G. **Pyrolysis Experiments.**[19]—Samples of the aryl perfluoroalkyl ethers were distilled into an evacuated 10-ml. stainless steel pressure vessel connected to the inlet system of a mass spectrometer. The vessel was heated for 20-min. periods in succession at temperatures of 400, 475, 550, 625 and 700°. After each period, a sample was removed for mass spectrometric analysis, and the per cent decomposition and major decomposition products were determined. In this study, $C_6H_5OCF_3$, $C_6H_5OCF_2CF_3$, $C_6H_5OCF_2CF_2H$, and p-$(CF_3O)_2C_6H_4$ were compared with benzotrifluoride and fluorobenzene. In each case a measurable amount of decomposition (5 to 10%) was noted between 550 and 570°. At 625° the decomposition was 60–70% for the pentafluoro- and tetrafluoroethyl ethers, but only 30 to 40% for the other compounds in the series. The initial course of decomposition in all cases appeared to be formation of biphenyls. For the ethers, formation of carbon monoxide, carbon dioxide, and fluorobenzene derivatives becomes significant at higher temperatures.

H. **Spectral Properties.**—A description of the infrared and n.m.r. spectra of the aryl perfluoroalkyl ethers was presented in the discussion. The ultraviolet spectra of these ethers are in general very similar to those of corresponding toluene derivatives, as illustrated by the following examples in Table V.

TABLE V

	λ_{max} mμ (log ε)			
$C_6H_5OCF_3$[a]	267 (2.2)	264 (2.4)	255 (2.2)	249 (2.2)
$C_6H_5CH_3$[b]	268 (2.4)	262 (2.5)	255 (2.4)	248 (2.2)
p-$C_6H_4(OCF_3)_2$[a]		269 (2.5)	264 (2.6)	259 (2.5)
p-$C_6H_4(CH_3)_2$[b]	275 (2.7)	268 (2.7)	261 (2.5)	256 (2.3)

[a] The solvent was isooctane. [b] Literature value.

Acknowledgment.—The author is grateful to Dr. R. V. Lindsey, Jr., and Dr. P. E. Aldrich for helpful discussions and suggestions during the course of this work and wishes to acknowledge the special assistance of Mr. R. M. Berdt for the pyrolysis studies employing the mass spectrometer and Mrs. Adah Richmond for the gas chromatographic analysis.

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[19] A qualitative study of the stability of derivatives of perfluorobenzene was described recently by L. A. Wall, R. E. Donadia, and W. J. Pummer, *J. Am. Chem. Soc.*, **82**, 4846 (1960).

α-Fluorinated Ethers. II. Alkyl Fluoroalkyl Ethers[1]

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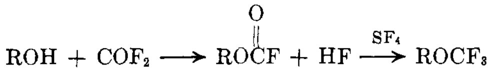
Aliphatic alcohols are converted to the corresponding trifluoromethyl ethers by reaction with carbonyl fluoride and treatment of the resulting fluoroformate with sulfur tetrafluoride. This reaction has synthetic value only when the alcohol is substituted with a deactivating substituent in the β-position. The scope and extensions of this reaction and the physical and chemical properties of these ethers, particularly trifluoromethyl vinyl ether and substituted ethyl trifluoromethyl ethers, are described.

Perfluoroalkyl ethers have been prepared in low yield by electrolytic fluorination.[2] Other methods useful for preparation of α-fluorinated ethers are base-catalyzed additions of alcohols to fluoroolefins and fluoride exchange reactions with chlorinated ethers. However, none of these methods is generally useful for the preparation of alkyl trifluoromethyl ethers.[3]

Results and Discussion

Synthesis.—The new general method for preparation of aryl trifluoromethyl ethers described in the previous paper[1] has been extended to the aliphatic series.



$$ROH + COF_2 \longrightarrow RO\overset{O}{\overset{\|}{C}}F + HF \xrightarrow{SF_4} ROCF_3$$

Alcohols were converted to the corresponding fluoroformates by reaction with carbonyl fluoride[4,5] in an autoclave at 100 to 200°. In a second step, the fluoroformates were converted to trifluoromethyl ethers by reaction with sulfur tetrafluoride[6] at 150 to 200°. In general, the intermediate fluoroformate was not isolated, and the hydrogen fluoride by-product from the first step served as a catalyst and/or solvent for the sulfur tetrafluoride reaction. In one case where the fluoroformate was isolated, anhydrous hydrogen fluoride was added with the sulfur tetrafluoride, since it had been shown with aryl fluoroformates and other carbonyl derivatives[1] that hydrogen fluoride is necessary to catalyze the conversion to the respective α-fluorinated ethers and difluoro derivatives.

This reaction is useful as a synthetic method only if the β-carbon is substituted with one or more electron-withdrawing groups, such as F, Cl, Br, OCF_3 (or $O\overset{O}{\overset{\|}{C}}F$), and fluoroalkyl groups. Although methanol afforded methyl trifluoromethyl ether, other aliphatic alcohols composed of only hydrocarbon chains gave tars or carbonaceous products. With one electronegative substituent, the over-all yield of ether from alcohol was in the range of 30 to 40% but increased to 50 to 60% when three deactivating substituents were present in the β-position. These reactions are summarized in Table I, and the trifluoromethyl ethers,

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[1] Paper I: W. A. Sheppard, *J. Org. Chem.*, **29**, 1 (1964).

[2] A general review describing synthesis and properties of fluoroalkyl ethers is presented in (a) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, Chap. V, p. 155; (b) M. Hudlicky, "Chemistry of Organic Fluorine Compounds," The MacMillan Co., New York, N. Y., 1962, pp. 141 and 238. (c) K. Weissermel and M. Lederer, *Ber.*, **96**, 77 (1963), describe preparation of α-fluorinated ethers by addition of t-butyl hypochlorite to fluoroolefins.

[3] A trichlorodimethyl ether has been treated with antimony trifluoride to give a trifluorodimethyl ether, H. S. Booth and P. E. Burchfield, *J. Am. Chem. Soc.*, **57**, 2070 (1935). No proof of structure was presented, but, on the basis of physical properties (see Discussion) and ease of hydrolysis, the structure must have been FCH_2OCF_2H and not CH_2OCF_3 as suggested in ref. 2a.

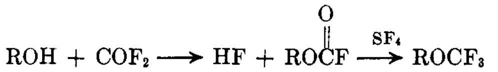
[4] Fluoroformates also may be obtained by fluoride ion exchange on chloroformates (ref. 2b, page 111).

[5] Carbonyl fluoride was prepared by a convenient new synthesis from sodium fluoride and phosgene in acetonitrile as described by F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 4275 (1962).

[6] (a) C. W. Tullock, F. S. Fawcett, W. C. Smith, and D. D. Coffman, *ibid.*, **82**, 539 (1960); (b) W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *ibid.*, **82**, 543 (1960).

TABLE I

PREPARATION OF ALKYL TRIFLUOROMETHYL ETHERS BY TWO-STEP METHOD FROM ALCOHOLS[a]



$$ROH + COF_2 \longrightarrow HF + RO\overset{O}{\overset{\Vert}{C}}F \xrightarrow{SF_4} ROCF_3$$

Alcohol	G.	(Moles)	COF₂ G.	COF₂ (Moles)	SF₄ G.	SF₄ (Moles)	Product	Yield G.	Yield %
$ClCH_2CH_2OH$	61.2	(0.76)	75	(1.14)	90	(0.83)	$ClCH_2CH_2OCF_3$	28–48	24–42
$BrCH_2CH_2OH$	50	(0.40)	40	(0.61)[b]	44	(0.41)	$BrCH_2CH_2OCF_3$	30	15
CH_3OH	15.8	(0.50)	50	(0.76)[b]	60	(0.56)	CH_3OCF_3[c]	17	29
CCl_3CH_2OH	200	(1.34)	125	(2.00)	180	(1.65)	$CCl_3CH_2OCF_3$	208	72
$CClF_2CH_2OH$	140	(1.20)	84	(1.28)	132	(1.22)	$CClF_2CH_2OCF_3$	84.5	38
$HCF_2CF_2CH_2OH$[d]	132	(1.00)	90	(1.35)	150	(1.40)	$HCF_2CF_2CH_2OCF_3$	127.1	63.5
$H(CF_2CF_2)_2CH_2OH$	34.8	(0.15)	15	(0.27)	18	(0.17)	$H(CF_2CF_2)_2CH_2OCF_3$	15.7	35
							$H(CF_2CF_2)_2CH_2O\overset{O}{\overset{\Vert}{C}}F$	14.3	29
$H(CF_2CF_2)_3CH_2OH$[d]	166	(0.50)	45	(0.68)	70	(0.65)	$H(CF_2CF_2)_3CH_2OCF_3$	102.1	51
							$H(CF_2CF_2)_3CH_2O\overset{O}{\overset{\Vert}{C}}F$	70.8	37

[a] Reactions were run in "Hastelloy"-lined pressure vessel of 140-, 240-, 500-, or 1000-ml. capacity at autogenous pressure. Normal heating pattern was 1–2 hr. at 100° followed by 1–4 hr. at 140–150° for the reaction with COF_2, and 2 hr. successively at 100°, 150° and 175° for the reaction with SF_4. [b] Heated only at 100° for 2 hr. [c] Gas chromatographic analysis indicated that the product was 85% pure. [d] Additional 2 hr. at 200° added to heating schedule for the SF_4 reaction.

TABLE II

PREPARATION OF α-FLUORINATED ETHERS BY REACTION OF CARBONATES OR ESTERS WITH SULFUR TETRAFLUORIDE[a]

$$RO\overset{O}{\overset{\Vert}{C}}R_f + SF_4 \xrightarrow{HF} ROCF_2R_f\ (R_f = F,\ CF_3,\text{ or }OR)$$

Reactants (carbonate or ester)	G.	(Moles)	SF₄ G.	SF₄ (Moles)	HF, g.	Product	Yield G.	Yield %
$F\overset{O}{\overset{\Vert}{C}}OCH_2CH_2O\overset{O}{\overset{\Vert}{C}}F$	183	(1.19)	270	(2.50)	10	$CF_3OCH_2CH_2OCF_3$	128	54
						$CF_3OCH_2CH_2O\overset{O}{\overset{\Vert}{C}}F$	6.5	3
$CF_3OCH_2CH_2O\overset{O}{\overset{\Vert}{C}}F$[b]	224	(1.27)	160	(1.48)	25	$CF_3OCH_2CH_2OCF_3$	132.5	53
						$CF_3OCH_2CH_2F$	31[c]	
$(CF_3\overset{O}{\overset{\Vert}{C}}O)_2CH_2$	18.8	(0.078)	19.0	(0.18)	3	$CF_3CF_2OCH_2F$	[d]	
						$CF_3\overset{O}{\overset{\Vert}{C}}F$		
$(CF_3CH_2O)_2C{=}O$[e]	16.7	(0.074)	10	(0.093)	5	$(CF_3CH_2O)_2CF_2$	3.4	18
						Recovered starting material	3.5	21
$(HCF_2CF_2CH_2O)_2C{=}O$[e]	29.0	(0.10)	15	(0.14)	5	$(HCF_2CF_2CH_2O)_2CF_2$	7.2	23
						Recovered starting material	8.6	30
$[H(CF_2CF_2)_2CH_2O]_2C{=}O$[e]	49.0	(0.10)	20	(0.18)	4	$[H(CF_2CF_2)_2CH_2O]_2CF_2$	17.5	34
						Recovered starting material	20.7	42

[a] Reactions were run in "Hastelloy"-lined pressure vessel of 140-, 240-, or 1000-ml. capacity at autogenous pressure. Normal heating pattern was 2 hr. successively at temperatures of 100, 150, and 175°. [b] Obtained in large quantities from reaction of COF_2 with ethylene oxide in presence of pyridine (see paper IV in this series by F. S. Fawcett). [c] Forecut, b.p. 50–68°, also contained $CF_3OCH_2CH_2OCF_3$. [d] Yield, 5 ml.; from low-temperature distillation; yield approximates 60%. [e] Heated at 150° for 2 hr., 200° for 2 hr., 225° for 2 hr., 250° for 4 hr.

with physical properties and analytical data, are listed in Table III.

In the preparation of 1,2-bis(trifluoromethoxy)ethane, it was necessary to prepare and isolate the bisfluoroformate of ethylene glycol by a low-temperature reaction of glycol with excess carbonyl fluoride in the presence of sodium fluoride as base. From the reaction of this fluoroformate with sulfur tetrafluoride in the presence of hydrogen fluoride (see Table II), two byproducts were isolated in addition to the normal product. One was β-trifluoromethoxyethyl fluoroformate, a product of incomplete reaction; the other was β-fluoroethyl trifluoromethyl ether[7] which can form by fluoride ion displacement of the fluoroformate group or by intramolecular decomposition of the fluoroformate.[4]

Extension of the reaction to preparation of alkyl

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(7) This product has been reported from reaction of CF_3OF with ethylene, J. A. C. Allison and J. H. Cady, *J. Am. Chem. Soc.*, **81**, 1089 (1959).

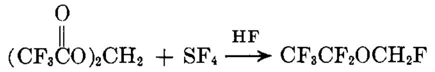
TABLE III

ALKYL FLUOROALKYL ETHERS AND ESTERS[a]

Compound	B.p. (mm.), °C.	$n^{25}D$	F^{19} n.m.r.[b] chemical shifts in c.p.s. (relative intensity), 40 Mc./sec.	Analyses							
				Carbon[c]		Hydrogen		Fluorine		Other	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
CH_3OCF_3	−25 to −19[d]		e							(Mass spectrometry)	
$ClCH_2CH_2OCF_3$	62–65	1.3292	e	24.3	24.5	2.71	2.72	38.3	38.6	Cl, 23.9	23.8
$BrCH_2CH_2OCF_3$	77–81	1.3605	e					29.5	29.3	Br, 41.4	41.5
$CCl_3CH_2OCF_3$	98.5	1.3769	−233	16.6	16.9	0.93	1.12	26.2	25.8	Cl, 48.9	48.9
$CClF_2CH_2OCF_3$	34–35		e	19.5	19.4	1.1	1.3				
$CH_2{=}CHOCF_3$	−18 to −15		e					50.9	50.9		
$CCl_2{=}CHOCF_3$	63.5	1.3572	−191[f]	19.9	20.2	0.56	0.75	31.5	31.2	Cl, 39.2	39.0
$CF_3OCH_2CH_2OCF_3$	71	<1.30	−208[g]	24.3	24.8	2.04	2.35	57.6	57.6		
$CF_3OCH_2CH_2O\overset{\overset{O}{\Vert}}{C}F$	117		−288 (3) −1933 (1)	27.3	28.0	2.29	2.63	43.2	43.1		
$CF_3OCHClCHClOCF_3$ (2)[h] $CF_3OCH_2CCl_2OCF_3$ (1)	91.0	1.3209	−505 (1) −266 (2) −257 (2) −233 (1)	18.0	18.2	0.76	0.92	42.7	42.2	Cl, 26.6	26.4
$CF_3OCCl_2CClHOCF_3$	110	1.3455	−475 (1) −223 (1)	15.9	16.3	0.34	0.84	37.8	38.2	Cl, 35.3	35.7
$CF_3OCCl_2CCl_2OCF_3$	128	1.3690	−257	14.3	14.7			34.0	33.7	Cl, 42.2	42.6
$CF_3OCH{=}CClOCF_3$[i]	54	1.299	−231 (1)[h] −177 (1) −139 (1) −128 (1)	20.9	21.1	0.44	0.88	49.5	49.3	Cl, 15.4	16.0
$CF_3OCCl{=}CClOCF_3$[i]	73	1.3270	−336 (1) −327 (1)	18.1	18.5			43.0	43.6	Cl, 26.8	26.5
$CF_3OCClBrCBrHOCF_3$	94–95	1.3920	e	12.3	12.8	0.26	0.67	29.2	29.1	Cl, 9.1 Br, 40.9	9.5 41.0
$HCF_2CF_2CH_2OCF_3$	45.5	<1.30	−531[k]	24.0	25.0	1.51	2.00	66.5	66.3		
$H(CF_2CF_2)_2CH_2OCF_3$	99	<1.30	−569[k]	24.0	24.4	1.01	1.20	69.7	70.7		
$H(CF_2CF_2)_3CH_2OCF_3$	140–141	<1.30	−534[k]	24.0	24.7	0.76	0.96	71.2	72.7		
$CF_2CF_2OCH_2F$	16		e					67.8	68.3		
$(CF_3CH_2O)_2CF_2$	89.5	<1.30	406[l] (3) 0 (1)	24.2	24.6	1.63	2.24				
$(HCF_2CF_2CH_2O)_2CF_2$	83–86 (50)	1.3129	e	26.9	27.3	1.94	2.25	60.9	59.8		
$[H(CF_2CF_2)_2CH_2O]_2CF_2$	68 (1.7)	1.3123	−50[m]	25.8	26.2	1.16	1.54	66.8	66.7 66.6		
$H(CF_2CF_2)_2CH_2O\overset{\overset{O}{\Vert}}{C}F$	127	<1.30	−2255[n]	25.9	26.2	1.09	1.23				
$(CF_3\overset{\overset{O}{\Vert}}{C}O)_2CH_2$	108	1.3091	e					47.5	47.3		

[a] Compounds reported in this table also were characterized generally by infrared and proton n.m.r. spectra. [b] Neat, relative to external $ClCF_2CF_2Cl$ at 0 c.p.s., no solvent; n.m.r. spectrometer was operated at approximately 9988 gauss. Negative frequency displacement indicates resonance occurring at lower field relative to the reference. [c] Carbon analyses of highly fluorinated compounds have frequently been found 0.4 to 0.7% high, although not reproducibly so. Purified by preparative gas chromatography for n.m.r. and mass spectrometric analysis. [e] Calibrated spectrum not obtained. [f] Proton n.m.r. single resonance at −6.55 p.p.m. relative to tetramethylsilane. [g] Proton n.m.r. single resonance at −4.16 p.p.m. relative to tetramethylsilane. [h] Approximate relative amounts estimated from F^{19} n.m.r. resonances. [i] Approximately 1:1 *cis–trans* mixture. Approximately equal proton resonances occur at −6.08 and −6.58 p.p.m. relative to tetramethylsilane. [j] Approximately 1:1 *cis–trans* mixture. [k] Resonances for OCF_3 group only. Other resonances (F^{19} and H^1 with proper relative intensities) observed at approximately same frequencies as in parent alcohols. [l] F^{19} resonance at 406 c.p.s. assigned to CF_3 group appeared as triplet (J = 9–10 c.p.s.) with additional fine structure. Resonance at 0 c.p.s. assigned to CF_2 group showed incompletely resolved fine structure. Proton n.m.r. quadruplet centered at −4.20 p.p.m. relative to tetramethylsilane with J = 9 c.p.s. [m] Assigned to CF_2; the remainder of the F^{19} spectra and the proton spectra approximately the same as parent alcohol. [n] Assigned to $\overset{\overset{O}{\Vert}}{C}F$.

perfluoroalkyl ethers was not investigated to any extent but is expected to proceed in a fashion analogous to that found for the aromatic ethers.[1] Partial success was attained in the one case studied. From the reaction of bis(trifluoroacetoxy)methane (**1**) with sulfur tetrafluoride in hydrogen fluoride only fluoromethylpentafluoroethyl ether (**2**) was isolated. Replacement of an acetoxy group by fluoride ion could occur either before or after one acetoxy group had reacted with sulfur tetrafluoride.



$$\underset{1}{(CF_3\overset{\overset{O}{\|}}{C}O)_2CH_2} + SF_4 \xrightarrow{HF} \underset{2}{CF_3CF_2OCH_2F}$$

This reaction was extended to the preparation of 1,1-difluoroformals (**3**), a new class of α-fluorinated ethers. The carbonate of a fluoroalkylmethyl alcohol (**4**) was treated with sulfur tetrafluoride in the presence

$$\underset{4}{(R_fCH_2O)_2C{=}O} + SF_4 \xrightarrow{HF} \underset{3}{(R_fCH_2O)_2CF_2}$$

of anhydrous hydrogen fluoride. In this case a higher temperature (about 225°, compared to a temperature of 175° normally used in the fluoroformate reaction) was required to obtain the difluoroformal in yields ranging from 20 to 30% (30% of the starting carbonate was recovered).

Chemical and Physical Properties.—The trifluoromethyl ethers are mobile, colorless liquids (with the exception of CH_3OCF_3 which has b.p. −25°) which are thermally and chemically stable.

β-Haloethyl trifluoromethyl ethers (**5**) were readily converted to vinyl ethers (**6**) by treatment with base.

$$\underset{5}{XCY_2CH_2OCF_3} \xrightarrow[\text{base}]{} \underset{6}{CY_2{=}CHOCF_3}$$

X = Cl or Br
Y = H, Cl

However, in the case of $ClCH_2CH_2OCF_3$, elimination of the OCF_3 group occurred to a significant extent so that the product was a mixture of vinyl ether **6** (Y = H) and $ClCH{=}CH_2$ in a ratio of three to one as determined by gas chromatography. No conclusion can be drawn from this experiment as to ease of elimination of $^{\ominus}OCF_3$ compared with $Cl^{\ominus}$ since the rate-controlling factor may be the acidity of the protons α to the trifluoromethoxy group in compound **5** (X = Cl, Y = H). The trifluoromethyl vinyl ether (**6**, Y = H) could be polymerized under the influence of radical initiators, but the dichloro analog (**6**, Y = Cl) was inert.

1,2-Bis(trifluoromethoxy)ethane was not attacked by bromine radicals but could be chlorinated photochemically to give a mixture of all possible isomers. By adjustment of time and temperature, the amount of chlorination could be controlled to make one isomer predominant.

$$CF_3OCH_2CH_2OCF_3 \xrightarrow[h\gamma]{Cl_2} \underset{7}{CF_3OCHClCH_2OCF_3} + \underset{8}{CF_3OCH_2CCl_2OCF_3} + \underset{9}{CF_3OCHClCHClOCF_3} + \underset{10}{CF_3OCCl_2CHClOCF_3} + \underset{11}{CF_3OCCl_2CCl_2OCF_3}$$

The trichloro and tetrachloro compounds (**10** and **11**) were readily separated in pure form by distillation. The dichloro substitution product distilled as a mixture with **9** predominant over **8** (ratio approximately two to one). Monochloro compound **7** codistilled with the starting material and could only be isolated in pure form by gas chromatography. Zinc dehalogenation of the tetrachloro derivative (**11**) gave the ethylene $CF_3OCCl{=}CClOCF_3$ (*cis–trans* mixture) and of the trichloro derivative (**10**) gave the ethylene $CF_3OCCl{=}CHOCF_3$. These ethylenes were stable to further treatment with dehalogenating reagents or to dehydrohalogenation with bases, but the monochloroethylene added bromine to give the ethane $CF_3OCBrClCHBrOCF_3$.

The trifluoromethyl ethers have boiling points 30 to 40° below those of the aliphatic analogs as would be expected from complete replacement of hydrogens on the methyl group by fluorines. These compounds are sweet smelling liquids. Toxicity studies conducted on a selection of these ethers indicate that they are toxic at 0.1 to 11% concentration in vapor inhalation.[8] For example, it was found that 2,2,3,3-tetrafluoropropyl trifluoromethyl ether at a vapor concentration of 0.5% caused violent convulsions and death of mice within 30 to 120 sec.

The infrared spectra of these ethers showed a typical strong C–O absorption in the 7.8 to 8-μ region and very strong C–F absorption in 8–9-μ region. The remainder of the spectra contain absorptions normal for the substituents and for the aliphatic system. F^{19} and H^1 n.m.r. spectra were obtained on the majority of compounds and conformed with predicted spectra. For the aryl trifluoromethyl ethers a single resonance was found for the OCF_3 group in the region of −700 to −800 c.p.s. at 40 Mc./sec. relative to CF_2ClCF_2Cl. For the aliphatic series, the resonance frequency was in the range of −130 to −500 c.p.s. under the aforementioned conditions. The lower frequency in aromatic systems is expected since ring currents generally cause a shift to lower fields. In the aliphatic series, the substituent is much closer to the OCF_3 group and has a more profound influence on the field with resultant greater frequency shifts.

Experimental

Materials.—The alcohols were purchased from chemical supply houses with the exception of the telomer alcohols $H(CF_2CF_2)_nCH_2OH$, which were obtained from Organic Chemicals Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware. Carbonyl fluoride was prepared by the recently reported synthesis from phosgene and sodium fluoride in acetonitrile.[5] Sulfur tetrafluoride was obtained from Organic Chemicals Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware. Anhydrous hydrogen fluoride was purchased from Harshaw Chemical Company. Bis(2,2,3,3-tetrafluoro-*n*-propyl)- and bis(octafluoro-*n*-amyl)-carbonates were supplied by Dr. W. B. McCormack of Jackson Laboratory, Organic Chemicals Department, E. I. du Pont de Nemours and Company.

Preparation of Alkyl Trifluoromethyl Ethers. General Two-Step Procedure from Alcohols.—The procedure described previously[1] for the conversion of phenols to aryl trifluoromethyl ethers was followed for the reaction of the aliphatic alcohols in two steps with carbonyl fluoride, then sulfur tetrafluoride. In general, a maximum temperature of 175° was employed for the sulfur tetrafluoride reaction since higher temperatures usually caused extensive formation of tar. However, the highly fluorinated alcohols were not prone to side reactions and were heated in the sulfur tetrafluoride reaction at 200° for several hours in order to improve the yield of ether.

The product was cautiously poured into a well-stirred slurry of a threefold molar excess of sodium fluoride powder or pellets in dichloromethane or xylene to remove hydrogen fluoride. (Dichloromethane was frequently used for the less volatile ethers.) The product was distilled through a spinning-band or packed column. Trifluoromethyl methyl ether is a gas at room temperature and was purified by passage through a tower of sodium fluoride pellets followed by distillation through a low-tempera-

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[8] The authors are indebted to the Haskell Laboratory for Toxicology and Industrial Medicine, E. I. du Pont de Nemours and Co., for toxicological studies.

ture column. The experimental details are given in Table I, and the physical properties and analytical data of the ethers are given in Table III.

Ethylene Glycol Bisfluoroformate.—A mixture of 50 g. (1.2 moles) of sodium fluoride powder in 300 ml. of ether was cooled to −80° in a 1-l. four-necked flask fitted with a "Tru-bore" paddle stirrer addition funnel, gas inlet tube, and a methanol-slush condenser. Carbonyl fluoride (100 g., 1.5 moles) was condensed into the ether solution, and 31.0 g. (0.50 mole) of anhydrous ethylene glycol (purified by distillation) was added dropwise. The reaction was exothermic; after the addition was complete, the reaction mixture was allowed to warm gradually to room temperature while the excess of carbonyl fluoride was retained under reflux for 1 hr. The solid was separated by suction filtration and washed with ether. The ether solution was evaporated to give 58 g. of oil. Distillation afforded 56.0 g. (79%) of the bisfluoroformate, b.p. 36° (1.7 mm.). The fluoroformate decomposes at approximately 100–120°, and precautions were taken to avoid overheating the pot during distillation.

Methylene Bis(trifluoroacetate). **A.**—A 500-ml. flask with reflux condenser and drying tube was charged with 150 ml. of dimethylformamide (distilled from phosphorus pentoxide). Dry silver trifluoroacetate (81.7 g., 0.37 mole) was dissolved in the dimethylformamide, and methylene diiodide (49.3 g., 0.184 mole) was added. In a few minutes the mixture became warm, and a yellow precipitate formed. The temperature was maintained at 60–70° for 1 hr., the silver iodide was filtered off, and the filtrate was distilled to give 28 g. (58%) of methylene bis-(trifluoroacetate), b.p. 108°. The infrared spectrum of the compound had ester carbonyl absorption at 5.60 μ.

B.—A 500-ml. flask with reflux condenser and drying tube was charged with 30 g. (1.00 mole, calculated as a monomer CH_2O) of paraformaldehyde (dried over phosphorus pentoxide), 200 ml. (298 g., 1.42 moles) of trifluoroacetic anhydride, and 50 ml. of trifluoroacetic acid. The mixture was refluxed until solution was complete and then was distilled to give 61.4 g. (26%) of methylene bis(trifluoroacetate), b.p. 108–110°, which was identical to that obtained *via* procedure A as shown by infrared spectra comparison.

In addition, higher boiling fractions, b.p. 75–76° (28 mm.) and 95–97° (28 mm.), were obtained. Since the infrared spectra of these fractions are similar to that of methylene bistrifluoroacetate, the structures $CF_3CO_2CH_2OCH_2O_2CCF_3$ and $CF_3CO_2CH_2OCH_2OCH_2O_2CCF_3$, respectively, are suggested.

Bis(2,2,2-trifluoroethyl)carbonate.—Trifluoroethanol (50 g., 0.50 mole) was added to a solution of 50 g. (0.50 mole) of phosgene in 39.5 g. (0.50 mole) of pyridine and 250 ml. of ether chilled in an ice bath. The pyridine hydrochloride was removed by suction filtration, and the ether solution was distilled. The bis(2,2,2-trifluoroethyl)carbonate, b.p. 62.5° (75 mm.), was obtained in a yield of 16%.

Reaction of Fluoroformates, Carbonates, and Esters with Sulfur Tetrafluoride.—The fluoroformates of ethylene glycol, the carbonate esters of the fluorinated alcohols, and methylene bistrifluoroacetate were treated with sulfur tetrafluoride in the presence of hydrogen fluoride as catalyst as described previously. In this case, the carbonyl reactant was charged into the pressure vessel with anhydrous hydrogen fluoride and sulfur tetrafluoride. The experimental details of the reactions are summarized in Table II, and the physical properties and analytical data of the products are given in Table III. For the conversion of carbonates to difluoroformates, heating the reactants for several hours at 225–250° (instead of 175°) was required.

Trifluoromethyl Vinyl Ether.—A three-necked flask was equipped with a dropping funnel, magnetic stirrer, and reflux condenser. The top of the condenser was connected to a trap cooled by solid carbon dioxide and acetone.

Into a refluxing solution of 56 g. (1 mole) of potassium hydroxide in 210 ml. of ethanol was dropped 41.3 g. (0.214 mole) of 2-bromoethyl trifluoromethyl ether or 36.6 g. (0.246 mole) of 2-chloroethyl trifluoromethyl ether. Refluxing was continued until no additional condensate gathered in the trap.

A.—The condensate from the addition of 2-bromoethyl trifluoromethyl ether was distilled in a low-temperature still to give 15 g. (63%) of vinyl trifluoromethyl ether, b.p. −18° to −15°. Gas chromatographic analysis indicated that the sample was 90% pure. The infrared spectrum of vinyl trifluoromethyl ether showed a strong absorption band at 6.00 μ (vinyl double bond) and very strong bands at 7.75, 8.05, and 8.40 μ (associated with the OCF_3 group).

B.—The condensate from the addition of 2-chloroethyl trifluoromethyl ether was distilled to give 18.8 g. of product, b.p. −18° to −14°. Gas chromatographic analysis of the product showed two peaks in the ratio 76:24. The retention time of the smaller peak was the same as that of vinyl chloride (b.p. −12°) while the retention time of the larger peak was the same as that of trifluoromethyl vinyl ether. The identities of these products were confirmed by separation of the components by preparative gas chromatography and examination of their infrared spectra.

2,2-Dichlorovinyl Trifluoromethyl Ether.—A solution of 3.8 g. (0.0175 mole) of 2,2,2-trichloroethyl trifluoromethyl ether and 2.0 g. (0.036 mole) of potassium hydroxide in 20 ml. of ethylene glycol was gradually heated at 100–120°, and the product was allowed to distil as formed. Redistillation of the product gave 2.25 g. (71%) of 2,2-dichlorovinyl trifluoromethyl ether, b.p. 63.5°.

Chlorination of 1,2-Bis(trifluoromethoxy)ethane.—1,2-Bis-(trifluoromethoxy)ethane (30 to 50 g.) was placed in a quartz tube fitted with a gas inlet tube and a condenser charged with wet ice–acetone mixture. A slow stream of dry chlorine gas was bubbled through the ethane, which was irradiated with a low-pressure mercury lamp. After approximately 2 hr., evolution of hydrogen chloride ceased, and distillation of the product afforded a 72% yield of tetrachloro-1,2-bis(trifluoromethoxy)-ethane (**11**), b.p. 128°. By chlorinating over a shorter period or by bubbling a stoichiometric amount (1, 2, or 3 moles) of chlorine condensed in a calibrated trap through the irradiated ethane, one could control the reaction to give a mixture of isomers (**7** to **11**), with the predominant isomer corresponding to the molar quantity of chlorine added. The monochloro derivative was never obtained in a pure state since it always codistilled with recovered starting material, but separation on a preparative scale could be accomplished by gas chromatography. The dichloroproduct was determined to be a mixture of the two possible isomers by F^{19} n.m.r. analysis. The isomer found in lesser amount appeared to be unsymmetrical by virtue of two resonances of equal intensity, one occurring at low field and the other at much higher field. The predominant isomer of symmetrical form also showed two resonances very close together and at an intermediate frequency shift. The two resonances are thought to arise from restricted rotation.[9]

1,2-Bis(trifluoromethoxy)ethylenes. A. Dichloro Derivative.—A mixture of 10 g. of zinc and 60 ml. of acetic anhydride was heated to reflux (140°) for approximately 10 min. in a flask fitted with magnetic stirrer, thermometer, and a Vigreux column. The reaction mixture was cooled to 100–120° and 28.7 g. (0.086 mole) of tetrachlorobis(trifluoromethoxy)ethane (**11**) was added dropwise. The product, boiling range 72–85°, distilled as formed. The crude product (25.5 g.) was fractionated through a 45-cm. spinning-band column, and 14.7 g. (65%) of 1,2-dichloro-1,2-bis-(trifluoromethoxy)ethylene was obtained as a colorless liquid, b.p. 72.0–73.5°. From the appearance of two F^{19} n.m.r. resonances, the product was characterized as approximately an equal mixture of *cis* and *trans* isomers. Although partial separation of the two isomers could be accomplished by analytical gas chromatography, separation was not successful on a preparative scale.

B. Monochloro Derivative.—Twenty-five grams (0.083 mole) of trichloro-1,2-bis(trifluoromethoxy)ethane (**10**) was dechlorinated with 10 ml. of zinc and 50 ml. of acetic anhydride as previously described. The product, chloro-1,2-bis(trifluoromethoxy)ethylene, was purified by fractionation through a 45-cm. spinning-band column, b.p. 54°, 19.1-g. (59%) yield; 4.8 g. (19%) of starting trichloro derivative (**10**) was recovered. From F^{19} and H^1 n.m.r. analysis, this material also was shown to be approximately an equal mixture of *cis* and *trans* isomers.

C. Chloro-1,2-dibromo-1,2-bis(trifluoromethoxy)ethylene.—A solution of 3.20 g. (0.020 mole) of bromine in 5.2 g. (0.023 mole) of crude chloro-1,2-bis(trifluoromethoxy)ethylene was allowed to stand in a stoppered flask. After 2 hr., all of the bromine color disappeared, and the colorless liquid was distilled to give 3.58 g. (41%) of bromo-1,2-dichloro-1,2-bis(trifluoromethoxy)ethane, b.p. 94–95° (200 mm.).

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(9) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 377.