filtered off and the solvent was evaporated. The mixture was distilled under reduced pressure to give a mixture of *trans*- and *cis*-**3b,e**.

2β-Methyl-1-oxa-4-decalone[29,31] (**3b**): yield 85%; bp 76–78 °C (0.5 mmHg); cis/trans ratio 45:55.

2β-*tert*-Butyl-1-oxa-4-decalone[28] (**3e**): yield 83%; bp 82–84 °C (0.5 mmHg); cis/trans ratio 75:25. Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.23; H, 10.55. Pure epimers were obtained by GLC as described above.

Equilibration of 1-Oxa-4-decalones 3. A solution of cis and trans isomers **3** (10 mmol) in ethanol (15 mL) and triethylamine (1.46 g, 15 mmol) was refluxed for 48 h and concentrated in vacuo. The residue was distilled under reduced pressure and analyzed by GLC. The trans/cis ratios were 9:1 for **3a–c,e** and 65:35 for **3d**.

Registry No. **1a**, 29798-89-8; **1b**, 13738-56-2; **1c**, 29798-90-1; **1d**, 91743-36-1; **2a**, 51599-61-2; **2b**, 91743-37-2; **2c**, 91743-38-3; **2d**, 91743-39-4; *trans*-**3a**, 51600-19-2; *cis*-**3a**, 51600-16-9; **3b**, 55023-43-3; *trans*-**3c**, 91743-40-7; *cis*-**3c**, 91743-43-0; **3d**, 91743-41-8; **3e**, 91743-42-9; *trans*-**4b**, 91743-44-1; *cis*-**4b**, 91743-48-5; *trans*-**4e**, 91743-45-2; *cis*-**4e**, 91743-49-6; *trans*-**5b**, 91743-46-3; *cis*-**5b**, 91743-50-9; *trans*-**5e**, 91743-47-4; *cis*-**5e**, 91743-51-0; 4-*tert*-butyl-1-morpholino-1-cyclohexene, 16963-28-3; 3-methyl-2-butenoyl chloride, 3350-78-5; ethyl acetylacetate, 141-97-9; ethyl pivaloylacetate, 17094-34-7; 3,4,5,6-tetrahydrobenzoyl chloride, 36278-22-5.

Catalytic Conversion of Fluoroalkyl Alkyl Ethers to Carbonyl Compounds

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Fluoroalkyl alkyl ethers are generally available by attack of alkoxide ion on fluoro olefins. In the presence of Lewis acid catalysts, such methyl and ethyl ethers have now been found to lose methyl or ethyl fluoride, respectively, to give fluorinated carbonyl compounds. The carbonyl compounds include acid fluoride, ketone, keto ester, vinyl ketone, acyl ketene, ketene, and acryloyl fluoride.

Fluorine atoms attached to carbon which also bears an alkyl ether group are known to be labile to electrophilic reagents. They are readily hydrolyzed in concentrated sulfuric acid, thus providing a route to some esters of fluoroacids.[2] The use of sulfur trioxide or fluorosulfonic acid gives acid fluorides, and chlorosulfonic acid gives acid chlorides.[3]

$$R_fCOF + CH_3OSO_2F \xleftarrow{SO_3} R_fCF_2OCH_3 \xrightarrow[H_2SO_4]{H_2O} R_fCOOCH_3 + HF$$

$$\xrightarrow{ClSO_3H} R_fCOCl + CH_3OSO_2F + HF \qquad \xrightarrow{FSO_3H} R_fCOF + CH_3OSO_2F + HF$$

The use of sulfur trioxide has been especially valuable to prepare, from methyl ethers, acid fluorides which were desired in our research. However, sulfur trioxide (bp 42 °C) and the toxic byproduct, methyl fluorosulfate (bp 92 °C), are difficult to handle and must be separated from the desired acid fluoride product.

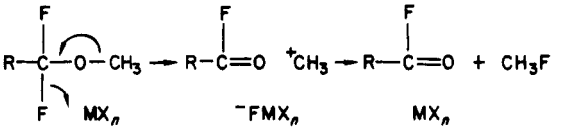
Results and Discussion

In an early experiment,[4] 1 mol of 3-methoxyperfluoropropionyl fluoride[5] was heated with 1.5 mol of titanium tetrafluoride in a sealed vessel at 175 °C to give a 77% yield of perfluoromalonyl fluoride (**2**) and methyl fluoride.

$$\underset{\mathbf{1}}{CH_3OCF_2CF_2COF} \xrightarrow{TiF_4} \underset{\mathbf{2}}{CF_2(COF)_2} + CH_3F$$

It was subsequently shown that this reaction is catalytic and can be carried out exothermally at atmospheric pressure and at low temperatures in high yield on a number of related compounds.[4] Antimony pentafluoride is one of many effective metal halide, Lewis acid type catalysts.[4] Because the reaction is clean and gives only a gas, methyl fluoride (bp −80 °C), as byproduct, it provides an excellent replacement for the use of sulfur trioxide to prepare acid fluorides from methyl fluoro ethers.

The mechanism may involve abstracting fluorine from a C–F bond giving the acid fluoride, a metal fluoride anion, and a methyl cation. The latter two unite to give methyl fluoride and regenerate the catalyst. Alternately, a concerted, cyclic transition state may be involved.[6] If a metal halide other than fluoride is used as catalyst, that methyl halide is evolved in initial stages of the reaction along with methyl fluoride.



The exothermic reaction is best controlled by regulating addition of the ether with stirring into a pot containing the neat catalyst. The product can often act as a moderating solvent; boiling lower than starting material, it can be fractionated from the mixture. Methyl fluoride is evolved as gas. Fresh catalyst can be added as required.

In addition to the preparation of acid fluorides by removal of CH_3F from the $-CF_2OCH_3$ group, ketones can be prepared from the $-CF(OCH_3)-$ group and ketenes and/or acryloyl fluorides from $FC(OCH_3)=C(F \text{ or } CF_3)CF_3$ where

(1) Contribution no. 3388.
(2) Young, J. A.; Tarrant, P. *J. Am. Chem. Soc.* **1979**, *71*, 2432.
(3) England, D. C.; Solomon, L.; Krespan, C. G. *J. Fluorine Chem.* **1973/74**, *3*, 63.
(4) Anderson, D. G.; England, D. C.; Milian, A. S., Jr. U.S. Patent 4 357 282, 1982.
(5) Fawcett, F. S.; Tullock, C. W.; Coffman, D. D. *J. Am. Chem. Soc.* **1962**, *84*, 4280.

(6) The author is indebted to referees for this suggestion which avoids formation of a methyl cation. One has suggested that the use of a butyl ether would be informative, since the cation would be expected to rearrange to give *sec*-butyl fluoride.

0022-3263/84/1949-4007$01.50/0

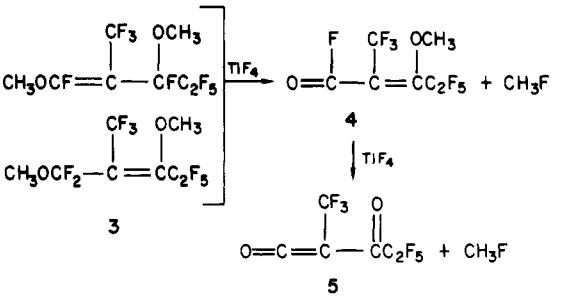
Table I. Catalytic (SbF_5) Elimination of CH_3F

no.	starting material → product	SbF_5, g	weights, g	% yield
1	[a] $HCF_2CF_2OCH_3$	1.8	32.5	
	→ HCF_2COF		12.3	88
2	[b] $CF_3CHFCF_2OCH_3$	2.7	49.5	
	→ $CF_3CHFCOF$		33	82
3	[c] $(CF_3)_2CHCF_2OCH_3$	2.2	77	
	→ $(CF_3)_2CHCOF$		55	83
4	[d] $CHF(CF_2OCH_3)_2$	2.5	15	
	→ $CHF(COF)_2$		8.2	84
5	[e] $CF_3CF_2OCHFCF_2OCH_3$	3.3	40	
	→ $CF_3CF_2OCHFCOF$ +		20.7	60
	$CF_3CF_2OCF_2H$		8.1	27
6	[f] $(CF_3)_2CHCF(OCH_3)C_2F_5$	1.0	38	
	→ $(CF_3)_2CHCOC_2F_5$		30	88
7	[g] $CH_3OCF{=}CFCF_3$	2.8	20	
	→ $CF_2{=}CFCOF$		7.5	47
8	[h] $CH_3OCF{=}C(CF_3)_2$	2.4	29	
	→ $O{=}C{=}C(CF_3)_2$ +		8.5	35
	$FOCC(CF_3){=}CF_2$		9.0	37
9	[i] $CH_3OCF{=}C(CF_3)CF(OCH_3)$-$CF(OCH_3)CF_3$	14.5	75	
	→ $CH_3OCF{=}C(CF3)$-$COCOCF_3$		24.5	37
10	[j] $CH_3OCF{=}C(CF_3)CF$-$(OCH_3)C_2F_5$ + $CH_3OCF_2C(CF_3){=}C(OC$-$H_3)C_2F_5$	4.4	73	
	→ $O{=}C{=}C(CF_3)COC_2F_5$		43	67
11	[k] $H_5C_2OOCCF(CF_3)OC_2H_5$	19.5	340.3	
	→ $H_5C_2OOCCOCF_3$		220	83
12	[m] $(CF_3)_2CHCF_2OC_2H_5$	7.3	99.2	
	→ $(CF_3)_2CHCOF$		61	77

[a] Reacted below room temperature with rapid evolution of product (bp 0 °C) causing some codistillation with starting material (bp 33 °C). [b] Reacted below room temperature; product bp 25 °C. [c] Reacted below room temperature; product bp 33 °C. [d] Reacted below room temperature; product bp 72 °C. [e] Reaction vigorous at room temperature; products bp 52 °C and −12 °C (decarbonylation by SbF_5). [f] Reacted below room temperature; product bp 60 °C. [g] Reaction very exothermic and gave some high boiling residue. [h] Reacted at room temperature; ketene product bp 5 °C; acryloyl product bp 52 °C. [i] Reacted at room temperature; distilled crude product (bp 32–75 °C (55 mm)) and redistilled from 5.5 g of SbF_5 to give the diketone; bp 91 °C (60 mm); n^{25}_D 1.3648; IR 5.40 and 5.95 μm (C=O); ^1H NMR 4.05 ppm (q, J = 2.0 Hz, 3 H); ^{19}F NMR −53.9 (q, J = 2.0 Hz, d, J = 2.Hz, 3 F), −81.6 (d, J = 4.0 Hz, 3 F) and −133.9 ppm (q, J = 4.0 Hz, q, J = 2.0 −81.6 (d, J = 4.0 Hz, 3 F) and −133.9 ppm (q, J = 4.0 Hz, q, J = 2.0 Hz, 1 F). Anal. Calcd for $C_7H_3F_7O_3$: C, 31.36; H, 1.13; F, 49.61. Found: C, 31.58; H, 1.21; F, 50.76. [j] Mixture of isomers. [k] Ethyl fluoride was evolved; product bp 89 °C. [m] Ethyl fluoride evolved.

a 1,3-fluoride shift is possible. Examples are given in Table I.

The reaction is particularly useful for the preparation of perfluoromethylpropionylketene (**5**) from the isomeric mixture of unsaturated ethers (**3**). In the previously reported[7] method using sulfur trioxide, removal of the toxic byproduct, methyl fluorosulfate, is especially difficult because it codistills with the desired product. The preparation of perfluoromethylpropionylketene is now accomplished in one step with SbF_5 catalyst. When the less active TiF_4 catalyst is used, it is possible to carry out the reaction in two steps, isolating the intermediate acryloyl fluoride (**4**).



The scope of the reaction is not limited to methyl ethers. Catalytic removal of ethyl fluoride from two ethyl ethers was demonstrated (see Table I, run no. 11 and 12).

Experimental Section

Melting points and boiling points are uncorrected. ^{19}F NMR spectra were obtained with a Varian XL-100 spectrometer operating at 94.1 MHz using $CFCl_3$ as internal standard. Upfield shifts are reported as negative values.

General Reaction Method. Reactions summarized in Table I were carried out by adding the catalyst to a dried still pot with magnetic stirrer, followed by addition of a small portion of the starting material from a dropping funnel through a side arm of the still pot. Most reactions were very exothermic, but heat was applied when necessary to start the reaction and to maintain distillation of product while more starting material was added. Some reactions started well below room temperature.

Conversion of 1,3-Dimethoxy-2-(trifluoromethyl)pentafluoropent-1- and -2-ene (3) to 3-Methoxyoctafluoro-2-methyl-2-pentenoyl Fluoride (4) and Perfluoromethylpropionylketene[7] (5). The isomeric mixture of methyl ethers **3** (34 g) was added to 2.3 g of TiF_4 in a 100-mL still pot, and the mixture was heated in a still as described above. Methyl fluoride was evolved, and 26.3 g (86.5%) of the acryloyl fluoride **4**, bp 103 °C, was distilled. ^{19}F NMR showed two isomers in the ratio of about 1:4: IR 5.36 μm (COF), 5.99 μm (C=C); ^{19}F NMR: +55.95 and +52.80 (minor) (1 F), −59.40 and −54.97 (minor) (3 F), −114.8 and −114.9 ppm (minor) (2 F). Anal. Calcd for $C_7H_3F_9O_6$: C, 29.98; H, 1.04; F, 58.94. Found: C, 29.10; H, 1.31; F, 58.95.

Part of the above product (19.6 g) was recharged to the still pot with 2.5 g of TiF_4 and heated to distill 15.7 g (90.8%) of the acylketene **5**, bp 79 °C.

Registry No. **3** (isomer 1), 84047-24-5; (*E*)-**3** (isomer 2), 59754-88-0; (*Z*)-**3** (isomer 2), 59736-18-4; (*E*)-**4**, 91686-80-5; (*Z*)-**4**, 91686-81-6; **5**, 53352-88-8; HCF_2COF, 2925-22-6; $CF_3CHFCOF$, 6065-84-5; $(CF_3)_2CHCOF$, 382-22-9; $CHF(COF)_2$, 77946-94-2; $CF_3CF_2OCHFCOF$, 77946-91-9; $CF_3CF_2OCF_2H$, 53997-64-1; $(CF_3)_2CHCOC_2F_5$, 61637-91-0; $CF_2{=}CFCOF$, 667-49-2; $O{=}C{=}C(CF_3)_2$, 684-22-0; $FOCC(CF_3){=}CF_2$, 684-36-6; $CH_3OCF{=}C(CF_3)COCOCF_3$, 77946-93-1; $H_5C_2OOCCOCF_3$, 13081-18-0; $HCF_2CF_2OCH_3$, 425-88-7; $CF_3CHFCF_2OCH_3$, 382-34-3; $(CF_3)_2CHCF_2OCH_3$, 382-26-3; $CHF(CF_2OCH_3)_2$, 758-62-3; $CF_3CF_2OCHFCF_2OCH_3$, 84047-27-8; $(CF_3)_2CHCF(OCH_3)C_2F_5$, 54376-60-2; $CH_3OCF{=}CFCF_3$, 666-92-2; $CH_3OCF{=}C(CF_3)_2$, 360-53-2; $CH_3OCF{=}C(CF_3)CF(OCH_3)CF(OCH_3)CF_3$, 59736-15-1; $H_5C_2OOCCF(CF_3)OC_2H_5$, 10186-66-0; $(CF_3)_2CHCF_2OC_2H_5$, 380-30-3; CH_3F, 593-53-3; CH_3CH_2F, 353-36-6; TiF_4, 7783-63-3; SbF_5, 7783-70-2.

(7) England, D. C. *J. Org. Chem.* **1981**, *46*, 152.