ion peak, but rather a prominent peak at m/e 119, attributed to the 2-phenyl-2-propyl cation. 1-Phenyl-3-methyl-2-butanone was characterized by its infrared, nmr, and mass spectra; the mass spectrum showed a molecular ion peak at m/e 162 but no peak at m/e 119.

Registry No.—Bromobenzene, 108-86-1; 5-phenyl-1-pentene, 1075-74-7; 1-phenyl-2-pentene, 27911-12-2; 5-phenyl-1,3-pentadiene, 1007-52-9; 1-phenyl-1,3-pentadiene, 1608-27-1; 3-phenyl-2-butanone, 769-59-5; 1-phenyl-2-butanone, 1007-32-5; 3-phenyl-3-methyl-2-butanone, 770-85-4.

The Preparation of Highly Fluorinated Ethers

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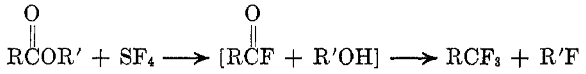
Received March 21, 1973

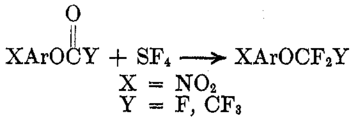
Highly fluorinated ethers are prepared by reducing their corresponding esters in HF at elevated temperature. Under the appropriate conditions the isolated yields of ethers exceed 80%; acyl-oxygen cleavage is negligible. The relative rates of reduction of a series of esters are reported and discussed.

Sulfur tetrafluoride[1] is a useful reagent for converting, among others, carbonyl to difluoromethylene and hydroxyl to fluoro groups. Our interest in this area stems from reports based on the attempted sulfur tetrafluoride reduction of esters to α,α-difluoro ethers. Pioneering investigations[2] dealing with reactions between sulfur tetrafluoride and various functional groups indicate that hydrocarbon aliphatic esters are reduced with predominant concomitance of acyl–oxygen cleavage. A subsequent study,[3] however,



$$R\overset{\overset{O}{\|}}{C}OR' + SF_4 \longrightarrow [R\overset{\overset{O}{\|}}{C}F + R'OH] \longrightarrow RCF_3 + R'F$$

demonstrates the conversion of aryl fluoroformates and trifluoroacetates to ethers by treatment with this reagent. Along these lines highly fluorinated aliphatic esters conceivably could be reduced to their corresponding ethers, a class of compound that would be difficult to prepare by alternate routes. The sulfur tetrafluoride reductions of this latter and related systems are described in this report.



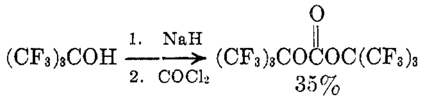
$$XAr O\overset{\overset{O}{\|}}{C}Y + SF_4 \longrightarrow XArOCF_2Y$$
$$X = NO_2$$
$$Y = F,\ CF_3$$

Results and Discussion

Preparation of Esters and a Carbonate.—Esters of perfluoroalkyl acids were prepared by the reaction between acid chlorides and $C_2F_5CH_2OH$, $(CF_3)_2CHOH$, and $(CF_3)_3COH$. In the presence of DMF, the reaction between acid chlorides and $C_2F_5CH_2OH$ proceeds at 25°; however, higher reaction temperatures (50–60°) were required for esters derived from $(CF_3)_2CHOH$. The yields of the fluorinated propyl esters range from 70 to 90%. A side product, the corresponding acid, is suspected to have resulted from the presence of adventitious moisture which hydrolyzed the ester during distillation.

The reaction between perfluorooctanoyl chloride and perfluoro-*tert*-butyl alcohol afforded the corresponding ester languidly at 50° (17% conversion after 90 hr). However, the addition of a stoichiometric amount of Et_3N[4] effected complete alcohol to ester conversion under mild conditions. When reactions between acid fluorides and $C_2F_5CH_2OH$ or $(CF_3)_2CHOH$ were run in glass vessels, water was inevitably introduced into the reaction. A good yield of ester can be obtained by running acid fluoride esterifications in stainless steel vessels. The esters prepared by the reactions between acid chlorides or fluorides are presented in Table I; yields, reaction conditions, and by-products are included for convenience.

Perfluoro-*tert*-butyl carbonate was prepared by the reaction between sodium perfluoro-*tert*-butoxide (prepared *in situ*) and phosgene.



$$(CF_3)_3COH \xrightarrow[2.\ COCl_2]{1.\ NaH} \underset{35\%}{(CF_3)_3CO\overset{\overset{O}{\|}}{C}OC(CF_3)_3}$$

The yield obtained is not representative of the reaction. The reaction proceeded smoothly; however, the unexpected physical properties of the carbonate led to losses during work-up.

Reductions of Esters and Related Compounds with SF_4.—The literature[1] indicates that Lewis and Brønsted acids, BF_3 and HF being the most popular, catalyze the SF_4 reduction of carbonyl compounds. However, to the best of our knowledge, there has been no reported comparative study concerning the relative effectiveness of these catalysts on the reduction of carbonyl compounds by SF_4. To this end, preliminary experiments were run under similar conditions using several preselected catalysts. The results are summarized in Table II.

Apparently, HF is the most effective catalyst in this group, and the rate of reduction of the ester is faster when HF is used as solvent rather than in catalytic amounts.

For each ester small-scale experiments were run to determine the temperature and reaction time neces-

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[1] For recent reviews on this reagent, see W. C. Smith, *Angew Chem., Int. Ed. Engl.*, **1**, 467 (1962); D. G. Martin, *Ann. N. Y. Acad. Sci.*, **145**, 161 (1967); P. Boissin and M. Carles, *Commis. Energ. At. [Fr.] Serv. Doc., Ser. Bibliogr.*, **98**, 29 (1967); J. V. Urenovitch, "Sulfur Tetrafluoride," Technical Bulletin, Air Products and Chemicals, Inc.

[2] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **82**, 543 (1960), and references stated therein.

[3] W. A. Sheppard, *J. Org. Chem.*, **29**, 1 (1964); J. A. Webster, Seventh Quarterly Progress Report, Contract NAS8-21401, "Thermally Resistant Polymers for Fuel Tank Sealants," Oct 1970.

[4] For an alternate preparation of a perfluoro-*tert*-butyl ester, see F. J. Pavlik and P. E. Toren, *J. Org. Chem.*, **35**, 2054 (1970).

TABLE I

SYNTHESIS OF ESTERS

Ester (% yield[a])	Acid (% yield[a])	Reactants (g, mol)	Registry no.	Conditions
$C_7F_{15}CO_2CH_2C_2F_5$ (71)	$C_7F_{15}CO_2H$ (16)	$C_7F_{15}COCl$ (41.5, 0.096) $C_2F_5CH_2OH$ (23.5, 0.156)	335-64-8 422-05-9	1 drop of DMF, reflux 5 hr
$C_7F_{15}CO_2CH(CF_3)_2$ (77)	$C_7F_{15}CO_2H$ (6)	$C_7F_{15}COCl$ (25, 0.058) $(CF_3)_2CHOH$ (12.6, 0.075)	920-66-1	5 drops of DMF, 60°, 24 hr
$C_7F_{15}CO_2C(CF_3)_3$ (17)		$C_7F_{15}COCl$ (20.0, 0.0462) $(CF_3)_3COH$ (14.1, 0.0597)	2378-02-1	DMF (0.5 ml), 50°, 90 hr
$C_7F_{15}CO_2C(CF_3)_3$ (83)				Et_3N (7.0 g, 0.046 mol), −100° → room temperature
$[(CF_3)_2CHO_2CCF_2CF_2]_2$ (92)		$(ClOCCF_2CF_2)_2$ (15.0, 0.046) $(CF_3)_2CHOH$ (20.0, 0.119)	336-06-1	DMF (0.1 ml), 60°, 18 hr
$C_3F_7O(\underset{F}{\overset{CF_3}{C}}CF_2O)_2\underset{F}{\overset{CF_3}{C}}CO_2CH(CF_3)_2$ (58)	Corresponding acid (20)	$C_3F_7O(\underset{F}{\overset{CF_3}{C}}CF_2O)_2\underset{F}{\overset{CF_3}{C}}C({=}O)F$ (20.5, 0.037) $(CF_3)_2CHOH$ (10.4, 0.062)	27639-98-1	2 drops of DMF, NaF (anhydrous, 5.2 g), 60°, 60 hr[b]
$C_2F_5O(CF_2CF_2O)_2CF_2CO_2CH_2C_2F_5$ (76)	Corresponding acid (13)	$C_2F_5O(CF_2CF_2O)_2CF_2C({=}O)F$ (15.0, 0.324) $C_2F_5CH_2OH$ (6.0, 0.040)	13071-66-4	DMF (0.1 ml), 65°, 16 hr[c]
$+C({=}O)(CF_2)_3CO_2CH_2(CF_2)_3CH_2O+_n$ (98)		$ClC({=}O)(CF_2)_3C({=}O)Cl$ (28.9, 0.10) $HOCH_2(CF_2)_3CH_2OH$ (22.4, 0.10)	678-77-3 376-90-9	DMF (0.5 ml), 140°, 5 hr

[a] Yield of isolated product. [b] Reaction run in glass flask. [c] Reaction run in stainless steel autoclave.

TABLE II

CATALYST SCREENING[a]

Catalyst (mol)	Conversion of ester	Selectivity to ether
	<1	
HF (0.01)	25	>98
HF (0.35)	56	>98
BF_3 (0.01)	<1	
SbF_5 (0.01)	<1	
AsF_3 (0.01)	<1	

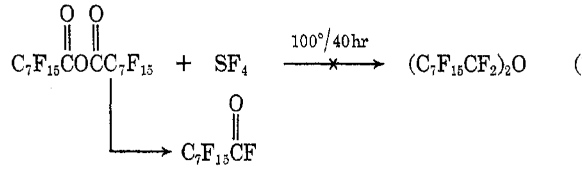
[a] $C_7F_{15}CO_2CH_2C_2F_5$ (1.0 g, 1.83 mmol), Freon E4 standard (0.5 g), and SF_4 (2.16 g, 20.0 mmol) were charged with or without added catalyst into a 30-ml stainless steel autoclave and heated with shaking at 85° for 20 hr.

sary to give the highest conversion of the ester and selectivity to the ether. To minimize a competing cleavage reaction, the lowest reaction temperature was chosen which would afford essentially complete conversion of the ester in a reasonable time interval. Once these conditions were found, the reaction was scaled up roughly by a factor of ten (see Table III). From examination of glc results obtained in these experiments, it was noted that ester to ether conversions were essentially quantitative under the given conditions. The yields of ethers shown in Table III presumably reflect losses due to handling.

In all of the runs, *ca.* a tenfold excess of SF_4 is used along with anhydrous HF as the solvent. No attempts were made to determine the minimum amount of SF_4 needed to effect complete conversion of esters to ethers at a given temperature.

It has been reported[2] that anhydrides can be converted to acid fluorides and under extreme conditions to trifluoromethyl groups. In several instances[2] an ether can be obtained from an anhydride.

Since these reactions were not run in HF solvent, an attempt was made to convert a linear anhydride to the homologous ether with SF_4/HF. The results are shown schematically in eq 1. Under the reaction

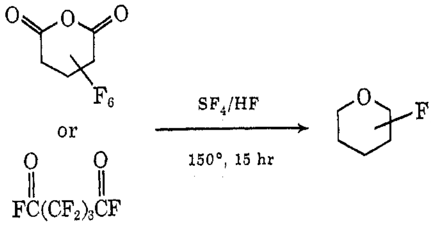


(1)

conditions essentially complete consumption of the anhydride was observed while no other appreciable products were detected in the crude reaction mixture. In another experiment run under milder conditions, the acid fluoride was the only identifiable product with unreacted acid accounting for the remainder of the reaction.

It is interesting that in our SF_4/HF reactions the anhydride, $[C_7F_{15}C({=}O)]_2O$, undergoes acyl–oxygen cleavage while the ester, $C_7F_{15}C({=}O)OCH_2C_2F_5$, gives carbonyl reduction without cleavage. This could be attributed to the cleavage of the anhydride by HF to an acid fluoride–acid mixture, folowed by the reduction of the acid to the acid fluoride by SF_4. The HF cleavage reaction has previously been reported[5] as a method for the preparation of CF_3COF from $(CF_3CO)_2O$.

However, we have observed that under more severe reaction conditions perfluoro cyclic anhydrides and certain perfluoro diacid fluorides are converted to cyclic ethers by SF_4/HF treatment. In separate experiments perfluoroglutaric anhydride and perfluoro-



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[5] G. A. Olah and S. J. Kuhn, *J. Org. Chem.*, **26**, 237 (1961).

TABLE III

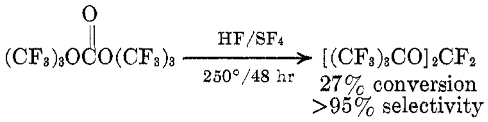
REDUCTION OF ESTERS TO ETHERS BY SF_4 IN HF[a]

Ester (mol)	SF_4, mol	Ether, % yield[b]	Reaction conditions, °C, hr	Acid fluoride (yield)[c]
$C_7F_{15}CO_2CH_2C_2F_5$ (0.0183)	0.22	92	150, 15	<1
$C_7F_{15}CO_2CH(CF_3)_2$ (0.0177)	0.21	81	185, 15	<1
$C_7F_{15}CO_2C(CF_3)_3$ (0.0136)	0.29	83	180, 100	1
$(CF_3)_2CHO_2C(CF_2)_4CO_2CH(CF_3)_2$ (0.017)	0.42	89	185, 16	<1
$C_2F_5O(CF_2CF_2O)_2CF_2CO_2CH_2C_2F_5$ (0.0168)	0.252	83	150, 15	<1
$-\!\!\left[C(=O)(CF_2)_3CO_2CH_2(CF_2)_3CH_2O\right]\!\!-_n$ (0.024)	0.36	89 (polyether)	150, 16	

[a] Reactions run in 300-ml stainless steel autoclave with 50 ml of anhydrous HF. [b] Isolated yield of distilled product. [c] Estimated by glc of the crude reaction mixture.

glutaryl fluoride are converted to perfluoropentamethylene oxide. A common intermediate (possibly a perfluorolactone) is suspected to be involved in these reactions.

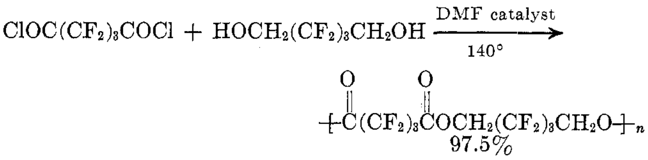
Perfluoro di-*tert*-butyl carbonate is unaffected by SF_4/HF treatment at 85° for 20 hr. Similar experiments run at 200° for 24 hr and 250° for 48 hr afforded 7 and 27% conversions, respectively, of the carbonate to a sole product (>95% selectivity). The product was tentatively assigned the structure $[(CF_3)_3CO]_2CF_2$ from glc mass spectra and ^{19}F nmr data.



$$(CF_3)_3O\overset{O}{\overset{\|}{C}}O(CF_3)_3 \xrightarrow[250°/48\ hr]{HF/SF_4} [(CF_3)_3CO]_2CF_2$$

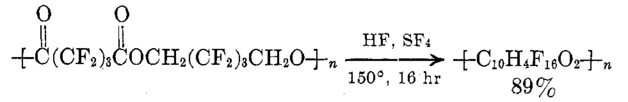
27% conversion
>95% selectivity

To test the applicability of these reactions for polymers, the polyester $-\!\!\left[OC(CF_2)_3COOCH_2(CF_2)_3CH_2O\right]\!\!-_n$ was prepared from perfluoroglutaryl chloride and hexafluoro-1,5-pentanediol. When the polyester was treated with excess SF_4 in HF at 150° for 16 hr, a polyether was isolated in 89% yield.



$$ClOC(CF_2)_3COCl + HOCH_2(CF_2)_3CH_2OH \xrightarrow[140°]{DMF\ catalyst} -\!\!\left[\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}OCH_2(CF_2)_3CH_2O\right]\!\!-_n$$

97.5%



$$-\!\!\left[\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}OCH_2(CF_2)_3CH_2O\right]\!\!-_n \xrightarrow[150°,\ 16\ hr]{HF,\ SF_4} -\!\!\left[C_{10}H_4F_{16}O_2\right]\!\!-_n$$

89%

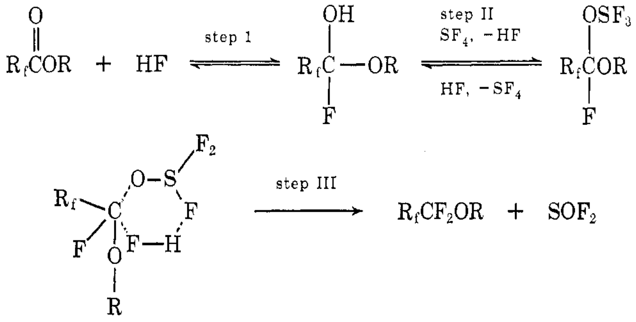
Relative Rate Data.—As a supplement to estimating the ease of reaction of an ester with SF_4 by comparing reaction conditions, semiquantitative data were obtained from a relative rate study. From these and our previously collected data, reasonable predictions could be made as to the feasibility of completely reducing a certain highly fluorinated ester with SF_4.

The relative rates of reaction between four pairs of esters were measured. In these experiments roughly a tenfold excess of SF_4 was employed to approach psuedo-first-order kinetics. The following rate expression was used to calculate the realtive rates.

$$k = \frac{\log A/A_0}{\log B/B_0}$$

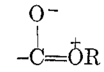
The rates were measured at 85 ± 2° (Chart I). The reported values are essentially the rates of consumption of the parent esters.

Mechanistic Implication.—The mechanism proposed[1,6] for the reduction of ketones with SF_4 seems consistent with the data accumulated on the reduction of the fluorinated esters.



The facts that our reactions do not proceed at moderate temperatures in the absence of HF and that the reactions proceed faster when HF is used as a solvent rather than in catalytic amounts suggest the incorporation of HF in the actual rate expression. This is consistent with an equilibrium involving HF in step I or (and) the HF facilitation of step III in the reaction as depicted in the mechanism.[7]

Our relative rate data indicate that steric effects influence the rates of these reactions more than electronic effects. The ester carbonyl absorption occurs at higher energy when a CF_3 is substituted for an H in the alkoxy substituent. This is in keeping with the intuitive expectation that such substitution reduces the electron density at the carbonyl group; *i.e.*, the ester stabilizing contribution[9] a becomes less important



$$-\overset{O^-}{\overset{|}{C}}=\overset{+}{O}R$$

a

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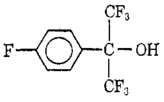
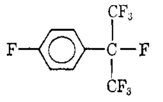
[6] W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1969, p 126.

[7] With regard to the SF_4 reduction of hydrocarbon, carbonyl-containing compounds, the authors in ref 2 make the reasonable suggestion that step I rather than step III is rate determining. However, the paucity of data demonstrating the ease of an S_Ni or S_N2 process at a highly F or R_f substituted, four-coordinate carbon atom limits our assignment of the slow step from the available data. Reactions analogous to step III do not appear to proceed[8] under mild conditions.

[8] For example, the conversion of i to ii is effected by SF_4 at 150°; see W. A. Sheppard, *J. Amer. Chem. Soc.*, **87**, 2410 (1965).



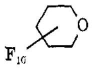
i



ii

[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, p 182.

TABLE IV
PROPERTIES OF ESTERS, ETHERS, AND CARBONATE

Registry no.	Compd	Bp, °C (mm)	Mass spectra
40719-59-3	$C_7F_{15}CO_2CH_2C_2F_5{}^a$	81–84 (25)	
40719-60-0	$C_7F_{15}CF_2OCH_2C_2F_5{}^a$	75–78 (28)	M − 19, 549
40719-61-7	$C_7F_{15}CO_2CH(CF_3)_2{}^a$	73–75 (28)	
40719-62-8	$C_7F_{15}CF_2OCH(CF_3)_2{}^a$	82–84 (41)	
40719-63-9	$C_7F_{15}CO_2C(CF_3)_3{}^a$	60–62 (1)	M − 19, 613
40691-16-5	$C_7F_{15}CF_2OC(CF_3)_3{}^a$	93 (41)	M − 19, 635
40719-64-0	$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)CO_2CH(CF_3)_2{}^a$	103 (27)	
40719-65-1	$C_2F_5O(CF_2CF_2O)_2CF_2CO_2CH_2C_2F_5{}^a$	88–91 (41)	
40719-66-2	$C_2F_5O(CF_2CF_2O)_2CF_2CF_2OCH_2C_2F_5{}^a$	87–88 (41)	
40719-67-3	$[(CF_3)_2HCO_2CCF_2CF_2]_2{}^a$	93–95 (41)	
40719-68-4	$[(CF_3)_2HCOCF_2CF_2CF_2]_2{}^a$	99–101 (40)	
355-79-3			M − 19, 247
40719-69-5	$(CF_3)_3COC(=O)OC(CF_3)_3{}^a$	(40–42)[b]	
40719-70-8	$(CF_3)_3COCF_2OC(CF_3)_3$		M − 19, 501
26546-05-4	$[C(=O)(CF_2)_3CO_2CH_2(CF_2)_3CH_2O]_n{}^a$	(~45)[b]	
40719-25-3 (polymer)	$(C_{10}H_4F_{16}O_2)_n{}^a$		

[a] Satisfactory combustion data for C and H (±0.7%) were provided for these compounds: Ed. [b] Melting point.

CHART I

$$k\frac{C_7H_{15}CO_2CH_2C_2F_5}{C_7F_{15}CO_2CH(CF_3)_2} = 1.8$$

$$k\frac{C_7H_{15}CO_2CH_2C_2F_5}{C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)CO_2CH(CF_3)_2} = 21$$

$$k\frac{C_7F_{15}CO_2CH(CF_3)_2}{C_7F_{15}CO_2C(CF_3)_3} = 6.0$$

$$k\frac{C_2F_5O(CF_2CF_2O)_2CF_2CO_2CH_2C_2F_5}{C_7F_{15}CO_2CH_2C_2F_5} = 11$$

Substrate	Relative rate
$C_2F_5O(CF_2CF_2O)_2CF_2CO_2CH_2C_2F_5$	230
$C_7H_{15}CO_2CH_2C_2F_5$	21
$C_7F_{15}CO_2CH(CF_3)_2$	12
$C_7F_{15}CO_2C(CF_3)_3$	2
$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)CO_2CH(CF_3)_2$	1

as the electron-withdrawing power of the R group increases. Consequently, the rate of step I and from a related argument step III (mechanism) would be expected to increase in the series $R_fCO_2C(R_f)_3 > R_fCO_2CH(R_f)_2 > R_fCO_2CH_2R_f$. Substitution of a CF_3 for an F or an R_fO for an F group α to the carbonyl, *e.g.*, $R_fCF_2CO_2R$, $R_fCF(R_f)CO_2R$, and $R_fOCF_2CO_2R$, does not appreciably change the carbonyl frequency of the esters. In this series F, R_f, and R_fO exert similar electronic effects.[10] Since the data accumulated from the relative rate study is not interpretable from arguments based on the above electronic effects, steric factors must govern the rates of these reactions.

To summarize the rate data, as the bulk of the substituent is increased at sites 1 or 2 (below) of a fluorinated ester, the rate decreases. Rate decline is more pronounced by substitution at site 1 rather than site 2.

$$\begin{array}{cccc} R_0 & CR_2 & CO_2 & CR_3 \\ & 1 & & 2 \end{array}$$

It is notable that $C_2F_5O(CF_2CF_2O)_2CF_2CO_2CH_2C_2F_5$ (TFEO ester) is reduced by an order of magnitude faster than $C_7F_{15}CO_2CH_2C_2F_5$. While most, if not all, of this rate enhancement may be attributed to the smaller steric bulk at site 1 of the ether ester, the possibility of a change in mechanism cannot be dismissed. In the ether ester step III may involve a prior ionization (HF assisted) of the $C–OSF_3$ bond. The resulting carbocation could be partially stabilized by the neighboring oxygen atoms in the fluorocarbon ether backbone. If this were the case, it might be anticipated that $R_fOCF(CF_3)CF_2OCF(CF_3)CO_2R$ (HFPO ester) would undergo reduction *via* the normal route since substitution of a CF_3 for an F at site 1 would destabilize[11] the incipient carbocation. This could account partially for the difference in the rates of reduction of the TFEO and HFPO esters.

Experimental Section

The highly fluorinated alcohols, acid chlorides, anhydrides, and hexafluoroglutaryl fluoride used in this work are supplied commercially by PCR, Inc. The acid fluorides derived from HFPO[12] and TFEO[13] were prepared by published procedures.

Vapor phase chromatographic analysis was performed on a Hewlett-Packard Model 700 instrument using an 8 ft × 0.25 in. 15 or 35% PFO-XR on Gas-Chrom R 60–80 mesh column. Infrared spectra were recorded on a Perkin-Elmer Infracord spectrometer. ^{19}F nmr spectra were recorded on a Varian XL-100 spectrometer at 94.1 MHz. The mass spectra were recorded on Model 14-107 Bendix time of flight spectrometer.

Preparation of Partially Fluorinated Esters. General Procedure.—The esters were prepared from the appropriate alcohols and acid chlorides or fluorides. The lower boiling component was added to the higher boiling component dropwise at room temperature. Several drops of DMF were added to catalyze the reactions. The esterifications with $C_2F_5CH_2OH$ proceeded at 25°; however, the reactions were run at reflux. It was necessary to heat the reaction mixture to 50–60° to observe appreciable reaction when $(CF_3)_2CHOH$ was used as reactant. Esters were isolated by distilling the crude reaction mixtures. Table I gives the stoichiometries, yields, etc., of these runs. Table IV and V give the properties of these materials.

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[10] Similar conclusions can be arrived at from the similarity of the ionization constants of perfluoroalkyl acids; see also W. A. Sheppard, *J. Amer. Chem. Soc.*, **92**, 5419 (1970).

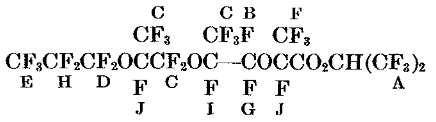
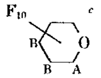
[11] G. A. Olah, R. D. Chambers, and M. B. Comisarow, *J. Amer. Chem. Soc.*, **89**, 1268 (1967); G. A. Olah and C. U. Pittman, Jr., *ibid.*, **88**, 3310 (1966).

[12] C. G. Fritz, E. P. Moore, and S. Selman, U. S. Patent 3,114,778 (1963); *Chem. Abstr.*, **60**, 6750*B* (1964).

[13] J. C. Warnell, U. S. Patent 3,250,806 (1966); *Chem. Abstr.*, **65**, 15230*F* (1966).

Table V

^{19}F[a] and ^{1}H Nmr[b] Data

Compd	A	B	C	D	E	F	G	H	I	J	^{1}H nmr
$\underset{A}{CF_3}\underset{G}{CF_2}\underset{D}{(CF_2)_4}\underset{F}{CF_2}\underset{C}{CF_2}OCH_2\underset{E}{CF_2}\underset{B}{CF_3}$	3.7 (t, $J \sim 10$)	6.7 (s)	9.1 (br s)	44.6 (br m)	46.6 (t of t)	47.4 (m)	48.6 (m)				3.95 (t, $J = 12$)
$\underset{B}{CF_3}\underset{E}{CF_2}\underset{D}{(CF_2)_4}\underset{C}{CF_2}CO_2CH\underset{A}{(CF_3)_2}$	−2.7 (d, $J \sim 6$)	5.0 (t of t)	41.4 (t)	45 (br)	49.5 (m)						6.1 (sept, $J = 6$)
$\underset{B}{CF_3}\underset{E}{CF_2}\underset{D}{(CF_2)_5}\underset{C}{CF_2}OCH\underset{A}{(CF_3)_2}$	−2.1 (d, $J \sim 5$)	5.2 (t, $J \sim 10$)	8.0 (br)	45.2 (m)	48.4 (br)						4.84 (sept, $J = 5.5$)
$\underset{B}{CF_3}\underset{E}{CF_2}\underset{D}{(CF_2)_4}\underset{C}{CF_2}CO_2C\underset{A}{(CF_3)_3}$	−6.6 (s)	4.9 (t of t)	40.4 (t of t)	45.1 (br)	49.4 (m)						
$\underset{C}{CF_3}\underset{F}{CF_2}\underset{D}{(CF_2)_4}\underset{E}{CF_2}\underset{B}{CF_2}OC\underset{A}{(CF_3)_3}$	−7.0 (t, $J = 9$)	2.9 (br)	5.0 (t, $J \sim 10$)	44.3 (br)	47.2 (br)	48.8 (br)					
 $\underset{E}{CF_3}\underset{H}{CF_2}\underset{D}{CF_2}O\overset{\overset{C}{CF_3}}{\underset{\underset{J}{F}}{C}}\underset{C}{CF_2}O\overset{\overset{C}{CF_3}}{\underset{\underset{I}{F}}{C}}{-}\overset{\overset{B}{F}}{\underset{\underset{G}{F}}{C}}O\overset{\overset{F}{CF_3}}{\underset{\underset{J}{F}}{C}}CO_2CH\underset{A}{(CF_3)_2}$	−2.9 (m)	1.9 (d, $J \sim 150$)	3.5 (br)	4.7 (br)	5.2 (t, $J = 7$)	5.8 (d, $J \sim 6$)	7.9 (d, $J \sim 150$)	53.0 (s)	54.7 (m)	67.9 (m)	6.0 (sept, $J = 6$)
$[\underset{C}{CF_2}\underset{B}{CF_2}CO_2CH\underset{A}{(CF_3)_2}]_2$	−2.9 (d, $J = 6$)	41.5 (m)	45.2 (m)								5.88 (sept, $J = 6$)
$[\underset{C\text{ or }D}{CF_2}\underset{B}{CF_2}CF_2OCH\underset{A}{(CF_3)_2}]_2$	−2.3 (q, $J = 5$)	7.9 (m)	45.2 (m)	48.1 (m)							4.88 (sept, $J = 5$)
$\underset{B}{CF_3}\underset{C}{CF_2}O(\underset{C}{CF_2}\underset{C}{CF_2}O)_2\underset{A}{CF_2}CO_2CH_2\underset{D}{CF_2}\underset{C}{CF_3}$	0.8 (t, $J = 12$)	8.1 (s)	10.9 (s)	47.6 (t, $J = 12$)							4.76 (t, $J = 12$)
$\underset{A}{CF_3}\underset{E}{CF_2}O(\underset{D}{CF_2}\underset{D}{CF_2}O)_2\underset{D}{CF_2}\underset{C}{CF_2}OCH_2\underset{F}{CF_2}\underset{B}{CF_3}$	8.3 (s)	11.2 (br s)	11.7 (m)	12.5 (m)	16.5 (s)	48.3 (t of t, $J = 11.5, 2$)					4.34 (t, $J = 12$)
$\underset{A}{(CF_3)_3}COCOOC(CF_3)_3$	−6.8 (s)										
$\underset{B}{(F_3C)_3}CO\underset{A}{CF_2}OC(CF_3)_3$	−20.6 (m, $J = 8$)	−6.4 (t, $J = 8$)									
 [c]	14.5	60.6									

[a] ^{19}F nmr spectra were recorded on a Varian XL-100 spectrometer at 94.1 MHz. The liquids were run neat with an external lock using a substitute tube of trifluoroacetic acid as reference. The solid samples were run in acetone-d_6 as solvent. Chemical shifts are reported in parts per million from the standard (J in hertz). [b] ^{1}H nmr spectra were run on the same instrument at 100 MHz as neat liquids or in acetone-d_6 using tetramethylsilane as internal standard. Chemical shifts are reported in parts per million from standard (J in hertz). [c] Gas phase.

Table VI

Relative Rate Data

Substrate		Substrate				
A_0, mmol	A, mmol	B_0, mmol	B, mmol	SF_4, g (mmol)	E4, g	Reaction time, hr
$C_7F_{15}CO_2CH_2C_2F_5$		$C_7F_{15}CO_2CH(CF_3)_2$		2.16 (20)	0.4739	15
0.820	0.390	0.886	0.585			
$C_7F_{15}CO_2CH(CF_3)_2$		$C_7F_{15}CO_2C(CF_3)_3$		2.92 (27)	0.503	15
0.604	0.389	1.87	1.74			
$C_7F_{15}CO_2CH_2C_2F_5$		$C_3F_7O[C(CF_3)FCF_2O]_2C(CF_3)FCO_2CH(CF_3)_2$		2.16 (20)	0.5076	15
0.825	0.389	0.905	0.845			
$C_2F_5O(CF_2CF_2O)_2CF_2CO_2CH_2C_2F_5$		$C_7F_{15}CO_2CH_2C_2F_5$		1.73 (16)	0.4954	10
0.421	0.037	0.892	0.702			

Preparation of Perfluoro Di-*tert*-Butyl Carbonate.—Sodium hydride (6.12 g, 0.255 mol, 50% mineral oil dispersion) was added to a flask equipped with an acetone–Dry Ice condenser. This material was slurried with 200 ml of anhydrous THF. Then perfluoro-*tert*-butyl alcohol (20.0 g, 0.085 mol) was added dropwise maintaining 20° in the flask by external cooling. The reaction mixture was allowed to stir overnight at 25°. The vessel was cooled to 5° and then phosgene (4.2 g, 0.0425 mol) was condensed into the flask rapidly. The reaction was exothermic and the temperature rose to 18°. The reaction was stirred at 5° for 1 hr and then at 25° for 24 hr. The solution was filtered under N_2 and the salts were dried with a N_2 flow. The salts were then washed with Freon-113 (2 × 100 ml). Distillation of the THF solution gave an azeotrope which was collected; on cooling, a solid crystallized from the distillate and was filtered cold under N_2 leaving 3.5 g of a white solid, mp 40–42°. Careful fractionation of the Freon wash solution gave a material (bp 84–87°, 3.0 g) which solidified on standing (mp 40–42°). These materials had identical ir spectra (C=O at 5.32 μ) and were found to be the carbonate (7.5 g, theory 21.1 g, 35% yield). Properties are reported in Tables IV and V.

SF_4 Reductions. General Procedure.—The ester was charged into a 300-ml, 316 stainless steel autoclave equipped with a 3000-psi bursting disk. The vessel was cooled to −183° and evacuated, and the appropriate amount of HF, then SF_4, was introduced by vacuum techniques. The autoclave was heated in a rocker for a given period; then the clave was removed, cooled, and vented at atmospheric or slightly reduced pressure through a steel trap packed with NaF. The SF_4 and SOF_2 were collected in a trap cooled at −183°. After the removal of the HF and SF_4 had been effected, the clave was opened and the contents were diluted with Freon-113 and transferred to a flask containing NaF to scavenge residual HF. This solution is referred to in the text as crude product. Concentration of the solution and distillation afforded the product. Yields are reported in Table III, properties in Table IV and V.

Reaction between Perfluorooctanoic Anhydride and SF_4.—Perfluorooctanoic anhydride (10.0 g, 0.0123 mol), HF (50.0 g, 2.5 mol), and SF_4 (70 g, 0.65 mol) were charged to a 300-ml stainless steel autoclave and heated at 100° for 40 hr. The autoclave was vented at 25° (720 mm) through NaF into traps cooled by ice and liquid O_2 consecutively. The autoclave was removed after the vapors were vented. By applying vacuum (0.1 mm) to the NaF and ice trap, $C_7F_{15}C(=O)F$ (6.0 g, >95%) was collected and identified by comparison of glc retention time and ir with those of an authentic sample. The autoclave was opened and Freon-113 (15 ml) was added. Glc of this solution showed that a trace (<1%) of perfluorooctanoic anhydride remained; perfluorooctanoyl fluoride was the only product detected. Distillation afforded 1.5 g of the acid fluoride, bp 105–107° (total 7.5 g, theory 10.2 g, 74%). The bottoms from the distillation (1.7 g) consisted of ~60:40 mixture of $C_7F_{15}C(=O)F$ and $C_7F_{15}C(=O)OH$, respectively, by ir analysis.

The reaction was repeated under milder conditions, *i.e.*, 60° for 24 hr, and gave the same product with perfluorooctanoic acid accounting for ~30% of the mixture. No appreciable amounts of products assignable to a perfluoroether or ester were detected.

Reaction between Perfluoroglutaric Anhydride and SF_4.—Perfluoroglutaric anhydride (5.0 g, 0.0225 mol), SF_4 (48.5 g, 0.45 mol), and HF (50 ml) were charged to a 300-ml stainless steel autoclave and heated at 150° for 15 hr with rocking. The autoclave was cooled and the contents were passed through a steel trap containing NaF to remove the HF. The volatiles were collected at liquid oxygen temperature and weighed 53.2 g. Analysis by glc showed SF_4, SOF_2, and an unknown product in a 50:6:6 ratio, respectively. The unknown product was shown to be perfluoropentamethylene oxide (see Tables IV and V). When the reaction was repeated using perfluoroglutaryl fluoride as starting material, the same results were obtained under analogous reaction conditions.

The SF_4 Reduction of Perfluoro-*tert*-butyl Carbonate.—The carbonate (1.3 g, 2.6 mmol), C_6F_6 (0.6 g, internal standard), HF (5 ml), and SF_4 (5.4 g, 50 mmol) were charged and heated with shaking in a 30-ml stainless steel autoclave at 250° for 48 hr. The contents were cooled and vented through a NaF trap at atmospheric pressure. Then vacuum was applied and the remainder of the material was collected in a trap cooled at −183°. Glc showed a 63:27 ratio of carbonate to product. Tables IV and V recorded the spectral properties of the product.

Competitive Experiments.—Pairs of esters were charged into 30-ml stainless steel autoclaves with 7.0 ml of HF, SF_4, and Freon E4 as a standard. The vessels were heated at 85 ± 2° with shaking for the appropriate time intervals, then cooled to room temperature, and vented. The contents were dissolved in Freon-113 (15 ml), and the resulting solution stored over NaF and then analyzed by glc. The details of these experiments are shown in Table VI.

Acknowledgments.—The author wishes to thank Dr. K. B. Baucom of PCR, Inc., for helpful suggestions as as well as a sample of the polyester. Thanks are due to Drs. W. S. Brey and R. J. Hanrahan of the University of Florida for obtaining and interpreting the nmr and mass spectral data, respectively, reported in this work. This work was sponsored by the Air Force under Contract No. F33615-70-C-1343.

Registry No.—Perfluorooctanoic anhydride, 33496-48-9; perfluorooctanoyl fluoride, 335-66-0; perfluoroglutaric anhydride, 376-68-1; perfluoroglutaryl fluoride, 678-78-4; SF_4, 7783-60-0.