

THE PREPARATION AND PROPERTIES
OF VINYL AND GLYCIDYL FLUOROETHERS

By

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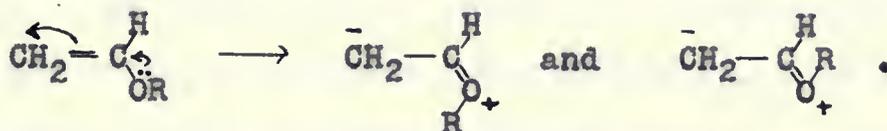
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CHAPTER I

PURPOSE AND SCOPE OF RESEARCH

The infrared spectra of vinyl alkyl ethers have unusual characteristics which have not been completely explained. The carbon-carbon double bond stretching absorption near six microns is split into two bands, and the carbon-oxygen stretch is at a much lower wave length (8.3 microns) than in saturated unsubstituted ethers (about 9.0 microns). The purpose of this work has been to account for these peculiarities in a qualitative way in terms of the structure of vinyl ethers.

In a study of the Raman spectra of vinyl alkyl ethers, Batuev et al. (3) observed a similar split in the double bond stretching frequency. They attributed the doublet to rotational isomerism, the restricted rotation enhanced by a resonance effect:



However, they did not attempt to prove their theory.

In the present study, two methods for testing the existence of the proposed resonance effect and resulting isomerism were undertaken. In order to demonstrate the

presence of rotational isomers, a study of the effect of a change in temperature on the intensities of the two double bond bands was made. Moreover, the presence of an electro-negative substituent in the alkyl group would be expected to decrease or perhaps prevent entirely such an electron shift. Since fluorine is the most electronegative element, the preparation of vinyl fluoroethers* and a study of their infrared absorption was an important phase of this work.

The preparation of the vinyl fluoroethers was carried out by a three-step procedure: (1) synthesis of the corresponding β -hydroxyethyl ether, (2) substitution of the hydroxyl group by chlorine, and (3) dehydrochlorination to the vinyl ether.

In addition, a series of glycidyl fluoroethers was prepared. By the reaction of a fluoroalcohol with epichlorohydrin in the presence of excess base, the glycidyl fluoroether was obtained in one step:



The ethylene oxide ring is opened by a wide variety of reagents, and the glycidyl fluoroethers can thus be made the basis for many further reactions.

*The term "vinyl fluoroether" is used in this dissertation to designate an ether having the vinyl group unsubstituted and the alkyl group substituted with one or more fluorine atoms.

CHAPTER II

MATERIALS

The fluorochemicals used on this project are of special interest because they have been commercially available for a relatively short time. The 1,1-difluoroolefins, chlorotrifluoroethylene, unsymmetrical dichlorodifluoroethylene, and vinylidene fluoride, were furnished by General Chemical Division, Allied Chemical and Dye Corporation. The trifluoroethyl alcohol was a product of Pennsylvania Salt Manufacturing Company, and the α,α -dimethyl- β,β,β -trifluoroethyl alcohol was supplied by Peninsular Chemresearch. The perfluoropropionic and perfluorobutyric acids were commercial products of Minnesota Mining and Manufacturing Company.

The reagent grade chemicals which were used were potassium hydroxide and sodium hydroxide pellets, obtained from Fisher Scientific Company; sulfuric acid, a Baker Analyzed Reagent; and phosphorus pentachloride and anhydrous sodium sulfate, from General Chemical Division, Allied Chemical and Dye Corporation.

Tetrafluoroethylene and perfluoropropylene were prepared by pyrolysis of the sodium salts of perfluoropropionic and perfluorobutyric acids, respectively, according

to the procedure of Hals and co-workers (23).

The α,α -dihydroperfluoropropyl and α,α -dihydroperfluorobutyl alcohols were prepared from perfluoropropionic and perfluorobutyric acid, respectively, by the preparation of the acid chloride and its reduction with lithium aluminum hydride, according to the method of Henne et al. (26).

CHAPTER III

ADDITION OF ETHYLENE GLYCOL TO FLUOROOLEFINS

A. Introduction

The base-catalyzed addition of an alcohol to a 1,1-difluoroolefin is a convenient method for the preparation of α,α -difluoroethers. The reaction was first reported in 1946 in a patent by Hanford and Rigby (24). They reacted various alcohols with tetrafluoroethylene, chlorotrifluoroethylene, and chlorodifluoroethylene ($\text{CF}_2=\text{CHCl}$) in the presence of the corresponding sodium alkoxide in a pressure vessel. Independently, Miller and co-workers (42) added methyl alcohol to tetrafluoroethylene, chlorotrifluoroethylene, and unsymmetrical dichlorodifluoroethylene in the presence of sodium methoxide. The tetrafluoroethylene reaction was carried out under pressure, while the others were reacted at atmospheric pressure. Park et al. (46) found that potassium hydroxide was also an effective catalyst for such reactions. Knunyants and co-workers (31) showed that alcohols add to perfluoropropylene in an analogous manner to form ethers of the type, $\text{CF}_3\text{CHFCF}_2\text{OR}$.

Ethylene glycol has been added to chlorotrifluoroethylene (34, 44) and to tetrafluoroethylene (24). In

both cases the β -hydroxyethyl ether was obtained, but with tetrafluoroethylene some of the diether, $(\text{CHF}_2\text{CF}_2\text{OCH}_2\text{CH}_2\text{OCF}_2\text{CHF}_2)_2$, was also formed.

Young and Tarrant (65) showed that α, α -difluoroethers are easily hydrolyzed to the corresponding esters by treatment with concentrated sulfuric acid. This property provided a convenient method for the preparation of fluoroacids and for the determination of the structure of the ethers.

B. Experimental

1. Discussion of procedure

In this work ethers were prepared by addition of ethylene glycol to the following olefins: chlorotrifluoroethylene, unsymmetrical dichlorodifluoroethylene, and perfluoropropylene. No reaction occurred when ethylene glycol was treated with tetrafluoroethylene and vinylidene fluoride. All reactions were carried out in a pressure vessel, with the exception of that employing tetrafluoroethylene, which was bubbled through the reaction mixture at atmospheric pressure.

Hydrolysis of the β -hydroxyethyl ethers to esters by the use of concentrated sulfuric acid proved unsuccessful. Higher boiling materials were formed which were believed to

be ethers of diethylene glycol. For example:



The β -chloroethyl ethers were hydrolyzed without difficulty.

The dehydration of the β -hydroxyethyl ethers to the corresponding vinyl ethers was tried, using both phosphorus pentoxide and boric acid (10) as dehydrating agents; however, only higher boiling materials were formed.

The addition of ethylene chlorohydrin to chlorotrifluoroethylene, in the presence of potassium hydroxide, was also attempted, but only a small amount of the desired β -chloroethyl ether was obtained.

2. Procedures and results

a. Addition of $\text{CH}_2\text{OHCH}_2\text{OH}$ to $\text{CF}_2=\text{CFCl}$

A solution of 94 g. (1.7 moles) of potassium hydroxide in 500 ml. of ethylene glycol was prepared and allowed to cool. It was then placed in an autoclave (capacity about 1300 ml.) which was chilled in a Dry Ice-acetone bath. Three hundred grams (2.6 moles) of chlorotrifluoroethylene was collected in a Dry Ice trap and added to the contents of the bomb, which was then sealed and rocked overnight at room temperature. The vessel was opened, and the reaction mixture was poured into ice water in order to separate the product from the potassium hydroxide and unreacted ethylene glycol. The organic layer was separated from the lighter

water layer and washed several times with water. It was dried over anhydrous sodium sulfate and distilled at reduced pressure through a 65-cm. column packed with Berl saddles. There was obtained 250 g. (1.4 moles, a 54% yield) of the ether, $\text{CH}_2\text{OHCH}_2\text{OCF}_2\text{CHFCl}$, b.p. $114-18^\circ/100$ mm.¹, n_D^{21} 1.3795². Lawson (34) reported the following constants: n_D^{25} 1.3808, d_{20}^{25} 1.456; while Park and co-workers (44) reported b.p. $40^\circ/1$ mm.

No other fraction was obtained and very little residue was left in the distilling flask.

b. Addition of $\text{CH}_2\text{OHCH}_2\text{OH}$ to $\text{CF}_2=\text{CCl}_2$

Unsymmetrical dichlorodifluoroethylene (300 g., 2.25 moles) was reacted with ethylene glycol by the procedure described above. Fractionation of the dried product resulted in 131 g. (0.67 mole, a 30% yield) of the ether, $\text{CH}_2\text{OHCH}_2\text{OCF}_2\text{CHCl}_2$, boiling in the range $71^\circ/4$ mm. - $74^\circ/3$ mm. A center fraction had the following properties: b.p. $62.5 - 63.0^\circ/2.2$ mm., n_D^{25} 1.4245, d_4^{25} 1.4905, $\text{MR}_{\text{calc.}}$ 33.57, MR_{found} 33.42³. Anal. Calc. for $\text{C}_4\text{H}_6\text{Cl}_2\text{F}_2\text{O}_2$: Cl,

¹All temperatures are given in degrees Centigrade.

²Refractive indices were measured with the D line of sodium.

³The molar refraction values (MR_{found}) were calculated from experimental data using the Lorenz-Lorentz equation; theoretical values were determined from the additive values

36.36. Found: Cl, 36.04⁴.

Sixty-five grams of a material boiling at 82-6°/2 mm. was also obtained. This material was later shown to be the diether of ethylene glycol, $\text{CHCl}_2\text{CF}_2\text{OCH}_2\text{CH}_2\text{OCF}_2\text{CHCl}_2$ (0.20 mole, an 18% yield). An analytical sample had the following constants: b.p. 90°/2.2 mm., n_D^{25} 1.4194, d_4^{25} 1.5786, $\text{MR}_{\text{calc.}}$ 52.66, MR_{found} 52.50. Anal. Calc. for $\text{C}_6\text{H}_6\text{Cl}_4\text{F}_4\text{O}_2$: C, 21.97; H, 1.84. Found: C, 22.33; H, 2.08.

Proof of structure of the diether

(1) Hydrolysis to the ester

Twenty-two grams (0.067 mole) of $\text{CHCl}_2\text{CF}_2\text{OCH}_2\text{CH}_2\text{OCF}_2\text{CHCl}_2$ was placed in a 200 ml, three-necked flask equipped with mechanical stirrer, reflux condenser, and thermometer. Three ml. of concentrated sulfuric acid was added, and the mixture was heated cautiously, with stirring. A vigorous reaction occurred, with evolution of hydrogen fluoride and heat. After the initial reaction had subsided, the reaction mixture was heated with for elements and bondings given in Lange's Handbook of Chemistry, 8th Ed., 1952.

⁴This analysis was performed by the writer; however, with two other exceptions which will be noted, the analyses were performed by the Clark Microanalytical Laboratory, Urbana, Illinois.

stirring for an hour. It was then allowed to cool and poured over cracked ice. The organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. Distillation through a 15-cm. column packed with Berl saddles resulted in approximately 6 g. (0.021 mole, a 31% yield) of the ester, $\text{CHCl}_2\overset{\text{O}}{\parallel}\text{COCH}_2\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{COCHCl}_2$, b.p. 148-

50°/3 mm., n_D^{25} 1.4840, d_4^{25} 1.5386, $\text{MR}_{\text{calc.}}$ 52.68, MR_{found} 52.79. Anal. Calc. for $\text{C}_6\text{H}_6\text{Cl}_4\text{O}_4$: Cl, 49.95. Found: Cl, 48.39. The infrared spectrum exhibited a doublet for the carbonyl stretching wave length at 5.62 and 5.70 microns.

(2) Esterification of ethylene glycol with dichloroacetic acid

Since no reference was found in the literature concerning this ester, synthesis by reaction of ethylene glycol with the appropriate acid was carried out.

Eight grams (0.13 mole) of ethylene glycol, 42 g. (0.32 mole) of dichloroacetic acid, and 2 ml. of concentrated sulfuric acid were mixed well in a 200 ml., round-bottom flask. A distilling head was attached to the flask, and the mixture was refluxed gently for two hours. About 3.5 g. of water was collected during the reaction. The crude ester was distilled from the reaction flask at reduced pressure. The distillate was washed with sodium

carbonate solution, then water, and dried over anhydrous sodium sulfate. Distillation through the 15-cm. column resulted in 16 g. (0.056 mole, a 43% yield) of the ester, b.p. 139-49°/3 mm. A center fraction had the constants: b.p. 146-47°/3 mm., n^{25}_D 1.4839, d^{25}_4 1.5337. Its infrared spectrum was identical with that of the hydrolysis product of the diether.

c. Addition of $\text{CH}_2\text{OHCH}_2\text{OH}$ to $\text{CF}_2=\text{CFCF}_3$

Perfluoropropylene (304 g., 2.03 moles) was reacted with ethylene glycol by the same procedure to form 106 g. (0.50 mole, 25% yield) of the ether, $\text{CH}_2\text{OHCH}_2\text{OCF}_2\text{OHCF}_3$, boiling in the range 71-75°/39 mm. An analytical sample had the constants: b.p. 72-74°/40 mm., n^{25}_D 1.3192, d^{25}_4 1.5227, $\text{MR}_{\text{calc.}}$ 28.45, MR_{found} 27.57. Anal. Calc. for $\text{C}_5\text{H}_6\text{F}_6\text{O}_2$: C, 28.31; H, 2.85. Found: C, 28.27; H, 2.89*.

Attempts were made to dehydrofluorinate this ether by treatment with both aqueous and alcoholic potassium hydroxide. However, in each case only starting material was recovered.

Hydrogen fluoride was evolved during the distillation, probably from hydrolysis of the ether to the ester. Seventeen grams of higher-boiling material was obtained;

*This analysis was performed by the microanalytical laboratory of Dr. G. Weiler and Dr. F. B. Strauss, Oxford, England.

it was collected over the range $63^{\circ}/2.5$ mm.- $85^{\circ}/3$ mm.

Sixty-five grams of very high boiling material remained in the distilling flask. Refractionation of the higher boiling material resulted in 6 g. of a compound, b.p. $84-87^{\circ}/10$ mm., which appeared to be the ester, $\text{CH}_2\text{OHCH}_2\text{OCCHFCF}_3$. It



had the constants: n_{25}^{25} 1.3545, d_4^{25} 1.4895, $\text{MR}_{\text{calc.}}$ 28.46, MR_{found} 27.78. A strong infrared absorption band at 5.60 microns indicated the presence of a carbonyl group in the compound. However, its analysis was not in close agreement with the theoretical values.

d. Attempted addition of $\text{CH}_2\text{OHCH}_2\text{OH}$ to $\text{CF}_2=\text{CH}_2$

The low boiling point of vinylidene fluoride (-32°) made it necessary to introduce it into the 1300 ml. autoclave in the gaseous state. It was added to a reaction mixture of 94 g. of potassium hydroxide dissolved in 500 ml. of ethylene glycol to a pressure of 500 lb./sq. in. Rocking overnight at room temperature resulted in only a slight decrease in pressure. The reaction mixture was then heated to 100° and rocked two hours, after which the pressure dropped to 75 lb./sq. in. The bomb was rocked overnight at 110° , but there was no further change in pressure. It was then cooled in ice, the unreacted gas was allowed to escape, and the contents were poured into about one liter of ice water. There was no separation of layers;

but hydrogen fluoride was evolved, as shown by etching of the glass container. β -Hydroxyethyl acetate, which would be formed by hydrolysis of the ether, $\text{CH}_2\text{OHCH}_2\text{OCF}_2\text{CH}_3$, is soluble in water. Separation of the ester from the aqueous mixture was not deemed worthwhile.

e. Attempted addition of $\text{CH}_2\text{OHCH}_2\text{OH}$ to $\text{CF}_2=\text{CF}_2$

Tetrafluoroethylene boils at -76° ; thus it is not condensed by Dry Ice cooling. It sometimes polymerizes explosively when under pressure. For these reasons the preparation of the ether was attempted by bubbling the olefin through an ethylene glycol-potassium hydroxide solution at atmospheric pressure.

A solution of 170 g. of potassium hydroxide in 900 ml. of ethylene glycol was placed in a one liter, three-necked flask equipped with mechanical stirrer and inlet and outlet tubes. The olefin was generated by the cautious heating of 502 g. (2.13 moles) of sodium perfluorobutyrate. As the olefin formed, it was passed through soda lime tubes to remove the carbon dioxide, which is formed simultaneously, and then through the ethylene glycol solution with vigorous stirring. After all the olefin had been bubbled through the solution, the reaction mixture was poured into ice water, but no organic layer formed.

Table I

Compounds Prepared from the Reaction
of Ethylene Glycol with Fluoroolefins

<u>Compound</u>	<u>Yield</u>	<u>B.P.</u>	<u>n_D²⁵</u>	<u>d₄²⁵</u>
(1) CH ₂ OHCH ₂ OCF ₂ CHFCI*	54%	114-18°/100 mm.	1.3795 (21°)	-
(2) CH ₂ OHCH ₂ OCF ₂ CHCl ₂	30%	62-3°/2.2 mm.	1.4245	1.4905
(3) (CHCl ₂ CF ₂ OCH ₂ -) ₂	18%	90°/2.2 mm.	1.4194	1.5786
(4) (CHCl ₂ COCH ₂ -) ₂	31%	148-50°/3 mm.	1.4840	1.5386
(5) CH ₂ OHCH ₂ OCF ₂ CHFCF ₃	25%	72-4°/40 mm.	1.3192	1.5227

<u>Compound</u>	<u>MR</u>		<u>Calc.</u>			<u>Found</u>		
	<u>Calc.</u>	<u>Found</u>	<u>%C</u>	<u>%H</u>	<u>%Cl</u>	<u>%C</u>	<u>%H</u>	<u>%Cl</u>
(2)	33.57	33.42	-	-	36.36	-	-	36.04
(3)	52.66	52.50	21.97	1.84	-	22.33	2.08	-
(4)	52.68	52.79	-	-	49.95	-	-	48.39
(5)	28.45	27.57	28.31	2.85	-	28.27	2.89	-

*Lawson (34) reported for this compound n_D²⁵ 1.3808,
d₂₀²⁵ 1.456; Park and co-workers (44) reported b.p. 40°/
1 mm.

f. Attempted addition of $\text{CH}_2\text{ClCH}_2\text{OH}$ to $\text{CF}_2=\text{CFCl}$

Ethylene chlorohydrin (220 g., 2.7 moles) was placed in an autoclave having a capacity of 300 ml. and cooled in a Dry Ice-acetone bath. Twenty-eight grams of potassium hydroxide and 100 g. (0.86 mole) of chlorotrifluoroethylene, which was collected in a Dry Ice trap, were added. The vessel was sealed with a rupture disk attached and rocked at room temperature overnight.

When the contents of the bomb were poured into water, a small amount of organic layer formed. This was separated, washed, and dried over anhydrous sodium sulfate. There was obtained 4.5 g. of material, the infrared spectrum of which was identical with that of $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHFCl}$. (The preparation of this compound is described in Chapter V.)

The reaction was also run at 50° and 100° under pressure and at -30° at atmospheric pressure. However, the best yield was only 10 g. (at -30°). Considerable amounts of ethylene oxide and potassium chloride were formed in the reaction.

C. Discussion of Results

In all the base-catalyzed additions of alcohols to fluoroolefins which have been reported, only one of the two possible isomers, the α, β -difluoroether, has been formed.

the diether was obtained.

The lack of reaction of tetrafluoroethylene at atmospheric pressure, reported by Park et al. (45), was confirmed in this work.

None of the adduct of ethylene glycol and vinylidene fluoride was isolated, although there was evidence of reaction. The probable ease of hydrolysis of the expected adduct, $\text{CH}_3\text{CF}_2\text{OCH}_2\text{CH}_2\text{OH}$, to the ester, β -hydroxyethyl acetate, would make isolation of the ether unlikely. Young (64) was unable to isolate the corresponding ethyl ether, $\text{CH}_3\text{CF}_2\text{OCH}_2\text{CH}_3$, and obtained only the hydrolysis product, ethyl acetate.

The infrared spectra of all compounds were obtained from freshly distilled samples. All were consistent, as far as could be determined, with the assigned structures. The β -hydroxyethyl ethers exhibited the broad O-H stretch at 3.00 microns, and this band was absent in the spectrum of the diether of ethylene glycol. Strong carbonyl absorption at 5.62 and 5.70 microns was present in the spectrum of $\text{CHCl}_2\text{COCH}_2\text{CH}_2\text{OCCHCl}_2$.

CHAPTER IV

ADDITION OF FLUOROALCOHOLS TO THE ETHYLENE OXIDE RING

A. Introduction

The addition of alcohols and phenols to the ethylene oxide ring has long been a subject of study. In 1859 Roithner (52) observed the addition of phenol to ethylene oxide to form β -phenoxyethyl alcohol by heating the two materials in a sealed tube at 150° for ten hours. In 1860 Reboul (49) reported the reaction of ethyl alcohol with epichlorohydrin which occurred when he heated them in a closed container at 180° for ten hours. He obtained the simple adduct, $C_2H_5OCH_2CHOHCH_2Cl$, as well as two other compounds, $CH_2ClCHOHCH_2Cl$ and $C_2H_5OCH_2CHOHCH_2OC_2H_5$. He isolated the first compound by treating the mixture with potassium hydroxide solution, thus forming the lower boiling ethyl glycidyl ether, $C_2H_5OCH_2\underset{\text{O}}{\text{C}}HCH_2$.

Repeated experiments (5, 20, 21, 29) have shown that alcohols add to the ethylene oxide ring when a catalytic amount of acid, such as sulfuric acid, is present. The addition of phenols to the ethylene oxide ring, however, is not aided appreciably by acids but is effectively catalyzed by organic or inorganic base (7, 9, 59). However,

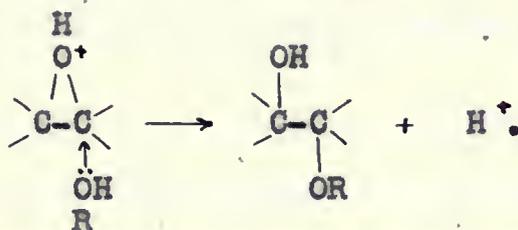
boron trifluoride (35) and stannic chloride (39) do serve as catalysts for the reaction of phenols with epichlorohydrin. Regardless of catalyst, the direction of addition of hydroxy compounds to epichlorohydrin is the same, resulting in a secondary alcohol:



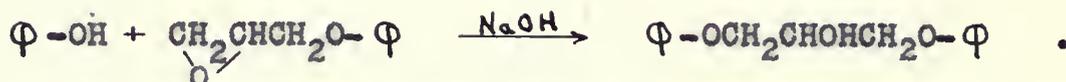
The opening of the ethylene oxide ring takes place by the attack of a nucleophilic reagent on carbon (17). In basic solution the attacking reagent is the alkoxide ion:



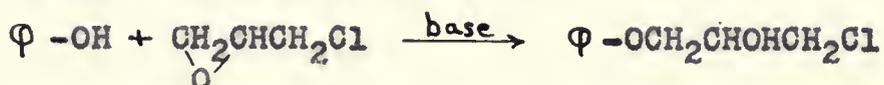
In the presence of an acid catalyst, the conjugate acid of ethylene oxide is attacked by the alcohol:



In 1891 Lindeman (36) reported the preparation of glycidyl ethers in one step by the addition of a phenol to epichlorohydrin in the presence of excess sodium hydroxide. The mixture was allowed to stand for ten to twelve hours with frequent shaking. A considerable amount of the symmetrical diphenyl glyceryl ether was also formed, by the further reaction of the glycidyl ether with phenol:



If the glycidyl ether is the desired product, it can be obtained in higher yields by using only a catalytic amount of base. The chlorohydrin is formed and separated and is then converted to the glycidyl ether by treatment with an equivalent amount of base:



B. Experimental

1. Discussion of procedure

In this research the addition of fluoroalcohols to ethylene oxide and epichlorohydrin was attempted in an effort to obtain β -hydroxyethyl fluoroethers and glycidyl fluoroethers, reactions which are analogous to those just described for unsubstituted alcohols and phenols.

The fluoroalcohols which were available were trifluoroethyl alcohol; α,α -dihydroperfluoropropyl alcohol; α,α -dihydroperfluorobutyl alcohol; and α,α -dimethyl- β,β,β -trifluoroethyl alcohol.

It should be noted that the ethers which may be prepared by this reaction will all have fluorine beta to the ether oxygen. Therefore the vinyl ethers which could possibly be made from them will be vinyl β -fluoroethers.

All attempts to add trifluoroethyl alcohol to epichlorohydrin using concentrated sulfuric acid resulted in only very small yields of the adduct, $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CHOHCH}_2\text{Cl}$. However, in the presence of base, trifluoroethyl alcohol added to epichlorohydrin and to ethylene oxide in good yield.

2. Procedures and Results

a. Addition of $\text{CF}_3\text{CH}_2\text{OH}$ to epichlorohydrin

(1) With a catalytic amount of sulfuric acid

One hundred grams (1.0 mole) of trifluoroethyl alcohol and 46 g. (0.5 mole) of epichlorohydrin were placed in a 500 ml. flask equipped with a reflux condenser. Two ml. of concentrated sulfuric acid was added dropwise to the mixture through the condenser while the flask was gently shaken. The mixture was refluxed twenty hours. Barium carbonate was added to the cooled solution, which was then distilled through the 65-cm. column. A small amount of the adduct, $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CHOHCH}_2\text{Cl}$, b.p. $73-5^\circ/17$ mm., was obtained.

(2) With a catalytic amount of pyridine

One hundred grams (1.0 mole) of trifluoroethyl alcohol, 185 g. (2.0 moles) of epichlorohydrin, and 2 ml. of pyridine were placed in a 500 ml. flask equipped with mechanical stirrer, reflux condenser, and thermometer. The mixture was heated to 80-90° for 12 hours. Fractional distillation of the reaction mixture through the 65-cm. column resulted in 39 g. of unreacted trifluoroethyl alcohol, b.p. 74°, excess epichlorohydrin, and 95.5 g. (0.50 mole, a 50% yield) of the ether, $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CHOHCH}_2\text{Cl}$, collected over the range 61°/17 mm. - 73°/14 mm. A center fraction had the constants: b.p. 85-6°/19 mm., n^{25}_D 1.3951, d^{25}_4 1.3716, $\text{MR}_{\text{calc.}}$ 33.33, MR_{found} 33.67. Anal. Calc. for $\text{C}_5\text{H}_8\text{ClF}_3\text{O}_2$: Cl, 18.41. Found: Cl, 18.91.

Six grams of unidentified material boiling at 80-2°/4 mm. was also obtained.

(3) Use of excess sodium hydroxide with refluxing

Fifty grams (0.5 mole) of trifluoroethyl alcohol, 46 g. (0.5 mole) of epichlorohydrin, and a solution of 25 g. (0.62 mole) of sodium hydroxide in 300 ml. of water were placed in a one liter flask and refluxed eight hours. The oily layer was separated, and the aqueous layer was extracted with ether. The organic layer and ether extracts were combined and dried over anhydrous sodium sulfate. Fractionation through a 50-cm. column packed with glass

helices resulted in 18 g. (0.07 mole, 28% yield) of the glyceryl diether of trifluoroethyl alcohol, $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CHOHCH}_2\text{OCH}_2\text{CF}_3$, b.p. $86^\circ/16$ mm., n_{D}^{25} 1.3528, d_4^{25} 1.3890, $\text{MR}_{\text{calc.}}$ 39.34, MR_{found} 39.97. Anal. Calc. for $\text{C}_7\text{H}_{10}\text{F}_6\text{O}_3$: C, 32.82; H, 3.93. Found: C, 31.87; H, 3.53.

(4) Use of excess sodium hydroxide without heating

Trifluoroethyl alcohol (50 g., 0.50 mole) and epichlorohydrin (46 g., 0.50 mole) were added to a cooled solution of 25 g. (0.62 mole) of sodium hydroxide in 300 ml. of water. The reactants were mixed thoroughly, and the mixture was allowed to stand at room temperature overnight. The organic layer was then separated, dried over anhydrous sodium sulfate, and distilled through the 50-cm. column. There was obtained 24 g. (0.15 mole, a 31% yield) of glycidyl trifluoroethyl ether, $\text{CH}_2\text{CHCH}_2\text{OCH}_2\text{CF}_3$, b.p. $82-5^\circ/120$ mm. ($132-5^\circ/\text{atm. press.}$), n_{D}^{25} 1.3560, d_4^{25} 1.2666, $\text{MR}_{\text{calc.}}$ 26.62¹, MR_{found} 26.93. Anal. Calc. for $\text{C}_5\text{H}_7\text{F}_3\text{O}_2$: C, 38.47; H, 4.52. Found: C, 38.98; H, 4.51².

In addition, 12 g. (0.047 mole, a 19% yield) of the

¹The atomic refraction value used for "epoxy" oxygen was 1.890, determined by Flores-Gallardo and Pollard (20).

²This analysis was performed by the microanalytical laboratory of Dr. G. Weiler and Dr. F. B. Strauss, Oxford, England.

glyceryl diether, $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CHOHCH}_2\text{OCH}_2\text{CF}_3$, was also obtained.

(5) Reaction of $\text{CF}_3\text{CH}_2\text{OH}$ with $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CHOHCH}_2\text{Cl}$

Forty-six grams (0.24 mole) of $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CHOHCH}_2\text{Cl}$ was placed in a 500 ml., round-bottom flask equipped with reflux condenser. To this was added 25 g. (0.25 mole) of trifluoroethyl alcohol and 12 g. (0.30 mole) of sodium hydroxide dissolved in 150 ml. of water. The mixture was refluxed for one hour and allowed to stand overnight. The organic layer was separated, and the aqueous layer was extracted with ether. Fractional distillation of the combined organic layer and ether extracts resulted in 11 g. of $\text{CH}_2\text{CHCH}_2\text{OCH}_2\text{CF}_3$, identified by its infrared spectrum, and about 23 g. (0.09 mole, 37% yield) of the glyceryl diether, $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CHOHCH}_2\text{OCH}_2\text{CF}_3$, b.p. $99-101^\circ/23$ mm. The infrared spectrum of the latter was identical with that of the high boiling fraction obtained from the trifluoroethylalcohol-epichlorohydrin reaction.

(6) Reaction of $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CHCH}_2$ with HCl

Glycidyl trifluoroethyl ether (45 g., 0.29 mole) and 40 ml. of chloroform were mixed in a 250 ml. flask and cooled in ice water. Fifty ml. (about 0.6 mole) of concentrated hydrochloric acid was added gradually, with stirring and cooling of the mixture. After all the acid

was added, the organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. Fractionation through a 15-cm. column packed with Berl saddles resulted in 30 g. (0.16 mole, a 54% yield) of $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CHOHCH}_2\text{Cl}$, b.p. $85-6^\circ/19$ mm. Its infrared spectrum was identical with that of the product obtained in (2) above.

b. Addition of $\text{C}_2\text{F}_5\text{CH}_2\text{OH}$ to epichlorohydrin

Forty-two grams (0.28 mole) of $\text{C}_2\text{F}_5\text{CH}_2\text{OH}$, 29 g. (0.31 mole) of epichlorohydrin, and a cooled solution of 16 g. (0.4 mole) of sodium hydroxide in 150 ml. of water were mixed in a 500 ml. flask and allowed to stand overnight. The procedure described for trifluoroethyl alcohol was followed. Fractional distillation resulted in 5 g. of a mixture of the alcohol, water, and probably some of the glycidyl ether; and a second fraction of 11 g. (0.053 mole, 19% yield) of the ether, $\text{CH}_2\text{CHCH}_2\text{OCH}_2\text{C}_2\text{F}_5$, b.p. $78^\circ/96$ mm.-
 $50^\circ/20$ mm. A center fraction of this material had the constants: b.p. $81^\circ/86$ mm. - $79^\circ/84$ mm., n_D^{25} 1.3419, d_4^{25} 1.3534, $\text{MR}_{\text{calc.}}$ 31.24, MR_{found} 32.08. Anal. Calc. for $\text{C}_6\text{H}_7\text{F}_5\text{O}_2$: C, 34.96; H, 3.42. Found: C, 35.15; H, 3.36.

Four grams of material boiling in the range $84^\circ/18$ mm. - $104^\circ/12$ mm. was also obtained. It was believed to be chiefly the diether, $\text{C}_2\text{F}_5\text{CH}_2\text{OCH}_2\text{CHOHCH}_2\text{OCH}_2\text{C}_2\text{F}_5$.

c. Addition of $C_3F_7CH_2OH$ to epichlorohydrin

Twenty-seven grams (0.135 mole) of α, α -dihydroperfluorobutanol, 12.5 g. (0.135 mole) of epichlorohydrin, and 6.5 g. (0.16 mole) of sodium hydroxide dissolved in 24 ml. of water were mixed and allowed to stand overnight at room temperature. Fractionation of the dried product resulted in 8 g. (0.031 mole, a 23% yield) of the glycidyl ether, $CH_2CHCH_2OCH_2C_3F_7$, b.p. $79^\circ/49$ mm., n^{25}_D 1.3350, d^{25}_4 1.4429, $MR_{calc.}$ 36.96, MR_{found} 36.71. Anal. Calc. for $C_7H_7F_7O_2$: C, 32.82; H, 2.76. Found: C, 32.10, H, 2.81.

In addition, there was obtained 7.5 g. (0.016 mole, a 24% yield) of the glyceryl diether, $C_3F_7CH_2OCH_2CH(OH)CH_2OCH_2C_3F_7$, b.p. $112-15^\circ/15$ mm., n^{25}_D 1.3338, d^{25}_4 1.5569, $MR_{calc.}$ 57.81, MR_{found} 60.40. Anal. Calc. for $C_{11}H_{10}F_{14}O_3$: C, 28.96; H, 2.21. Found: C, 28.81; H, 1.91.

d. Attempted addition of $CF_3C(CH_3)_2OH$ to epichlorohydrin

Attempts to add this tertiary alcohol to epichlorohydrin using an excess of sodium hydroxide, as in the above procedure, and with a catalytic amount of pyridine, were unsuccessful. In both cases only starting material was recovered.

e. Addition of CF_3CH_2OH to ethylene oxide

Five grams of potassium hydroxide was dissolved in

150 g. (1.5 mole) of trifluoroethyl alcohol. The cooled solution was placed in the small autoclave, which was cooled in a Dry Ice-acetone bath. Forty-four grams (1.0 mole) of ethylene oxide was collected in a Dry Ice trap and added to the contents of the autoclave. The latter was sealed and rocked at 70° for 4 hours. It was cooled to room temperature, opened, and the reaction mixture was distilled through the 65-cm. fractionation column. Forty-three grams of excess trifluoroethyl alcohol was recovered, and 107.5 g. (0.75 mole, ^{~75} ~~58%~~ yield) of the ether, $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$, was collected over the range 82°/85 mm.-68°/50 mm. A center fraction had the constants: b.p. 84°/80 mm., n_D^{25} 1.3502, d_4^{25} 1.2902, $\text{MR}_{\text{calc.}}$ 23.84, MR_{found} 24.04. Anal. Calc. for $\text{C}_4\text{H}_7\text{F}_3\text{O}_2$: C, 33.34; H, 4.90. Found: C, 33.10; H, 4.86.

f. Addition of $\text{C}_2\text{F}_5\text{CH}_2\text{OH}$ to ethylene oxide

Four grams of powdered potassium hydroxide, 105 g. (0.70 mole) of $\text{C}_2\text{F}_5\text{CH}_2\text{OH}$, and 29.5 g. (0.67 mole) of ethylene oxide were reacted in the usual manner. Three grams of the alcohol was recovered, and 42 g. (0.22 mole, 32% yield) of the ether, $\text{C}_2\text{F}_5\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$, b.p. 85-95°/87 mm., was obtained. A center fraction had the properties: b.p. 87°/84 mm., n_D^{25} 1.3370, d_4^{25} 1.3806, $\text{MR}_{\text{calc.}}$ 28.46, MR_{found} 29.24. Anal. Calc. for $\text{C}_5\text{H}_7\text{F}_5\text{O}_2$: C, 30.94; H, 3.63. Found: C, 30.66; H, 3.77.

g. Addition of $C_3F_7CH_2OH$ to ethylene oxide

Three grams of powdered potassium hydroxide, 125 g. (0.62 mole) of $C_3F_7CH_2OH$, and 13.5 g. (0.31 mole) of ethylene oxide were reacted by the same procedure. Distillation through the 65-cm. column resulted in 44 g. of the alcohol and 47 g. (0.19 mole, a 62% yield) of $C_3F_7CH_2OCH_2CH_2OH$, collected over the range 83-94°/54 mm. A center cut had the constants: b.p. 91-2°/54 mm. (159°/atm. press.), n_D^{28} 1.3300, d_4^{28} 1.4695, $MR_{calc.}$ 33.08, MR_{found} 33.90. Anal. Calc. for $C_6H_7F_7O_2$: C, 29.51; H, 2.89. Found: C, 29.24; H, 2.87.

h. Addition of $CF_3C(CH_3)_2OH$ to ethylene oxide

Four grams of powdered potassium hydroxide, 77 g. (0.60 mole) of $CF_3C(CH_3)_2OH$ in azeotropic solution with about 19 g. of ethyl alcohol, and 22 g. (0.50 mole) of ethylene oxide were treated in the usual manner. As a result of distillation through the 65-cm. column, 50 g. of unreacted alcohol and 30 g. (0.174 mole, a 35% yield) of the desired ether, $CF_3C(CH_3)_2OCH_2CH_2OH$, collected over a boiling point range of 90°/80 mm. - 74°/33 mm., were obtained. A center fraction of the latter material had the constants: b.p. 92°/77 mm., n_D^{22} 1.3749, d_4^{22} 1.1931, $MR_{calc.}$ 33.08, MR_{found} 33.02. Anal. Calc. for $C_6H_{11}F_3O_2$: C, 41.86; H, 6.44. Found: C, 42.05; H, 6.81.

Table II

Compounds Prepared from the Reaction
of Fluoroalcohols with Epichlorohydrin

<u>Compound</u>	<u>Yield</u>	<u>B.P.</u>	<u>n²⁵</u>	<u>d₄²⁵</u>
(1) $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CHOHCH}_2\text{Cl}$	50%	85-6°/19 mm.	1.3951	1.3716
(2) $\text{CH}_2\text{CH}(\text{O})\text{CH}_2\text{OCH}_2\text{CF}_3$	31%	82-5°/120 mm., 132-5°/atm. press.	1.3560	1.2666
(3) $(\text{CF}_3\text{CH}_2\text{OCH}_2-)_2\text{CHOH}$	19%	86°/16 mm.	1.3528	1.3890
(4) $\text{CH}_2\text{CH}(\text{O})\text{CH}_2\text{OCH}_2\text{C}_2\text{F}_5$	19%	81°/86 mm.- 79°/84 mm.	1.3419	1.3534
(5) $\text{CH}_2\text{CH}(\text{O})\text{CH}_2\text{OCH}_2\text{C}_3\text{F}_7$	23%	79°/49 mm.	1.3350	1.4429
(6) $(\text{C}_3\text{F}_7\text{CH}_2\text{OCH}_2-)_2\text{CHOH}$	24%	112-15°/ 15 mm.	1.3338	1.5569

<u>Compound</u>	<u>MR</u>		<u>Calc.</u>			<u>Found</u>		
	<u>Calc.</u>	<u>Found</u>	<u>%C</u>	<u>%H</u>	<u>%Cl</u>	<u>%C</u>	<u>%H</u>	<u>%Cl</u>
(1)	33.33	33.67	-	-	18.41	-	-	18.91
(2)	26.62	26.93	38.47	4.52	-	38.98	4.51	-
(3)	39.34	39.97	32.82	3.93	-	31.87	3.53	-
(4)	31.24	32.08	34.96	3.42	-	35.15	3.36	-
(5)	36.96	36.71	32.82	2.76	-	32.10	2.81	-
(6)	57.81	60.40	28.96	2.21	-	28.81	1.91	-

Table III

Compounds Prepared from the Reaction
of Fluoroalcohols with Ethylene Oxide

<u>Compound</u>	<u>Yield</u>	<u>B.P.</u>	<u>n²⁵</u>	<u>d₄²⁵</u>
(1) $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	50%	84°/80 mm.	1.3502	1.2902
(2) $\text{C}_2\text{F}_5\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	32%	87°/84 mm.	1.3370	1.3806
(3) $\text{C}_3\text{F}_7\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	62%	91-2°/54 mm., 159°/atm. press.	1.3300 (28°)	1.4695 (28°)
(4) $\text{CF}_3\text{C}(\text{CH}_3)_2\text{OCH}_2\text{CH}_2\text{OH}$	35%	92°/77 mm.	1.3749 (22°)	1.1931 (22°)

<u>Compound</u>	<u>MR</u>		<u>Calc.</u>		<u>Found</u>	
	<u>Calc.</u>	<u>Found</u>	<u>%C</u>	<u>%H</u>	<u>%C</u>	<u>%H</u>
(1)	23.84	24.04	33.34	4.90	33.10	4.86
(2)	28.46	29.24	30.94	3.63	30.66	3.77
(3)	33.08	33.90	29.51	2.89	29.24	2.87
(4)	33.08	33.02	41.86	6.44	42.05	6.81

C. Discussion of Results

The ability of fluorine to alter the properties of a molecule is again exhibited in the reaction of fluoroalcohols with epoxy compounds. Unsubstituted alcohols add readily to the ethylene oxide ring if a catalytic amount of sulfuric acid is present. However, this work has shown that fluoroalcohols require a basic catalyst for an efficient reaction. Only a slight amount of adduct was obtained when sulfuric acid was the catalyst employed, but yields of about 20-60% were obtained when sodium hydroxide or pyridine was used. In this respect the fluoroalcohols resemble the phenols; this is probably due to their similarity in acidity: K_a perfluoroalcohols 10^{-12} (27), K_a phenol 10^{-10} .

The lack of reactivity of the fluoroalcohols and phenols in acid solution is probably due to the low concentration of electrons on the hydroxyl oxygen available for nucleophilic attack on the carbon of the ring. Likewise, the fact that unfluorinated alcohols do not react as readily in basic solution as the phenols is probably due to the low concentration of alkoxide ion, the attacking reagent in basic solution. However, Boyd and Marle (8) found that the rate of addition of substituted phenoxides to ethylene oxide diminished with an increase in the acidity of the phenol. They attributed this fact to the increased

stability of the phenoxide ion with greater acidity of the phenol. The two effects appear to contradict each other: the more acidic the alcohol or phenol, the greater is the concentration of alkoxide or phenoxide ion, but it is also the more stable or less reactive. Probably both effects are important, and optimum conditions may be attained by a compound of intermediate acidity.

By the addition of fluoroalcohols to epichlorohydrin in the presence of at least an equivalent amount of base, the glycidyl ether is obtained in the one operation in yields of about 20-30%. However, the latter reacts with some of the fluoroalcohol to form the glyceryl diether, thus decreasing the yield of glycidyl ether. Heating the reaction mixture results in complete conversion of the glycidyl ether to the glyceryl diether. Supporting evidence for the structure of the diether was obtained by synthesis by the base-catalyzed reaction of trifluoroethanol with $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CHOHCH}_2\text{Cl}$. The latter compound was obtained both from the pyridine-catalyzed reaction of trifluoroethanol with epichlorohydrin and by treatment of trifluoroethyl glycidyl ether with hydrochloric acid.

The addition of fluoroalcohols to ethylene oxide, catalyzed by a small amount of potassium hydroxide, was uncomplicated by major side reactions. Yields of about 30-60% of the adduct, a β -hydroxyethyl ether, were obtained.

The tertiary fluoroalcohol, $\text{CF}_3\text{C}(\text{CH}_3)_2\text{OH}$, differed from the primary fluoroalcohols in its lack of reactivity with epichlorohydrin; however, it added to ethylene oxide, resulting in a 35% yield of the ether.

The infrared spectra of the compounds described in this chapter were obtained and were consistent with the assigned structures. The spectra of the glycidyl ethers and a discussion of their characteristics are given in Chapter VII.

CHAPTER V

PREPARATION OF β -CHLOROETHYL FLUOROETHERS

A. Introduction

The replacement of the hydroxyl group with chlorine by treatment with phosphorus pentachloride is a well-known and useful organic reaction. Applications of the reaction to ethers of the type prepared in this work have been reported. Park and co-workers (44) prepared $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHFCl}$ by heating the β -hydroxyethyl ether with phosphorus pentachloride and phosphorus oxychloride. Boyd (6) treated glyceryl diphenyl ether, $\phi\text{-OCH}_2\text{CHOHCH}_2\text{O-}\phi$, with phosphorus pentachloride and thereby obtained the chloro derivative.

Park and co-workers (44) and Rapp et al. (48) have prepared α,α -difluoroethers by the addition of alcohols to fluoroolefins and have studied the effect of treatment with elemental chlorine. Both groups reported that the chlorinated ethers were very stable chemically; hydrolysis to the esters occurred with difficulty or not at all, depending on the degree of chlorine substitution.

B. Experimental

1. Discussion of procedure

By the methods described in chapters III and IV, β -hydroxyethyl ethers of two types were prepared: (1) $\text{CH}_2\text{OHCH}_2\text{OCF}_2\text{R}$ and (2) $\text{CH}_2\text{OHCH}_2\text{OCH}_2\text{R}_f$. The ethers of type (1) were successfully treated with phosphorus pentachloride by the method of Park and co-workers (44), in the presence of phosphorus oxychloride. However, it was later found that the absence of phosphorus oxychloride did not decrease the yield of chloroether. The ethers of type (2) were diluted with chloroform before treatment with phosphorus pentachloride, and much better yields of the β -chloroethyl ethers were obtained. The glyceryl diether, $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CHOHCH}_2\text{OCH}_2\text{CF}_3$, was also treated with phosphorus pentachloride, and the corresponding chloroether was obtained, with the chlorine in the beta position with respect to both of the ether oxygens.

The use of thionyl chloride as a chlorinating agent gave none of the desired β -chloroethyl ether.

Hydrolysis of two of the chlorinated ethers having fluorine in the alpha position was attempted, and the corresponding esters were obtained.

2. Procedures and resultsa. $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHFCl}$

(1) Preparation

The β -hydroxyethyl ether, $\text{CH}_2\text{OHCH}_2\text{OCF}_2\text{CHFCl}$ (59 g., 0.33 mole) was placed in a 500 ml., three-necked flask equipped with a mechanical stirrer and reflux condenser. Seventy-three grams (0.35 mole) of phosphorus pentachloride was added gradually, while the mixture was stirred vigorously. Each addition of phosphorus pentachloride resulted in immediate reaction, as shown by the evolution of hydrogen chloride and heating of the mixture, until about two-thirds of the chlorinating agent was added. Then the reaction subsided. After addition was complete, the reaction mixture was refluxed twenty minutes; it was then cooled and poured into ice water. The organic material settled to the bottom and was separated from the water. It was washed with sodium bicarbonate solution until neutral to litmus, then dried over anhydrous sodium sulfate. Finally, it was distilled through a 15-cm. fractionating column packed with Berl saddles. There was obtained 17.5 g. (0.089 mole, a 27% yield) of $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHFCl}$, b.p. $83^\circ/100$ mm. - $97^\circ/98$ mm., from which a center fraction had the constants: b.p. $85^\circ/100$ mm., n_D^{25} 1.3882, d_4^{25} 1.4471, $MR_{\text{calc.}}$ 32.05, MR_{found} 32.14. Park and co-workers (44) reported for this compound, b.p. $80^\circ/100$ mm., n_D^{20} 1.3929.

In addition, a higher boiling fraction was obtained which had the following properties: b.p. 95°/29 mm. - 94°/27 mm., n_{D}^{25} 1.3703, d_{4}^{25} 1.5385. An infrared spectrum of this material exhibited no OH stretching frequency or carbonyl band. It was probably chiefly the diether of diethylene glycol, $(\text{CHFC1CF}_2\text{OCH}_2\text{CH}_2-)_2\text{O}$.

(2) Hydrolysis

Forty grams (0.20 mole) of $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHFC1}$ was placed in a 500 ml. flask equipped with a mechanical stirrer, reflux condenser, and thermometer. Ten grams of concentrated sulfuric acid was added, and the mixture was heated cautiously, with stirring. When the temperature of the liquid reached 82°, a vigorous reaction began, with evolution of hydrogen fluoride and heat. After an hour of continued heating and stirring, the temperature had risen to 98°. The mixture was then allowed to cool and poured over cracked ice. The oily layer was separated, washed with water, and dried over anhydrous sodium sulfate. Distillation through the 15-cm. column resulted in about 12 g. (0.069 mole, a 34% yield) of the ester, $\text{CH}_2\text{ClCH}_2\text{OC}(=\text{O})\text{CHFC1}$,
 b.p. 106°/47 mm. - 105°/45 mm., n_{D}^{23} 1.4369, d_{4}^{25} 1.4256,
 $\text{MR}_{\text{calc.}}$ 32.06, MR_{found} 32.20. Anal. Calc. for $\text{C}_4\text{H}_5\text{Cl}_2\text{FO}_2$:
 Cl, 40.52. Found: Cl, 40.09.

b. $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHCl}_2$

(1) Preparation

Treatment of 45 g. (0.23 mole) of $\text{CH}_2\text{OHCH}_2\text{OCF}_2\text{CHCl}_2$ with 60 g. (0.29 mole) of phosphorus pentachloride by the procedure described above resulted in 13.5 g. (0.063 mole, a 27% yield) of $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHCl}_2$, boiling in the range 86-80°/33 mm. A center fraction had the constants: b.p. 87°/33 mm., n_D^{25} 1.4270, d_4^{25} 1.4833, $M_{r, \text{calc.}}$ 36.92, $M_{r, \text{found}}$ 36.95. Anal. Calc. for $\text{C}_4\text{H}_5\text{Cl}_3\text{F}_2\text{O}$: Cl, 49.83. Found: Cl, 50.94.

(2) Hydrolysis

The ether, $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHCl}_2$ (12.5 g., 0.058 mole), was treated with three ml. of concentrated sulfuric acid by the hydrolysis procedure just described for $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{-CHFCI}$. Four grams (0.021 mole, a 36% yield) of the ester, $\text{CH}_2\text{ClCH}_2\text{OCCHCl}_2$, was obtained. Its constants were: b.p. 207-11°/atm. press., n_D^{25} 1.4719, d_4^{25} 1.4544, $M_{r, \text{calc.}}$ 36.93, $M_{r, \text{found}}$ 36.85. The constants given in the literature (15) are: b.p. 209-12°/767 mm., d_4^{15} 1.200*.

*This density is believed to be in error. By comparing the values: $\text{CH}_3\text{COOC}_2\text{H}_5$, d_4^{20} 0.901, $\text{CH}_2\text{ClCOOC}_2\text{H}_5$, d_4^{20} 1.159, and $\text{CHCl}_2\text{COOC}_2\text{H}_5$, d_4^{20} 1.2821, one would expect an additional chlorine atom to raise the density at least 0.1 unit above that of $\text{CHCl}_2\text{CHOC}_2\text{H}_5$. (These values were obtained from the Handbook of Chemistry and Physics, 30th

$C_4H_5Cl_3O_2$: Cl, 55.56. Found: Cl, 54.85. This derivative serves as proof of structure of the ether.

c. Preparation of $CH_2ClCH_2OCF_2CHFClCF_3$

Treatment of 84 g. (0.40 mole) of $CH_2OHCH_2OCF_2CHFClCF_3$ with 88 g. (0.42 mole) of phosphorus pentachloride by the usual procedure resulted in 25 g. (0.11 mole, a 27% yield) of $CH_2ClCH_2OCF_2CHFClCF_3$, collected over the range $45^\circ/45$ mm.- $54^\circ/35$ mm. An analytical sample had the constants: b.p. $46^\circ/37$ mm., n_D^{25} 1.3349, d_4^{25} 1.4749, $MR_{calc.}$ 31.80, MR_{found} 32.33. Anal. Calc. for $C_5H_5ClF_6O$: Cl, 15.38. Found: Cl, 14.53.

Twenty-nine grams of a material boiling at $70^\circ/30$ mm.- $76^\circ/27$ mm. was also isolated. Its infrared spectrum showed the absence of hydroxyl and carbonyl groups and was very similar to that of the β -chloroethyl ether. It was believed to be the diether of diethylene glycol, $(CF_3CHFClCF_2OCH_2CH_2-)_2O$, and it had the constants: n_D^{28} 1.3281, d_4^{28} 1.5452, $MR_{calc.}$ 53.31, MR_{found} 53.35. However, analysis did not confirm the proposed structure.

d. Preparation of $CF_3CH_2OCH_2CHClCH_2OCH_2CF_3$

Fifty grams (0.19 mole) of $CF_3CH_2OCH_2CH(OH)CH_2OCH_2CF_3$ in 100 ml. of chloroform was treated with 44 g. (0.21 mole) of
Ed., Chemical Rubber Publishing Co., Cleveland, Ohio
 (1946).

phosphorus pentachloride by the same procedure as in the preceding reaction. Distillation resulted in 28 g. (0.10 mole, a 54% yield) of $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CHClCH}_2\text{OCH}_2\text{CF}_3$, b.p. $59^\circ/6$ mm. - $63^\circ/7$ mm., n^{26}_D 1.3587, d^{26}_4 1.3933, $\text{MR}_{\text{calc.}}$ 42.68, MR_{found} 43.35. Anal. Calc. for $\text{C}_7\text{H}_9\text{ClF}_6\text{O}_2$: Cl, 12.91. Found: Cl, 13.92.

e. Preparation of $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$

The ether, $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ (101 g., 0.70 mole) in 350 ml. of chloroform was treated with 167 g. (0.80 mole) of phosphorus pentachloride by the procedure just described. Fractionation of the dried reaction mixture resulted in 60 g. (0.37 mole, a 53% yield) of $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$, b.p. $114-15^\circ/\text{atm. press.}$, n^{27}_D 1.3590, d^{27}_4 1.3034, $\text{MR}_{\text{calc.}}$ 27.18, MR_{found} 27.46. Anal. Calc. for $\text{C}_4\text{H}_6\text{ClF}_3\text{O}$: C, 29.56; H, 3.72; Cl, 21.81. Found: C, 29.41; H, 3.68; Cl, 22.08.

f. Preparation of $\text{C}_2\text{F}_5\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$

Thirty-nine grams (0.20 mole) of $\text{C}_2\text{F}_5\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ in 100 ml. of chloroform was treated with 52 g. (0.25 mole) of phosphorus pentachloride by the customary procedure. Fractionation of the dried product resulted in 21 g. of $\text{C}_2\text{F}_5\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$ (0.099 mole, a 49% yield), b.p. $64^\circ/118$ mm. - $64^\circ/96$ mm. An analytical sample had the constants: b.p. $68^\circ/113$ mm. ($120-1^\circ/\text{atm. press.}$), n^{26}_D 1.3448, d^{26}_4 1.3792, $\text{MR}_{\text{calc.}}$ 31.80, MR_{found} 32.72. Anal. Calc. for

$C_5H_6ClF_5O$: C, 28.25; H, 2.85. Found: C, 27.61; H, 2.93.

g. Preparation of $C_3F_7CH_2OCH_2CH_2Cl$

Forty-four grams (0.18 mole) of $C_3F_7CH_2OCH_2CH_2OH$ in 100 ml. of chloroform was treated with 46 g. (0.22 mole) of phosphorus pentachloride by the usual procedure. There was obtained 31.5 g. (0.12 mole, a 67% yield) of $C_3F_7CH_2OCH_2CH_2Cl$ collected in the range $75^\circ/94$ mm. - $72^\circ/70$ mm. A center fraction had the properties: b.p. $75^\circ/80$ mm., n^{24}_D 1.3381, d^{24}_4 1.4673, $MR_{calc.}$ 36.42, MR_{found} 37.32. Anal. Calc. for $C_6H_6ClF_7O$: Cl, 13.50. Found: Cl, 13.04.

h. Preparation of $CF_3C(CH_3)_2OCH_2CH_2Cl$

Twenty-four grams (0.14 mole) of $CF_3C(CH_3)_2OCH_2CH_2OH$ in 65 ml. of chloroform was treated with 31 g. (0.15 mole) of phosphorus pentachloride. There was obtained 12 g. (0.063 mole, a 45% yield) of $CF_3C(CH_3)_2OCH_2CH_2Cl$, b.p. $71^\circ/92$ mm. - $69^\circ/75$ mm. A center fraction had the constants: b.p. $69^\circ/75$ mm. (135°/atm. press.), n^{24}_D 1.3784, d^{24}_4 1.2102, $MR_{calc.}$ 36.42, MR_{found} 36.34. Anal. Calc. for $C_6H_{10}ClF_3O$: C, 37.81; H, 5.29. Found: C, 37.74; H, 5.02.

C. Discussion of Results

The procedure which was adopted for replacing the

Table IV

Chloroethers Having Fluorine in the Alpha Position
and Ester Derivatives of the Ethers

<u>Compound</u>	<u>Yield</u>	<u>B.P.</u>	<u>n²⁵</u>	<u>d₄²⁵</u>
(1) $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHFC1}^*$	27%	85°/100 mm.	1.3882	1.4471
(2) $\text{CH}_2\text{ClCH}_2\text{OC(=O)CHFC1}$	34%	106°/47 mm.- 105°/45 mm.	1.4369 (23°)	1.4256
(3) $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHCl}_2$	27%	86-7°/33 mm.	1.4270	1.4833
(4) $\text{CH}_2\text{ClCH}_2\text{OC(=O)CHCl}_2$	36%	207-11°/atm. press.	1.4719	1.4544
(5) $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHFCF}_3$	27%	46°/37 mm.	1.3349	1.4749

<u>Compound</u>	<u>MR</u>		<u>%Cl</u>	
	<u>Calc.</u>	<u>Found</u>	<u>Calc.</u>	<u>Found</u>
(2)	32.06	32.20	40.52	40.09
(3)	36.92	36.95	49.83	50.94
(4)	36.93	36.85	55.56	54.85
(5)	31.80	32.33	15.38	14.53

*Prepared by Park and co-workers (44), who reported b.p. 80°/100 mm., n_D²⁰ 1.3929.

Table V

Chloroethers Having Fluorine in the Beta Position

<u>Compound</u>	<u>Yield</u>	<u>B.P.</u>	<u>n_D²⁴</u>	<u>d₄²⁴</u>
(1) (CF ₃ CH ₂ OCH ₂) ₂ CHCl	54%	59°/6 mm.- 63°/7 mm.	1.3587 (26°)	1.3933 (26°)
(2) CF ₃ CH ₂ OCH ₂ CH ₂ Cl	53%	114-15°/atm. press.	1.3590 (27°)	1.3034 (27°)
(3) C ₂ F ₅ CH ₂ OCH ₂ CH ₂ Cl	49%	68°/113 mm., 120-1°/atm. press.	1.3448 (26°)	1.3792 (26°)
(4) C ₃ F ₇ CH ₂ OCH ₂ CH ₂ Cl	67%	75°/80 mm.	1.3381	1.4673
(5) CF ₃ C(CH ₃) ₂ OCH ₂ CH ₂ Cl	45%	69°/75 mm., 135°/atm. press.	1.3784	1.2102

<u>Compound</u>	<u>MR</u>		<u>Calc.</u>			<u>Found</u>		
	<u>Calc.</u>	<u>Found</u>	<u>%C</u>	<u>%H</u>	<u>%Cl</u>	<u>%C</u>	<u>%H</u>	<u>%Cl</u>
(1)	42.68	43.35	-	-	12.91	-	-	13.92
(2)	27.18	27.46	29.56	3.72	21.81	29.41	3.68	22.08
(3)	31.80	32.72	28.25	2.85	-	27.61	2.93	-
(4)	36.42	37.32	-	-	13.50	-	-	13.04
(5)	36.42	36.34	37.81	5.29	-	37.74	5.02	-

hydroxyl group of the α,α -difluoroethers with chlorine was the gradual addition of phosphorus pentachloride to the ether, followed by refluxing for twenty minutes. Yields of 24-7% of the chloroethyl ethers were obtained. The low yields were believed to be due to further etherification of the hydroxyethers, as evidenced by higher boiling materials which were not positively identified. Additional refluxing of the reaction mixture resulted in lower yields of the chloroether and more of the high boiling material.

The chlorination of the β -fluoroethers, formed from the addition of fluoroalcohols to ethylene oxide, was carried out with chloroform as diluent. Yields of 45 - 67% were obtained, and very little higher boiling material was formed.

Two of the chloroethyl α,α -difluoroethers were hydrolyzed with no difficulty by heating with concentrated sulfuric acid. Yields of 34 and 36% of the esters were obtained. One of the esters thus formed, β -chloroethyl dichloroacetate, was a known compound and thus served as proof of structure of the ether, $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHCl}_2$, from which it was prepared.

The infrared spectra of the compounds described in this chapter were also obtained. Of especial interest was the carbonyl stretching absorption of the esters. Although the spectra of relatively few α -haloesters have

been published, it is known that the carbonyl stretch is shifted to shorter wave lengths from that which occurs in unsubstituted esters. Ethyl trichloroacetate absorbs at 5.65 microns (4), and the esters of perfluoroacids have an average value of 5.60 microns for the C=O stretch (25). Saturated, unsubstituted esters exhibit the carbonyl stretching absorption at 5.71 - 5.76 microns (4).

The esters prepared on this project had the following carbonyl absorption: $\text{CH}_2\text{ClCH}_2\text{OC}(=\text{O})\text{CHFCl}$, 5.60 microns; $\text{CH}_2\text{ClCH}_2\text{OC}(=\text{O})\text{CHCl}_2$, 5.67 microns; and $\text{CHCl}_2\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{OC}(=\text{O})\text{CHCl}_2$, 5.62 and 5.70 microns. Thus these esters also display a shift in carbonyl absorption to lower wave lengths from that of the unsubstituted esters.

CHAPTER VI

PREPARATION OF UNSATURATED ETHERS

A. Introduction

Like the glycidyl ethers, vinyl ethers have been known for many years. In 1878 Wislicenus (63) prepared vinyl ethyl ether by heating chloroacetal with sodium at 130-40°. Its synthesis from acetal by heating with phosphorus pentoxide and quinoline was reported in 1898 by Claisen (13).

Vinyl alkyl ethers are commonly prepared by the reaction of alcohols with acetylene at about 120-80° in strongly alkaline medium, a procedure which was patented by Reppe (51). Shostakovskii and Gracheva (56) have prepared α -methylvinyl alkyl ethers by the analogous reaction of primary alcohols with methylacetylene.

Several unconventional methods for the preparation of vinyl alkyl ethers have been reported. Adelman (1) described the reaction of primary aliphatic alcohols with vinyl acetate in the presence of mercuric sulfate at low temperatures to form the vinyl ether and acetic acid. Shostakovskii et al. (57) found that by heating unsymmetrical acetals to 140-50°, decomposition to a vinyl ether and an alcohol occurred. Reppe (50) reported the reaction of

vinyl chloride with sodium alkoxides in alcohol solution to form the corresponding vinyl ether when heated to 100° for about twelve hours.

The dehydrohalogenation of α - and β -haloethyl ethers has been reported by many workers. α -Chloroethyl ethers are rather unstable and form the corresponding vinyl ethers when they are heated with pyridine (28). The synthesis of the α -chloroethyl ethers is accomplished by the reaction of acetaldehyde with the appropriate alcohol and hydrogen chloride:



β -Haloethers are in general stable compounds and require much more drastic treatment in order to form the vinyl ethers. Chalmers (12) found that it was necessary to heat β -chloroethyl ethers with powdered sodium hydroxide. He obtained much lower yields of vinyl ethers from the β -bromoalkyl ethers, a result which he attributed to the formation of dialkyl ethers of diethylene glycol. Lawson (34) prepared $\text{CH}_2=\text{CHOCF}_2\text{CHFCl}$ by heating the β -iodoethyl ether with a mixture of powdered sodium hydroxide and soda lime. α,β -Unsaturated ethers of the type $\text{RCH}=\text{C}(\text{OR}')\text{R}''$ have been prepared by a four-step procedure, of which the final reaction was dehydrobromination of the β -bromoether by heating with finely powdered potassium hydroxide (33).

A study of the anesthetic properties of vinyl tri-

fluoroethyl ether and vinyl pentafluoropropyl ether ($\text{CH}_2=\text{CHOCH}_2\text{C}_2\text{F}_5$) has been made, and some physical constants of the former vinyl ether are reported (32,38). However, no description of the preparation of these vinyl fluoroalkyl ethers was found.

B. Experimental

1. Discussion of procedure

The final step in the proposed synthesis of vinyl fluoroalkyl ethers, the dehydrochlorination of the β -chloroethyl ethers, was the most difficult part of the procedure. Some of the desired vinyl ethers were prepared by reaction of the chloroethyl ethers with alcoholic potassium hydroxide, but the yields were low. Treatment of the chloroethyl ethers with powdered sodium or potassium hydroxide was ineffective as a means of obtaining the vinyl ethers.

Because of the limited success in dehydrochlorinating β -chloroethyl fluoroalkyl ethers, several other methods of preparing vinyl ethers, using fluoroalcohols, were attempted. The reaction of alcohols with acetylene was not used because of lack of proper safety equipment; however, the less hazardous methylacetylene was reacted with trifluoroethyl alcohol, and a small amount of α -methylvinyl

trifluoroethyl ether was obtained. The reaction of an alcohol with vinyl acetate by the procedure of Adelman (1) was unsuccessful, as was Reppe's (50) vinyl chloride reaction. Preparation of the β -chloroethyl ether of trifluoroethyl alcohol by reaction of the alcohol with acetaldehyde and hydrogen chloride was also attempted without success.

The preparation of allyl trifluoroethyl ether was carried out in order that a comparison of its spectrum with that of vinyl trifluoroethyl ether could be made.

2. Procedures and results

a. Dehydrochlorination of $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHFCl}$

Thirty-eight grams (0.19 mole) of $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHFCl}$ was placed in a 500-ml., three-necked flask equipped with mechanical stirrer, addition funnel, and distilling head. A solution of 18 g. (0.32 mole) of potassium hydroxide in 120 ml. of *n*-propyl alcohol was added dropwise to the ether, with heating and vigorous stirring. Salt formation began immediately. A distillate consisting of a mixture of vinyl ether and alcohol was collected over the approximate range 65-70°. It was poured into ice water, and the organic layer was separated, washed several times with water, and dried over anhydrous sodium sulfate. Fractionation through the 15-cm. column resulted in 16 g. (0.10

mole, 52% yield) of the vinyl ether, $\text{CH}_2=\text{CHOCF}_2\text{CHFC1}$, b.p. $71-3^\circ$, n_D^{25} 1.3531, d_4^{25} 1.2408, $\text{MR}_{\text{calc.}}$ 26.72, MR_{found} 28.06. Lawson (34) reported for this compound a boiling point of 71.4° .

Treatment of the β -chloroethyl ether with aqueous potassium hydroxide and with tri-n-butyl amine was ineffective as a means of preparing the vinyl ether.

b. Attempted dehydrochlorination of $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHCl}_2$

The dehydrochlorination of this ether was attempted by the procedure described above, using n-butyl and n-amyl alcohols, but none of the vinyl ether was isolated. Considerable salt formation occurred during the reaction, and a yellow-brown solid material, believed to be a polymer of the desired vinyl ether, remained in the reaction flask. A mixture of powdered sodium hydroxide and soda lime was also used with no success.

c. Attempted dehydrochlorination of $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHFCF}_3$

Solutions of potassium hydroxide in ethyl alcohol and n-propyl alcohol, and powdered potassium hydroxide, were all tried as dehydrochlorinating agents for $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHFCF}_3$. However, in no case was the vinyl ether isolated.

d. Dehydrochlorination of $\text{CH}_2\text{ClCH}_2\text{OCH}_2\text{CF}_3$

Twenty-five grams (0.15 mole) of $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$ was

treated with a solution of 17 g. (0.3 mole) of potassium hydroxide in 100 ml. of absolute ethyl alcohol by the procedure described in a. for $\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHFCl}$. Fractionation of the dried organic layer resulted in 6 g. (0.048 mole, a 32% yield) of the vinyl ether boiling over the range $42-55^\circ$. A low boiling fraction was collected which had the constants: b.p. $42-8^\circ$, n^{27} 1.3180, d_4^{27} 1.118, $\text{MR}_{\text{calc.}}$ 21.85, MR_{found} 22.24. The constants reported for $\text{CH}_2=\text{CHOCH}_2\text{CF}_3$ are as follows: b.p. 42.7° , d^{25} 1.13 (32, 38).

A sample furnished by Air Reduction Company, Inc., had the constants n^{27} 1.3168, d_4^{27} 1.118, when measured with the same equipment as the ether prepared above. Its infrared spectrum was almost identical with that of the prepared vinyl ether.

e. Dehydrochlorination of $\text{C}_2\text{F}_5\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$

Seventeen grams (0.080 mole) of $\text{C}_2\text{F}_5\text{OCH}_2\text{CH}_2\text{Cl}$ was treated with a solution of 11 g. (0.20 mole) of potassium hydroxide in 70 ml. of absolute ethyl alcohol by the usual procedure. Fractionation of the dried product resulted in about three grams (0.017 mole, 21% yield) of the vinyl ether, $\text{CH}_2=\text{CHOCH}_2\text{C}_2\text{F}_5$, boiling in the range $52-76^\circ$, of which a center fraction had the constants: b.p. $54-60^\circ$, n^{27} 1.3131, d_4^{27} 1.227, $\text{MR}_{\text{calc.}}$ 26.47, MR_{found} 27.92.

Anal. Calc. for $C_5H_5F_5O$: C, 34.10; H, 2.86. Found: C, 34.51; H, 3.22.

f. Dehydrochlorination of $C_3F_7CH_2OCH_2CH_2Cl$

The chloroether, $C_3F_7CH_2OCH_2CH_2Cl$ (25.5 g., 0.097 mole), was treated with a solution of 11 g. (0.20 mole) of potassium hydroxide in 70 ml. of absolute ethyl alcohol. There was obtained four grams (0.018 mole, an 18% yield) of $CH_2=CHOCH_2C_3F_7$ collected in the range 77 - 95°. From this an analytical sample had the constants: b.p. 78 - 82°, n_D^{26} 1.3111, d_4^{26} 1.343, $MR_{calc.}$ 32.56, MR_{found} 31.08.

Anal. Calc. for $C_6H_5F_7O$: C, 31.87; H, 2.23. Found: C, 32.01; H, 2.49.

g. Attempted dehydrochlorination of $CF_3C(CH_3)_2OCH_2CH_2Cl$

Nine grams (0.047 mole) of $CF_3C(CH_3)_2OCH_2CH_2Cl$ was treated with 5.5 g. (0.098 mole) of potassium hydroxide in 35 ml. of absolute ethyl alcohol. However, only starting material was recovered.

h. Dehydrochlorination of $CF_3CH_2OCH_2CHClCH_2OCH_2CF_3$

Thirty-six grams (0.13 mole) of the chloroether was placed in a 200 ml., three-necked flask equipped with mechanical stirrer, reflux condenser, and addition funnel. Fourteen grams (0.25 mole) of potassium hydroxide was dissolved in 30 ml. of methyl alcohol and added dropwise to the ether with stirring. A precipitate formed, and the

reaction mixture became warm. It was heated and stirred for an hour after the addition of the alcoholic potassium hydroxide. It was then filtered, and two layers became apparent. The lower layer was separated, dried over anhydrous sodium sulfate, and distilled. From it was obtained 19 g. of the original chloroether only. The upper or alcohol layer was distilled at reduced pressure, and a fraction boiling at 29 - 52°/28 mm. was obtained. This was washed with water and dried over anhydrous sodium sulfate. Fractionation through the 15-cm. column resulted in two grams (0.0084 mole, a 6.5% yield) of the unsaturated ether, $\text{CF}_3\text{CH}_2\text{OCH}=\text{CHCH}_2\text{OCH}_2\text{CF}_3$, b.p. 86 - 90°/34 mm., n_{24}^{24} 1.3536, d_4^{24} 1.3533, $\text{MR}_{\text{calc.}}$ 37.35, MR_{found} 38.21. Absorption of the C=O stretch was apparent in the infrared spectrum. However, the analyses were somewhat different from the theoretical values, probably indicating the presence of impurities.

1. Reaction of trifluoroethyl alcohol with methylacetylene

A solution of 9 g. of potassium hydroxide in 100 g. (1 mole) of trifluoroethyl alcohol was placed in the small autoclave, which was cooled in a Dry Ice-acetone bath. Fifty-two grams (1.3 moles) of methylacetylene was collected in a Dry Ice trap and added to the contents of the bomb, which was then sealed and rocked at 225° for 18 hours. It was cooled to room temperature, the excess methylacetylene

was allowed to escape, and the contents were poured into ice water. Twenty grams of an organic layer formed and was separated, washed, and dried over anhydrous sodium sulfate. Distillation resulted in 6 g. (0.04 mole, 4% yield) of material boiling over the range 50 - 67°, which was believed to be $\text{CH}_2=\text{C}(\text{CH}_3)\text{OCH}_2\text{CF}_3$, with the constants: n_D^{26} 1.3322, d_4^{26} 1.107, $\text{MR}_{\text{calc.}}$ 24.73, MR_{found} 25.98. Nine grams of unidentified higher boiling material was also obtained.

Although the α -methylvinyl ether was probably impure, as evidenced by unsatisfactory analyses, the compound is of interest for its infrared absorption in the double bond region. Impurities are likely to be polymers or hydrolysis products, which probably would not interfere in this region.

j. Reaction of trifluoroethyl alcohol with allyl chloride

Twenty-five grams (0.45 mole) of potassium hydroxide was dissolved in 115 g. (1.15 mole) of trifluoroethyl alcohol, and the solution was placed in a 500 ml., three-necked flask equipped with mechanical stirrer, reflux condenser, and addition funnel. Thirty-four grams (0.44 mole) of allyl chloride was added dropwise to the refluxing mixture, with stirring. A large amount of white precipitate was formed. The mixture was refluxed one hour after

Table VI

Unsaturated Fluoroethers

<u>Compound</u>	<u>Yield</u>	<u>B.P.</u> ¹	<u>n_D²⁵</u>	<u>d₄²⁵</u>
(1) $\text{CH}_2=\text{CHO CF}_2\text{CHFC l}^2$	52%	71-3°	1.3531	1.2408
(2) $\text{CH}_2=\text{CHOCH}_2\text{CF}_3^3$	32%	42-8°	1.3180 (27°)	1.118 (27°)
(3) $\text{CH}_2=\text{CHOCH}_2\text{C}_2\text{F}_5$	21%	54-60°	1.3131 (27°)	1.227 (27°)
(4) $\text{CH}_2=\text{CHOCH}_2\text{C}_3\text{F}_7$	18%	78-82°	1.3111 (26°)	1.343 (26°)
(5) $\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CF}_3$	21%	74.5-74.8°	1.3360	1.092 (24°)

<u>Compound</u>	<u>MR</u>		<u>Calc.</u>		<u>Found</u>	
	<u>Calc.</u>	<u>Found</u>	<u>%C</u>	<u>%H</u>	<u>%C</u>	<u>%H</u>
(3)	26.47	27.92	34.10	2.86	34.51	3.22
(4)	32.56	31.08	31.87	2.23	32.01	2.49
(5)	26.47	26.62	42.86	5.04	42.45	5.15

¹At atmospheric pressure.

²Lawson (34) prepared this ether, b.p. 71.4°.

³Air Reduction Company, Inc., reports the constants:

b.p. 42.7°/753 mm., n_D²⁰ 1.3193; Krantz et al. (32) report a specific gravity of 1.13 at 25°.

the addition of all the allyl chloride. It was then cooled, filtered, and distilled through the 65-cm. column at atmospheric pressure. The following fractions were obtained:

Fraction 1 -- b.p. 43-6° -- 9 g.

Fraction 2 -- b.p. 61-70° -- 26 g. (flat 66°)

Fraction 3 -- b.p. 73-6° -- 58 g.

Residue -- about 5 g.

Fraction 1 was probably unreacted allyl chloride, and 3 was chiefly trifluoroethyl alcohol. Fraction 2 was washed with cold water, dried over anhydrous sodium sulfate, and distilled through the 15-cm. column. Thirteen grams (0.093 mole, a 21% yield) of allyl trifluoroethyl ether boiling in the range 61 - 75° was obtained. From a center fraction of this an analytical sample had the constants: b.p. 74.5 - 74.8°, n_D^{24} 1.3360, d_4^{24} 1.092, $MR_{calc.}$ 26.47, MR_{found} 26.62. Anal. Calc. for $C_5H_7F_3O$: C, 42.86; H, 5.04. Found: C, 42.45; H, 5.15.

C. Discussion of Results

The results obtained from the dehydrochlorination of the β -chloroethyl ethers indicate that this is not a satisfactory method for the preparation of vinyl fluoroethers. Only one vinyl ether having fluorine in the alpha position was isolated: $CH_2=CHOCF_2CHFCl$. This compound

had been prepared earlier by Lawson (34). Some vinyl ethers having fluorine in the beta position were prepared but in low yields. These were $\text{CH}_2=\text{CHOCH}_2\text{CF}_3$, $\text{CH}_2=\text{CHOCH}_2\text{C}_2\text{F}_5$, and $\text{CH}_2=\text{CHOCH}_2\text{C}_3\text{F}_7$; and an impure sample of $\text{CF}_3\text{CH}_2\text{OCH}=\text{CHCH}_2\text{OCH}_2\text{CF}_3$ was obtained.

However, the ethers which were prepared were sufficient for the determination of the effect of fluorine substitution in the alkyl group of vinyl alkyl ethers on their infrared absorption spectra.

Inability to prepare vinyl ethers from two of the chloroethers having fluorine in the alpha position was probably due to the reactivity of both the chloro derivative and the corresponding vinyl ether.

The low yields of vinyl β -fluoroalkyl ethers were probably the result of the reactivity of the vinyl ethers, for there was evidence of both polymerization and hydrolysis. Considerable salt formation indicated that dehydrochlorination had occurred.

The lack of success with the other methods of preparing vinyl ethers may be due, at least in part, to the unusual acidic properties of the fluoroalcohols. Vinyl ethyl ether, for example, was prepared in fair yield by the reaction of acetaldehyde, ethyl alcohol, and hydrogen chloride to form ethyl α -chloroethyl ether, followed by dehydrochlorination with pyridine. However, when the same

reaction was attempted with trifluoroethyl alcohol, only a trace of the vinyl ether was obtained, as shown by the infrared absorption of the distillate.

The base-catalyzed addition of trifluoroethyl alcohol to methylacetylene resulted in a very low yield of impure α -methylvinyl trifluoroethyl ether.

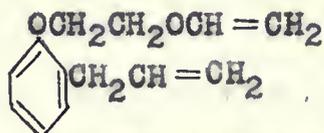
Allyl trifluoroethyl ether was prepared by the reaction of allyl chloride with trifluoroethyl alcohol and potassium hydroxide.

CHAPTER VII

PROPERTIES OF VINYL AND GLYCIDYL FLUOROETHERS

A. Introduction

This work on vinyl ethers grew out of an infrared spectral study by G. B. Butler (11) of the selective polymerization of monomers possessing both vinyloxy and allylic substituents, such as



Polymerization was carried out at low temperature with boron trifluoride as catalyst, a procedure which was believed to affect only the vinyloxy group, leaving the allyl double bond unchanged. The monomers exhibited two bands in the region of carbon-carbon double bond stretching absorption, one at 6.18 microns which disappeared entirely in the polymer and a second at 6.08 microns which was much weaker in the polymer; the portion of this band remaining in the polymer could be attributed to the allyl double bond. The strongest band in the spectrum of the monomer, at 8.32 microns, was also completely missing in the polymer spectrum. Because these three bands diminished in intensity or disappeared entirely when the vinyloxy group was lost in the polymerization process, they were believed to be associated with this group.

Recently, Haas and Simon (22) obtained analogous results in a study of the acid-catalyzed polymerization of β -vinylloxyethyl methacrylate, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COCH}_2\text{CH}_2\text{OCH}=\text{CH}_2$.

Infrared bands which they reported present in the monomer and diminished or missing from the spectrum of the polymer were: 6.10, 6.17, 7.58, 8.30, and 10.2 microns. They found similar changes in the spectra of vinyl butyl ether and its polymer.

The 6.08 and 6.18 micron bands can be assigned immediately to the carbon-carbon double bond stretching vibration; however, the very strong 8.32 micron band cannot be accounted for as easily. Saturated unsubstituted ethers are known to exhibit strong absorption near 9.00 microns which is believed to be due to a vibration involving the carbon-oxygen bond (2, 61). Esters and aromatic ethers have this band at a lower wave length, in the region of 8.00-8.30 microns (2). Thompson and Torkington (60) found a strong band near 8.00 microns in esters which they attributed to a vibration primarily controlled by a carbon-oxygen bond. Tschamler and Leutner (61) reported that compounds having the structure $-\text{C}-\text{O}-\text{C}-$, such as esters, acids, lactones, and mixed aliphatic aromatic ethers always have two intense bands, 7.87-8.70 and 8.92-9.70 microns. Thus the 8.32 band, present in the vinylloxy monomer and missing in the polymer spectrum, is probably the result of a

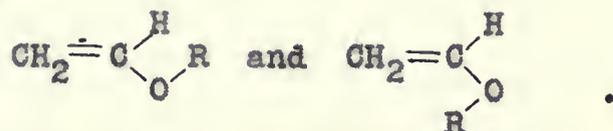
vibration associated with the carbon-oxygen bond of the vinyloxy group.

The substitution of electronegative atoms, such as chlorine or fluorine, alpha to an ether oxygen has been shown by E. W. McKisson (40) to shift the characteristic C-O-C band near 9.00 microns to lower wave lengths. Bands at 8.2-8.4 microns in the spectra of α, α -difluoroethers were believed to be analogous to the 9.00 micron band of saturated, unsubstituted ethers.

Several studies have been made of the vibration spectra of vinyl ethers. Davison and Bates (14) studied the infrared absorption due to carbon-carbon double bond stretch and olefinic carbon-hydrogen deformation vibrations of five vinyl alkyl ethers: ethyl, butyl, isobutyl, 2-ethylhexyl, and 2-chloroethyl. Kirrmann and Chancel (30) compared the infrared and Raman spectra of the first three vinyl ethers listed and of vinyl allyl ether. Both groups of investigators reported doubling of the carbon-carbon double bond stretching frequency and attributed it to rotational isomerism. The latter group listed the 8.30 micron band as present in the infrared spectra of all four vinyl ethers; but it was absent in their Raman spectra. They made no assignment of this band. Batuev, Prilezhaeva, and Shostakovskii (3) had earlier made a systematic study of the Raman spectra of eight vinyl ethers: methyl, ethyl,

propyl, isopropyl, butyl, isobutyl, isoamyl, and isooctyl. They found the very sharp and characteristic carbon-carbon double bond stretching vibration to be a triplet: 6.06, 6.10, 6.25 microns. This they believed to be due to rotational isomerism which results in the doublet 6.07, 6.25, along with Fermi-resonance splitting of the 6.07 (1645 cm.^{-1}) band through interaction with the overtone of a band at 12.2 microns (820 cm.^{-1}).

To explain the existence of rotational isomers, Batuev *et al.* (3) postulated a resonance structure for vinyl ethers, $\bar{\text{C}}\text{H}_2\text{-CH}=\overset{\dagger}{\text{O}}\text{-R}$, for which rotation of the alkyl group about the carbon-oxygen bond would be hindered, resulting in the isomers:



In addition to the infrared and Raman spectra of vinyl ethers, a number of independent lines of evidence lend support to the proposed resonance. For instance, the heat of hydrogenation (16) of ethyl vinyl ether is 26.7 kcal. per mole, while that of the corresponding hydrocarbon, butene-2, is 30.3 kcal. per mole, indicating a resonance energy of about 3.6 kcal. per mole. Allyl alcohol, on the other hand, shows a slight exaltation of the heat of hydrogenation, with a value of 31.6 kcal. per mole. It is interesting that the heat of hydrogenation of divinyl ether

is only 57.2 kcal., indicating the same resonance energy as in ethyl vinyl ether. Wheland (62) has explained this fact as due to the impossibility of maintaining without strain the planar molecule which would be required if resonance with both double bonds occurred.

Shostakovskii (54) originally proposed the resonance structure for vinyl ethers in order to explain their unusual chemical reactivity. Not only do numerous reagents add to the double bond, including alcohols, carboxylic acids, halogens, and hydrogen halides, but in addition vinyl ethers are readily hydrolyzed if a trace of acid is present and they are easily polymerized with acid catalysts (53, 55). In contrast, allyl ethers are not readily hydrolyzed, and more drastic conditions are required for their polymerization.

However, no direct proof of the existence of rotational isomerism in vinyl ethers has been reported. Mizushima et al. (43) demonstrated the presence of rotational isomers of chloroacetone by observing the effect of temperature changes on the intensities of infrared bands which were due to the isomers. A rise in temperature increases the intensity of the band resulting from the higher-energy form and decreases that of the lower-energy isomer. In the present work a similar procedure has been applied to the carbon-carbon double bond stretching bands

of a vinyl alkyl ether.

The infrared absorption spectra of epoxy compounds have recently been the subject of considerable study, and characteristic bands for the ethylene oxide ring have been reported. Field et al. (19) definitely identified a band at 7.94 - 8.07 microns as characteristic of the epoxy group. Shreve and co-workers (58) also noted the presence of the 8.0 micron band, but suggested that a pair of bands near 11 and 12 microns was more useful in identifying the epoxy structure. Patterson (47) studied a series of epoxy compounds, including glycidyl butyl ether, which had bands at 10.90 and 11.95 microns, and glycidyl phenyl ether, with corresponding absorption at 10.94 and 11.84 microns. A band at 13.2 microns was also observed which may be characteristic of the epoxy group.

B. Experimental

1. Discussion of procedure

a. Materials

The vinyl and glycidyl fluoroethers were prepared by the procedures described in the preceding chapters, and the freshly distilled analytical samples were used in determining their infrared spectra and other physical properties. In addition, a sample of vinyl trifluoroethyl ether was

generously supplied by Air Reduction Company, Inc. They reported it to be the purest they have been able to make, having the constants: b.p. $42.7^{\circ}/753$ mm., n_D^{20} 1.3193. Although it contained 0.01% phenyl α -naphthylamine as a stabilizer, this was too little to interfere with the infrared absorption at the concentration used.

The vinyl butyl ether was a product of Delta Chemical Works. It was fractionated through a 15-cm. column packed with Berl saddles, and a portion boiling at 93.3° was used.

The vinyl 2-ethylhexyl ether was obtained from Carbide and Carbon Chemicals Co. It was also distilled, and a center fraction having the following properties was used: b.p. $177^{\circ}/\text{atm. press.}$, n_D^{23} 1.4266, d_4^{23} 0.8055.

Glycidyl ethyl ether was prepared by the acid-catalyzed addition of ethyl alcohol to epichlorohydrin, followed by dehydrochlorination with aqueous sodium hydroxide. Its constants were: b.p. 128° , n_D^{25} 1.4070, d_4^{25} 0.9377, compared with b.p. $124-6^{\circ}$, n_D^{25} 1.406, d_4^{25} 0.94, reported by Fairbourne et al. (18).

b. Determination of spectra

The infrared spectra were determined with a Perkin-Elmer Model 21 double-beam infrared recording spectrophotometer equipped with sodium chloride optics. The region 3.75-5.75 microns was omitted from the figures because of

the absence of any significant absorption of the ethers in this range. The spectra were recorded at a speed of approximately 0.5 micron per minute. A slit schedule of 927 was used, response of 1, and gain of 6.

Most of the vinyl ethers were too volatile to allow the determination of their infrared absorption as liquids in a demountable cell. The spectrum of liquid vinyl 2-ethylhexyl ether is included, however, for comparison with its solution spectrum. Approximately 0.2 M solutions of the vinyl ethers in Eastman Spectro Grade carbon tetrachloride were prepared and placed in a cell of 0.1 mm. thickness, with compensating cell of about the same thickness containing carbon tetrachloride only.

The study of the effect of temperature on the intensity of the carbon-carbon double bond stretching bands was performed with a demountable cell which could be heated with less danger of serious damage to the cell. Vinyl 2-ethylhexyl ether was used because of its relatively high boiling point. The cell was heated by wrapping with heating tape. Attempts to obtain low-temperature spectra were unsuccessful because of interfering absorption from moisture which immediately condensed on the cold cell when it was exposed to the air.

The glycidyl ethers were less volatile than the vinyl ethers, and spectra of the liquids are given. The solution

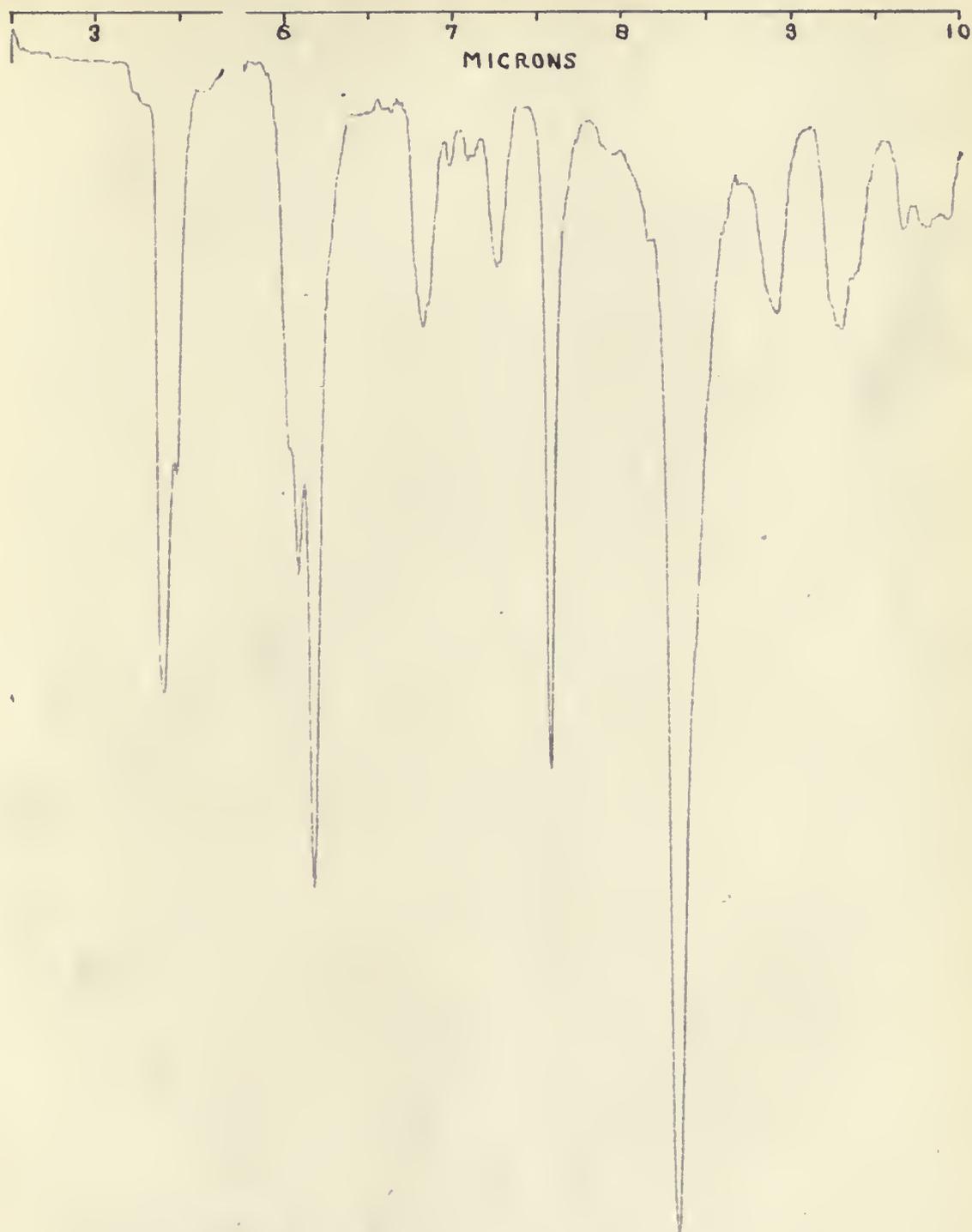


FIG. 1
 $\text{CH}_2=\text{CHOC}_4\text{H}_9$
SOLUTION IN CCl_4

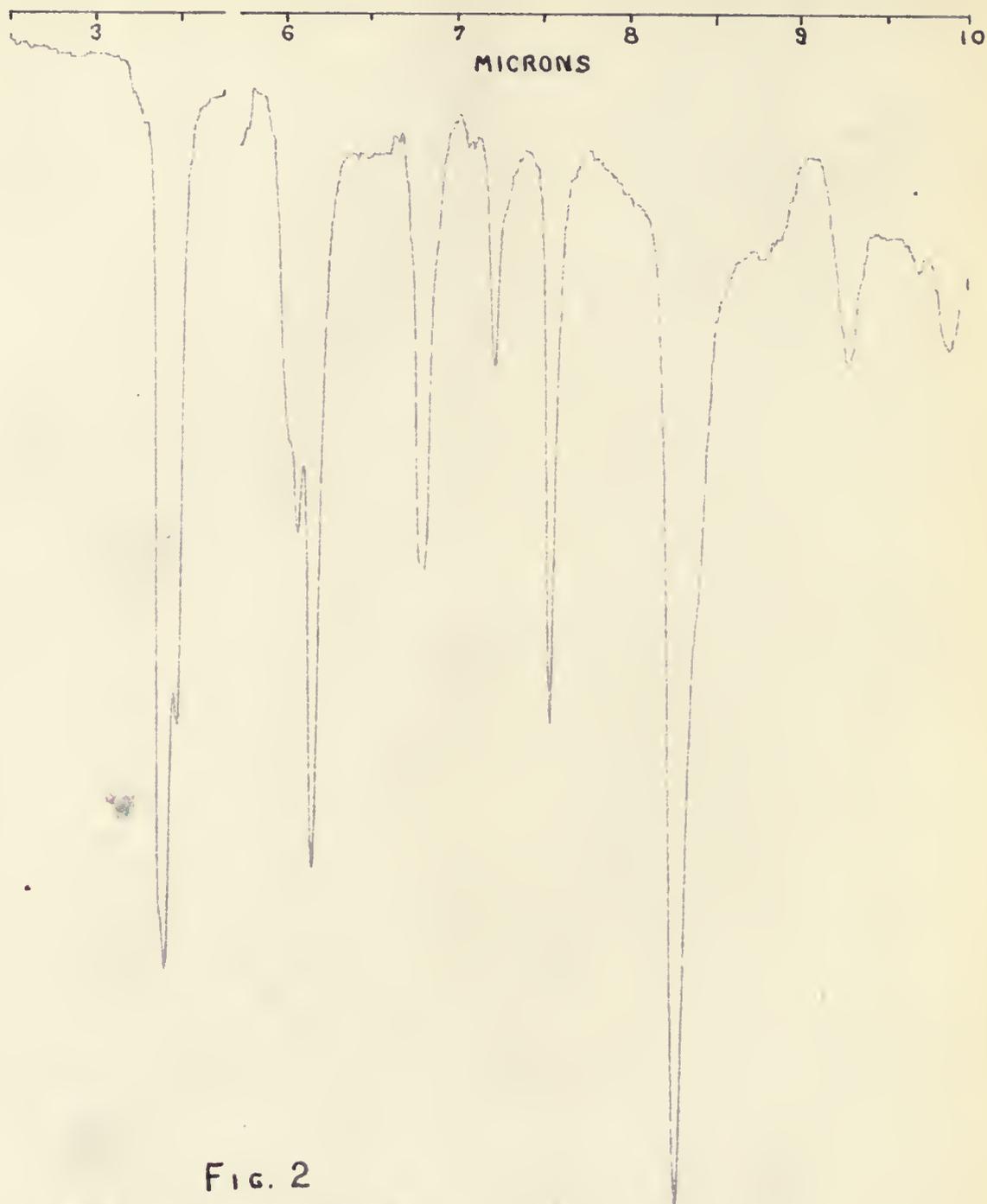


FIG. 2
 $\text{CH}_2=\text{CHOCH}_2\underset{\text{C}_2\text{H}_5}{\text{CH}}\text{C}_4\text{H}_9$
SOLUTION IN CCl_4

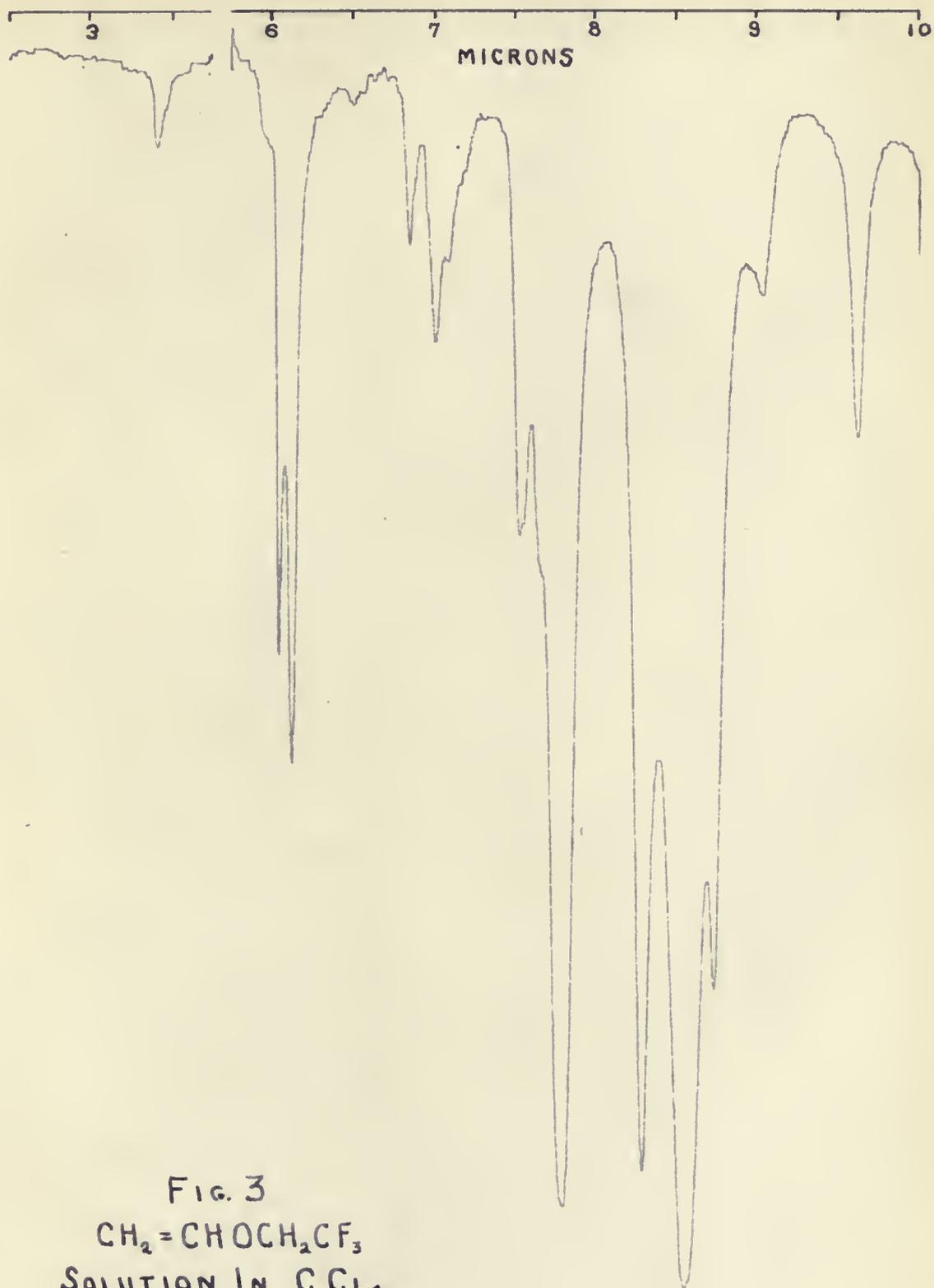


FIG. 3
 $\text{CH}_2=\text{CHOCH}_2\text{CF}_3$
SOLUTION IN CCl_4

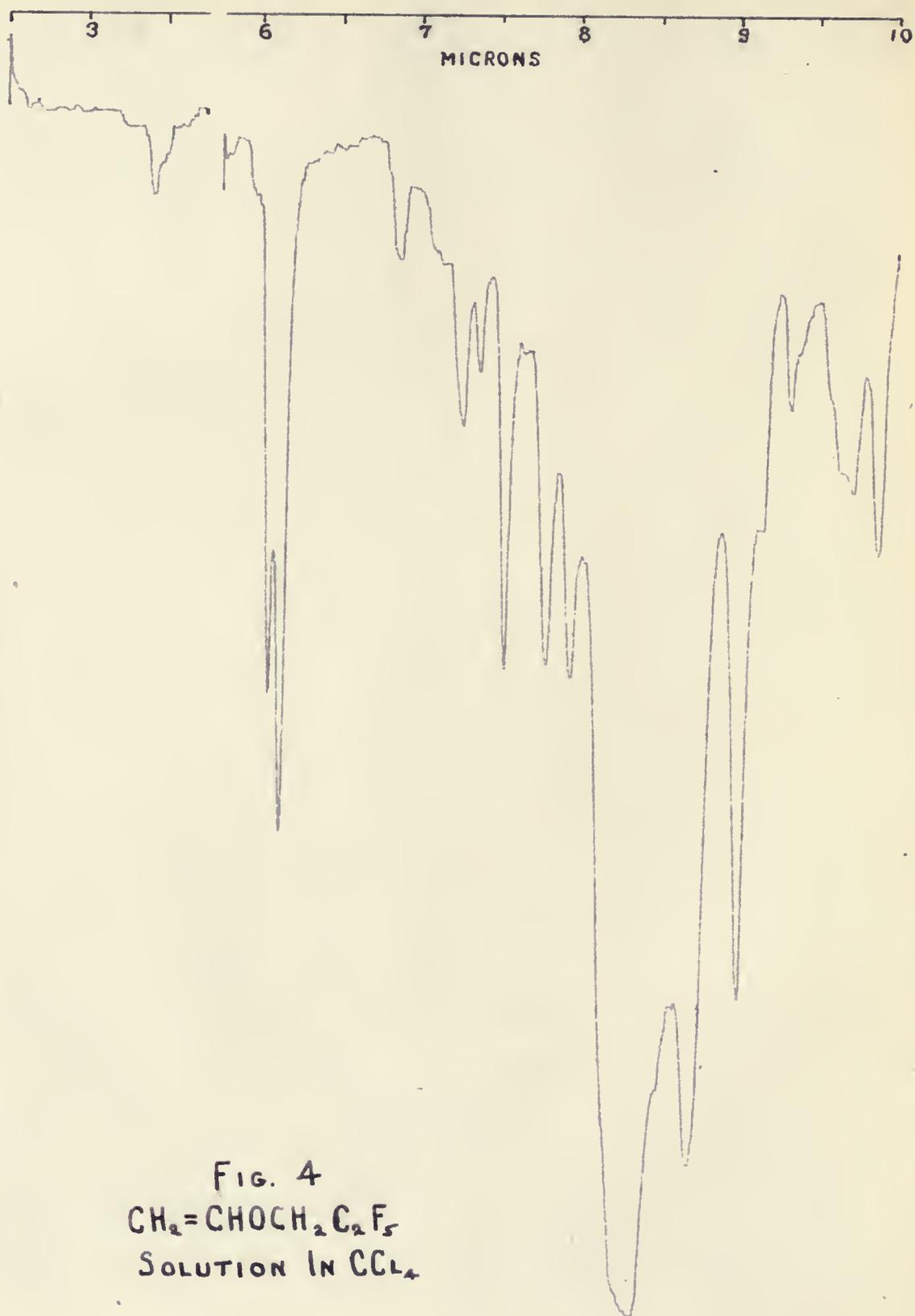


FIG. 4
 $\text{CH}_2=\text{CHOCH}_2\text{C}_2\text{F}_5$
SOLUTION IN CCl_4



FIG. 5
 $\text{CH}_2=\text{CHOCH}_2\text{C}_3\text{F}_7$
SOLUTION IN CCl_4

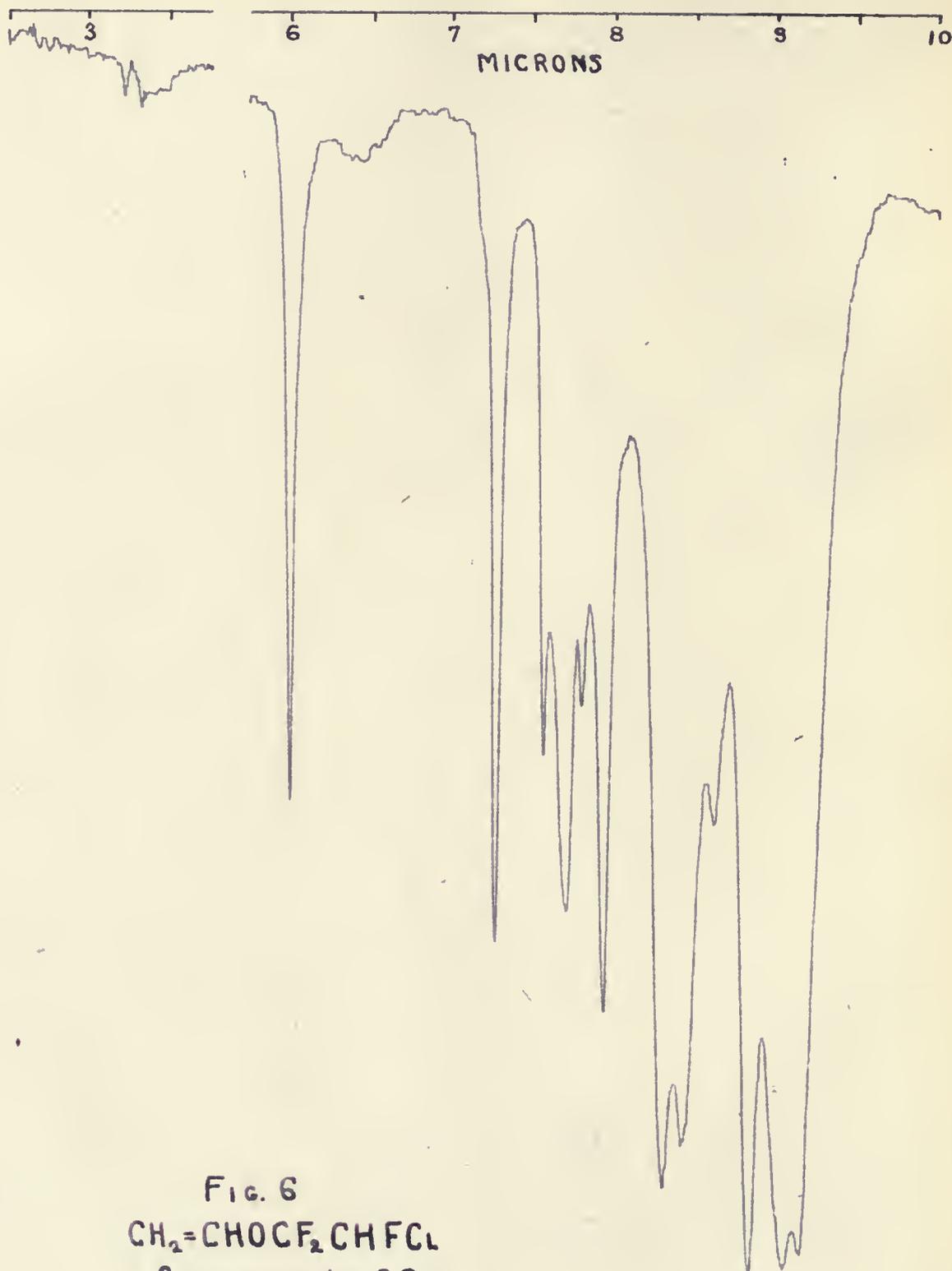
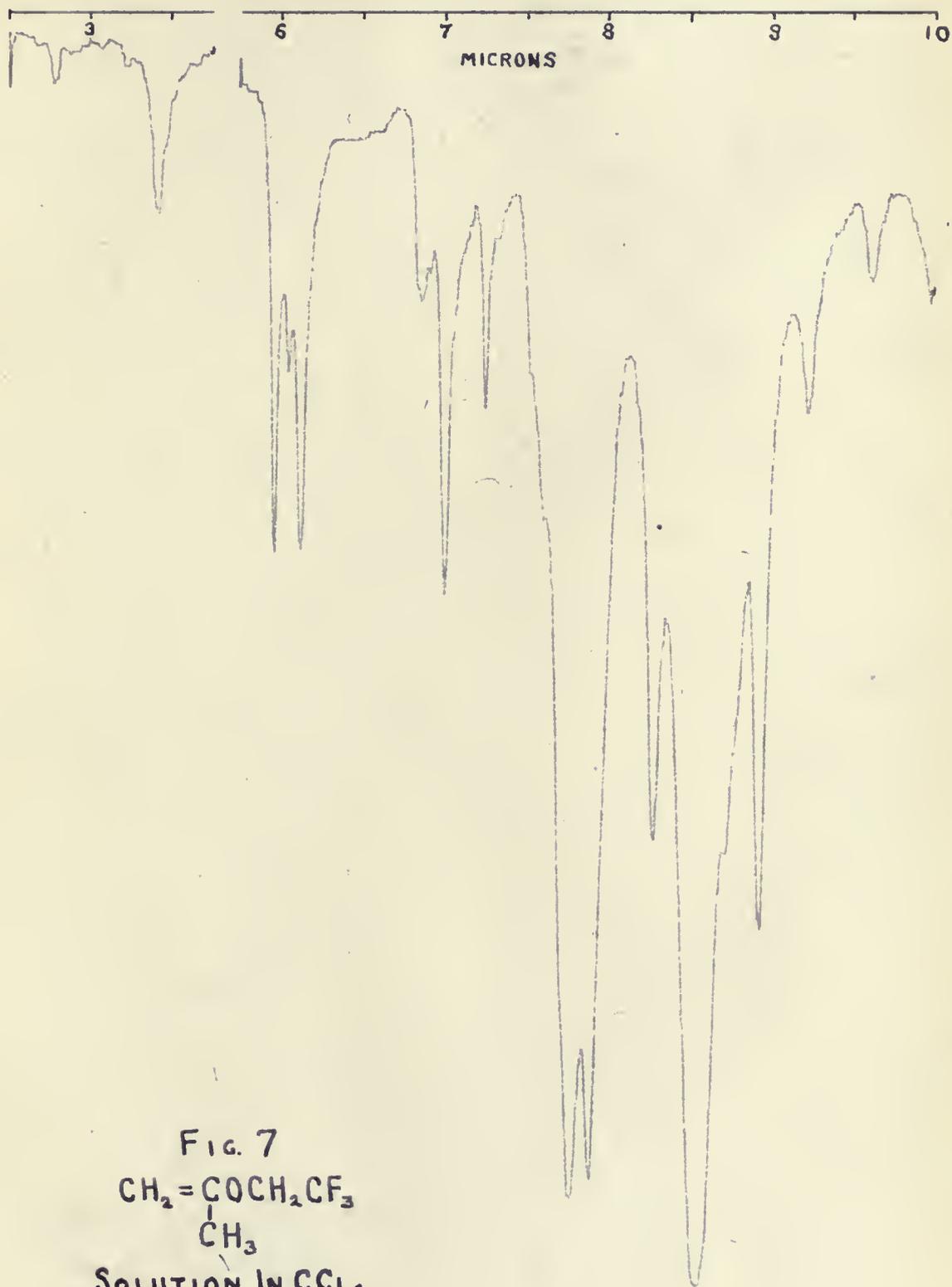
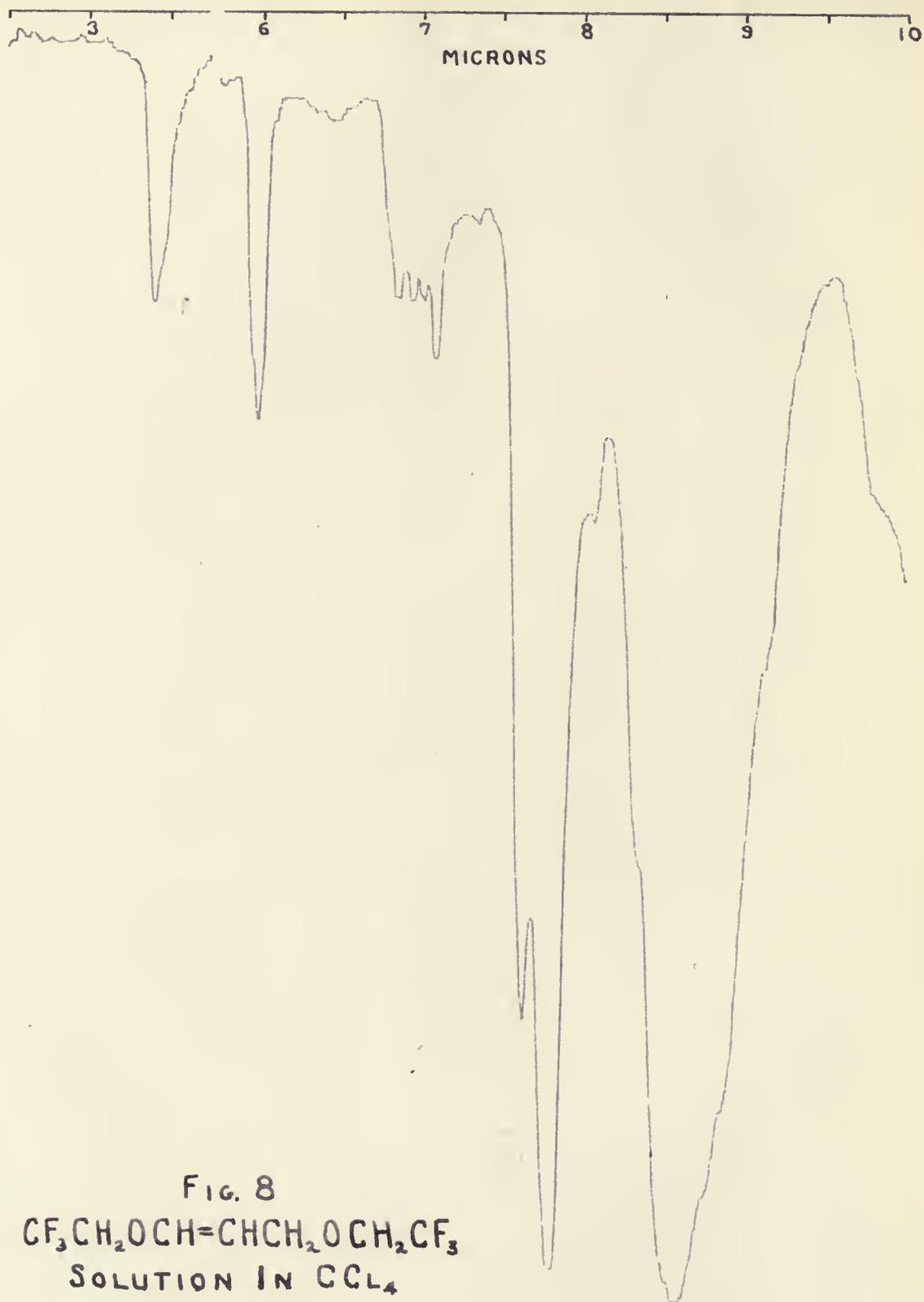


FIG. 6
 $\text{CH}_2=\text{CHO CF}_2\text{CH FCl}$
SOLUTION IN CCl_4





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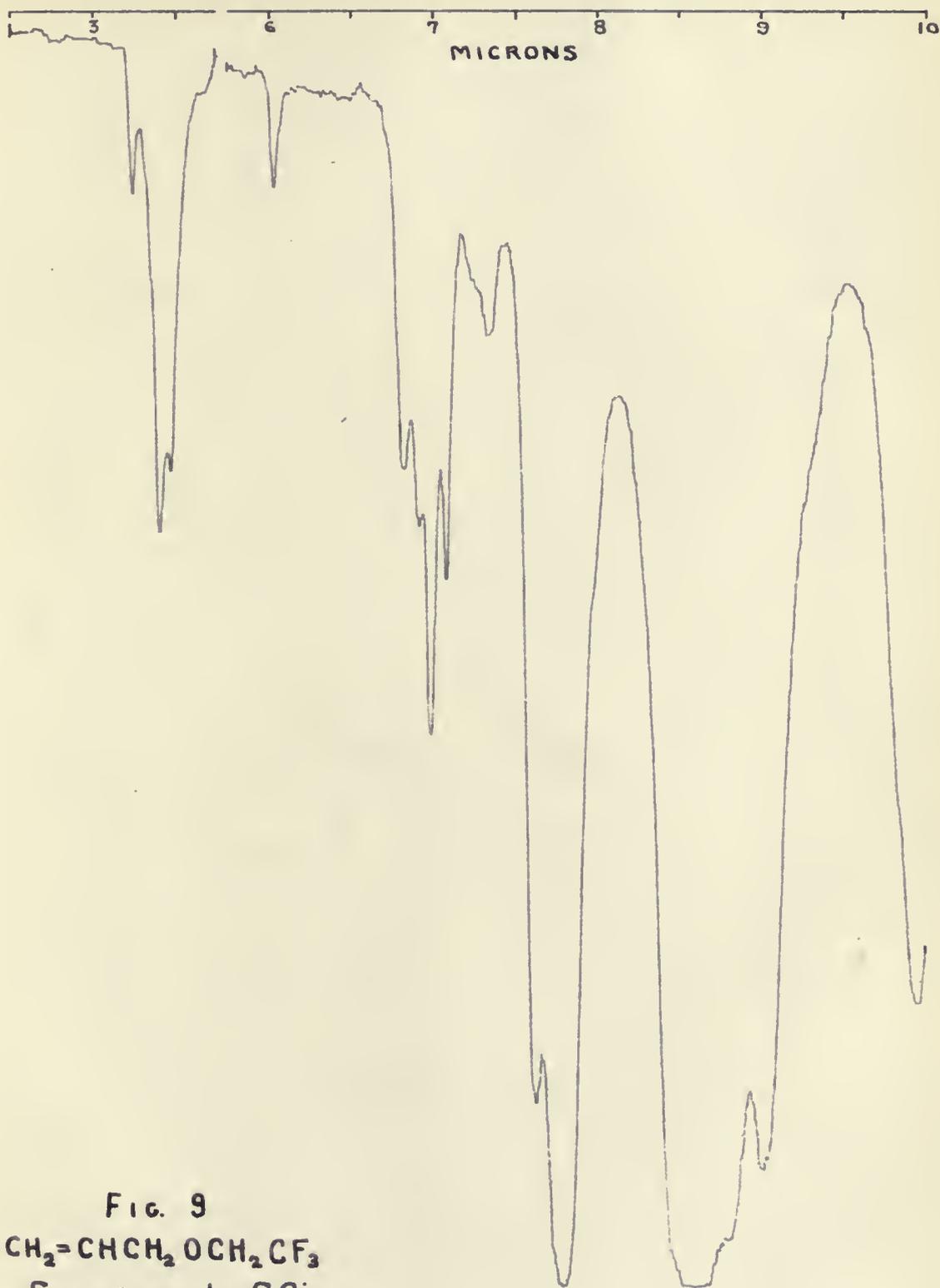


FIG. 9

$\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CF}_3$
SOLUTION IN CCl_4

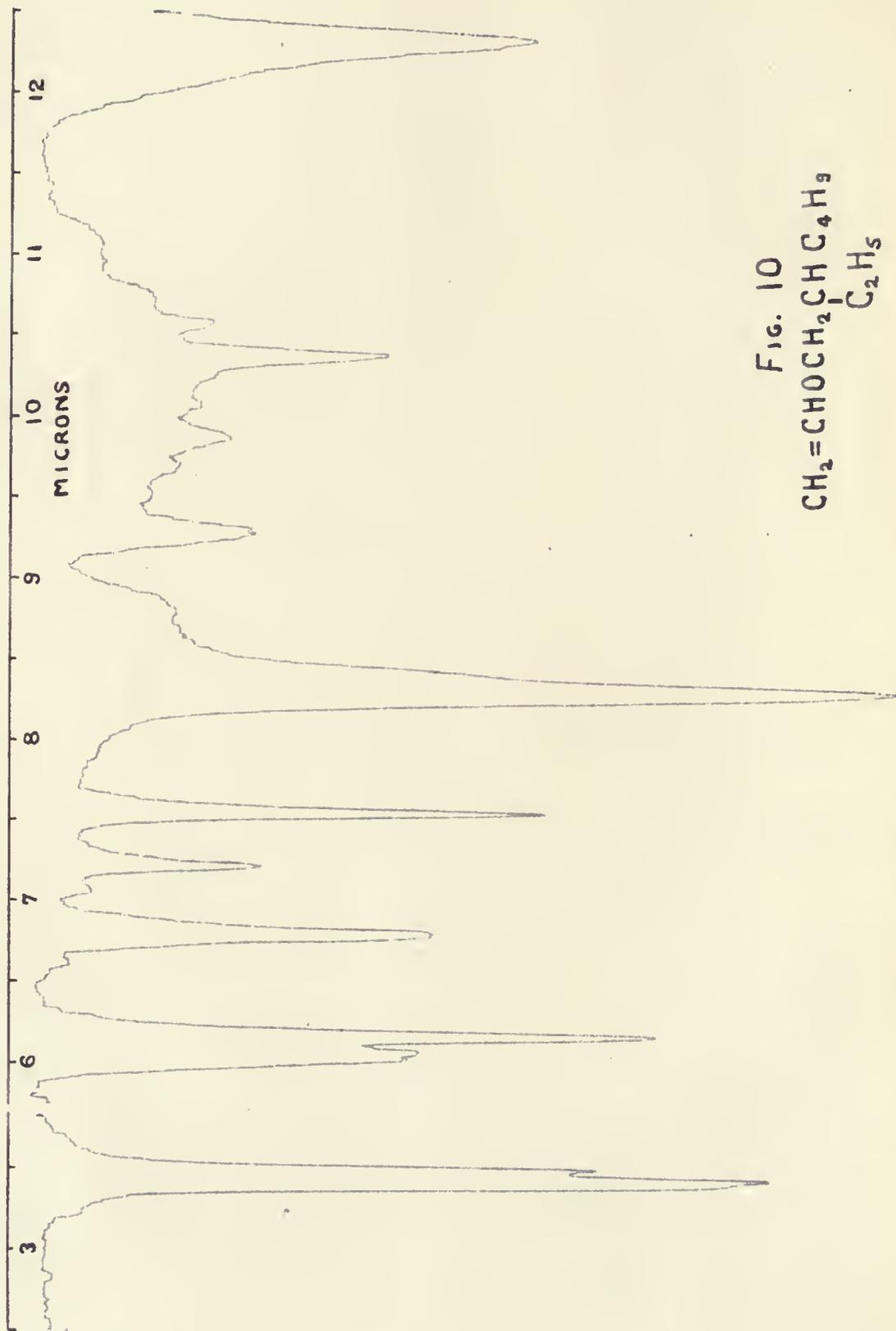
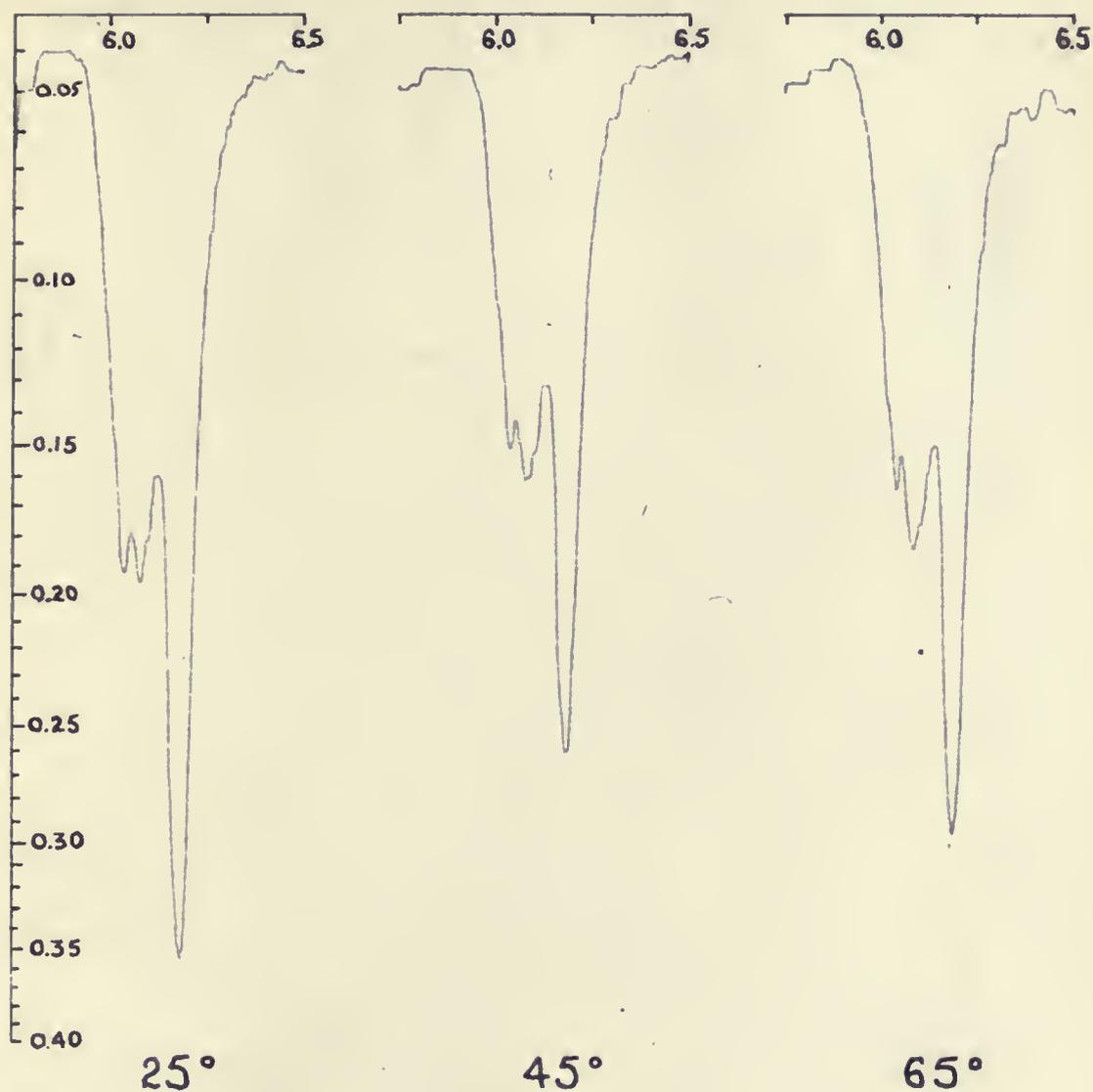


FIG. 10
 $\text{CH}_2=\text{CHOCH}_2\underset{\text{C}_6\text{H}_5}{\text{CH}}\text{C}_4\text{H}_9$



ABSORBANCE

FIG. 11
 EFFECT OF TEMPERATURE
 ON ABSORPTION NEAR SIX MICRONS
 OF $\text{CH}_2=\text{CHOCH}_2\underset{\text{C}_2\text{H}_5}{\text{CH}}\text{C}_2\text{H}_5$

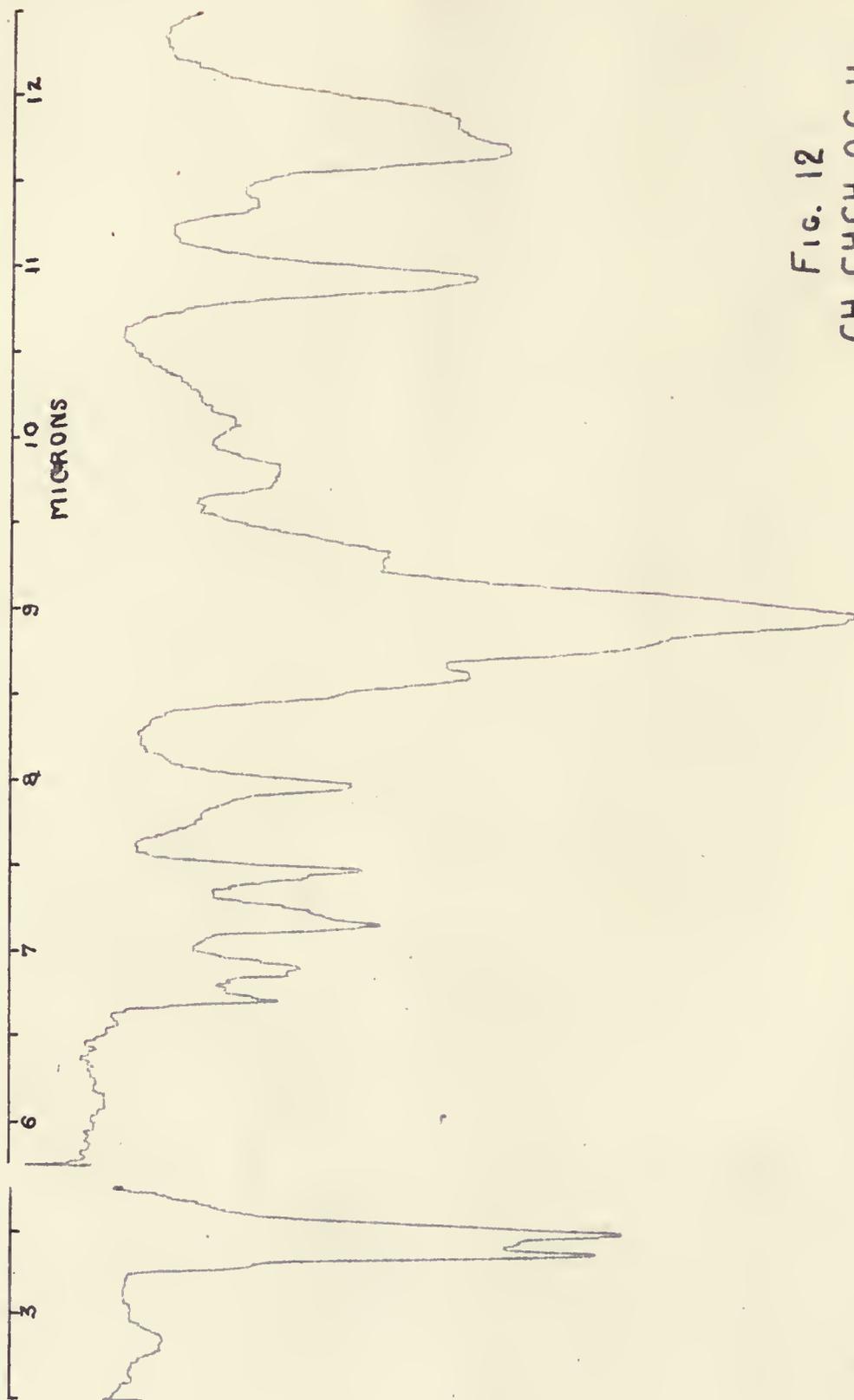


FIG. 12
 $\text{CH}_2\text{CHCH}_2\text{OC}_2\text{H}_5$

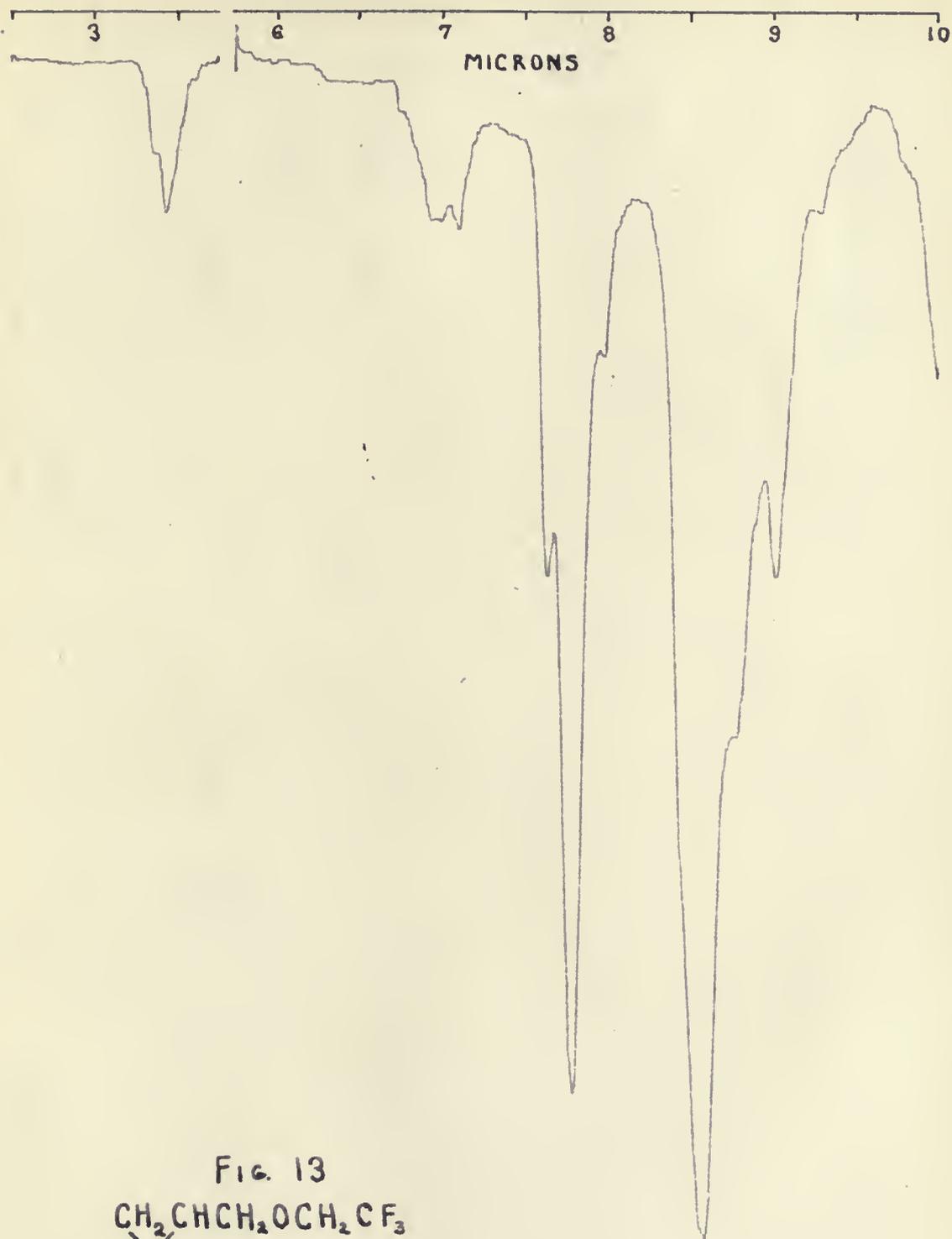


FIG. 13
 $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$
O
SOLUTION IN CCl_4

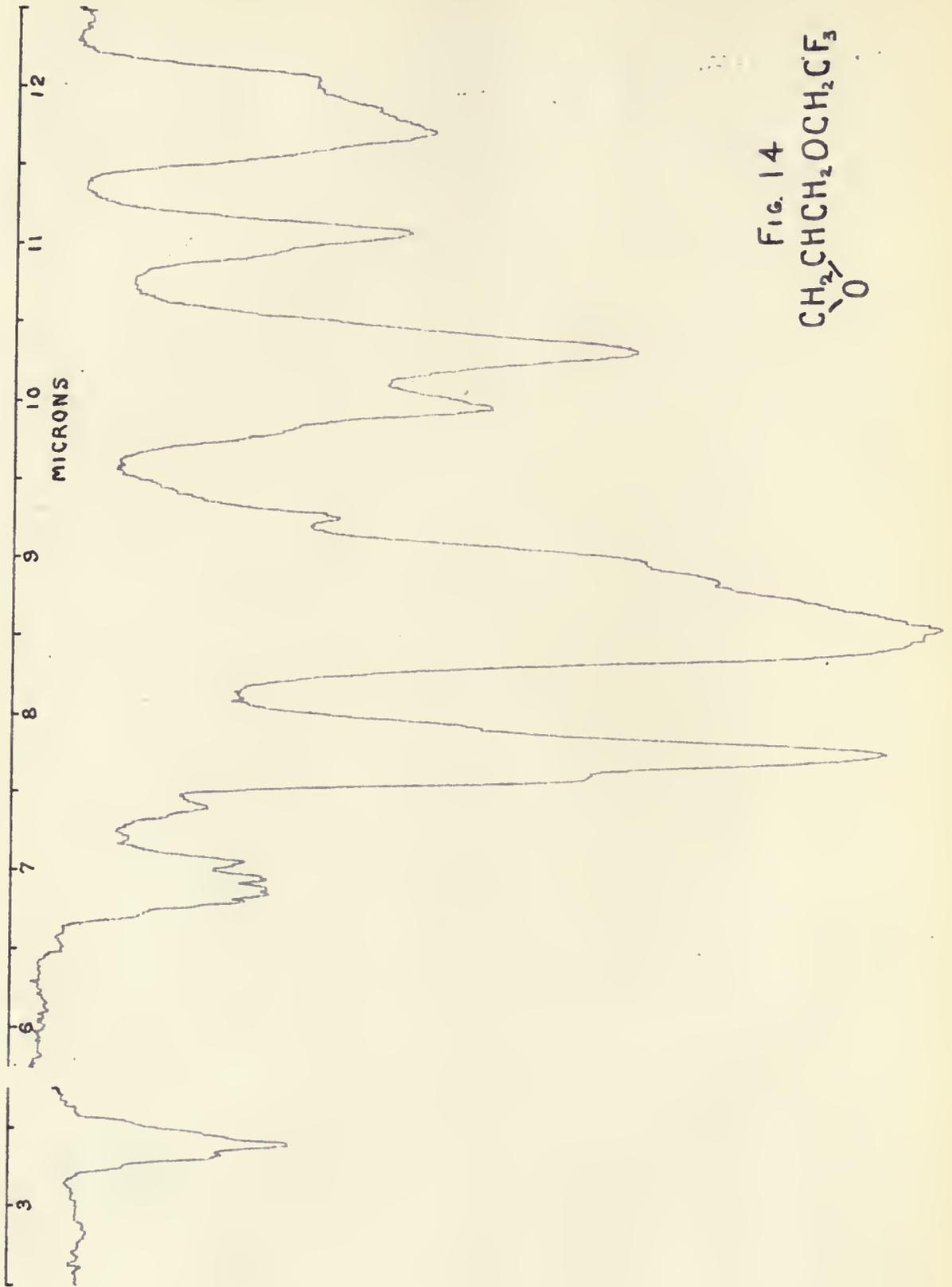


FIG. 14



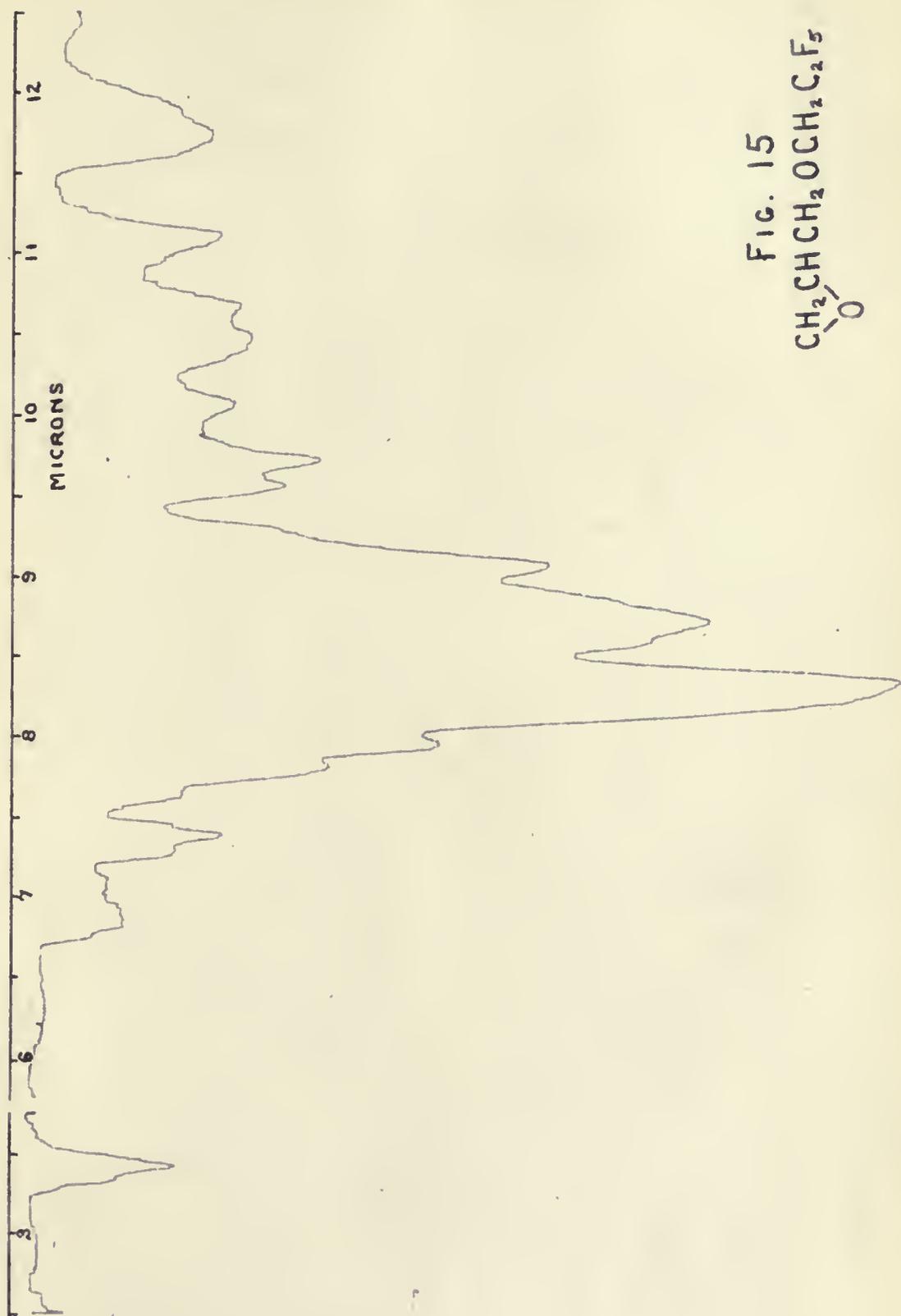


FIG. 15
 $\text{CH}_2\text{CHCH}_2\text{OCH}_2\text{C}_2\text{F}_5$

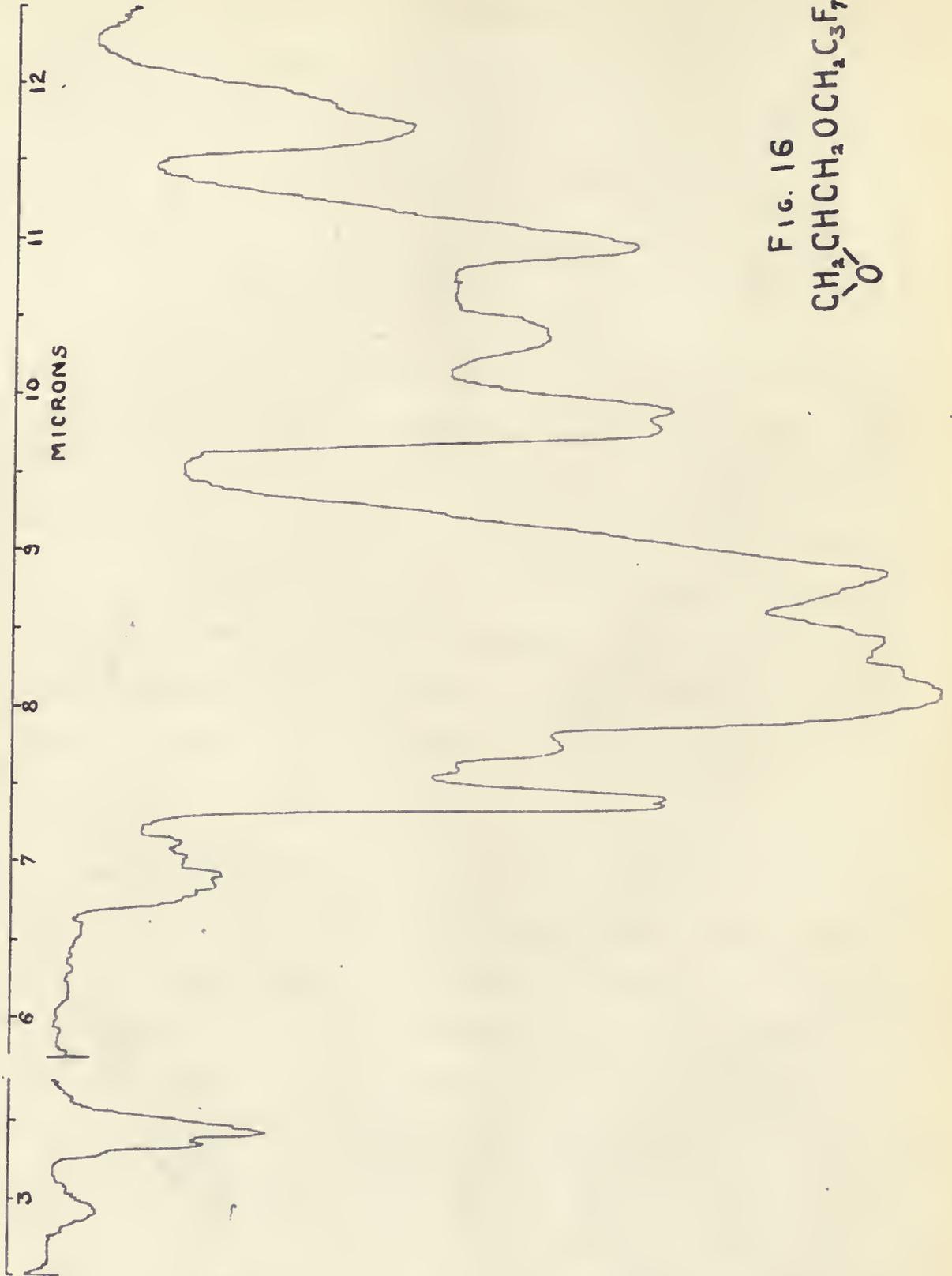


FIG. 16
 $\text{CH}_2\text{CHCH}_2\text{OCH}_2\text{C}_3\text{F}_7$

spectrum of glycidyl trifluoroethyl ether is also included for comparison with that of the liquid.

C. Discussion of Results

1. Vinyl ethers

C-H stretch

The olefinic carbon-hydrogen stretching vibrations near 3.25 and 3.30 microns (4) appear only as weak shoulders in the spectra of the vinyl ethers. Strong alkyl carbon-hydrogen stretching absorption is present in the spectra of the butyl and 2-ethylhexyl ethers at ca. 3.40 and 3.50 microns. The fluoroethers have much weaker absorption in this region, as a result of the relatively smaller number of alkyl hydrogen atoms present.

C=C stretch

In Table VII are shown the wave lengths in microns of the bands associated with the carbon-carbon double bond stretching vibration. For vinyl ethers, this vibration has been reported by Davison and Bates (14) and Kirrmann and Chancel (30) to appear in the infrared as the doublet 6.12, 6.20 microns, of which the latter band is always more intense. Batuev et al. (3) found that in the Raman spectra of vinyl ethers having a secondary alkyl group the 6.21 band was not as intense as the 6.05, 6.10 pair which they

reported present in all the vinyl ethers. This they attributed to different relative amounts of rotational isomers present.

Table VII

C=C Stretching Wave Lengths (Microns)

$\text{CH}_2=\text{CHOC}_4\text{H}_9$	-----6.05 shoulder, 6.10 medium, 6.19 strong
$\text{CH}_2=\text{CHOCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$	--6.06 weak, 6.09 weak, 6.20 strong
$\text{CH}_2=\text{CHOCH}_2\text{CF}_3$	-----6.08 medium, 6.15 medium
$\text{CH}_2=\text{CHOCH}_2\text{C}_2\text{F}_5$	-----6.06 medium, 6.13 medium
$\text{CH}_2=\text{CHOCH}_2\text{C}_3\text{F}_7$	-----6.06 medium, 6.13 medium
$\text{CH}_2=\text{CHOCF}_2\text{CHFCl}$	-----6.05 medium
$\text{CH}_2=\text{C}(\text{CH}_3)\text{OCH}_2\text{CF}_3$	-----5.99 medium, 6.07 weak, 6.16 medium
$\text{CF}_3\text{CH}_2\text{OCH}=\text{CHCH}_2\text{OCH}_2\text{CF}_3$	-----5.99 shoulder, 6.02 medium
$\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CF}_3$	-----6.06 weak

Perhaps the vinyl fluoroethers present an analogous situation. The intensity of the lower wave length band (6.06-6.08 microns) relative to that of the second band (6.13-6.15 microns) of the C=C doublet is lowest in $\text{CH}_2=\text{CHOCH}_2\text{CF}_3$, increases in $\text{CH}_2=\text{CHOCH}_2\text{C}_2\text{F}_5$, and is still greater in $\text{CH}_2=\text{CHOCH}_2\text{C}_3\text{F}_7$, so that in the last the bands are nearly equal in intensity. The steric hindrance of

the perfluoro groups may stabilize the isomer corresponding to the 6.06-6.08 micron band. These bands are at a slightly lower wave length than in nonfluorinated vinyl ethers.

The spectrum of vinyl butyl ether exhibits the typical doublet at 6.10, 6.19 microns. The shoulder at 6.05 microns may correspond to the 6.05 line of the triplet 6.05, 6.10, 6.21 reported by Batuev et al. (3) for the Raman spectrum of this ether. Meakins (41) has reported a shoulder in the infrared spectrum of this ether at 6.06 microns, but it is not mentioned for any of the vinyl ethers in the other infrared studies (14, 30). The solution spectrum of vinyl 2-ethylhexyl ether exhibits a similar shoulder at 6.06 microns, which becomes a distinct band in the liquid spectrum, in addition to the 6.09, 6.20 doublet. Davison and Bates (14) reported only two bands, at 6.13 and 6.21 microns, for this compound.

The α, α -difluoroether, $\text{CH}_2=\text{CHOCF}_2\text{CHFC1}$, has a single $\text{C}=\text{C}$ stretching band, at 6.05 microns. Thus the strong inductive effect of two fluorine atoms substituted in the alkyl group alpha to the oxygen atom prevents conjugation of the oxygen electrons with the double bond. The single bond character of the carbon-oxygen bond is restored, so that rotation is sufficiently free to prevent the existence of stable isomers. The inductive effect of fluorine in the beta position, insulated from the oxygen atom by a

methylene group, is not sufficient to overcome the resonance, as evidenced by the doublet at 6.06-6.08, 6.13-6.15 microns in the spectra of the vinyl β -fluoroethers.

The α -methylvinyl fluoroether, $\text{CH}_2=\text{C}(\text{CH}_3)\text{OCH}_2\text{CF}_3$, possesses three bands in this region: 5.99, 6.07, and 6.16 microns. The internal vinylic ether, $\text{CF}_3\text{CH}_2\text{OCH}=\text{CHCH}_2\text{OCH}_2\text{CF}_3$, exhibits a shoulder at 5.99 microns and a band at 6.02 microns.

The spectrum of allyl trifluoroethyl ether is shown for contrast with that of vinyl trifluoroethyl ether. The allyl ether has only a single weak band at 6.06 microns.

In Table VIII are shown the results of the study of the effect of temperature upon the intensities of the three bands in the carbon-carbon stretching absorption of vinyl 2-ethylhexyl ether as a liquid. It may be seen from this table that the ratio of band I (6.06 microns) to band III (6.20 microns) remains constant, within the experimental error of the measurement. The ratio of band II (6.09 microns) to band III (6.20 microns), however, increases noticeably with increasing temperature. Bands I and III must therefore be due to one isomer, the more stable form, and band II is then due to the higher-energy isomer. If these bands correspond to the triplet, 6.05, 6.10, 6.20 microns, reported by Batuev *et al.* (3) for vinyl alkyl ethers, then their explanation of the 6.05, 6.10 pair

Table VIII

Effect of Temperature on the C=C Absorption
of Vinyl 2-Ethylhexyl Ether

Band	<u>Absorbance</u>			<u>Ratio to Band III</u>		
	<u>I</u>	<u>II</u>	<u>III</u>	<u>I</u>	<u>II</u>	<u>III</u>
Microns	<u>6.06</u>	<u>6.09</u>	<u>6.20</u>	<u>6.06</u>	<u>6.09</u>	<u>6.20</u>
25°	*0.143	*0.147	*0.305	0.470	0.482	1
	0.188	0.198	0.391	0.481	0.506	1
	0.179	0.181	0.379	0.473	0.477	1
			Average	0.475	0.488	1
45°	*0.101	*0.111	*0.211	0.478	0.525	1
	0.153	0.172	0.326	0.468	0.526	1
	0.161	0.173	0.341	0.473	0.507	1
			Average	0.473	0.519	1
65°	*0.114	*0.134	*0.247	0.462	0.542	1
	0.131	0.149	0.260	0.505	0.632	1
			Average	0.483	0.587	1

*The first values shown at each temperature are those of the bands in Figure 11, page 77. The others are additional measurements for which the spectra are not given.

resulting from splitting of a 6.08 band and thus arising from the same isomeric form is unlikely.

C-H deformation

A series of lines from 6.7 to 7.7 microns present in the Raman spectra of vinyl ethers was attributed by Batuev *et al.* (3) to carbon-hydrogen deformation vibrations. A band at about 7.60 microns which appears in all the spectra of the vinyl ethers of this study and is not present in the substituted vinyl ethers or the allyl ether appears to be characteristic of the vinyloxy group. It is one of the bands reported by Haas and Simon (22) to disappear in the spectrum of the polymerized vinyl ether.

Davison and Bates (14) have reported 10.40 and 10.62 microns as average values for the out-of-plane olefinic carbon-hydrogen deformation bands in the infrared spectra of vinyl ethers. Although vinyl 2-ethylhexyl ether is the only ether for which the spectrum is here shown in the region beyond 10 microns, it was found that all the vinyl ethers studied exhibited the two bands in this region.

C-F stretch

Molecules possessing several fluorine atoms exhibit very intense absorption in the region 7.15 - 10.0 microns (4). Vinyl trifluoroethyl and allyl trifluoroethyl ether both have bands at 7.80 and 8.60 microns which seem to be

characteristic of the CF_3 group. Similar bands are also present in the spectra of $\text{CH}_2=\text{C}(\text{CH}_3)\text{OCH}_2\text{CF}_3$ and $\text{CF}_3\text{CH}_2\text{OCH}=\text{CHCH}_2\text{OCH}_2\text{CF}_3$.

Very strong bands in the spectra of the ethers, $\text{CH}_2=\text{CHOCH}_2\text{C}_2\text{F}_5$ and $\text{CH}_2=\text{CHOCH}_2\text{C}_3\text{F}_7$, also probably due to the carbon-fluorine stretch, occur in the 8-9 micron region.

C-O stretch

In Table IX are shown the wave lengths of a band which is characteristic of the infrared absorption of vinyl ethers and appears to be associated with the carbon-oxygen stretching vibration. This band is in the region

- - - - -

Table IX

C-O Stretching Wave Lengths

$\text{CH}_2=\text{CHOC}_4\text{H}_9$	8.31 microns
$\text{CH}_2=\text{CHOCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$	8.32 microns
$\text{CH}_2=\text{CHOCH}_2\text{CF}_3$	8.31 microns
$\text{CH}_2=\text{CHOCH}_2\text{C}_2\text{F}_5$	strong C-F
$\text{CH}_2=\text{CHOCH}_2\text{C}_3\text{F}_7$	strong C-F
$\text{CH}_2=\text{CHOCF}_2\text{CHFCl}$	8.34, 8.40 microns (?)

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reported by Tschamler and Leutner (61) for the $=\text{C}-\text{O}-\text{C}-$

group. In the case of the fluoroethers carbon-fluorine absorption makes such an assignment more difficult. However, vinyl trifluoroethyl ether does exhibit a band at 8.31 microns which is not present in the spectrum of the corresponding allyl ether.

2. Glycidyl ethers

Weak absorption near 3.27 and 3.33 microns, which is present in the spectra of all the glycidyl ethers in this study, can be attributed to the carbon-hydrogen stretching vibrations of the epoxy group (37). The alkyl carbon-hydrogen stretching vibrations are similar to those of the vinyl ethers. Most of the absorption in the 6.70 - 7.50 micron region is probably due to carbon-hydrogen deformation vibrations.

In the spectrum of glycidyl trifluoroethyl ether, bands at 7.70 and 8.60 microns which were attributed to the CF_3 group in the vinyl ethers are again present. In the region of 8-9 microns the spectrum of $\text{CH}_2\text{CH}(\text{O})\text{CH}_2\text{OCH}_2\text{C}_2\text{F}_5$ resembles that of the corresponding vinyl ether; the same similarity is present for $\text{CH}_2\text{CH}(\text{O})\text{CH}_2\text{OCH}_2\text{C}_3\text{F}_7$ and its corresponding vinyl ether.

From Table X it may be seen that the infrared absorption of the glycidyl ethers near 8.00 microns and near 11

and 12 microns is consistent with the previous studies which reported these bands as characteristic of the epoxy group (19, 47, 58).

Table X

Bands Characteristic of Epoxy Group

<u>Glycidyl Ether</u>	<u>Wave Length in Microns</u>		
C_2H_5-	7.97	10.95	11.70
CF_3CH_2-	7.98	11.08	11.78
$C_2F_5CH_2-$	7.95	11.10	11.74
$C_3F_7CH_2-$	(masked by C-F)	11.00	11.76

The strong band at 9.00 microns in the spectrum of glycidyl ethyl ether is due to a carbon-oxygen stretching vibration. However, strong carbon-fluorine absorption probably masks this band in the spectra of the glycidyl fluoroethers.

SUMMARY

Vinyl fluoroethers were prepared by a three-step procedure: (1) synthesis of a β -hydroxyethyl fluoroether, (2) replacement of the hydroxyl group with chlorine through use of phosphorus pentachloride, and (3) dehydrochlorination of the β -chloroethyl ether by treatment with alcoholic potassium hydroxide.

Two types of β -hydroxyethyl fluoroethers were prepared: those having fluorine present in the alpha position of the alkyl group, by the base-catalyzed addition of ethylene glycol to 1,1-difluoroolefins; and those with fluorine substituted in the beta position, by the addition, in basic medium, of fluoroalcohols to ethylene oxide. The new ethers prepared by the first method were

$\text{CH}_2\text{OHCH}_2\text{OCF}_2\text{CHCl}_2$ and $\text{CH}_2\text{OHCH}_2\text{OCF}_2\text{CHFCl}$. The new β -fluoroethers which were synthesized were $\text{CH}_2\text{OHCH}_2\text{OCH}_2\text{CF}_3$, $\text{CH}_2\text{OHCH}_2\text{OCH}_2\text{C}_2\text{F}_5$, $\text{CH}_2\text{OHCH}_2\text{OCH}_2\text{C}_3\text{F}_7$, and $\text{CH}_2\text{OHCH}_2\text{OC}(\text{CH}_3)_2\text{CF}_3$.

Treatment of the above ethers with phosphorus pentachloride resulted in formation of the corresponding β -chloroethyl ethers in yields of about 20-50%.

By means of the dehydrochlorination reaction, $\text{CH}_2=\text{CHOCH}_2\text{CF}_3$, $\text{CH}_2=\text{CHOCH}_2\text{C}_2\text{F}_5$, and $\text{CH}_2=\text{CHOCH}_2\text{C}_3\text{F}_7$ were prepared in low yields. Only the last-named vinyl ether is a new compound; however the physical constants of only $\text{CH}_2=\text{CHOCH}_2\text{CF}_3$ are present in the literature; no method of

preparation of these vinyl β -fluoroethers has been reported, nor have their infrared spectra been available.

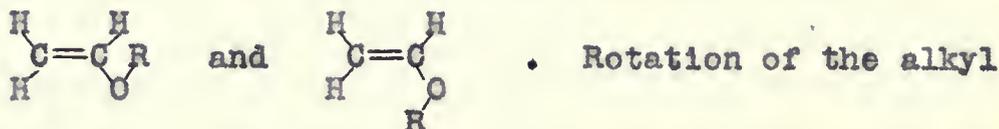
Attempts to prepare vinyl ethers from the chloroethers having fluorine present in the alpha position, $\text{CH}_2\text{ClCH}_2\text{OOCF}_2\text{CHCl}_2$ and $\text{CH}_2\text{ClCH}_2\text{OOCF}_2\text{CHFCl}_2$, were unsuccessful. However, a known vinyl ether, $\text{CH}_2=\text{CHOOCF}_2\text{CHFCl}$, was prepared by this procedure.

A method of preparing glycidyl fluoroethers in one step by the reaction of an α, α -dihydroperfluoroalcohol with epichlorohydrin and an equivalent amount of base was developed. The reaction is analogous to the addition of phenol to epichlorohydrin. The effectiveness of a basic catalyst was attributed to the relative acidity of the fluoroalcohols as compared with unsubstituted alcohols. Yields of glycidyl ethers were rather low when prepared by this procedure because of their further reaction with alcohol to form diethers. Three new glycidyl ethers were prepared: (1) $\text{CH}_2\text{CH}(\text{O})\text{CH}_2\text{OCH}_2\text{CF}_3$, (2) $\text{CH}_2\text{CH}(\text{O})\text{CH}_2\text{OCH}_2\text{C}_2\text{F}_5$, and (3) $\text{CH}_2\text{CH}(\text{O})\text{CH}_2\text{OCH}_2\text{C}_3\text{F}_7$. Diethers of (1) and (3) were isolated. The tertiary fluoroalcohol, $\text{CF}_3\text{C}(\text{CH}_3)_2\text{OH}$, gave none of the glycidyl ether when treated with epichlorohydrin by the same procedure.

The infrared spectra of vinyl and glycidyl fluoroethers are presented, and assignments of bands character-

istic of the functional groups are discussed.

Two lines of confirmatory evidence are given for the existence of vinyl ethers in two isomeric forms:



group about the carbon-oxygen bond is hindered as a result of the contribution of the resonance structure, $\bar{\text{C}}\text{H}_2-\text{CH}=\overset{+}{\text{O}}-\text{R}$. The carbon-carbon double bond absorption, always presenting at least two bands near 6.10, 6.20 microns in the spectra of unsubstituted vinyl alkyl ethers, is replaced by a single band at 6.05 microns in the spectrum of $\text{CH}_2=\text{CHOCF}_2\text{CHFCl}$. Thus the strong inductive effect of the alpha fluorine atoms prevents any conjugation of the unshared pair of oxygen electrons with the double bond. Fluorine substitution in the beta position, as in $\text{CH}_2=\text{CHOCH}_2\text{CF}_3$, does not prevent conjugation, for the usual doublet occurs, shifted to slightly lower wave lengths, in vinyl ethers of this type. The relative intensities of the double bond bands were found to be dependent upon temperature; this can only be explained by the existence of rotational isomers. The 6.20 micron band is attributed to the lower-energy form and the 6.10 micron band to the isomer of higher energy.

BIBLIOGRAPHY

- (1) R. L. Adelman, *J. Am. Chem. Soc.* 75, 2678 (1953).
- (2) R. B. Barnes, R. C. Gore, R. W. Stafford, and V. Z. Williams, *Anal. Chem.* 20, 402 (1948).
- (3) M. I. Batuev, E. N. Prilezhaeva, and M. F. Shostakovskii, *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1947, 123.
- (4) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, N.Y. (1954), p. 156.
- (5) L. Blanchard, *Bull. soc. chim.* 39, 1263 (1926).
- (6) D. R. Boyd, *J. Chem. Soc., Trans.*, 79, 1221 (1901).
- (7) D. R. Boyd and E. R. Marle, *J. Chem. Soc.* 93, 838 (1908).
- (8) D. R. Boyd and E. R. Marle, *J. Chem. Soc.* 105, 2117 (1914).
- (9) W. Bradley, J. Forrest, and O. Stephenson, *J. Chem. Soc.* 1951, 1589.
- (10) W. Brandenburg and A. Galat, *J. Am. Chem. Soc.* 72, 3275 (1950).
- (11) G. B. Butler, *J. Am. Chem. Soc.* 77, 482 (1955).
- (12) W. Chalmers, *Can. J. Research* 7, 464 (1932).
- (13) T. Claisen, *Ber.* 31, 1019 (1898).
- (14) W. H. T. Davison and G. R. Bates, *J. Chem. Soc.* 1953, 2607.

- (15) M. Delacre, Bull. soc. chim. 48, 708 (1887).
- (16) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith, and W. E. Vaughan, J. Am. Chem. Soc. 60, 440 (1938).
- (17) R. C. Elderfield, Heterocyclic Compounds, John Wiley and Sons, Inc., New York (1950), Vol. I, Ch. I.
- (18) A. Fairbourne, G. P. Gibson, and D. W. Stephens, J. Chem. Soc. 1932, 1965.
- (19) J. E. Field, J. O. Cole, and D. E. Woodford, J. Chem. Phys. 18, 1298 (1950).
- (20) H. Flores-Gallardo and C. B. Pollard, J. Org. Chem. 12, 831 (1947).
- (21) E. Fourneau and I. Ribas, Bull. soc. chim. 39, 1584 (1926); 41, 1046 (1927).
- (22) H. G. Haas and M. S. Simon, J. Polymer Sci. 17, 421 (1955).
- (23) L. J. Hals, T. S. Reid, and G. H. Smith, J. Am. Chem. Soc. 73, 4054 (1951).
- (24) W. E. Hanford and G. W. Rigby, U. S. 2,409,274, Oct. 15, 1946; C.A. 41, 982b (1947).
- (25) M. Hauptschein, C. S. Stokes, and E. A. Nodiff, J. Am. Chem. Soc. 74, 4005 (1952).
- (26) A. L. Henne, R. M. Alm, and M. Smook, J. Am. Chem. Soc. 70, 1968 (1948).
- (27) A. L. Henne and W. C. Francis, J. Am. Chem. Soc. 75,

991 (1953)

- (28) C. D. Hurd and D. G. Botteron, *J. Am. Chem. Soc.* 68
1200 (1946).
- (29) M. S. Kharasch and W. Nudenberg, *J. Org. Chem.* 8,
189 (1943).
- (30) A. Kirrmann and P. Chancel, *Bull. soc. chim. France*
1954, 1338.
- (31) I. L. Knunyants, A. I. Shechekotikhin, and A. V.
Fokin, *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*
1953, 282; *C.A.* 47, 3221b (1953).
- (32) J. C. Krantz, Jr., G. J. Carr, G. Lu, and F. K. Bell,
J. Pharmacol. Exptl. Therapy 108, 488 (1953).
- (33) W. M. Lauer and M. A. Spielman, *J. Am. Chem. Soc.* 53,
1533 (1931).
- (34) J. K. Lawson, Jr., U. S. 2,631,975, Mar. 17, 1953;
C.A. 47, 6702a (1953).
- (35) E. Levas and H. Lefebvre, *Compt. rend.* 222, 555 (1946).
- (36) T. Lindemann, *Ber.* 24, 2145 (1891).
- (37) R. C. Lord and B. Nolin, *J. Chem. Phys.* 24, 656 (1956).
- (38) G. Lu, J. S. L. Ling, and J. C. Krantz, Jr., *Anes-
thesiology* 14, 466 (1953).
- (39) K. E. Marple, E. C. Shokal, and T. W. Evans, U. S.
2,428,235, Sept. 30, 1947; *C.A.* 42, 601 (1948).
- (40) E. W. McKisson, An Infrared Study of Halogen Substi-
tuted Ethers, Dissertation, University of Florida

(1954).

- (41) G. D. Meakins, J. Chem. Soc. 1953, 4170.
- (42) W. T. Miller, Jr., E. W. Fager, and P. H. Griswold, J. Am. Chem. Soc. 70, 431 (1948).
- (43) S. Mizushima, T. Shimanouchi, T. Miyazawa, I. Ichishima, K. Kuratani, I. Nakagawa, and N. Shido, J. Chem. Phys. 21, 815 (1953).
- (44) J. D. Park, D. M. Griffin, and J. R. Lacher, J. Am. Chem. Soc. 74, 2292 (1952).
- (45) J. D. Park, M. L. Sharrah, W. H. Breen, J. R. Lacher, J. Am. Chem. Soc. 73, 1329 (1951).
- (46) J. D. Park, D. K. Vail, K. R. Lea, and J. R. Lacher, J. Am. Chem. Soc. 70, 1550 (1948).
- (47) W. A. Patterson, Anal. Chem. 26, 823 (1954).
- (48) K. E. Rapp, J. T. Barr, R. L. Pruett, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., J. Am. Chem. Soc. 74, 749 (1952).
- (49) M. Reboul, Ann. chim. et phys. (3) 60, 57 (1860).
- (50) W. Reppe, U. S. 1,941,108, Dec. 26, 1933; C.A. 28, 1357⁶ (1934).
- (51) W. Reppe, U. S. 1,959,927, May 22, 1934; C.A. 28, 4431⁶ (1934).
- (52) E. Roithner, Monatsh. 15, 674 (1894).
- (53) G. E. Schildknecht, A. O. Zoss, and C. McKinley, Ind. Eng. Chem. 39, 180 (1947).

- (54) M. F. Shostakovskii, Doklady Akad. Nauk S.S.S.R. 41, 124 (1943); Bull. acad. sci. U.R.S.S., classe sci. chem. 1943, 156; C.A. 38, 3607⁷ (1944).
- (55) M. F. Shostakovskii, Zhur. Obshchei Khim. 20, 608 (1950); C.A. 44, 7754c (1950).
- (56) M. F. Shostakovskii and E. P. Gracheva, Zhur. Obshchei Khim. 23, 1153, 1320 (1953); C.A. 47, 12217d (1953), 48, 9899h (1954).
- (57) M. F. Shostakovskii, B. I. Mikhant'ev, and N. N. Ovchinnikova, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1952, 1099; C.A. 48, 1242c (1954).
- (58) O. D. Shreve, M. R. Heether, H. B. Knight, and D. Swern, Anal. Chem. 23, 277 (1951).
- (59) O. Stephenson, J. Chem. Soc. 1954, 1571.
- (60) H. W. Thompson and P. Torkington, J. Chem. Soc. 1945, 640.
- (61) H. Tschamler and R. Leutner, Monatsh. 83, 1502 (1952).
- (62) G. W. Wheland, Resonance in Organic Chemistry, John Wiley and Sons, Inc., New York, N. Y. (1955), p. 160.
- (63) J. Wislicenus, Ann. 92, 106 (1878); J. Chem. Soc. Abstracts 34, 776 (1878).
- (64) J. A. Young, The Preparation and Reactions of Some Aliphatic Fluoroethers, Dissertation, University of Florida (1950).
- (65) J. A. Young and P. Tarrant, J. Am. Chem. Soc. 71,

2432 (1949); 72, 1860 (1950).

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

June 4, 1956

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