 (w), 585 (w), 570 (w) cm^{-1}; ^{19}F NMR ($CF_3{}^AOCHF^BCHF_2{}^C$) $\phi_A{}^*$ −61.6 (d), $\phi_B{}^*$ −146.2 (m), $\phi_C{}^*$ −136.0 (m), J_{AB} = 4.5, J_{BC} = 6.5, $J_{H^BF^B}$ = 56.0, $J_{H^CF^C}$ = 54.0, $J_{H^BF^C}$ = 3.5, $J_{H^CF^B}$ = 2.0 Hz.

$CH_2{=}CHCH_3$. The reaction mixture was separated through traps cooled to −78 and −195 °C. The addition product and some Freon-11 (used as solvent) collected in the −78 °C trap. Reseparation of the −78 °C trap through −70 and −195 °C traps gave the products in the −70 °C trap. ^{19}F NMR indicated the presence of both regioisomers. $CF_3OCH_2CHFCH_3$ and $CF_3OCH(CH_3)CH_2F$: colorless liquids; IR 2985 (w), 2975 (sh, w), 2935 (sh, vw), 1280 (vs), 1237 (vs), 1165 (vs), 622 (w) cm^{-1}; ^{19}F NMR ($CF_3{}^AOCH_2CHF^BCH_3$) $\phi_A{}^*$ −62.2 (d), $\phi_B{}^*$ −182.3 (m), J_{AB} = 1.5 Hz; ($CF_3{}^AOCH(CH_3)CH_2F^B$) $\phi_A{}^*$ −59.8 (d), $\phi_B{}^*$ −228.5 (m), $^2J_{HF}$ = 47.0, $^3J_{HF}$ = 8.5, J_{AB} = 2.0 Hz.

$CH_2{=}CHCH_2Cl$. The reaction mixture was analyzed after separation through −45 and −195 °C traps. The addition product collected in the −45 °C trap. ^{19}F NMR indicated the presence of both regioisomers. $CF_3OCH_2CHFCH_2Cl$ and $CF_3OCH(CH_2Cl)CH_2F$: colorless liquids; IR 2970 (w), 1405 (w), 1320 (sh, m), 1285 (vs), 1240 (vs), 1175 (vs), 1090 (w, br), 1030 (w), 930 (w), 848 (w), 778 (w), 725 (vw) cm^{-1}; prominent peaks in the mass spectrum (EI) 160, 162 $(M - HF)^+$, 131 $(CF_3OCH_2CHF)^+$, 125 $(M - HF - Cl)^+$, 99 $(CF_3OCH_2)^+$, 69 $(CF_3)^+$, (CI) 161, 163 $(CF_3OCH_2CHCH_2Cl)^+$, 95, 97 $(CH_2CHFCH_2Cl)^+$; ^{19}F NMR ($CF_3{}^AOCH_2CHF^BCH_2Cl$) $\phi_A{}^*$ −62.4 (d), $\phi_B{}^*$ −188.8 (m), J_{AB} = 1.5, $^2J_{HF}$ = 46.5 Hz; ($CF_3{}^AOCH(CH_2Cl)CH_2F^B$) $\phi_A{}^*$ −60.1 (d), $\phi_B{}^*$ −234.5 (m), J_{AB} = 2.5, $^2J_{HF}$ = 49.0, $^3J_{HF}$ = 18.5 Hz.

***cis*-$ClCH_2CH{=}CHCH_2Cl$.** The products were separated through −40 and −195 °C traps. The addition product collected in the −40 °C trap as a heavy liquid. ^{19}F NMR indicated the presence of both stereoisomers. *erythro*- and *threo*-$CF_3OCH(CH_2Cl)CHFCH_2Cl$: colorless liquids; IR 2980 (vw), 1450 (vw), 1285 (s), 1240 (s), 1175 (s), 1120 (vw), 1070 (m), 1030 (m), 978 (vw), 942 (vw), 870 (vw), 845 (vw), 780 (m) cm^{-1}; prominent peaks in the mass spectrum (EI) 179, 181 $[CF_3OCH(CH_2Cl)CHF]^+$, 147, 149 $(CF_3OCHCH_2Cl)^+$, 81, 83 $(FCHCH_2Cl)^+$, 69 $(CF_3)^+$, (CI) 209, 211, 213 $[CF_3OCH(CH_2Cl)CHCH_2Cl]^+$, 193, 195 $[CF_3OCH(CH_2Cl)CHFCH_2]^+$, 143, 145, 147 $(ClCH_2CHCHFCH_2Cl)^+$, 89, 91 $(ClCH_2CHCHCH_2)^+$; ^{19}F NMR (*threo*-$CF_3{}^AOCH(CH_2Cl)CHF^BCH_2Cl$) $\phi_A{}^*$ −59.4 (d), $\phi_B{}^*$ −195.8 (m), $^2J_{HF}$ = 46.5, J_{AB} = 1.0; (*erythro*-$CF_3{}^AOCH^C(CH_2Cl)CHF^BCH_2{}^DCl$) $\phi_A{}^*$ −59.7 (d), $\phi_B{}^*$ −199.6 (m), J_{AB} = 1.0, $^2J_{HF}$ = 46.5, J_{BC} = 21.0, J_{BD} = 15.0 Hz.

$CH_2{=}CHOCOCF_3$. The reaction mixture was separated by distillation through traps cooled to −78 and −195 °C. The addition products collected in the −78 °C trap. ^{19}F NMR indicated the presence of both regioisomers. $CF_3OCH_2CHFOCOCF_3$ and $CF_3OCH(OCOCF_3)CH_2F$: colorless liquids; IR 2990 (vw), 2960 (vw), 1798 (s), 1410 (w), 1370 (sh, w), 1320 (m), 1278 (vs), 1235 (vs), 1185 (vs), 1175 (sh, s), 1133 (vs), 1100 (s), 1090 (sh, s), 1060 (s), 1055 (sh, m), 1022 (m), 988 (w), 910 (w), 852 (w), 758 (w), 735 (m) cm^{-1}; prominent peaks in the mass spectrum (EI) 159 $(CH_2CHFOCOCF_3)^+$, 145 $(CHFOCOCF_3)^+$, 131 $(CF_3OCH_2CHF)^+$, 99 $(CF_3OCH_2)^+$, 97 $(CF_3CO)^+$, 85 $(CF_3O)^+$, 69 $(CF_3)^+$, 65 $(FCH_2CHF)^+$, (CI) 245 $(CF_3OCH_2CHFOCOCF_3H)^+$, 225 $(CF_3OCH_2CHOCOCF_3)^+$, 159 $(CH_2CHFOCOCF_3)^+$, 131 $(CF_3OCH_2CHF)^+$; ^{19}F NMR ($CF_3{}^AOCH_2CHF^BOCOCF_3{}^C$) $\phi_A{}^*$ −62.8 (d), $\phi_B{}^*$ −140.3 (m), $\phi_C{}^*$ −76.07 (s), J_{AB} = 1.2, $^2J_{HF}$ = 53.5, $^3J_{HF}$ = 12.0 Hz; ($CF_3{}^AOCH(OCOCF_3{}^C)CH_2F^B$) $\phi_A{}^*$ −60.8 (d), $\phi_B{}^*$ −234.9 (m), $\phi_C{}^*$ = −76.12 (s), J_{AB} = 1.0, $^2J_{HF}$ = 53.0, $^3J_{HF}$ = 6.5 Hz.

$CH_2{=}CHF$. The reaction mixture was separated through −111 and −195 °C traps. The addition product collected in the −111 °C trap. ^{19}F NMR indicated the presence of both regioisomers. $CF_3OCH_2CHF_2$ and $CF_3OCHFCH_2F$: colorless liquids; IR 2980 (w), 1455 (sh, vw), 1428 (m), 1373 (m), 1325 (sh, s), 1282 (vs), 1245 (vs), 1172 (vs), 1140 (vs), 1105 (vs, 910 (m), 875 (m), 630 (w), 480 (w) cm^{-1}; prominent peaks in the mass spectra [EI] 99 $(CF_3OCH_2)^+$, 85 $(CF_3O)^+$, 69 $(CF_3)^+$, 65 $(CH_2CF_2H)^+$, (CI) 151 $(CF_3OCH_2CHF_2H)^+$, 149 $(CF_3OCH_2CF_2)^+$, 131 $(CF_3OCH_2CHF)^+$, 85 $(CF_3O)^+$, 65 $(CH_2CHF_2)^+$; ^{19}F NMR ($CF_3{}^AOCH_2CHF_2{}^B$) $\phi_A{}^*$ −62.85 (d), $\phi_B{}^*$ −126.6 (m), J_{AB} = 1.4, $^2J_{HF}$ = 55.5, $^3J_{HF}$ 12.2 Hz; ($CF_3{}^AOCHF^BCH_2F^C$) $\phi_A{}^*$ −60.7 (d), $\phi_B{}^*$ −139.6 (m), $\phi_C{}^*$ −237.3 (m), J_{AB} = 4.7, J_{BC} = 21.0, $^2J_{HF^C}$ = 46.0, $^3J_{HF^C}$ = 6.0 Hz.

$CH_2{=}CHBr$. The reaction mixture was separated through traps cooled to −65 and −195 °C. The adduct collected in the −65 °C trap. $CF_3{}^AOCH_2CHBrF^B$: colorless liquid; IR 2975 (vw), 1455 (w), 1405 (m), 1350 (s), 1285 (vs), 1235 (vs), 1175 (vs), 1115 (s), 1090 (sh, s), 1055 (s), 900 (br, w), 840 (w), 745 (s), 660 (w), 620 (sh, w), 600 (m), 460 (w) cm^{-1}; prominent peaks in the mass spectrum (EI) 131 $(CF_3OCH_2CHF)^+$, 125, 127 $(CH_2CHFBr)^+$, 111, 113 $(CHFBr)^+$, 99 $(CF_3OCH_2)^+$, 69 $(CF_3)^+$, 65 $(FCH_2CHF)^+$, (CI) 209, 211 $(CF_3OCHCHFBr)^+$, 191, 193 $(CF_3OCH_2CHBr)^+$, 131 $(CF_3OCH_2CHF)^+$, 125, 127 $(CH_2CHFBr)^+$; ^{19}F NMR ($CF_3{}^AOCH^BH^CCHBrF^D$) $\phi_A{}^*$ −62.2 (d), $\phi_D{}^*$ −147.2 (m), J_{AB} = 2.0, $^2J_{HF}$ = 53.0, $^3J_{H^BF}$ = 23.0, $^3J_{H^CF}$ = 16.0 Hz.

$CH_2{=}CHOCOCH_3$. The reaction mixture was separated through traps cooled to −35, −75, and −195 °C. The −35 °C trap contained unreacted olefin and some addition product. The −75 °C trap contained pure addition product. ^{19}F NMR indicated the presence of both regioisomers and a trace of the fluorination product. $CF_3OCH_2CHFOCOCH_3$, $CF_3OCH(OCOCH_3)CH_2F$, and $FCH(OCOCH_3)CH_2F$: colorless liquids; IR 2998 (w), 2971 (w), 2905 (vw), 1943 (w), 1922 (w), 1786 (s), 1460 (vw), 1418 (w), 1366 (m), 1327 (m), 1280 (vs), 1240 (sh, s), 1198 (vs), 1172 (vs), 1115 (s), 1070 (s), 1025 (s), 1010 (sh, m), 941 (w), 879 (w), 844 (w), 765 (vw), 733 (w), 587 (w), 531 (w) cm^{-1}; prominent peaks in the mass spectrum (EI) 105 $[CH(OCOCH)_3CH_2F]^+$, 85 $(CF_3O)^+$, 69 $(CF_3)^+$, 65 $(FCHCH_2F)^+$, 43 $(CH_3CO)^+$, (CI) 191 $(MH)^+$, 171 $[CF_3OCH(OCOCH_3)CH_2]^+$, 105 $[CH(OCOCH_3)CH_2F]^+$, 67 $(COF_2H)^+$, ^{19}F NMR ($CF_3{}^AOCH_2CHF^BOCOCH_3$) $\phi_A{}^*$ −62.3 (d), $\phi_B{}^*$ −139.3 (q, t, d), J_{AB} = 1.0, $^2J_{HF}$ = 55.0, $^3J_{HF}$ = 13.5 Hz; ($CF_3{}^AOCH(OCOCH_3)CH_2F^B$) $\phi_A{}^*$ −59.8 (d), $\phi_B{}^*$ −234.1 (q, d, t), J_{AB} = 1.2, $^2J_{HF}$ = 48.0, $^3J_{HF}$ = 7.5 Hz; ($F^ACH(OCOCH_3)CH_2F^B$) $\phi_A{}^*$ −142.0 (m), $\phi_B{}^*$ −237.7 (m), J_{AB} = 18.0, $^2J_{HF^A}$ = 55.0, $^2J_{HF^B}$ = 47.5, $^3J_{HF^B}$ = 8.7 Hz.

$CF_3CF{=}CF_2$. The reaction mixture was separated through −78, −111, and −195 °C traps. The addition products collected in the −111 °C trap. ^{19}F NMR indicated the presence of both regioisomers, $CF_3OCF_2CF_2CF_3$ and $CF_3OCF(CF_3)_2$. ^{19}F NMR and IR data for these compounds agreed well with those reported in the literature.[21]

Norbornylene. The reaction was attempted by dissolving norbornylene in $CFCl_3$, cocondensing appropriate amounts of CF_3OF, and allowing the reaction mixture to warm up slowly from −160 to 22 °C. On analyzing the reaction mixture, no volatile products could be characterized, and only a charred solid remained behind in the reaction vessel.

Cyclohexene. The reaction was attempted under a variety of conditions to control the reaction. First, a neat reaction was tried on a 1-mmol scale, but the reaction mixture exploded as soon as it was warm to −78 °C. The reaction was repeated with 20 mmol of $CFCl_3$ as solvent, but again only charred products were obtained. Carrying out the reaction by bubbling CF_3OF diluted with Ar (1:24) slowly into a solution of cyclohexene (4 mmol) in 25 mmol of $CFCl_3$ at −78 °C also produced charred products.

***cis*- and *trans*-2-Butene.** This reaction was also attempted under a variety of conditions as follows: (a) Cocondense 2 mmol of each reactant into a glass reactor and warm up slowly from −160 to 22 °C. (b) Condense 2 mmol of the olefin and 20 mmol of CF_2Cl_2 solvent and warm to dissolve, and then condense 2 mmol of CF_3OF and warm the reaction mixture slowly from −155 to 22 °C. (c) Similar to b but this time in the presence of 5A molecular sieves to trap any HF released and (d) dissolve 3 mmol of the olefin in 20 mmol of CF_2Cl_2 (solvent) containing the same 5A sieves. Cool the system to −130 °C and introduce CF_3OF (cooled to −78 °C) slowly to the solution so that the pressure of CF_3OF is never greater than 5 torr. Under all the above conditions, the majority of the products were black tars. Small amounts of very low volatile material were isolated. This exhibited at least six resonances in the CF_3O region of ^{19}F NMR. Thus it was probably a mixture of oligomers.

Reactions of CF_3OCl. *trans*-CHCl═CHCl. The reaction products were separated through traps cooled to −30, −60, and −195 °C. The addition product collected in the −60 °C trap. ^{19}F NMR indicated the presence of $CF_3OCHClCHCl_2F_2$ and FCH-$ClCHCl_2$. $CF_3OCHClCHCl_2$ and $FCHClCHCl_2$: colorless liquids; IR 2990 (w), 1452 (w), 1360 (w), 1300–1270 (vw), 1240–1180 (vs), 1112 (m), 1045 (m), 1070 (m), 1050 (m), 1030 (m), 990 (w), 892 (m), 815 (m), 790 (s), 748 (s), 692 (w), 628 (m), 555 (w), 535 (w) cm^{-1}; ^{19}F NMR ($CF_3OCHClCHCl_2$) ϕ_F^* −60.8 (s); ($FCHClCHCl_2$) ϕ_F^* −137.2 (d, d), $^2J_{HF} = 49.0$, $^3J_{HF} = 8.7$ Hz.

CH_2═CCl_2. The reaction mixture was analyzed by separating it through −30, −65, and −195 °C traps. The adduct along with some unreacted olefin collected in the −65 °C trap. Further purification of the −65 °C trap product was done by redistilling the contents through −60 and −195 °C traps. Pure addition product was obtained in the −60 °C trap. $CF_3OCCl_2CH_2Cl$: colorless liquid; mol wt 216.8 (calcd 217.5); IR 2760 (w), 1410 (w), 1265 (s), 1230 (vs), 1190 (vs), 1135 (m), 1100 (m), 1030 (m), 950 (sh, w), 938 (m), 865 (sh, w), 842 (m), 803 nw), 758 (m), 640 (m) cm^{-1}; ^{19}F NMR ϕ_F^* −54.8 (s).

CH_2═CF_2. The products were distilled through traps cooled to −60, −111, and −195 °C. The addition products collected in the −111 °C trap. ^{19}F NMR of the contents of this trap indicated the presence of $CF_3OCF_2CH_2Cl$ and CF_3CH_2Cl. $CF_3OCF_2CH_2Cl$ and CF_3CH_2Cl: colorless liquids; IR 2965 (m), 1420 (m), 1280 (vs), 1245 (vs), 1205 (vs), 1160 (vs), 1125 (vs), 1060 (w), 1035 (w), 960 (m), 932 (m), 900 (sh, m), 890 (m), 862 (m), 850 (s), 805 (s), 770 (w), 735 (w), 645 (s), 610 (w), 580 (m), 530 (w): ^{19}F NMR ($CF_3{}^AOCF_2{}^BCH_2Cl$) ϕ_A^* −56.2 (t), ϕ_B^* −77.7 (m), $J_{AB} = 9.5$, $^3J_{HF} = 9.5$ Hz; (CF_3CH_2Cl) ϕ_F^* −72.6 (t), $^3J_{HF} = 8.3$ Hz. The values for $CF_3OCF_2CH_2Cl$ agree well with those reported previously.[17]

CF_2═CCl_2. The products were separated through traps cooled to −45, −78, and −195 °C. Most of the addition product collected in the −78 °C trap. ^{19}F NMR indicated the presence of regioisomers. $CF_3OCCl_2CF_2Cl$ and $CF_3OCF_2CCl_3$: colorless liquids; mol wt 252.0 (calcd 253.5); IR 1280 (vs), 1232 (vs), 1205 (vs), 1180 (sh, vs), 1122 (vs), 1045 (vs), 905 (s), 878 (vs), 855 (sh, s), 812 (vs), 685 (s), 643 (s), 610 (s), 575 (vw), 520 (w) cm^{-1}; ^{19}F NMR ($CF_3{}^AOCCl_2CF_2{}^BCl$) ϕ_A^* −54.7 (s), ϕ_B^* −67.9 (s); ($CF_3{}^AOCF_2{}^BCCl_3$) ϕ_A^* −56.5 (t), ϕ_B^* −85.0 (q), $J_{AB} = 9.5$ Hz.

CF_2═CBr_2. The reaction mixture was distilled through traps cooled to −50 and −195 °C. The addition product and some unreacted olefin collected in the −50 °C trap. Reseparation of contents of the −50 °C trap through −35 and −195 °C traps gave pure product in the −35 °C trap. ^{19}F NMR indicated the presence of regioisomers. $CF_3OCF_2CBr_2Cl$ and $CF_3OCBr_2CF_2Cl$: colorless liquids: IR 1715 (w), 1300 (s), 1275 (s), 1230 (vs), 1195 (vs), 1170 (s), 1145 (s), 1120 (s), 1030 (s), 945 (w), 880 (m), 825 (m), 800 (w), 775 (m), 755 (m), 718 (m), 688 (w), 655 (w), 633 (w), 603 (w); prominent peaks in the mass spectrum (CI) 320, 322, 324, 326 ($CF_3OCFCBr_2Cl$), 304, 306, 308 $(CF_3OCF_2CBr_2)^+$, 261, 263, 265 $(CF_3OCF_2CBrCl)^+$, (EI) 261, 263, 265 $(CF_3OCF_2CBrCl)^+$, 91, 93 $(CBr)^+$, 85, 87 (CF_2Cl), 69 $(CF_3)^+$, 50 $(CF_2)^+$; ^{19}F NMR ($CF_3{}^AOCBr_2CF_2{}^BCl$) ϕ_A^* −55.1 (s), ϕ_B^* −64.7 (s), ($CF_3{}^AOCF_2{}^BCBr_2Cl$) ϕ_A^* −56.5 (t), ϕ_B^* −83.04 (q), $J_{AB} = 10.0$ Hz.

CF_2═CHBr. The products of the reaction were distilled through traps cooled to −55 and −195 °C. The addition compound collected in the −55 °C trap contaminated with some $CF_3CHBrCl$ as shown by ^{19}F NMR. $CF_3OCF_2CHBrCl$ and $CF_3CHBrCl$: IR 2995 (w), 1300 (vs), 1290 (sh, s), 1245 (vs), 1205 (vs), 1175 (vs), 1135 (vs), 1105 (vs), 970 (w), 950 (w), 930 (m), 890 (w), 845 (m), 815 (s), 753 (m), 720 (w), 650 (br, m), 555 (w) cm^{-1}; ^{19}F NMR ($CF_3{}^AOCF_2{}^BCHBrCl$) ϕ_A^* −56.3 (t), ϕ_B^* −80.8 (m), $J_{AB} = 9.3$, $^3J_{HF} = 5.7$ Hz, ($CF_3CHBrCl$) ϕ_F^* −76.8 (d), $J_{HF} = 5.0$ Hz.

CF_2═CFBr. The products of the reaction were distilled through traps cooled to −65 and −195 °C. The addition products collected in the −65 °C trap. ^{19}F NMR indicated the presence of two regioisomers. $CF_3OCFBrCF_2Cl$ and $CF_3OCF_2CFBrCl$: colorless liquids; IR 1352 (m), 1280 (vs), 1250 (vs), 1205 (s), 1185 (vs), 1142 (vs), 1108 (vs), 978 (m), 960 (s), 940 (sh, m), 890 (vs), 838 (s), 738 (m), 720 (w), 672 (w), 652 (m), 632 (sh, w), 552 (w) cm^{-1}; ^{19}F NMR ($CF_3{}^AOCF^BBrCF_2{}^CCl$) ϕ_A^* −55.4 (d), ϕ_B^* −73.8 (m), ϕ_C^* −69.0 (m), $J_{AB} = 10.8$, $J_{BC} = 7.2$ Hz, ($CF_3{}^AOCF_2{}^BCF^CBrCl$) ϕ_A^* −56.3 (t), ϕ_B^* −86.4 (m), ϕ_C^* −76.3, $J_{AB} = 9.5$, $J_{BC} = 9.5$ Hz.

***cis*-CHF═CHF.** The products of the reaction were separated through −60, −111, and −195 °C traps. The addition product collected in the −111 °C trap. *erythro*-$CF_3OCHFCHFCl$: colorless liquid; mol wt 195.6 (calcd 194.5); IR 2990 (m), 1410 (m), 1355 (m), 1285 (vs), 1238 (vs), 1208 (vs), 1165 (s), 1115 (vs), 1075 (vs), 1055 (sh, s), 1020 (sh, m), 952 (m), 910 (w), 885 (m), 838 (s), 775 (m), 710 (sh, w), 700 (m), 675 (m), 618 (w), 585 (w), 570 (w) cm^{-1}; ^{19}F NMR (*erythro*-$CF_3{}^AOCHF^BCHF^CCl$) ϕ_A^* −60.62 (d), ϕ_B^* −136.2 (m), ϕ_C^* −154.0 (m), $J_{AB} = 4.5$, $J_{BC} = 15.6$, $^2J_{HF^B} = 57.0$, $^3J_{HF^B} = 4.5$, $^2J_{HF^C} = 49.0$, $^3J_{HF^C} = 3.5$, $^3J_{HH} = 3.8$ Hz.

***trans*-CHF═CHF.** The products of the reaction were separated through traps cooled to −60, −111, and −195 °C. The addition product collected in the −111 °C trap. *threo*-$CF_3OCHFCHFCl$: colorless liquid, mol wt 194.0 (calcd 194.5); IR similar to erythro isomer; ^{19}F NMR ($CF_3{}^AOCHF^BCHF^CCl$) ϕ_A^* −60.57 (d), ϕ_B^* −138.9 (m), ϕ_C^* −154.1 (m), $J_{AB} = 4.5$, $J_{BC} = 20.0$, $^2J_{HF^B} = 55.0$, $^3J_{HF^C} = 4.2$, $^2J_{HF^C} = 48.0$, $^3J_{HF^C} = 4.5$ $^3J_{HH} \approx 3.8$ Hz.

***cis*- (8) and *trans*-CHF═CHF (5).** The reaction products were erythro and threo isomers in the ratio of 8:5 by ^{19}F NMR.

CH_2═$CHCH_3$. The reaction mixture was separated through traps cooled to 70 and −195 °C. The addition product collected in the −70 °C trap, and the ^{19}F NMR indicated the presence of both regioisomers. $CF_3OCH(CH_3)CH_2Cl$ and $CF_3OCH_2CHClCH_3$: colorless liquids; IR 2995 (m), 2900 (sh, w), 1452 (w), 1395 (sh, w), 1365 (w), 1345 (w), 1290 (vs), 1250 (s), 1210 (s), 1168 (vs), 1065 (s), 1032 (sh, w), 985 (w), 905 (w), 870 (w), 828 (w), 775 (m), 725 (w), 675 (w), 605 (w) cm^{-1}; prominent peaks in the mass spectrum (EI) 147, 149 $(CF_3OCHCH_2Cl)^+$, 113 $(CF_3OCHCH_3)^+$, 99 $(CF_3OCH_2)^+$, 69 $(CF_3)^+$, (CI) 161, 163 $[CF_3OC(CH_3)CH_2Cl]^+$, 127 $[CF_3OCH(CH_3)CH_2]^+$, 113 $(CF_3OCHCH_3)^+$, 77, 79 $(CH_3CHCH_2Cl)^+$; ^{19}F NMR ($CF_3OCH(CH_3)CH_2Cl$) ϕ_F^* −59.6 (s), ($CF_3OCH_2CHClCH_3$) ϕ_F^* −61.9 (s).

CH_2═$CHCH_2Cl$. The reaction products were analyzed by separation through −45 and −195 °C traps. The addition product collected in the −45 °C trap, and the ^{19}F NMR indicated the presence of two regioisomers. $CF_3OCH(CH_2Cl)CH_2Cl$ and $CF_3OCH_2CHClCH_2Cl$: colorless liquids; IR 2980 (w), 1440 (w), 1365 (sh, w), 1345 (sh, w), 1290 (s), 1235 (s), 1170 (s), 1150 (sh, m), 1052 (w), 1025 (vw), 930 (w), 870 (vw), 823 (vw), 778 (w), 720 (vw), 705 (sh, vw) cm^{-1}; prominent peaks in the mass spectrum

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[21] Hohorst, F. A.; DesMarteau, D. D. *Inorg. Nucl. Chem. Lett.* **1976**, 63.

(EI) 147, 149 $(CF_3OCHCH_2Cl)^+$, 99 $(CF_3OCH_2)^+$, 81, 83 $(FCHCH_2Cl)^+$, 69 $(CF_3{}^+)$, (CI) 161, 163 $(CF_3OCH(CH_2Cl)CH_2)^+$, 111, 113, 115 $(ClCH_2CHCH_2Cl)^+$, 95, 97 $(ClCH_2CHFCH_2)^+$; ^{19}F NMR $(CF_3OCH(CH_2Cl)CH_2Cl)$ $\phi_F{}^*$ −59.9 (s), $(CF_3OCH_2CHClCH_2Cl)$ $\phi_F{}^*$ −62.1 (s).

***cis*-$ClCH_2CH{=}CHCH_2Cl$.** The products of the reaction were distilled through traps cooled to −40 and −195 °C. The addition product collected in the −40 °C trap. *erythro*-$CF_3OCH(CH_2Cl)CHClCH_2Cl$: colorless liquid; IR 1280 (s), 1240 (m), 1215 (m), 1178 (m), 1120 (br, m), 1028 (w), 955 (sh, w), 932 (w), 865 (sh, w), 843 (m), 775 (w), 750 (w), 715 (w), 605 (w) cm^{-1}; ^{19}F NMR $\phi_F{}^*$ −59.4 (s).

$CH_2{=}CHOCOCF_3$. The reaction products were separated through −65 to −195 °C traps. The addition product contaminated with some $ClCH_2CHFOCOCF_3$ collected in the 65 °C trap. $CF_3OCH(OCOCF_3)CH_2Cl$ and $ClCH_2CHFOCOCF_3$: colorless liquids; IR 2980 (vw), 1820 (s), 1750 (w), 1440 (w), 1360 (sh, w), 1340 (m), 1290 (s), 1240 (s), 1195 (s), 1150 (sh, s), 1132 (s), 1120 (sh, s), 1062 (m), 1020 (sh, m), 1010 (m), 978 (w), 940 (w), 895 (w), 880 (sh, w), 845 (w), 795 (w), 770 (sh, w), 738 (m) cm^{-1}; prominent peaks in the mass spectrum (EI) 211 $(CF_3OCHOCOCF_3)^+$, 183 (211 − CO), 175, 177 $[CH(OCOCF_3)CH_2Cl]^+$, 147, 149 $(CF_3OCHCH_2Cl)^+$, 81, 83 $(FCHCH_2Cl)^+$, 69 $(CF_3)^+$, (CI) 225 $[CF_3OCH(OCOCF_3)CH_2]^+$, 175, 177 $[CH(OCOCF_3)CH_2Cl]^+$, 147, 149 $(CF_3CHCH_2Cl)^+$; ^{19}F NMR $(CF_3{}^AOCH(OCOCF_3{}^B)CH_2Cl)$ $\phi_A{}^*$ −60.6 (s), $\phi_B{}^*$ −76.02 (s), $(F^ACH(OCOCF_3{}^B)CH_2Cl)$ $\phi_A{}^*$ −131.8 (t, d), $\phi_B{}^*$ −76.01 (s), $^2J_{HF}$ = 53.0, $^3J_{HF}$ = 11.5 Hz.

$CH_2{=}CHF$. The products were separated through traps cooled to −100 and −195 °C. The addition product contaminated with some F_2CHCH_2Cl collected in the −100 °C trap.

$CF_3OCHFCH_2Cl$ and F_2CHCH_2Cl: colorless liquids; IR 2985 (m), 1448 (m), 1408 (sh), 1395 (m), 1360 (m), 1292 (vs), 1250 (vs), 1205 (vs), 1132 (s), 1080 (vs), 1058 (vs), 950 (w), 900 (w), 870 (w), 803 (s), 665 (m), 615 (w), 500 (w), 470 (sh, w), 450 (m) cm^{-1}; prominent peaks in the mass spectrum (EI) 166, 168 (M^+), 117 $(CF_3OCHF)^+$, 100, 102 $(F_2CHCH_2Cl)^+$, 81, 83 $(CHFCH_2Cl)^+$, 69 $(CF_3)^+$, (CI) 147, 149 $(CF_3OCHCH_2Cl)^+$, 81, 83 $(FCHCH_2Cl)^+$; ^{19}F NMR $(CF_3{}^AOCHF^BCH_2Cl)$ $\phi_A{}^*$ −60.5 (d), $\phi_B{}^*$ −128.0 (m), J_{AB} = 4.5, $^2J_{HF}$ = 57.0, $^3J_{HF}$ = 11.6 Hz, (F_2CHCH_2Cl) $\phi_F{}^*$ −119.9 (t, d), $^2J_{HF}$ = 56.0, $^3J_{HF}$ = 13.5 Hz.

$CH_2{=}CHBr$. The reaction products were separated by distilling through −55 and −195 °C traps. The addition product collected in the −55 °C trap. $CF_3OCHBrCH_2Cl$: colorless liquid; IR 2980 (vw), 1440 (w), 1285 (vs), 1232 (vs), 1205 (vs), 1165 (sh, s), 1110 (s), 1035 (m), 938 (m), 880 (w), 845 (vw), 828 (vw), 790 (w), 765 (w), 690 (sh, s), 680 (s), 620 (w) cm^{-1}; prominent peaks in the mass spectrum (EI) 147, 149 $(CF_3OCHCH_2Cl)^+$, 81, 83 $(FCHCH_2Cl)^+$, 69 $(CF_3)^+$, (CI) 191, 193 $(CF_3OCHBrCH_2)^+$, 147, 149 $(CF_3OCHCH_2Cl)^+$; ^{19}F NMR $\phi_F{}^*$ −61.5 (s).

***cis*-$CH_3CH{=}CHCH_3$.** The reaction products were distilled through traps cooled to −40, −75, and −195 °C traps. The addition product collected in the −75 °C trap. *erythro*-$CF_3OCH(CH_3)CHClCH_3$: colorless liquid; mol wt 176.7 (calcd 178.5); IR 2960 (m), 2915 (m), 2855 (w), 1435 (m), 1375 (s), 1355 (s), 1285 (vs), 1240 (vs), 1115 (vs), 1080 (s), 1032 (m), 995 (m), 945 (w), 848 (m), 830 (m), 712 (m), 662 (w), 605 (m), 566 (m), 530 (m) cm^{-1}; ^{19}F NMR $\phi_F{}^*$ −59.4 (s).

***trans*-$CH_3CH{=}CHCH_3$.** The reaction products were distilled through traps cooled to −60 and −195 °C. The addition product collected in the −60 °C trap. *threo*-$CH_3OCH(CH_3)CHClCH_3$: colorless liquid; IR 2995 (m), 2950 (w), 2895 (vw), 1455 (m), 1380 (m), 1350 (m), 1282 (vs), 1250 (vs), 1225 (sh, s), 1160 (vs), 1095 (sh, s), 1078 (vs), 1025 (m), 950 (sh, vw), 930 (w), 845 (s), 795 (w), 720 (w), 660 (w), 602 (w) cm^{-1}; prominent peaks in the mass spectrum (EI) 113 $(CF_3OCHCH_3)^+$, 69 $(CF_3)^+$; ^{19}F NMR $\phi_F{}^*$ −59.1 (s).

***cis*- (1) and *trans*-$CH_3CH{=}CHCH_3$ (2).** Erythro and threo isomers were obtained in the ratio of 1:2, and the IR and NMR spectra were identical with the values reported above.

Cyclohexene. The reaction products were distilled through traps cooled to −45 and −195 °C. The addition product collected in the −45 °C trap. *cis*-1-Chloro-2-(trifluoromethoxy)cyclohexane: colorless liquid; IR 2930 (s), 2850 (m), 1450 (2), 1285 (sh, m), 1270 (s), 1230 (s), 1160 (s), 1055 (w), 1028 (sh, w), 1020 (sh, m), 1018 (s), 970 (w), 915 (w), 730 (br, s) cm^{-1}; ^{19}F NMR $\phi_F{}^*$ −58.8 (s).

$CH_2{=}CHOCOCH_3$. The products were separated through traps cooled to −50 and −195 °C. The addition product collected in the −50 °C trap. $CF_3OCH(OCOCH_3)CH_2Cl$: colorless liquid; IR 2960 (vw), 2920 (vw), 1760 (m), 1400 (w), 1350 (w), 1290 (m), 1255 (m), 1205 (sh, m), 1190 (s), 1118 (w), 1030 (br, m), 935 (w), 905 (vw), 880 (vw), 785 (w), 735 (w), 652 (w), 635 (vw), 620 (w), 530 (vw), 515 (vw) cm^{-1}; ^{19}F NMR $\phi_F{}^*$ −59.5 (s).

Norbornylene. The reaction product was analyzed after pumping off the volatile substances. The solid remaining behind was dissolved in $CFCl_3$ to run the ^{19}F NMR. *cis*-2-Chloro-3-(trifluoromethoxy)norbornane: white solid; ^{19}F NMR $\phi_F{}^*$ −59.4.

$CF_3CF{=}CF_2$. The reaction products were distilled through traps cooled to −50, −111, and −195 °C. The addition products collected in the −111 °C trap. ^{19}F NMR indicated presence of both regioisomers. $CF_3OCF_2CFClCF_3$ and $CF_3OCF(CF_3)CF_2Cl$: colorless liquids; IR 1300 (vs), 1255 (vs), 1168 (vs), 1155 (vs), 1140 (vs), 1080 (m), 1052 (s), 978 (vs), 910 (m), 890 (m), 850 (s), 820 (m), 760 (w), 740 (sh, m), 725 (s), 690 (w), 665 (w) cm^{-1}; prominent peaks in the mass spectrum (EI) 185, 187 $(CF_3CFClCF_2)^+$, 135 $(CF_3OCF_2)^+$, 85, 87 $(CF_2Cl)^+$, 69 $(CF_3)^+$, (CI) 251, 253 $(CF_3OCF_2CFClCF_2)^+$, 235 $(CF_3OCF_2CFCF_3)^+$, 185, 187 $(CF_3CFClCF_2)^+$, 135, 137 $(CF_3CFCl)^+$; ^{19}F NMR $(CF_3{}^AOCF_2{}^BCF^CClCF_3{}^D)$ $\phi_A{}^*$ −56.1 (t), $\phi_B{}^*$ −83.2 (m), $\phi_C{}^*$ −140.5 (m), $\phi_D{}^*$ −78.6 (d, t), J_{AB} = 10.0, J_{BD} = 10.0, J_{CD} = 6.5 Hz, $(CF_3{}^AOCF^B(CF_2{}^CCl)CF_3{}^D)$ $\phi_A{}^*$ −53.9 (m), $\phi_B{}^*$ −141.9 (m), $\phi_C{}^*$ −68.6 (m), $\phi_D{}^*$ −78.9 (m), J_{AB} = 9.0 Hz.

Results

The reactions of CF_3OF and CF_3OCl with a variety of alkenes are summarized in Tables I and II. The reaction conditions and the addition products formed are given for each reaction. The major emphasis of the reactions was to observe the regio- and stereospecificity of the additions of CF_3OF and CF_3OCl to alkenes under similar conditions. Therefore, some of the products were identified from mixtures and were not separated as pure compounds. A few of the reactions gave significant amounts of side products corresponding to fluorination with CF_3OF and chlorofluorination with CF_3OCl.[22] The relative yields of the reaction products indicated in Tables I and II are based on the integration intensities in the ^{19}F NMR. The absolute yields were not accurately determined for all reactions, but the total yield of the products listed were in general near 70–90%, based on the starting alkene. In most cases, it was obvious that for a given alkene, the amount of isolated addition products were greater with CF_3OCl than with CF_3OF, and the latter sometimes resulted in low-volatility polymeric materials.

Certain reactions of CF_3OF were attempted under a variety of conditions in order to observe the effect, if any, on the yield and on the regio- and stereospecificity of the reactions. In particular the experimental conditions in the reactions of CF_3OF with *trans*-$CHCl{=}CHCl$, $CH_2{=}CCl_2$, cyclohexene, and *cis*- and *trans*-2-butene were varied. Dilution of the CF_3OF with Ar, slow addition of the CF_3OF, very low reaction temperatures, and HF absorbants did not influence the products of the reactions significantly over that given in Table I. In addition, the reaction with $CH_2{=}CCl_2$ was also carried out in $CHCl_3$ and C_2H_5OH as solvents without effect on the observed regiospecificity from use of $CFCl_3$.

The identification of the various products was based on some or all of the following measurements: (a) molecular weight determinations, (b) ^{19}F or ^1H NMR spectra, (c)

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[22] In certain reactions of CF_3OF and CF_3OCl, products corresponding to the addition of F_2 and ClF, respectively, were observed. In reactions of CF_3OF, other investigators have often observed considerable fluorination with carbon–carbon double bonds (see ref 11). With CF_3OCl, chlorofluorinatioin is less common. Some ClF addition may result from ClF impurity present in the CF_3OCl. Also, CF_3OCl is sometimes sensitive toward decomposition to COF_2 and other products.

Table III. Typical Chemical Shifts of the CF_3O Group Bonded to Carbon[a]

C bonded to CF_3O	av chem shift[b]	C bonded to CF_3O	av chem shift[b]
CHClR	−60.6	CFBrR	−55.5
CH_2R	−62.3	CHFR	−60.8
CF_2R	−56.3	$CH(CH_3)R$	−59.5
CCl_2R	−54.8	$CH(CH_2Cl)R$	−59.7
CBr_2R	−55.1	$CH(OCOCF_3)R$	−60.7
CHBrR	−61.8	$CH(OCOCH_3)R$	−59.5

[a] Chemical shifts are in δ (ppm) relative to $CFCl_3$ as an internal standard. [b] Maximum deviation from the mean occurs with CH_2R (+0.8, −0.4). All others were ±0.4.

mass spectra, and (d) IR. Identification of products arising from addition of CF_3OF and CF_3OCl to fluorinated olefins was very clear from the ^{19}F NMR. Orientation of the additions were deduced from J_{FF} values. Typical $^4J_{FF}$ values were found to be 9–10 Hz, while $^5J_{FF}$ varied from 0 to 2 Hz. In the case of nonfluorinated olefins, the orientation of addition was easily determined in the case of CF_3OF from the value of J_{HF}. Typical $^2J_{HF}$ values ranged from 45 to 60 Hz, while $^3J_{HF}$ varied from 4 to 20 Hz. In the case of CF_3OCl reactions with nonfluorinated olefins, the situation was made more difficult by the lack of a C–F probe on the original alkene carbons. $^4J_{HF}$ couplings between CF_3O and CH of the olefin were always found to be near 0. Therefore, the orientation of addition in these compounds had to be based on the chemical shift of the CF_3O group and also the pattern of their mass spectrum. In Table III are listed typical chemical shifts of the CF_3O group bonded to carbon. Thus, in compounds like $CF_3OCH(CH_3)CH_2Cl$ and $CF_3OCH_2CHClCH_3$, arising from the addition of CF_3OCl to propylene, two resonances are observed in the CF_3O group chemical shift region at −59.1 and −61.9 ppm. Comparison with the Table III and the corresponding chemical shifts in the CF_3OF addition products with propylene clearly reveals that the resonance at −59.1 ppm must be due to $CF_3OCH(CH_3)CH_2Cl$ and that at −61.9 ppm belongs to the other regioisomer. Thus, the CF_3O group chemical shifts were very effective in assigning the orientation of addition of all isomers arising from the addition of CF_3OCl to olefins. The observed regioisomers could not be readily separated on our GLC system, and the proton NMR spectra of these compounds were rather complex and not easily interpreted.

Additional proof regarding the orientation of addition was also obtained from the mass spectra of the compounds. In comparison of the EI spectra for the additioin CF_3OF and CF_3OCl to $CHF{=}CH_2$, for example, the CF_3OF addition compound shows an intense fragment *m/z* 99, which can be assigned to $CF_3OCH_2^+$. Conversely, no ion is observed at *m/z* 117. On the other hand, the CF_3OCl addition product shows an intense fragment at *m/z* 117, which can be assigned to CF_3OCHF^+, and no ion at *m/z* 99. Similarly, in the mass spectrum for addition to $CH_2{=}CHCH_2Cl$, the CF_3OF product shows weak ions at *m/z* 147 and 149 due to $CF_3OCHCH_2Cl^+$ and a more intense ion *m/z* 99 due to $CF_3OCH_2^+$. This is consistent with the ^{19}F NMR, which indicates that $CF_3OCH_2CHFCH_2Cl$ is formed as a major product and $CF_3OCH(CH_2Cl)CH_2F$ as a minor one. The corresponding mass spectrum for the CF_3OCl addition exhibits intense ions at *m/z* 147 and 149 and only a very weak ion at *m/z* 99. This can be taken as evidence that in this case $CF_3OCH(CH_2Cl)CH_2Cl$ is the major fraction and $CF_3OCH_2CHClCH_2Cl$ the minor one. A final example of the application of mass spectrometry is the addition of CF_3OF and CF_3OCl to $CH_2{=}CHOCOCF_3$. Intense *m/z* values at 99 and 212 for CF_3OF and CF_3OCl, respectively, are indicative of the products $CF_3OCH_2CHFOCOCF_3$ and $CF_3OCH(OCOCF_3)CH_2Cl$.

The assignment of diastereomers as erythro and threo in the case of CF_3OCl additions was based mainly on 1,2-difluoroethylene. Previous work by us has shown that the $^3J_{FF}$ value in erythro and threo diastereomers of $CF_3OCHFCHFCl$ will be larger for the threo than for the erythro isomer.[23,24] Thus the isomer formed with *cis*-$CHF{=}CHF$ is erythro ($^3J_{FF}$ = 15.6 Hz) and with *trans*-$CHF{=}CHF$, threo ($^3J_{FF}$ = 20.0 Hz). This means the addition of CF_3OCl is syn, and it was then assumed to be syn in all other cases.

The infrared spectra of these compounds were very typical and showed a very characteristic pattern of three strong absorptions at ~1280, ~1240, and ~1180 cm^{-1} due to the CF_3O group. C–H stretching frequencies were always <3000 cm^{-1}, indicating H bonded to a saturated four-coordinated carbon atom. Starting olefins exhibited C–H stretching >3000 cm^{-1}. Physical constants other than molecular weights were not measured.

Discussion

The reactions of CF_3OF and CF_3OCl with a variety of simple olefins were carried out under very similar conditions to compare their reactivity. It is obvious from inspection of Tables I and II that they are rather different. In most instances, CF_3OCl is more selective in its reactions, and the observed products are often very different. In several cases, stereospecific reactions are observed with CF_3OCl, while none were found for CF_3OF.

In Table IV, the major addition products for the reaction of CF_3OF and CF_3OCl with simple alkenes are compared along with some related results of other investigations with unsymmetrical olefins. These results offer considerable insight into the probable mechanism for the reaction of CF_3OCl and CF_3OF with compounds containing carbon–carbon double bonds. On the other hand, this work does not prove any operative mechanism for either CF_3OF or CF_3OCl.

The results of these studies will be discussed in terms of whether the additioins of CF_3OCl and CF_3OF to simple olefins are consistent with a classical electrophilic addition mechanism.[26] If such a mechanism is operative, certain predictions may be valid. In particular for CF_3OX (X = F, Cl), X may be considered the positive end of a dipole or induced dipole which first interacts with the π electrons of the olefin. From this interaction, a variety of processes could lead to syn and/or anti addition of CF_3OX, depending on reaction conditions and the nature of the olefin. In any of these processes, electron-donating groups on the olefin are expected to increase the reactivity and vice versa. Furthermore, with unsymmetrical olefins one expects to observe some regioselectivity, with X ending up on a particular side of the double bond in accord with Markovnikov's rule. Finally, with appropriate olefins the stereoselectivity of the reaction may be observed, and this selectivity will depend on the details of the above.

First, the relative reaction rates of CF_3OF and CF_3OCl should be compared. No quantitative rate data are available, but qualitative comparisons can be made. Trifluoromethyl hypochlorite reacts much faster with ac-

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Table IV. CF_3OX Addition Products with Alkenes[a]

alkene	X = F	X = Cl
trans-$CHCl{=}CHCl$	*threo*-$CF_3OCHClCHClF$ (50), *erythro*-$CF_3OCHClCHClF$ (50),	$CF_3OCHClCHCl_2$ (100)
$CH_2{=}CCl_2$	$CF_3OCH_2CCl_2F$ (100)	$CF_3OCCl_2CH_2Cl$ (100)
$CH_2{=}CF_2$	$CF_3OCH_2CF_3$ (97.5), $CF_3OCF_2CH_2F$ (2)	$CF_3OCF_2CH_2Cl$ (100)
$CF_2{=}CCl_2$	$CF_3OCF_2CCl_2F$ (84), $CF_3OCCl_2CF_3$ (16)	$CF_3OCCl_2CF_2Cl$ (86), $CF_3OCF_2CCl_3$ (14)
$CF_2{=}CBr_2$	$CF_3OCF_2CBr_2F$ (42), $CF_3OCBr_2CF_3$ (58)	$CF_3OCBr_2CF_2Cl$ (56.5), $CF_3OCF_2CBr_2Cl$ (43.5)
$CF_2{=}CHBr$	CF_3OCF_2CHBrF (74), $CF_3OCHBrCF_3$ (26)	$CF_3OCF_2CHBrCl$ (100)
$CF_2{=}CFBr$	$CF_3OCF_2CF_2Br$ (80), $CF_3OCFBrCF_3$ (20)	$CF_3OCFBrCF_2Cl$ (71), $CF_3OCF_2CFBrCl$ (29)
cis-$CHF{=}CHF$	$CF_3OCHFCHF_2$ (100)	*erythro*-$CF_3OCHFCHFCl$ (100)
trans-$CHF{=}CHF$		*threo*-$CF_3OCHFCHFCl$ (100)
cis- and *trans*-$CHF{=}CHF$ (8:5)		*erythro*- and *threo*-$CF_3OCHFCHFCl$ (8:5) (100)
$CH_2{=}CHCH_3$	$CF_3OCH_2CHFCH_3$ (80), $CF_3OCH(CH_3)CH_2F$ (20)	$CF_3OCH(CH_3)CH_2Cl$ (78), $CF_3OCH_2CHClCH_3$ (22)
$CH_2{=}CHCH_2Cl$	$CF_3OCH_2CHFCH_2Cl$ (84), $CF_3OCH(CH_2Cl)CH_2F$ (16)	$CF_3OCH(CH_2Cl)CH_2Cl$ (78), $CF_3OCH_2CHClCH_2Cl$ (22)
cis-$ClCH_2CH{=}CHCH_2Cl$	*threo*-$CF_3OCH(CH_2Cl)CHFCH_2Cl$ (35), *erythro*-$CF_3OCH(CH_2Cl)CHFCH_2Cl$ (65)	*erythro*-$CF_3OCH(CH_2Cl)CHClCH_2Cl$ (100)
$CH_2{=}CHOCOCF_3$	$CF_3OCH_2CHFOCOCF_3$ (77), $CF_3OCH(OCOCF_3)CH_2F$ (23)	$CF_3OCH(OCOCF_3)CH_2Cl$ (100)
$CH_2{=}CHF$	$CF_3OCH_2CHF_2$ (87), $CF_3OCHFCH_2F$ (13)	$CF_3OCHFCH_2Cl$ (100)
$CH_2{=}CHBr$	CF_3OCH_2CHBrF (100)	$CF_3OCHBrCH_2Cl$ (100)
$CH_2CHOCOCH_3$	$CF_3OCH_2CHFOCOCH_3$ (61), $CF_3OCH(OCOCH_3)CH_2F$ (39)	$CF_3OCH(OCOCH_3)CH_2Cl$ (100)
cis-$CH_3CH{=}CHCH_3$		*erythro*-$CH_3OCH(CH_3)CHCHCH_3$ (100)
trans-$CH_3CH{=}CHCH_3$		*threo*-$CF_3OCH(CH_3)CHCHClCH_3$ (100)
cis- and *trans*-$CH_3CH{=}CHCH_3$ (1:2)		*erythro*- and *threo*-$CH_3OCH(CH_3)$-$CHClCH_3$ (1:2) (100)
$CF_3CF{=}CF_2$	$CF_3OCF_2CF_2CF_3$ (67), $CF_3OCF(CF_3)_2$ (33)	$CF_3OCF_2CFClCF_3$ (71.5), $CF_3OCF(CF_3)CF_2Cl$ (28.5)
cyclohexene		*cis*-1-chloro-2-(trifluoromethoxy)cyclohexane
norbornylene		*cis*-2-chloro-3-(trifluoromethoxy)-norbornane
$CF_2{=}CFCl$	$CF_3OCF_2CF_2Cl$ (?), $CF_3OCFClCF_3$ (?)[25]	$CF_3OCF_2CFCl_2$ (45), $CF_3OCFClCF_2Cl$ (55)[17,18]
$CHCl{=}CFCl$	$CF_3OCHClCF_2Cl$ (?), $CF_3OCFClCHClF$ (?)[25]	
$CH_2{=}CHCl$		$CF_3OCHClCH_2Cl$ (100)[17]
$CF_3OCH{=}CH_2$		$(CF_3O)_2CHCH_2Cl$ (?), $CF_3OCH_2CHClOCF_3$ (?)[17]

[a] Relative yields of CF_3OCCX as determined by ^{19}F NMR.

tivated olefins than with deactivated olefins. Thus the addition to propene or 2-butene occurs rapidly at low temperatures (<−111 °C), whereas the addition to $CF_2{=}CCl_2$ or $CF_3CF{=}CF_2$ is much slower and will only proceed at significantly higher temperatures (∼−50 °C). On the other hand, CF_3OF is extremely reactive with nearly all olefins. Thus with propene the reaction is difficult to control even at −150 °C, and no conditions could be found to control the reaction with 2-butene. Similarly, the reactions with $CF_2{=}CCl_2$ and $CF_3CF{=}CF_2$ are rapid at much lower temperatures than those observed with CF_3OCl. Qualitatively, these observations are consistent with an eelctrophilic addition mechanism for CF_3OCl but not for CF_3OF.

Next, the regioselectivity of CF_3OF and CF_3OCl can be compared. Overall, the regioselectivity of CF_3OCl is far greater than that of CF_3OF, although both compounds gave regiospecific addition products with some olefins. In the case of CF_3OCl, all additions were highly regioselective except with some 1,1,2-trihalo- and 1,1,2,2-tetrahaloalkenes. With CF_3OF, two regioisomers were the rule, and only with $CH_2{=}CHBr$ and $CH_2{=}CCl_2$ were the reactions regiospecific. Some regioselectivity, however, is clearly evident in some other reactions. For those unsymmetrical olefins where CF_3OCl adds in a regiospecific manner, the chlorine was always bound to a specific carbon in accord with Markovnikov's rule.[27] In contrast, the two regiospecific additions of CF_3OF are anti-Markovnikov, and in the other cases where a high regioselectivity is observed, the major regioisomer corresponds to an anti-Markovnikov addition in contrast to the regioselective reactions of CF_3OCl. These observations again are consistent with an electrophilic addition mechanism for CF_3OCl but not for CF_3OF.

Next, it is very informative to compare the stereoselectivity of the reactions of CF_3OF and CF_3OCl. In every case where the stereoselectivity could be observed, the reactions of CF_3OCl were stereospecific and those with CF_3OF were not. The number of cases where this selectivity could be observed was less with CF_3OF than CF_3OCl (2 vs. 8), and the reactions could only be controlled in the case of CF_3OF by using the deactivated olefins *trans*-$CHCl{=}CHCl$ and *cis*-1,4-dichloro-2-butene. In contrast, stereospecific additions of CF_3OCl were observed with cyclohexene, norbornylene, *cis*- and *trans*-2 butene, *cis*- and *trans*-1,2-difluoroethylene, *cis*-1,4-dichloroethylene, and cis/trans mixtures of 2-butene and 1,2-difluoroethylene. These results for CF_3OCl are very consistent with that expected for an electrophilic addition mecha-

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[27] It is interesting to note that a photochemical reaction of CF_3OCl with $CF_2{=}CCl_2$ has been reported, and the major product is $CF_3OCF_2CCl_3$, as expected for a free-radical reaction. Dicelio, L.; Schumacher, H. J. *J. Photochem.* **1979**, *11*, 1.

nism, but for CF_3OF they are unsupportive. For the one case (*cis*-1,4-dichloro-2-butene) in which the stereoselectivity can be observed for both CF_3OF and CF_3OCl, one would have to conclude that the mechanism of addition is rather different in this case. Quite probably, the mechanisms are different in nearly every case.

In conclusion, it is clear from this and other work with CF_3OCl that this hypohalite is an excellent source of electrophilic chlorine, and the reactions with simple alkenes are entirely consistent with this concept. The best explanation for the observed products is that CF_3OCl adds to most carbon–carbon double bonds in a highly concerted manner, giving rise to syn addition products. In contrast, our work offers little evidence in support of electrophilic fluorine in CF_3OF. The reaction products found with CF_3OF are most readily accounted for on the basis of a free-radical reaction mechanism, which would account for the observed reactivity, regioselectivity, and low stereoselectivity.

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Registry No. CF_3OCl, 22082-78-6; CF_3OF, 373-91-1; *trans*-$CHCl{=}CHCl$, 156-60-5; *erythro*-$CF_3OCHClCHClF$, 84010-97-9; *threo*-$CF_3OCHClCHClF$, 84010-98-0; $CH{=}CCl_2$, 75-35-4; $CF_3OCH_2CCl_2F$, 84010-99-1; $CH_2{=}CF_2$, 75-38-7; $CF_3OCH_2CF_3$, 20193-67-3; $CF_3OCF_2CH_2F$, 84011-00-7; $CF_2{=}CCl_2$, 79-35-6; $CF_3OCF_2CCl_2F$, 25476-71-5; $CF_3OCCl_2CF_3$, 25476-71-5; CF_3CCl_2F, 374-07-2; $CF_3{=}CBr_2$, 430-85-3; CF_3CBr_2F, 27336-23-8; $CF_3OCBr_2CF_3$, 84011-01-8; $CF_3OCF_2CBr_2F$, 84011-02-9; $CF_2{=}CHBr$, 359-08-0; CF_3OCF_2CHBrF, 84011-03-0; $CF_3OCHBrCF_3$, 84011-04-1; $CF_2{=}CFBr$, 598-73-2; $CF_3OCF_2CF_2Br$, 1561-51-9; $CF_3OCFBrCF_3$, 84011-05-2; *cis*-$CHF{=}CHF$, 1630-77-9; $CF_3OCHFCHF_2$, 84011-06-3; $CH_2{=}CHCH_3$, 115-07-1; $CF_3OCH_2CHFCH_3$, 84011-07-4; $CF_3OCH(CH_3)CH_2F$, 84011-08-5; $CH_2{=}CHCH_2Cl$, 107-05-1; $CF_3OCH_2CHFCH_2Cl$, 84011-09-6; $CF_3OCH(CH_2Cl)CH_2F$, 84011-10-9; *cis*-$ClCH_2CH{=}CHCH_2Cl$, 1476-11-5; *erythro*-$CF_3OCH(CH_2Cl)CHFCH_2Cl$, 84011-11-0; *threo*-$CF_3OCH(CH_2Cl)CHFCH_2Cl$, 84011-12-1; $CH_2{=}CHOCOCF_3$, 433-28-3; $CF_3OCH_2CHFOCF_3$, 84011-13-2; $CF_3OCH(OCOCF_3)CH_2F$, 84011-14-3; $CH_2{=}CHF$, 75-02-5; $CF_3OCH_2CHF_2$, 84011-15-4; $CF_3OCHFCH_2F$, 84011-16-5; $CH_2{=}CHBr$, 593-60-2; CF_3OCH_2CHBrF, 84011-17-6; $CH_2{=}CHOCOCH_3$, 108-05-4; $CF_3OCH_2CHFOCOCH_3$, 84011-18-7; $CF_3OCH(OCOCH_3)CH_2F$, 84011-19-8; $FCH(OCOCH_3)CH_2F$, 3852-06-0; $CF_3CF{=}CF_2$, 116-15-4; $CF_3OCF_2CF_2CF_3$, 59426-77-6; $CF_3OCF(CF_3)_2$, 60901-74-8; $CF_3OCHClCHCl_2$, 84011-20-1; $FCHClCHCl_2$, 359-28-4; $CF_3OCCl_2CH_2Cl$, 84011-21-2; $CF_3OCF_2CH_2Cl$, 25957-33-9; CF_3CH_2Cl, 75-88-7; $CF_3OCCl_2CF_2Cl$, 84011-22-3; $CF_3OCF_2CCl_3$, 54362-34-4; $CF_3OCF_2CBr_2Cl$, 84011-23-4; $CF_3OCBr_2CF_2Cl$, 84011-24-5; $CF_3OCF_2CHBrCl$, 84011-25-6; $CF_3CHBrCl$, 151-67-7; $CF_3OCFBrCF_2Cl$, 84011-26-7; $CF_3OCF_2CFBrCl$, 84011-27-8; *erythro*-$CF_3OCHFCHFCl$, 84011-28-9; *threo*-$CF_3OCHFCHFCl$, 84011-29-0; $CF_3OCH(CH_3)CH_2Cl$, 84011-30-3; $CF_3OCH_2CHClCH_3$, 84011-31-4; $CF_3OCH(CH_2Cl)CH_2Cl$, 84011-32-5; $CF_3OCH_2CHClCH_2Cl$, 84011-33-6; *erythro*-$CF_3OCH(CH_2Cl)CHClCH_2Cl$, 84011-34-7; $CF_3OCH(OCOCF_3)CH_2Cl$, 84011-35-8; $ClCH_2CHFOCOCF_3$, 84011-36-9; $CF_3OCHFCH_2Cl$, 84011-37-0; F_2CHCH_2Cl, 338-65-8; *erhthro*-$CF_3OCH(CH_3)CHClCH_3$, 84011-38-1; *threo*-$CH_3OCH(CH_3)CHClCH_3$, 84011-39-2; $CF_3OCH(OCOCH_3)CH_2Cl$, 84011-41-6; $CF_3OCF_2CFClCF_3$, 41255-96-3; $CF_3OCF(CF_3)CF_2Cl$, 41255-97-4; norbornylene, 498-66-8; cyclohexene, 110-83-8; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; *cis*-1-chloro–2–(trifluoromethoxy)cyclohexane, 84011-40-5; 2-chloro–3-(trifluoromethoxy)norbornane, 84011-42-7.

Notes

Desulfurization of Thiols and Thioketones by Sodium Triethylborohydride and Iron(II) Chloride on Alumina

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The extrusion of sulfur from organic compounds is relevant to the problem of the desulfurization of crude oil. Of the various organic sulfur compounds known, thiols and thioketones are the most susceptible to desulfurization. Therefore, if one is to have reasonable expectations that a process for the removal of sulfur from fuel oil will be successful, it is almost mandantory that such a method be applicable to thiols and thioketones.

One class of desulfurization agents are metal carbonyls which can convert thioketones to either alkenes [$Co_2(CO)_8$, $C_5H_5Fe(CO_2)_2$] or hydrocarbons [$Fe(CO)_5$, KOH]^2. Two of us have also recently found that mixed-metal hydride/transition-metal halide reagents are useful for the preparation of hydrocarbons from thiols. The most suitable reagent combination is sodium triethylborohydride and ferrous chloride.[3]

There has been considerable interest in the use of reagents deposited on refractory oxides for effecting organic transformations.[4,5] The principal advantages of carrying out organic synthesis by using such supported reagents include the ease of product separation at the end of the reaction and the mild conditions often used. We now report that thiols can be desulfurized by treatment with iron(II) chloride and sodium triethylborohydride on alumina. In addition, thioketones undergo desulfurization in this manner as does crude oil and Athabasca bitumen.

A variety of experimental conditions were used for the reaction of a thiol (1) with sodium triethylborohydride and $FeCl_2$ on alumina. The best results were obtained by the use of a 1:2:4 ratio of $1/FeCl_2/Na(C_2H_5)_3BH$ (eq 1) in

$$\underset{1}{RSH} \xrightarrow[FeCl_2,\ THF-C_6H_6]{Na(C_2H_5)_3BH/Al_2O_3} \underset{2}{RH} + \underset{3}{RR} \qquad (1)$$

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