Preparation and Properties of Alkyl Trifluorovinyl Ethers and Related Compounds[1]

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Since 1946[2], many fluoroethers have been synthesized by the addition of alcohols to fluoroölefins under alkali catalysis, and a mechanism has also been presented[3]. These fluoroethers are usually saturated addition products, and some fluoroethers easily split off hydrogen fluoride to give vinyl ethers[4-6]. According to previous reports[5,6], it can be inferred that the larger the number of fluorine attached to the olefin carbons, the higher the stability of the resulting fluoroether. It was for this reason that the dehydrofluorination of methyl 1, 1, 2-trifluoro-2-chloroethyl ether was found to require a prolonged refluxing over solid potassium hydroxide[7].

Another procedure for preparing fluorovinyl ether has been presented by Meier and Böhler[8]. They synthesized ethyl 1, 2-difluoro-2-chlorovinyl ether directly by the reaction of trifluorochloroethylene with alcohol-free sodium ethylate.

By using the same method, trifluorovinyl, methyl, ethyl, isopropyl and *tert*-butyl ethers were prepared, the first of which has already been described by Dixon[9]. In our experiment the accompanying formation of the corresponding saturated tetrafluoroethyl ethers could not be avoided because highly alcohol-free sodium alcoholates were not available.

$$CF_2{=}CF_2 + NaOR \rightarrow CF_2{=}CFOR + NaF$$

$$CF_2{=}CF_2 + HOR \rightarrow CF_2HCF_2OR$$

$$R;\ CH_3,\ C_2H_5,\ CH(CH_3)_2,\ C(CH_3)_3$$

The apparent reactivity of the alcoholates toward tetrafluoroethylene increased in the following order: methyl, ethyl < isopropyl, *tert*-butyl.

In the alkyl trifluorovinyl ethers, the absorption peak of C=C occurs within the range 5.46~5.50 μ (1832~1818 cm^{-1}). This position seems exceptionally short for C=C, but it is reasonably correlated with those of reference compounds, as is shown in Table II.

Trifluorovinyl and 1, 2-difluoro-2-chlorovinyl ethyl ethers give chlorine and bromine addition products. They are easily hydrolyzed to the corresponding esters according to the method that was used for the hydrolysis of α, α-difluoroethers by Tarrant and Young[10]. The adducts and esters are given in Table III. The adducts are so reactive that crude adducts from the

TABLE I. REACTION OF TETRAFLUOROETHYLENE AND SODIUM ALCOHOLATES

Alcoholate	Temp. °C	Time hr.	Yield[a] %	Product	B. p., °C Found	B. p., °C Reported	Fluorine, % Found	Fluorine, % Calcd.
Methyl	20~40	145	28	$CF_2{=}CFOCH_3$	12	10.5~12.5[9]	50.0	50.9
			7	$CF_2HCF_2OCH_3$	36	36.5[3]		
Ethyl	40	120	53	$CF_2{=}CFOC_2H_5$	38.5		44.1	45.2
			4	$CF_2HCF_2OC_2H_5$	57	57.5[2]		
Isopropyl	10	96	26	$CF_2{=}CFOCH(CH_3)_2$	58.5		38.5	40.7
			20	$CF_2HCF_2OCH(CH_3)_2$	70		45.3	47.5
tert-Butyl	10	27		$CF_2{=}CFOC(CH_3)_3$	56/375 mmHg			
				$CF_2HCF_2OC(CH_3)_3$	73/375 mmHg	87[11]		

a) Based upon the charged alcoholate.

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[1] Presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

[2] W. E. Hanford and G. W. Rigby, U. S. Pat. 2409274 (1946).

[3] W. T. Miller, Jr., E. W. Fager and P. H. Griswold, *J. Am. Chem. Soc.*, **70**, 431 (1948).

[4] J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., ibid., **72**, 4480 (1950).

[5] P. Tarrant and H. C. Brown, ibid., **73**, 1781 (1951).

[6] J. D. Park, W, M. Sweeney, S. L. Hopwood, Jr. and J. R. Lacher, ibid., **78**, 1685 (1956).

[7] R. S. Corley, J. Lal and M. W. Kane, idid., **78**, 3489 (1956).

[8] R. Meier and F. Böhler, *Chem. Ber.*, **90**, 2342 (1957).

[9] During the course of our investigation, Dixon has prepared a number of trifluorovinyl ethers of the type $RCH_2OCF{=}CF_2$ by the same method, and has stated that they can be converted into high molecular weight polymers; U. S. Pat. 2917548 (1959).

[10] J. A. Young and P. Tarrant, *J. Am. Chem. Soc.*, **71**, 2432 (1949).

TABLE II. ABSORPTION PEAK OF C=C IN TRIFLUOROVINYL ALKYL ETHERS AND REFERENCE COMPOUNDS

	Wavelength, μ^{a}
$CF_2=CF_2$	5.34[b,c]
$CF_2=CFOCH_3$	5.46[b]
$CF_2=CFOC_2H_5$	5.46
$CF_2=CFOCH(CH_3)_2$	5.48
$CF_2=CFOC(CH_3)_3$	5.50
$CFCl=CF_2$	5.55[b]
$CFCl=CFOC_2H_5$	5.70

a) Liquid unless otherwise mentioned.
b) Gas
c) Raman spectrum data: J. R. Nielsen and H. H. Claassen, *J. Chem. Phys.*, **18**, 812 (1950).

reaction mixtures were always accompanied by the corresponding esters. Furthermore, in the absence of potassium carbonate, some decomposition to acyl fluoride and alkyl halide could not be avoided during the fractional distillation the crude reaction product.

Methyl trifluorovinyl ether polymerized, even when stored in a refrigerator, to give a white solid deposit. Ethyl trifluorovinyl ether became viscous upon standing in a sealed tube at room temperature, and was polymerized with common free-radical initiators to give a balsam-like mass. Propyl trifluorovinyl ether could not be polymerized. These facts are interesting when compared with the facts[12] that the high polymers of vinyl methyl, ethyl and other alkyl ethers can be obtained only by cationic polymerization, and that isopropyl vinyl ether is also capable of forming a polymer.

tert-Butyl trifluorovinyl ether was very unstable and decomposed, upon standing, to the acyl fluoride and isobutene. This is analogous to the decomposition of 1, 1, 2, 2-tetrafluoro- and 1, 1, 2-trifluoro-2-chloroethyl *tert*-butyl ethers[5,11]. It is noteworthy that the vinyl ether decomposed as easily as the saturated ether.

Postulated Carbonium Ion of the Type $-\text{O}-\overset{\text{F}}{\underset{+}{\text{C}}}-$.—The high reactivity of the fluoroethers prepared, and of other α-haloethers, seems to be explained by assuming the formation of a carbonium ion* of the type $-\text{O}-\overset{|}{\underset{+}{\text{C}}}-$. Tiers postulated carbonium-oxonium ion in the transformation of α-fluoroethers with aluminum trichloride to the corresponding α-chloroethers[13].

With this group of compounds, not only the halogen exchange and the hydrolysis to esters, but also the decomposition to alkyl and acyl halides, are subject to acid catalysis. The operation of acid catalysis is supported by the facts that *tert*-butyl 1, 1, 2-trifluoro-2-chloroethyl ether from which hydrogen fluoride had been removed by adsorption was fairly stable[4], and that potassium carbonate is effective as the stabilizer of the ethers prepared in this experiment. The three reactions, decomposition, halogen exchange and hydrolysis, are thought to proceed through the same intermediate, carbonium-oxonium ion.

As this type of compound is relatively stable when acids are removed, an intramolecular reaction through a cyclic transition state[7] is not sufficient to explain the decomposition. It rather seems to be an intermolecular reaction and to proceed by a chain mechanism. With the compound of the type $-\text{O}-\overset{\text{F}}{\underset{\text{X}}{\text{C}}}-$ (where

TABLE III. ETHERS AND ESTERS DERIVED FROM TRIFLUOROVINYL AND DIFLUOROCHLOROVINYL ETHYL ETHERS

	B. p., °C	Halogen, %		Fluorine, %	
		Found	Calcd.	Found	Calcd.
$C_2H_5OCFBrCFClBr$	170			12.5	12.6
$C_2H_5OCOCFClBr$	145[a]				
$C_2H_5OCFBrCF_2Br$	135.5	55.5	55.9	19.7	19.9
$C_2H_5OCOCF_2Br$	113	39.7	39.4	18.6	18.7
$C_2H_5OCFClCFCl_2$	134	49.9	49.8	17.7	17.8
$C_2H_5OCFClCF_2Cl$	ca. 95[b]				
$CH_3CHClOCFClCFCl_2$	157	56.8	57.2	15.3	15.3
$CH_3CHClOCFClCF_2Cl$	121	45.4	46.0	24.3	24.6

a) F. Swarts, *Bull. soc. chim. France*, [3], **15**, 1135 (1896), reports b. p. 151°C.
b) Impure. See the last part of Experimental.

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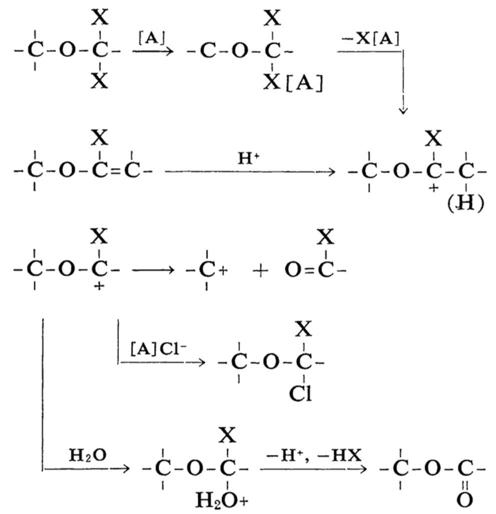
[11] D. E. England, L. R. Melby, M. A. Dietrich and R. V. Lindsey, Jr., ibid., **82**, 5116 (1960).

[12] C. E. Schildknecht, "Vinyl and Related Polymers", John Wiley and Sons, Inc., New York (1952), pp. 593, 599.

* For simplicity, the carbonium ion of the type $-\text{O}-\overset{|}{\underset{+}{\text{C}}}-$ stabilized by carbonium-oxonium resonance will be called carbonium-oxonium ion in the following discussions.

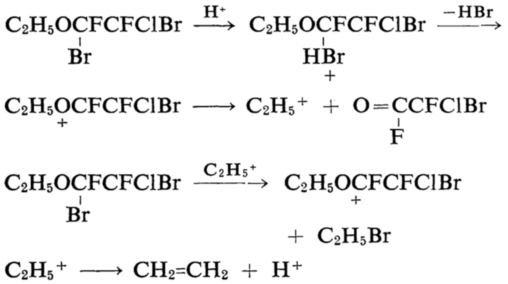
[13] G. V. D. Tiers, *J. Am. Chem. Soc.*, **77**, 4837, 6703 (1955).

Chart I. Formation of carbonium-oxonium ion and its secondary transformations.



[A] = H^+ or other acid such as $AlCl_3$
X = F or other halogen

X is Cl or Br), X^- is preferentially removed and fluorocarbonium-oxonium ion is formed, judging from the decomposition products of 1, 2-difluoro-2-chloro-1, 2-dibromoethyl- and 1, 2-difluoro-1, 2, 2-trichloroethyl ethyl ethers.



$$C_2H_5O\underset{Br}{C}FCFClBr \xrightarrow{H^+} C_2H_5O\underset{\underset{+}{HBr}}{C}FCFClBr \xrightarrow{-HBr}$$

$$C_2H_5O\underset{+}{C}FCFClBr \longrightarrow C_2H_5^+ + O{=}\underset{F}{C}CFClBr$$

$$C_2H_5O\underset{Br}{C}FCFClBr \xrightarrow{C_2H_5^+} C_2H_5O\underset{+}{C}FCFClBr + C_2H_5Br$$

$$C_2H_5^+ \longrightarrow CH_2{=}CH_2 + H^+$$

Compounds which are capable of forming carbonium-oxonium ion and thus undergoing a similar decomposition (rearrangement, in the case of cyclic ethers) are not only α-halo and vinyl ethers, but also α-carboxy ethers(14), haloformates(15), etc.

In the hydrolysis of α, α-difluoroethers to the esters, it is inconsistent with experimental findings to assume that the reaction proceeds through the oxonium ion in which a proton is attached to the oxygen of the ether(10). A route through carbonium-oxonium ion could explain the hydrolysis of both α, α-difluoroethers and α-fluorovinyl ethers(8).

Reactions that could be interpreted as electrophilic aromatic substitution involving carbonium-oxonium ion have also been reported(16).

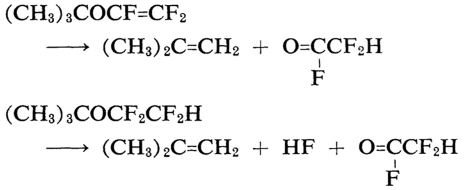
Experimental

Ethyl Trifluorovinyl Ether.—A mixture of 164 g. of sodium ethylate and 450 ml. of dioxane was placed in a 2 l. autoclave. After moderate evacuation, the autoclave was charged with about 200 g. of tetrafluoroethylene at one time and shaken until the pressure was constant. The pressure readings during the shaking were 30 kg./cm^2 (initial), 23 kg./cm^2 (1 hr.), 13 kg./cm^2 (22 hr.), and 5 kg./cm^2 (120 hr.; final). The liquid products were separated by centrifuguration or suction filtration from the solid products and the liquid remaining on the solid was evaporated under reduced pressure and collected in cold traps. The rectification of the combined dioxane solution over potassium carbonate under nitrogen atmosphere gave ethyl trifluorovinyl ether (161 g., 53% yield), boiling at 38.5°C, and 1, 1, 2, 2-tetrafluoroethyl ether (15 g., 4% yield), boiling at 57°C.

Methyl trifluorovinyl ether was prepared in a similar fashion, but in one experiment a violent explosion of the charged tetrafluoroethylene occurred.

In the preparation of isopropyl trifluorovinyl ether, the first portion (69 g., 15 kg./cm^2) of tetrafluoroethylene was taken up completely by 250 g. of sodium isopropylate within 15 min. at 10°C and considerable heat was generated.

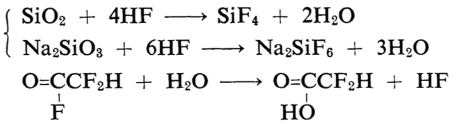
***tert*-Butyl Trifluorovinyl Ether.**—Both trifluorovinyl and 1, 1, 2, 2-tetrafluoroethyl *tert*-butyl ethers were unstable and decomposed to form two layers on storage in a sealed tube at room temperature. The decomposition products were not thoroughly examined, but their infrared spectra showed that the upper layers from both compounds are polyisobutene, the lower layer from the vinyl ether is an acyl fluoride, while the one from the tetrafluoroether is a mixture of a carboxylic acid and a small amount of the acyl fluoride. Based upon similar dicomposition(4,5,11), the acyl fluoride is assumed to be difluoroacetyl fluoride and the acid to be difluoroacetic acid.



$$(CH_3)_3COCF{=}CF_2 \longrightarrow (CH_3)_2C{=}CH_2 + O{=}\underset{F}{C}CF_2H$$

$$(CH_3)_3COCF_2CF_2H \longrightarrow (CH_3)_2C{=}CH_2 + HF + O{=}\underset{F}{C}CF_2H$$

In the latter case, the hydrogen fluoride and the acyl fluoride may have reacted with the glass wall to yield the carboxylic acid.



$$\left\{\begin{array}{l} SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O \\ Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O \end{array}\right.$$

$$O{=}\underset{F}{C}CF_2H + H_2O \longrightarrow O{=}\underset{HO}{C}CF_2H + HF$$

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14) J. Meinwald, H. Hwang, D. Cristman and A. P. Wolf, ibid., **82**, 483 (1960).

15) S. Nakanishi, T. Myers and E. V. Jensen, ibid., **77**, 5033 (1955).

16) A. Rieche, H. Gross and E. Hoft, *Chem. Ber.*, **93**, 88 (1960); C. T. Mason and L. A. Gist, Jr., *J. Am. Chem. Soc.*, **73**, 4644 (1951).

Bromine Derivatives of 1, 2-Difluoro-2-chlorovinyl Ethyl Ether.—Difluorochlorovinyl ethyl ether[8] (26.0 g.) in chloroform (11 g.) was added dropwise to a solution of bromine (29.7 g.) in chloroform (60 g.) with stirring and cooling. The resultant solution was washed with aqueous potassium carbonate-sodium thiosulfate, dried over sodium sulfate, and fractionated. After the chloroform was distilled, the temperature at the head of the column suddenly dropped and fluctuated between 41 and 48°C, showing the occurrence of a decomposition. The liquid decomposition product (37.1 g.) was shown to be a mixture of an acyl fluoride (5.35 μ) and ethyl bromide (reported b. p. 38.4°C) by its infrared spectra. The fluoride is most likely to be fluorochlorobromoacetyl fluoride. (Ref. a of Table III reports b. p. 51°C.) Ethylene was also noted in the gaseous decomposition product by its characteristic multiplet around 10.5 μ.

In order to prevent decomposition, potassium carbonate was added to the still-pot, and the distillation was successfully carried out. A duplicate run, but with distillation over potassium carbonate, gave 1, 2-difluoro-2-chloro-1, 2-dibromoethyl ethyl ether (33.7 g., 61% yield), boiling at 170°C. Sodium carbonate was not so effective as potassium carbonate in preventing such decompositions.

The bromoether (17.8 g.) was treated with 98% sulfuric acid (70 g.) for 50 min. without cooling, poured into ice-water, extracted with chloroform, washed with aqueous potassium carbonate and dried over sodium sulfate. Distillation of the resultant solution gave ethyl fluorochlorobromoacetate (6.7 g. 53% yield), boiling at 145°C.

Chlorine Derivatives of 1, 2-Difluoro-2-chlorovinyl Ethyl Ether.—Chlorine was bubbled through a solution of difluorochlorovinyl ethyl ether (22.0 g.) in chloroform (83 g.) until the solution turned yellow from an excess of chlorine under ice-salt cooling. The resultant solution was washed with aqueous potassium carbonate, dried over sodium sulfate and distilled. A saturated ether (15.4 g., 39% yield) boiling at 157°C was obtained. The elementary analysis showed that three chlorines were introduced during the chlorination. The ether was tentatively identified as 1-chloroethyl 1, 2-difluoro-1, 2, 2-trichloroethyl ether by its infrared spectrum (6.75 μ, 6.90 μ and 7.27 μ), compared with that of 1, 2-difluoro-1, 2, 2-trichloroethyl ethyl ether (6.91 μ, 7.20 μ).

Dioxane was found to be a suitable solvent to stop the reaction at the stage of chlorine addition. Thus, chlorine was bubbled through a solution of difluorochlorovinyl ethyl ether (15 g.) in dioxane (30 g.) until the solution turned yellow from an excess of chlorine. The resultant dioxane solution was poured into aqueous potassium carbonate, and the lower layer was separated, dried over sodium sulfate and distilled over potassium carbonate. 1, 2-Difluoro-1, 2, 2-trichloroethyl ethyl ether (10.4 g., 46% yield), boiling at 134°C, was obtained. A duplicate distillation without potassium carbonate gave no difluorotrichloroethyl ethyl ether. However, ethyl chloride and ethylene, but no ethyl fluoride, were noted in the gaseous decomposition product.

The ethers and ester from ethyl trifluorovinyl ether were obtained like those from 1, 2-difluoro-2-chlorovinyl ethyl ether; their boiling points and analytical data are given in Table III. However, ethyl 1, 2, 2-trifluoro-1, 2-dichloroethyl ether could not be obtained in a pure state, being contaminated with the corresponding ester, ethyl difluorochloroacetate (reported[17] b. p. 97°C).

summary

Trifluorovinyl methyl, ethyl, isopropyl and *tert*-butyl ethers have been prepared. These trifluorovinyl ethers show C=C absorption at such a short wavelength as 5.46$\sim$5.50 μ. The methyl and ethyl ethers can be polymerized by free-radical initiators. Halogen addition products of trifluorovinyl- and 1, 2-difluoro-2-chlorovinyl ethers have also been prepared. With α-halo or vinyl ethers, the reactions that are catalyzed by acids, including decomposition, are best interpreted as proceeding through the carbonium ion stabilized by carbonium-oxonium resonance.

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[17] F. Swarts, *Rec. trav. chim.*, **27**, 128 (1908).