UNCLASSIFIED

AD NUMBER
AD912520
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies only; Test and Evaluation: May 1973. Other requests shall be referred to Air Force Materials Lab., Wright-Patterson AFB, OH 45433.
AUTHORITY
AFWAL ltr, 3 Nov 1983

THIS PAGE IS UNCLASSIFIED

AFML-TR-73-144
PART I
AD0912520

OFFICIAL FILE COPY

PERFLUOROCARBON EPOXIDES
Part I

A-18

Ralph J. De Pasquale
Calvin D. Padgett
Jerry R. Patton

PCR, Inc.

TECHNICAL REPORT AFML-TR-73-144

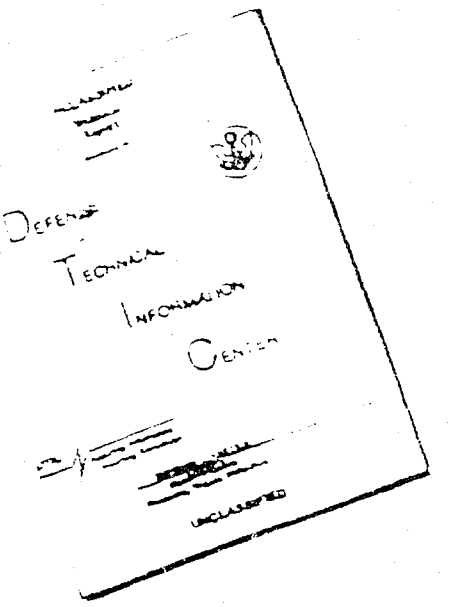
Distribution limited to U. S. Government agencies only; (test and evaluation). May 1973. Other requests for this document must be referred to the Air Force Materials Laboratory, Nonmetallic Materials Division, Polymer Branch, AFML/MBP, Wright-Patterson Air Force Base, Ohio 45433.

Air Force Materials Laboratory
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio 45433

20040301096

Best Available Copy
OFFICIAL FILE COPY

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

REPRODUCED FROM
BEST AVAILABLE COPY

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

PERFLUOROCARBON EPOXIDES

Ralph J. De Pasquale
Calvin D. Padgett
Jerry R. Patton

Distribution limited to U. S. Government agencies only; (test and evaluation). May 1973. Other requests for this document must be referred to the Air Force Materials Laboratory, Nonmetallic Materials Division, Polymer Branch, AFML/MBP, Wright-Patterson Air Force Base, Ohio 45433.

Best Available Copy

FOREWORD

This report was prepared by PCR, Inc., Gainesville, Florida, under Contract No. F33615-72-C-1550, Project No. 7340, Task No. 734004, administered by the Polymer Branch, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. Dr. Robert C. Evers (AFML/MBP) was the Project Scientist for the Air Force.

This is the First Annual Report under this contract and covers the period 1 April 1972 to 31 March 1973.

Personnel who have contributed to this research are Dr. E. C. Stump, Vice President, Contract Research Division; Dr. R. J. De Pasquale, Project Director; Mr. C. D. Padgett, Mr. J. R. Patton, and Mr. J. Middleton, Research Chemists. Analyses were carried out under the supervision of Dr. D. A. Warner, Director of Analytical Services. ^{19}F-NMR analysis and mass spectral analysis were done by Professor W. S. Brey and Professor R. H. Hanrahan, respectively, of the University of Florida.

This report was submitted by the authors May 1973.

This technical report has been reviewed and is approved.

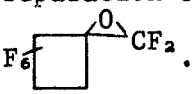
R. L. VAN DEUSEN
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

Potential solvents of the general formula

$$MeO(CH_2CH_2O)_3\overset{OCF_3}{\overset{\|}{C}}\overset{|}{C}F(OCF_2\overset{CF_3}{\overset{|}{C}}F)_nF$$

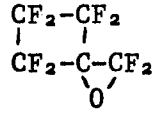
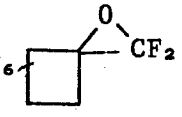
were prepared, tested for stability toward fluoride ion, and used as solvents in HFPO oligomerizations. These materials were found to be inferior to the conventional glyme solvents in HFPO oligomerizations. Areas for further investigation were suggested.

Studies directed toward the preparation of a 2.3 spiroepoxide were culminated by the synthesis of  . Considerable effort was spent on obtaining perfluorocyclobutanone, an essential intermediate in the spiroepoxide synthesis. Under the appropriate conditions this fluorinated ketone can be converted to the spiroepoxide in excellent yield. Under specified conditions the attempted preparation of this epoxide leads to the isolation of an unusual series of compounds apparently derived from the spiroepoxide, itself. Attempted polymerization and reactions of the spiroepoxide are discussed.

A new class of compound, a perfluorinated ether epoxide, was prepared by the oxidation of the vinyl ether derived from HFPO trimer. Of the three reagents tested for this oxidation ($O_2/h\nu$, H_2O_2/Na_2CO_3, OF_2/O_2) the OF_2 catalyzed oxidation seemed best. Attempts to extend this reaction to the simplest homolog of this class of epoxide are discussed.

Several approaches leading to the preparation of perfluorinated-N-alkyl aziridines were investigated.

TABLE OF CONTENTS

I.	INTRODUCTION	1
II.	DISCUSSION	2
	A. Solvent Studies	2
	B. Fluorinated Spiroepoxides - Preparation	5
	C. Attempted Reactions of the Spiroepoxide	15
	D. Fluorinated Ether Epoxides	20
	E. Perfluoro-N-alkylaziridines	25
	F. Perfluoro Bis-Epoxides	28
III.	EXPERIMENTAL	29
	A. Solvent Studies	29
	1. Oligomerization of HFPO	29
	2. Reaction Between HFPO Dimer and Methoxytriglycol	29
	3. Reaction Between HFPO Trimer and Methoxytriglycol	30
	4. Reaction Between HFPO Tetramer and Methoxytriglycol	30
	5. General HFPO Oligomerization Procedure	30
	B. Fluorinated Spiroepoxides- Preparation	30
	1. Preparation of $C_3F_7O(C(CF_3)FCF_2O)_2CF{=}CF_2$ (II)	30
	2. Reaction Between II and Dichlorodifluoroethylene	31
	3. Attempted Hydrolysis of III	31
	4. Initial Preparation of 	32
	5. Preparation of Methyl Trifluorovinyl Ether	33
	6. Preparation of Methyl Perfluorocyclobutyl Ether	33
	7. Conversion of Methyl Perfluorocyclobutyl Ether to Perfluorocyclobutanone	35
	8. Reaction Between Perfluorocyclobutanone and HFPO in Glass Ampoules	35
	9. Preparation of 	36

10. Preparation of Trimethyl Trifluoromethyl Tin 36

11. Reaction Between Me_3SnCF_3 and Perfluorocyclobutanone 36

C. Reactions of the Spiroepoxide 37

1. Fluoride Ion Catalyzed Reaction of the Spiroepoxide 37

2. Reaction Between Spiroepoxide and $(\phi O)_3P$ 38

D. Fluorinated Ether Epoxides 38

1. The Preparation of $CF_3CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$ 38

2. Epoxidation of $CF_3CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$ Using 50% H_2O_2 39

3. Epoxidation of $CF_3CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$ Using O_2/OF_2 39

4. Epoxidation of $CF_2CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$ with O_2 and Sunlight 41

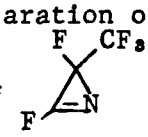
5. Preparation of Perfluoro(2-methoxypropionyl fluoride) 41

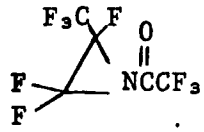
6. Preparation of Perfluoro(methyl vinyl ether) 42

7. Epoxidation of CF_3-O-$CF{=}CF_2$ 43

E. Perfluoro N-alkylaziridines 45

1. Attempted Preparation of a Fluorinated Aziridine 45

2. Preparation of  46

3. Preparation of  47

F. Perfluoro Bis-Epoxides 47

1. Attempted Synthesis of Decafluorodiiodohexane 47

APPENDIX 49

REFERENCES

LIST OF ILLUSTRATIONS

Figure 1 $C_3F_7OC(CF_3)F\overset{O}{\overset{\|}{C}}O(CH_2CH_2O)_3CH_3$ 52

Figure 2 $C_3F_7OC(CF_3)FCF_2OC(CF_3)F\overset{O}{\overset{\|}{C}}O(CH_2CH_2O)_3CH_3$ 53

Figure 3 $C_3F_7O[C(CF_3)FCF_2O]_2C(CF_3)F\overset{O}{\overset{\|}{C}}O(CH_2CH_2O)_3CH_3$ 54

Figure 4 $C_3F_7O(C\overset{CF_3}{\overset{|}{F}}CF_2O)_2CF=CF_2$ 55

Figure 5 $C_3F_7O(C\overset{CF_3}{\overset{|}{F}}CF_2O)_2\underset{Cl_2C}{\underset{|}{CF}}-\underset{CF_2}{\underset{|}{CF_2}}$ + (isomer ?) 56

Figure 6 $MeOCF=CF_2$ 57

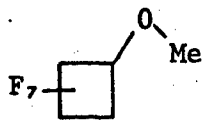
Figure 7  58

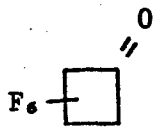
Figure 8  59

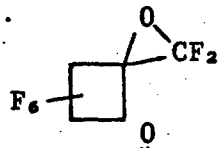
Figure 9  60

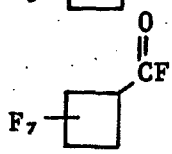
Figure 10  61

Figure 11 $C_3F_7O\overset{CF_3}{\overset{|}{C}}FCF_2OCF=CF_2$ 62

Figure 12 Crude Reaction Mixture $C_3F_7O\overset{CF_3}{\overset{|}{C}}FX$ 63

$X = CF_2OCF=CF_2$, COF, $CF_2O\overset{O}{\overset{/\backslash}{CF-CF_2}}$

Figure 13	$CF_3OCF(CF_3)-CF(=O)$	64
Figure 14	$CF_3OCF=CF_2$	65
Figure 15	$CF_3OCF=CF_2$ dimers	66
Figure 16	Crude $C_6F_5N=P(C_8H_{17})_3$	67
Figure 17	Crude Azirine	68
Figure 18	$F_3CCFHCF_2N_3$ (2.8, 4.6μ)	69
Figure 19	Amide	70
Figure 20	Cell Blank for Amide	71

I. INTRODUCTION

Technological advances in the field of aeronautics and astronautics have created a demand for materials of construction which will function for extended periods in extreme environments. These requirements have necessitated a broad research and development program by the Air Force, particularly in the area of non-metallic materials such as elastomers, designed to provide solutions to both immediate and anticipated problems.

Elastomers are required which exhibit high thermal stability, low temperature flexibility, impermeability to gases and liquid missile propellants, and resistance to fuels, oxidizers, oils, hydraulic fluids and other corrosive materials. Perfluoropolyethers are expected to meet these requirements if the polymerization of perfluoroepoxides can be carried to high molecular weight and if they can be cured. For this reason polymerization studies on new as well as existing perfluoroepoxides should receive top priority in elastomers research. During this first year of the contract, segements from these two areas were selected for investigation, i.e., a variation in the fluoride ion polymerization of HFPO and the attempted preparations of new fluoroepoxides.

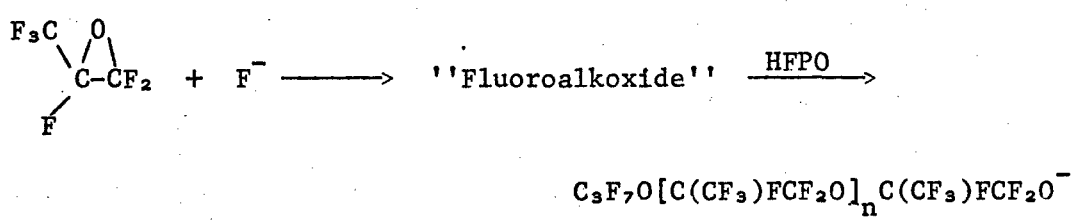
II. DISCUSSION

A. Solvent Studies

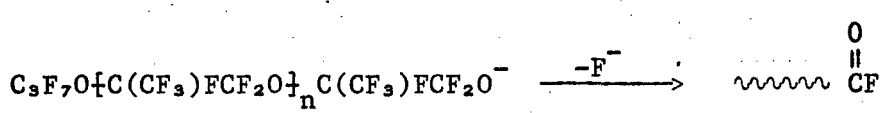
The preliminary concern is to attempt to increase the molecular weight of polyhexafluoropropylene oxide prepared from fluoride ion catalyzed polymerization of HFPO. One approach is described below.

With conventional solvents, nitriles or glyme ethers, as the polymerization proceeds, the initially homogeneous solution separates into a glyme-metal fluoride and fluorocarbon phase. It is conceivable that the phase separation restricts the formation of high molecular weight polymer according to the following rationale.

This assumes that the oligomerization proceeds predominantly in the glyme phase and continues as long as fluoroalkoxide remains as such.



However as soon as the fluoroalkoxide eliminates fluoride ion, the resulting acid fluoride redistributes into the fluorocarbon layer.



Essentially, then, the reverse reactions of F^- addition to acid fluoride to afford fluoroalkoxide is restricted as the molecular weight of the acid fluoride increases due to the solubility partitioning. Thus, the following propagation would be limited to low or moderate molecular weight

$$\sim\sim\sim\sim\overset{O}{\overset{\|}{C}}F + F^- \longrightarrow \sim\sim\sim\sim CF_2O^- \xrightarrow{HFPO} \text{high oligomer}$$

acid fluorides. This would result in a lower Mw polymer.

To test this hypothesis, a solvent system could be devised which would maintain homogeneous polymerization conditions and dissolve and activate metal fluoride as well as solublize broad molecular weight ranges of acid fluorides and fluoroalkoxides. To this end potential solvents were prepared containing fluorocarbon ether and hydrocarbon ether units linked by an ester group.[1]

HFPO was oligomerized under conditions where low molecular weight acid fluorides, $(HFPO)_n$ (n = 2 - 5), would predominate. The dimer, trimer and tetramer acid fluorides were separated and reacted with a methyl capped ethylene oxide trimer in separate experiments. The esters were isolated in purity of >99% (GLC) in yields ranging from 69-85% when reactions were carried out in stainless steel vessels. The mixed esters were tested for their stability toward F^- and then used as solvents in HFPO oligomerizations. The results from these runs were compared to runs using glyme solvents under a standard set of conditions.

$$C_3F_7O\{C(CF_3)FCF_2O\}_nC(CF_3)\overset{O}{\overset{\|}{F}}CF + HO(CH_2CH_2O)_3CH_3 \xrightarrow{-HF}$$

$$MeO(CH_2CH_2O)_3\overset{OCF_3}{\overset{|}{\overset{\|}{C}}}CF(OCF_2\overset{CF_3}{\overset{|}{C}}F)_nF$$

(I) n = 1 - 3

When samples of the esters (I, n = 1 - 3) were treated with anhydrous CsF at 25°/16 hr, then 80°/24 hr, less than 1% decomposition was observed. The trace of gaseous material that was isolated as a decomposition product is suspected to be a perfluoroalkane by infrared. In these experiments care must be taken to avoid adventitious moisture. It was noted that exposure of the reaction mixture to the moist Florida air for short intervals causes decomposition of these esters. For example, when a mixture containing I (n = 3) and CsF was exposed to the air for ca. 15 minutes, then stirred for 18 hr at 25°, 20% decomposition was observed.

Since these esters proved stable to CsF, attempts were made to use them as solvents in fluoride ion catalyzed HFPO oligomerizations. Oligomerizations reactions were studied using 0.5 g CsF/10 g ester solvent/3 g HFPO over ca. a 100° temperature range (-25° to 80°). A reaction was run using diglyme as a standard for comparison purposes. The results are shown in Table 1.

TABLE 1

HFPO OLIGOMERIZATIONS IN MIXED ESTER SOLVENTS[a]

Solvent	Conditions	Standard[b]	$(HFPO)_2$	$(HFPO)_3$	$(HFPO)_4$	$(HFPO)_{5+6}$
Diglyme (7 ml)	-25°, 30 min	1	0.075	0.83	1.53	0.01
	1 hr	1	0.03	0.75	2.26	1.3
	2 hr	1	0.1	1.5	2.9	1.3
I (n=3) (10 g)	-25°, 30 min	1	0.01	--	--	--
	2 hr	1	0.06	--	--	--
I (n=3) (10 g)	30°, 2 hr	1	0.12	--	--	--
I (n=1) (10 g)	30°, 2 hr	1	0.71	0.06	trace	--
I (n=1) (10 g)	80°[c], 14 hr	--	trace	trace	--	--
I (n=1) (7 g) Diglyme (1 cc)	30°, 2 hr	1	1	0.1	0.03	--
I (n=1) (7 g) Diglyme (3 cc)	30°, 2 hr	1	1.1	0.1	0.04	--

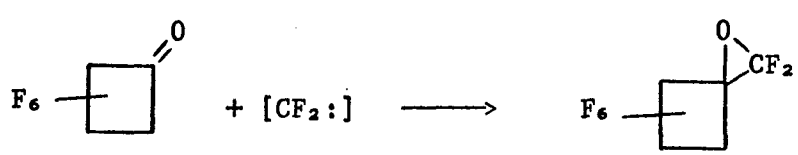
(a) Charge 3 g of HFPO, use 0.5 g CsF as catalyst
(b) 0.5 g Freon E4 standard.
(c) Reaction was run in a 80-ml SS autoclave. Isolation of volatiles showed that most of the HFPO was converted to hexafluoropropionyl fluoride.

To date, HFPO has shown little tendency to oligomerize in these neat solvents. With the ester solvents, <5% of the HFPO was converted predominately to dimer acid fluoride; with one exception, unreacted HFPO could be recovered. Hexafluoropropionyl fluoride was the major product at high temperature (see Table 1).

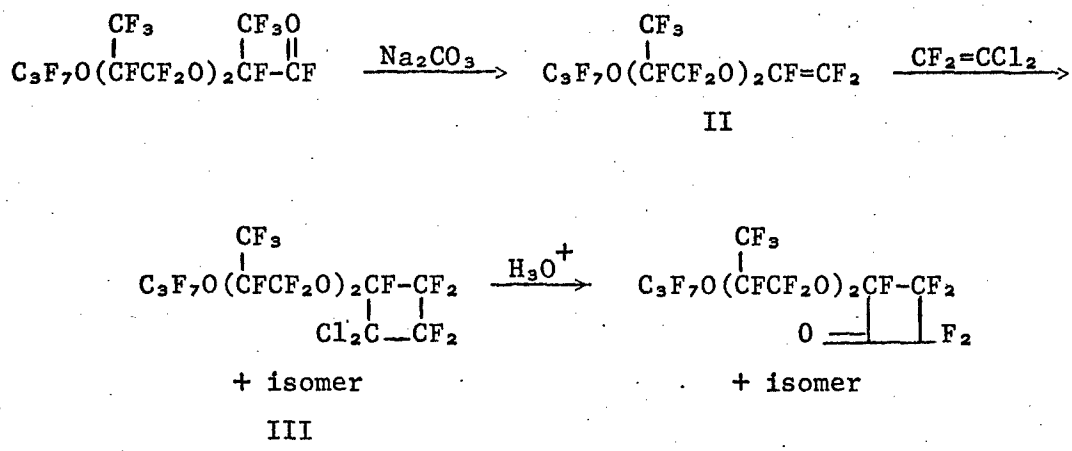
The oligomerization reaction proceeds best in the solvent with the greatest ratio of EO:HFPO, i.e., diglyme >>I (n=1) > I (n=3). There is a large difference in reactivity between diglyme and I type solvents. This is presumably due to the inability of the hydrocarbon part in the mixed ester solvent to complex CsF effectively. Since the solvent should be relatively low boiling (easily removed from the reaction mixture), there is a limit to the number of EO or HFPO units that can be used in these ester solvents. Perhaps an ester derived from 4 or 5 EO units and 2 or 3 HFPO units would be a better choice for a solvent. In attempts to estimate the potential of such a solvent, solutions of I (n=1) and diglyme (completely miscible) were used as reaction media. Unfortunately, these solutions gave marginally better results (see Table I) than neat I and were still inferior in both rate and product distribution to diglyme. With the exception of determining the effect of added metal fluoride complexing agents, further work with I type solvents will be temporarily discontinued.

B. Fluorinated Spiroepoxides - Preparation

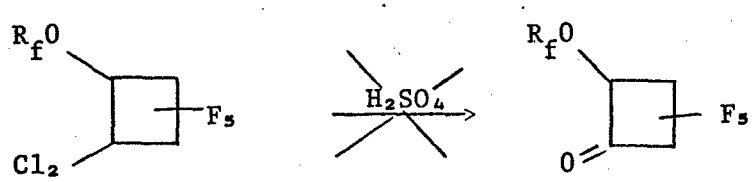
One of the most reactive and interesting fluorinated spiroepoxides could be derived from fluorocyclobutanones via CF_2 transfer reaction to the carbonyl group.



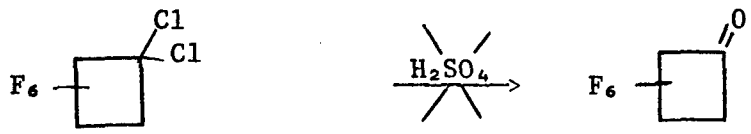
Due to the handling difficulties of perfluorocyclobutanone (toxic gas) a potential route has been devised to a more easily handled substituted cyclobutanone. The preparation of such a compound was attempted as follows.



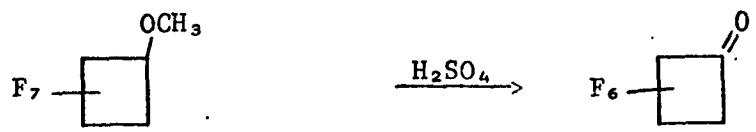
The first step of this route gave the vinyl ether (II) in 55% yield. Subsequent reactions of this ether with $CF_2{=}CCl_2$ showed that an excess of the chlorinated olefin is necessary to minimize the quantity of vinyl ether dimers. A product suspected to be the substituted cyclobutane (and isomer) was isolated in 52% yield at 82% vinyl ether conversion. The hydrolysis of the dichlorocyclobutane (III) to the cyclobutanone initially was attempted on a small scale. It was reported[2] that 95% H_2SO_4 containing Hg^+ and Hg^{++} salts was an effective reagent for converting a pendent CCl_3 group of a fluorocarbon chain to an acid group. Under similar conditions (100°) or more stringent conditions (175°) this reagent had no effect on III. Further attempts to hydrolyze III on larger scale to the desired cyclobutanone in 30% fuming sulfuric acid at 90°/16 hr, 120°/16 hr, 145°/60 hr, and 185°/60 hr gave recovered III with no detectable ketone.



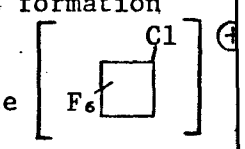
England[3] recently related similar experiences in the preparation of the parent compound, perfluorocyclobutanone. Apparently 1,1-dichlorohexafluorocyclobutane is stable to hydrolysis whereas methoxyheptafluorocyclobutane hydrolyzes readily to the cyclobutanone.

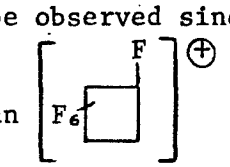


IV

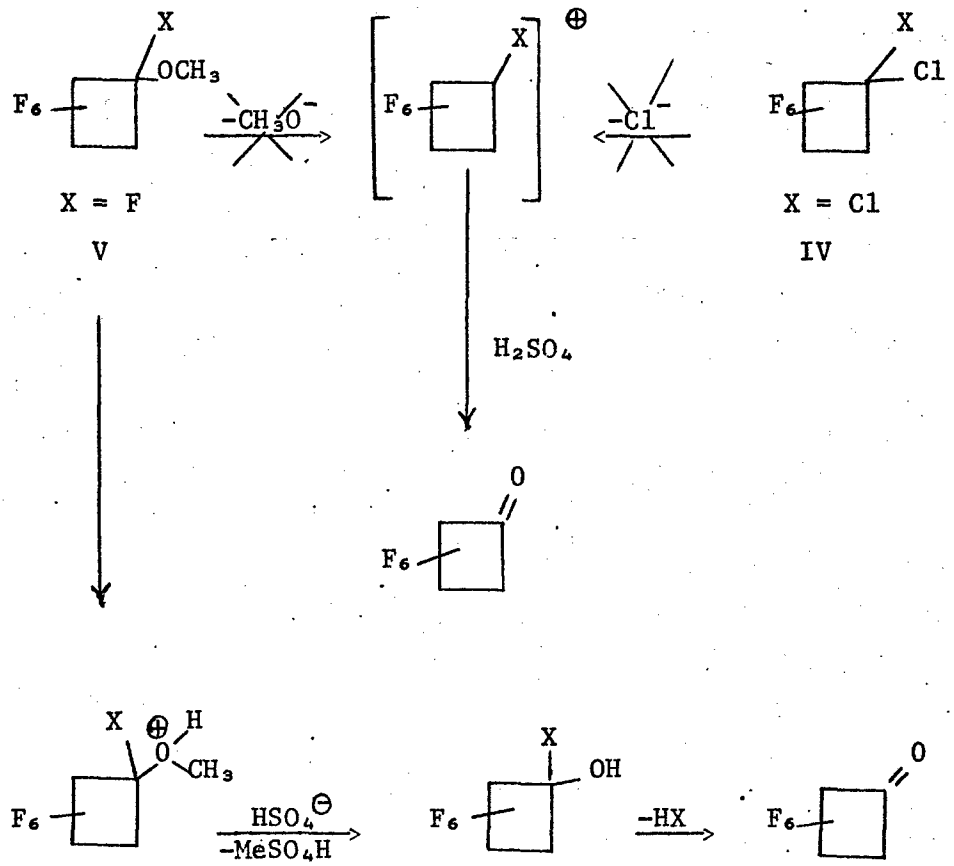


V

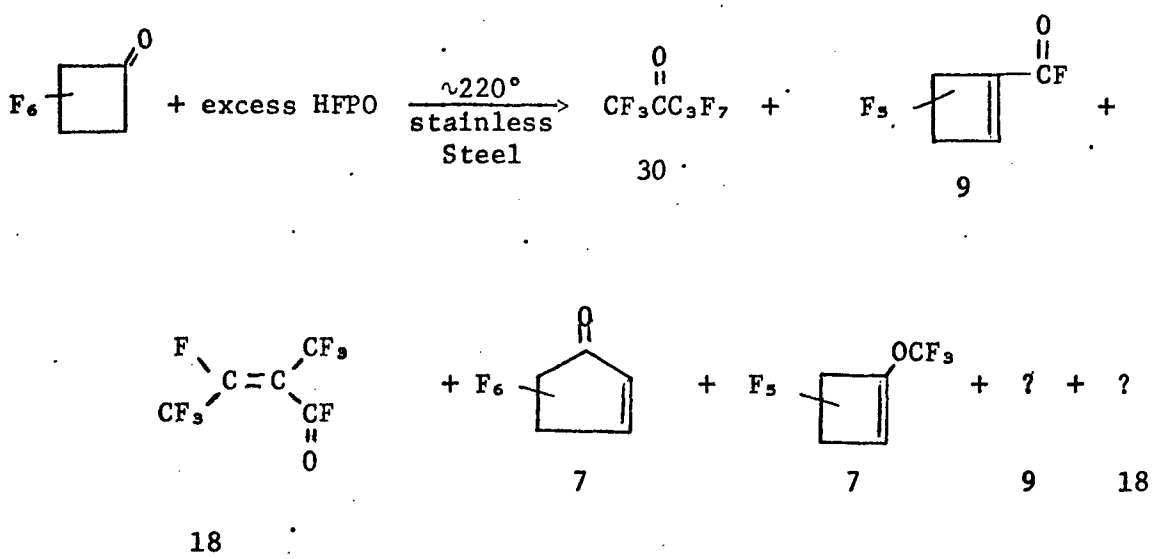
These data lead to conclusions of mechanistic significance. The fact that V is converted to the ketone at a faster rate than IV implies that a fluorinated cyclobutyl cation is not an intermediate in the formation of cyclobutanone. If it were, the reverse should be observed since 

would be expected to be formed at a faster rate than 

via ionization of a C-Cl bond in preference to a C-OCH_3 bond. Presumably, V hydrolyzes in a manner analogous to that below; this route is untenable for IV.


X
OCH3
F6
-CH3O-
X = F
V
X
F6
⊕
-Cl-
X
Cl
F6
X = Cl
IV
H2SO4
O
F6
X
⊕
H
O
CH3
F6
HSO4⊖
-MeSO4H
X
OH
F6
-HX
O
F6

Work was then shifted to the study of the reaction between perfluorocyclobutanone and HFPO. In an initial experiment, a complimentary sample[4] of the cyclic ketone was reacted with excess HFPO in a stainless steel autoclave at ca. 200°. This small scale run (1 g) afforded a material tentatively characterized as the spiroepoxide. The yield was ca. 25%. Scale-up, however, gave totally different results; no spiroepoxide was observed. GLC of the crude reaction mixture showed that all of the perfluorocyclobutanone and HFPO were consumed. Work-up gave trifluoroacetyl fluoride and perfluorocyclopropane as well as seven low boiling compounds. To date, five of these have been characterized by IR, mass spec, and NMR; their structures and ratios are shown below. Surprisingly, these seven products were formed in good yield.

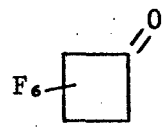


Since the above experiments depleted the complimentary sample of perfluorocyclobutanone, work was then initiated on attempting to reproduce the reported preparation of this cyclic ketone[5] shown schematically below.

$$F_2C{=}CF_2 + NaOMe \xrightarrow{\text{Dioxane}} MeOCF{=}CF_2$$

$$MeOCF{=}CF_2 + F_2C{=}CF_2 \xrightarrow{175°C} \begin{array}{l} MeOCF-CF_2 \\ \quad\;\; | \qquad\;\; | \\ \quad\;\; CF_2-CF_2 \end{array}$$

$$\begin{array}{l} MeOCF-CF_2 \\ \quad\;\; | \qquad\;\; | \\ \quad\;\; CF_2-CF_2 \end{array} \xrightarrow[\text{2) } P_2O_5\text{, distill}]{\text{1) } H_2SO_4\text{, 175°}}$$



Throughout this sequence difficulties were encountered in reproducing the literature data. As a consequence, considerable time was spent on developing reproducible procedures for the preparation of the intermediate compounds.

In the literature preparation[6] of methyl trifluorovinyl ether referred to in England's communication, NaOMe and dioxane were placed in an autoclave and heated with agitation at 100° while a continual pressure (300 psi) of TFE was applied. The author obtained a 27% yield of the desired ether when run on ca. 0.5 mole scale. Our attempts to reproduce this reaction on roughly a 4 mole scale gave less than 10% of the ether. The majority of the TFE was converted to the methanol addition product, $MeOCF_2CF_2H$. Later we observed that the formation of this side product is due to a combination of moisture (in the NaOMe or solvent) and the relatively high reaction temperature[7] used in the preparation. A procedure was developed in which a NaOMe/dioxane slurry was transferred into an evacuated autoclave by suction followed by TFE (slight deficiency relative to NaOMe) charging at -183°. The autoclave was allowed to warm to 25° with shaking; at this temperature the reaction proceeds nearly to completion in ca. 20 hr. According to the developed procedure, methyl trifluorovinyl ether was prepared in 46% yield on a 4 mole scale. At higher temperatures perfluorocyclobutane, $MeOCF_2CF_2H$, and another product believed to be derived from dimethoxy substitution were major side products. In our experiments we used unopened bottles of NaOMe that had been on the premises for about a year.

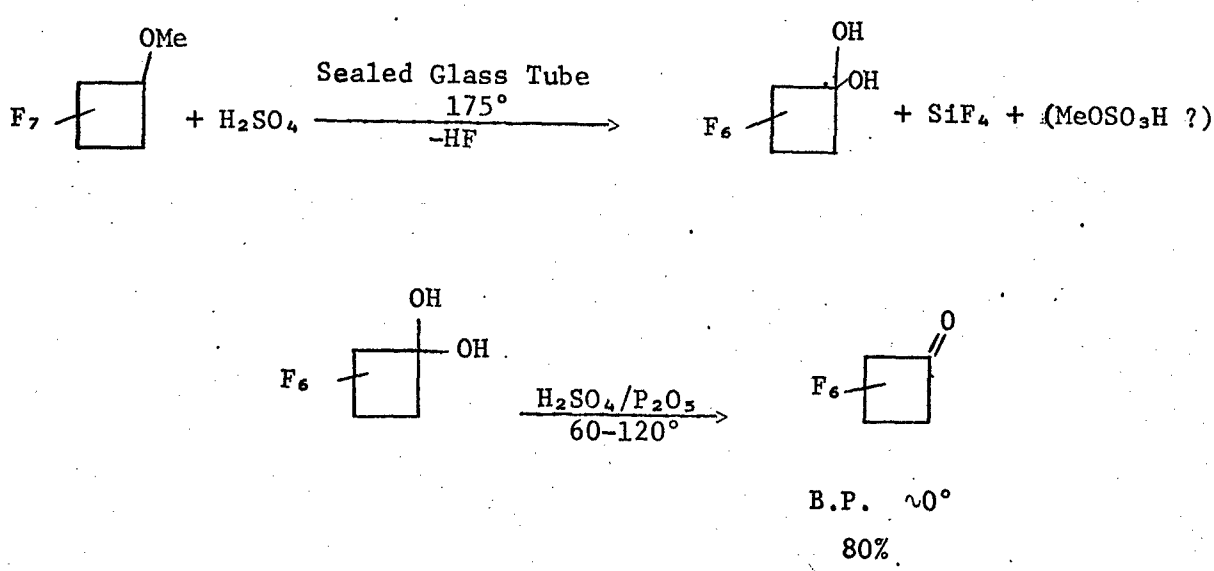
It was noticed, during subsequent experiments performed on another project, that the immediate use of purchased NaOMe afforded yields of the derived product in excess of 70% both reproducibly and without incident. Absolutely anhydrous, methanol free conditons are required for this reaction.

In the next sequence, reaction conditions were found that smoothly converted TFE and methyl trifluorovinyl ether (MTE) to methyl perfluorocyclobutyl ether. England reported[5] that the desired ether was prepared at 175°; no details were given. Our preliminary attempts to prepare this compound by charging a 3:1 ratio of TFE:MTE and dipentene inhibitor into a stainless steel vessel gave irreproducible results on warming to 175°. Several reactions exothermed and carbonized at temperature.

For example, the cyclobutanization reaction between TFE and methyl trifluorovinyl ether was run twice on a 10 g scale; one reaction exothermed and blew the bursting disc, the other gave a 34% yield of the cyclobutane derivative. In a personal discussion, England then indicated that his reactions were run in glass using a combination of a terpene and phenothiazine inhibitors on a 0.1 mole scale. The reaction was then investigated to determine conditions that would lead to facile scale-up in a stainless steel autoclave. By using a 2.5:1 ratio of TFE:MTE with the dual inhibitors, the reaction can be run on at least a mole scale without mishap provided that certain heating conditions are followed (see Experimental). In our hands yields of 60-70% of the isolated ether were obtained; we have prepared ca. 200 g of this material by this procedure.

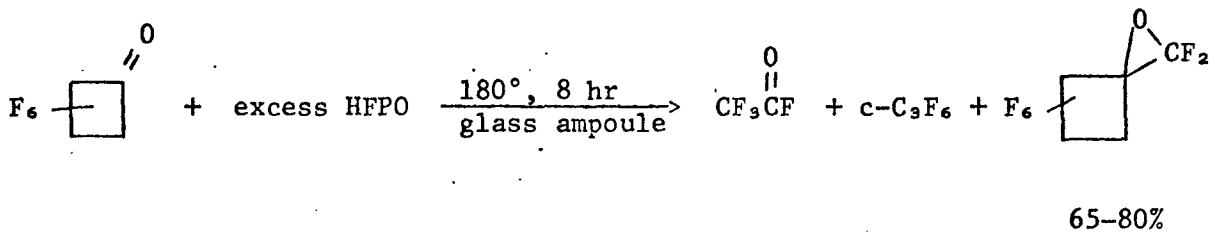
England converted methyl perfluorocyclobutyl ether to perfluorocyclobutanone by treatment with concentrated H_2SO_4 at 175°. In our hands several trial experiments were run to gain familiarization with the overall reaction. We observed that yields of perfluorocyclobutanone in excess of 80% can be obtained routinely. It would have been convenient to run this reaction in stainless steel since this would present a minimum of scale-up difficulties. Unfortunately, a reaction run in stainless steel at 175° for 12 hrs with rocking afforded <10% yield of ketone. While it is conceivable that this reaction could be run effectively in stainless steel under appropriate conditions, for time conservation all subsequent reactions were run in cylindrical glass ampoules. Under these conditions, we have prepared the ketone in 25 g

quantities/run. At 175° H_2SO_4 and the methyl perfluorocyclobutyl ether appear immiscible. Consequently, agitation rate dramatically affects the reproducibility and extent of the reaction. When the reactants are heated at temperature without shaking following a prescribed workup (vide infra) the yields of cyclobutanone are low (<25%) and irreproducible. When the tube is shaken along the longitudinal axis at 175°; the reaction is essentially complete (near coalescence of the two layers) after 24 hrs. This mixture is black and affords 50-60% yield of the fluorinated ketone. Lastly, when the tube is rocked at 175°, the reaction is complete in ca. 3 hr and affords a clear, amber solution from which yields of perfluorocyclobutanone can be obtained in excess of 80%. At temperature HF is presumably liberated and reacts with the glass yielding SiF_4. Thus, the tube is opened (cold) and vented at 25° to remove this undesirable component. Then, as suggested by England, P_2O_5 is gradually added to the H_2SO_4 solution. The resulting mixture is heated to drive off the desired fluoroketone. The overall scheme is shown schematically below.



As previously discussed, the reaction between perfluorocyclobutanone and HFPO in stainless steel vessels invariably gave poor yields of the spiroepoxide. We have demonstrated that under essentially the same conditions the reaction between these two substrates in a glass ampoule affords the spiroepoxide with the exclusion of the other side products.

Thus, reaction between perfluorocyclobutanone and HFPO in a 1:2 or 2:1 ratio, respectively, at 180°/8 hr in a glass ampoule gave >90% yields (GLC) of the spiroepoxide. Under these conditions the reaction is essentially complete. Even when the reaction is run at 200°C/48 hr in glass the only identifiable product is the spiroepoxide. Scale-up of this reaction affords isolated yields of spiroepoxide (98% purity) ranging from 65-80% depending on the scale of the experiment. The reaction is essentially quantitative, however, low temperature distillation leads to handling losses.



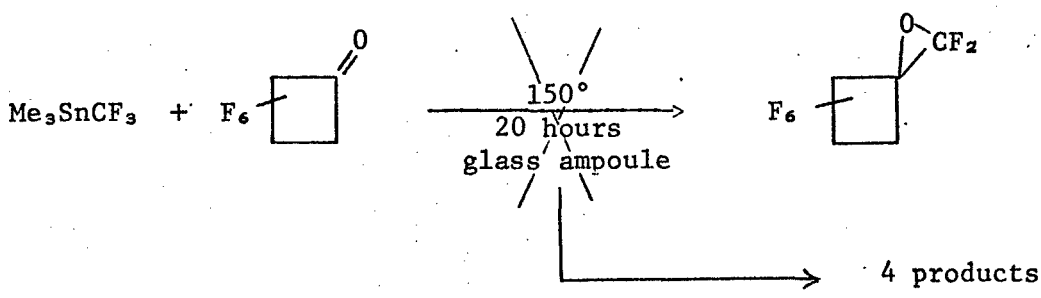
The results observed from the attempted preparation of the spiroepoxide in stainless steel are worthy of comment. In order to ascertain the probable course of the stainless steel reaction, the previously run large-scale experiment was repeated and interrupted after 18 hr at 200°. Analysis of the crude reaction mixture by GLC showed that all the perfluorocyclobutanone and HFPO had been consumed, and that 85% of the high boiling products was accountable for as spiroepoxide. The remaining 15% was a mixture of the seven products previously discussed. While the appearance of these seven products in the stainless steel reaction is reproducible, their rates of appearance are not. Thus, in one experiment at 200°/48 hr essentially all spiroepoxide was consumed affording the seven-product mixture. In a similar experiment only 30% of the spiroepoxide was consumed. It is notable

that pretreatment of the stainless steel reactor with 98% H_2SO_4 (150°/18 hr) followed by washing and drying, effectively reduces the rate of decomposition.

Thus, it appears that spiroepoxide is formed at comparable rates in glass and in stainless steel; however, some species in the stainless steel causes the conversion of the spiroepoxide[8] to the seven-product mixture. Further experimentation suggests that this transformation is not entirely a thermal reaction and is not generally catalyzed by Lewis acids or Lewis bases. Among others, it is possible that surface phenomona, carbonaceous material or transition metal complexes (perhaps fluorides) contribute to the decomposition.

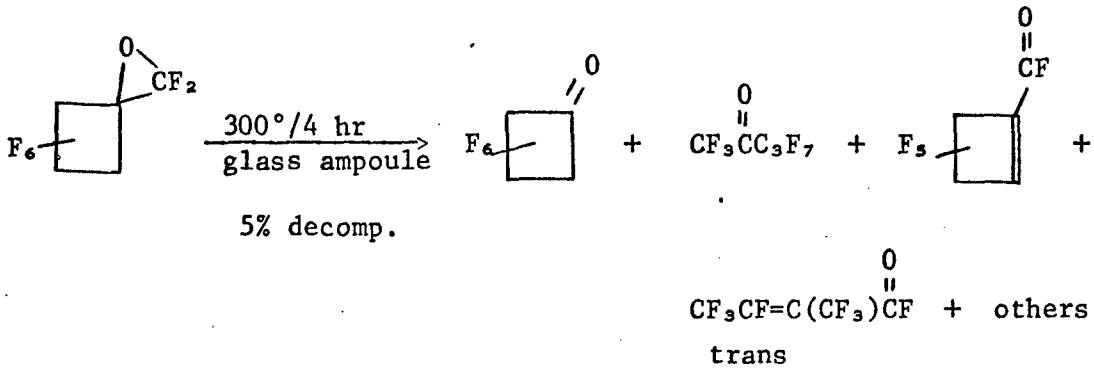
At the time that we encountered difficulties in the preparation of the spiroepoxide in stainless steel vessels, we considered an alternate (rather than HFPO), lower temperature source of ''CF_2''. The reagent Me_3SnCF_3 is known to decompose to Me_3SnF and CF_2 at 150° and as such its use seemed appropriate for the spiroepoxide preparation. The tin compound was prepared by the literature procedure,[9] and subsequently reacted with perfluorocyclobutanone. GLC and IR showed complete consumption of the cyclic ketone; however, no spiroepoxide was detected. Four products of similar retention time of the spiroepoxide were observed. Due to the success of spiroepoxide preparation in glass, no further sources of CF_2 other than HFPO were tested.

$$CF_3I + Me_3SnSnMe_3 \xrightarrow[5\ \text{days}]{75^\circ} Me_3SnCF_3 + Me_3SnI + \text{others}$$

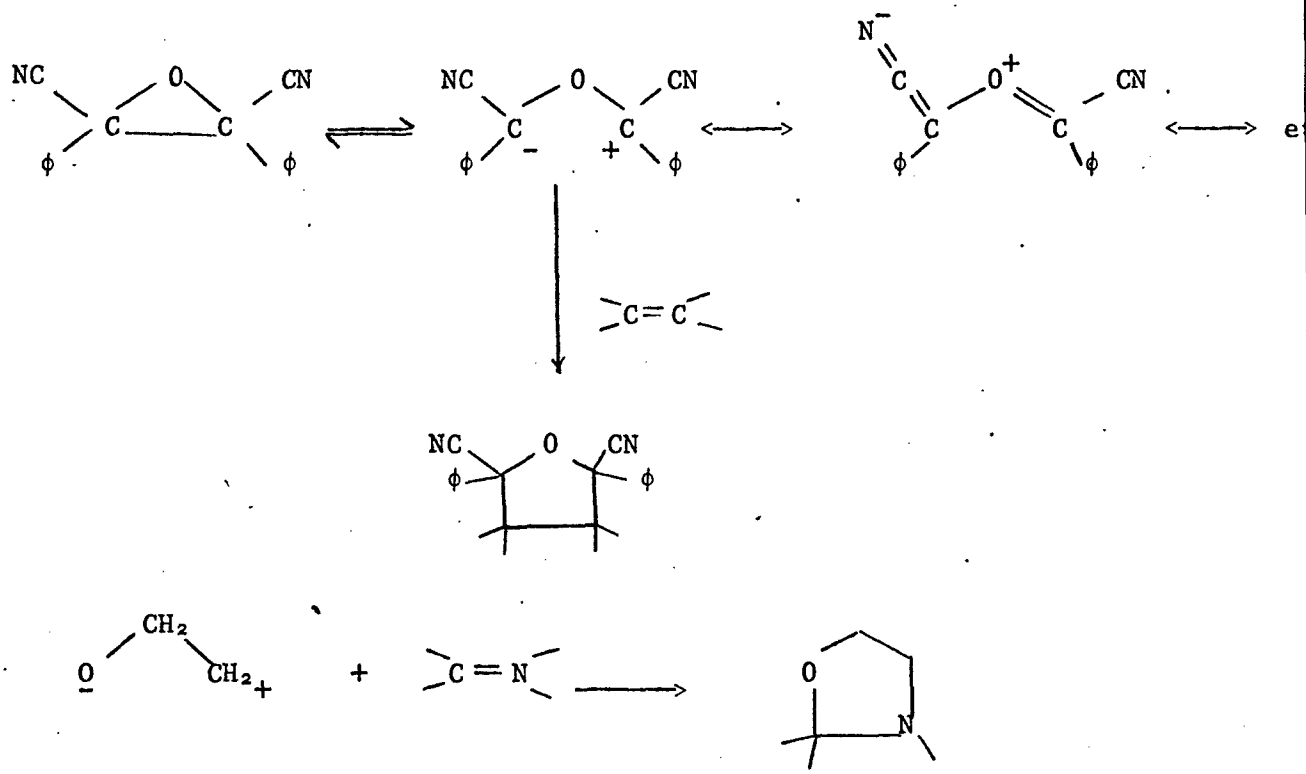


C. Attempted Reactions of the Spiroepoxide

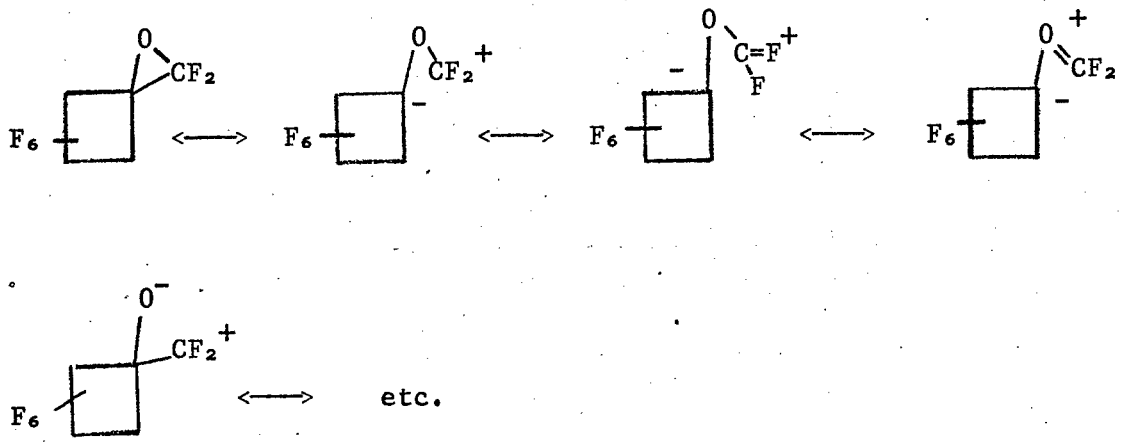
When the spiroepoxide is heated in a glass ampoule at 200°/48 hr no appreciable (<1%) decomposition is observed. Even when the spiroepoxide is heated at 300°/4 hr in glass, only 5% decomposition was detected. The tentatively assigned products from this decomposition are shown below.

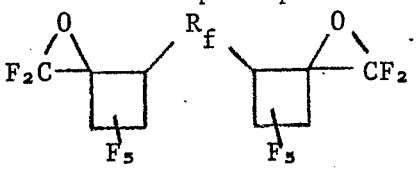


It is interesting that the epoxide displays such thermal stability. Unlike TFEO or HFPO which decompose[10] at 150-180° liberating CF_2, retro-carbene reaction of the spiroepoxide is minimal below 300°. This suggests that bis-spiroepoxides may be used as potential cross linking agents. Huisgen[11] et al reported that certain epoxides behave as 1,3-dipolarophiles towards various unsaturated compounds.



It is conceivable that the spiroepoxide may behave similarly, i.e., be polarized in such a manner by a reactive unsaturated group, since dipolar species derived from the spiroepoxide appear attractive from a theoretical viewpoint.



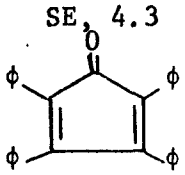
If the fluorinated spiroepoxide reacts in this manner, a bis-spiroepoxide e.g., 

may be useful for cross-linking fluoropolymers containing pendent C≡N, C≡C, or C=C groups.

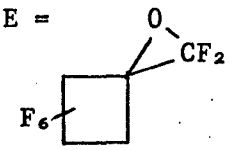
To this end model reactions between the spiroepoxide and several appropriate substrates were investigated. The results are shown in the Table II. Unfortunately, to date, no adducts were detected. In each case spiroepoxide was recovered unchanged. It is notable that during the reaction between the spiroepoxide and CF_3NO, the nitroso compound undergoes decomposition[12] which involves the intervention of free radicals. The spiroepoxide, apparently, is not attacked by radical intermediates. From these experiments it seems safe to conclude that the spiroepoxide does not behave as a 1,3-dipolarophile in cycloaddition reactions.

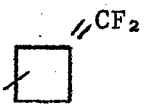
TABLE II

MISCELLANEOUS REACTIONS OF THE SPIROEPOXIDE[a]

Reactants mmoles	Conditions °C, hr	Comments
SE[b], 2.8	200, 48	No appreciable decomposition
SE, 4.2	300, 4	*ca.* 5% decomposition
SE, 2.8 C_2F_4, 5.5	200, 48	No adduct, c-C_4F_8 and unreacted SE, 95% wt recovery
SE, 3.2 $CH_3CH{=}CH_2$, 8.6	200, 8 then 280, 4	No adduct, recovered SE
SE, 2.4 CF_3NO, 2.4	200, 48	No adducts, recovered SE,(95%) decomposition of CF_3NO
SE, 4.3  , 4.3	220, 48	No adduct, recovered SE
SE, 4.0 BF_3, 0.8	200, 16	Unreacted SE, no detectable decomposition
SE, 4.3	Radiate with Co^{60} source at 25°, total of 40 meg rad	No reaction, recovered >95% SE
SE, 4.3 $(EtO)_3P$, 4.8	Let warm from -183° to RT, exotherm	Isolate EtF, no unreacted phosphite, IR shows P=0 as well as $-\overset{O}{\overset{\|\|}{C}}F$

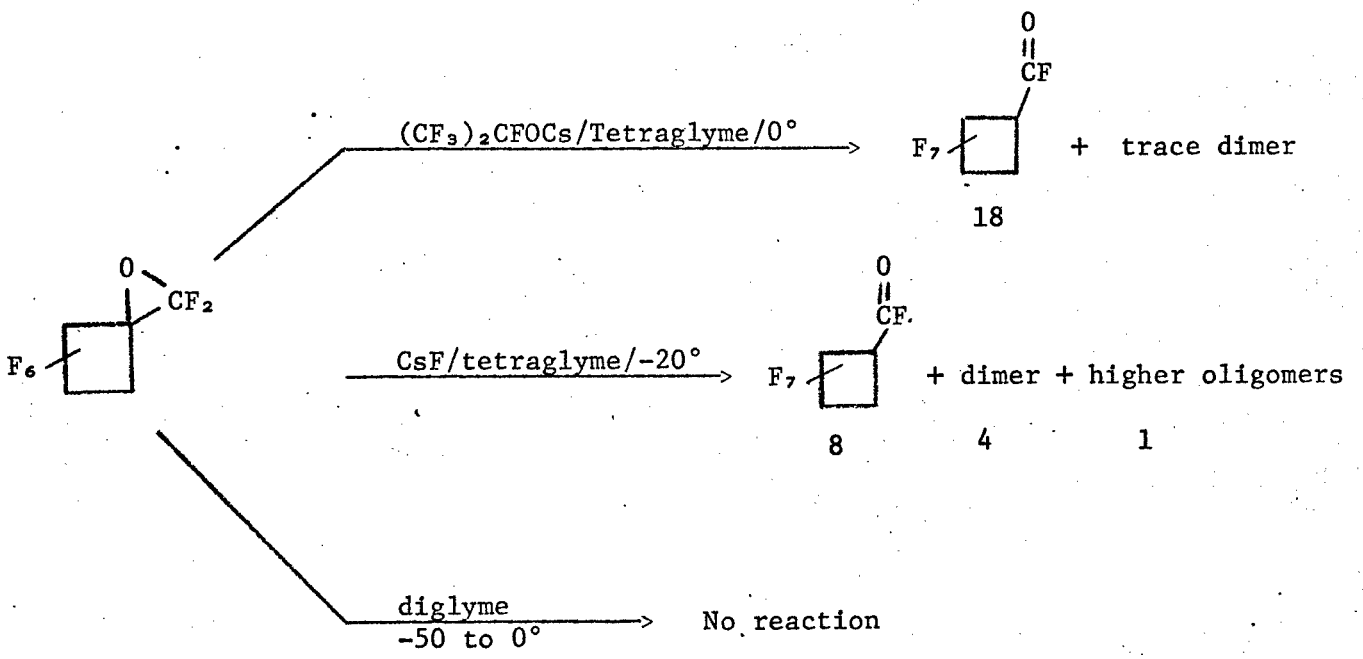
(a) All reactions were run in 20-cc glass ampoules

(b) SE = 

An unsuccessful attempt was made to prepare F_6  by deoxygenating the spiroepoxide with $(EtO)_3P$. The isolation of EtF as well as the observation of a $\overset{O}{\overset{\|}{C}}F$ group suggests that a scheme similar to the Arbusov reaction[13] is taking place. The desired olefin could be used as a precursor to a polymer (via Montecatini process) which would be esssentially similar to the polymer derived from fluoride ion catalyzed homopolymerization of the spiroepoxide.

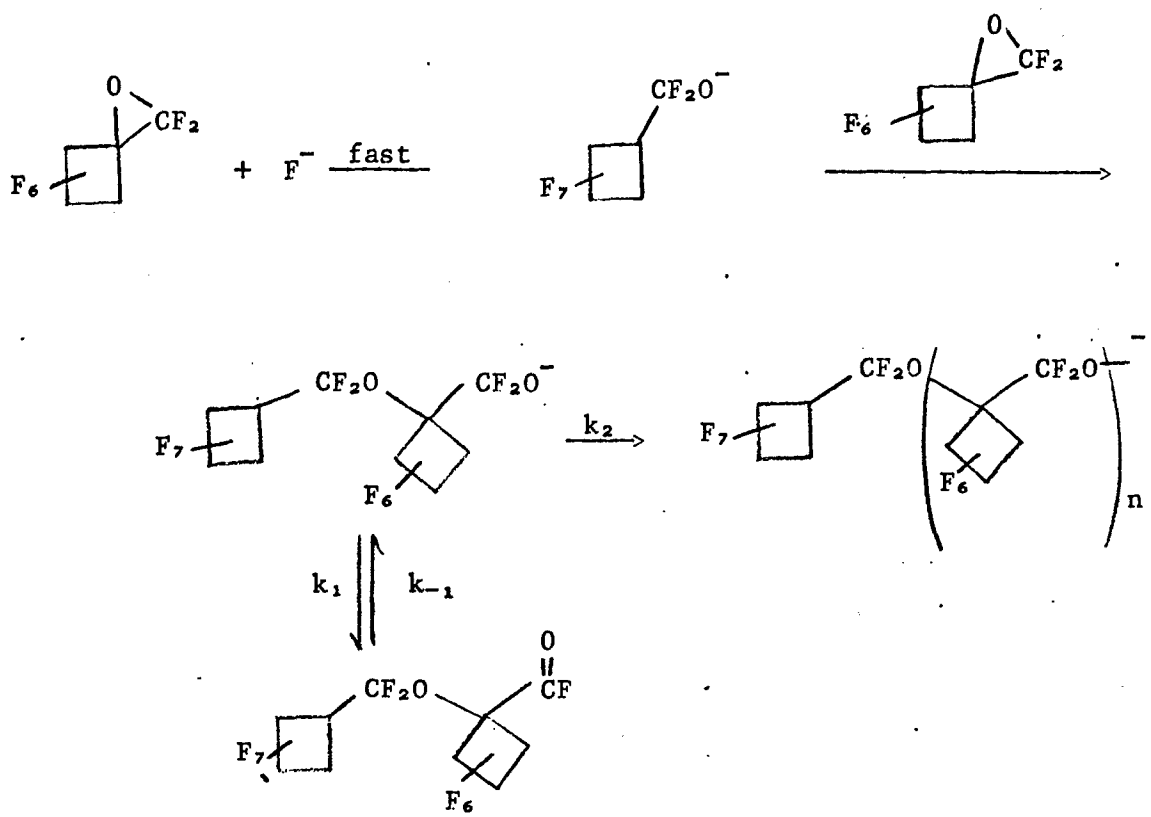
An attempt to prepare perfluoro(methylene cyclobutane) by reacting stoichiometric amounts of $P(O\phi)_3$ and spiroepoxide, surprisingly, gave a tacky resin. Both phosphite and spiroepoxide were consumed. It is notable that under similar conditions $P(O\phi)_3$ does not promote more than a stoichiometric amount of spiroepoxide consumption. The structure of the resin is being characterized.

Attempts to polymerize the spiroepoxide by radiation or with catalytic amounts of a is acid failed; Co^{60} radiation at 25° (40 meg. Rads) or BF_3 (200°/16 hr) did not affect the epoxide. The spiroepoxide is unstable to fluoride ion in glyme solvents; $CsOCF(CF_3)_2$/tetraglyme at 0° yields mostly rearranged acid fluoride while CsF/tetraglyme at -20° yields dimer with minor amounts of presumed trimer and tetramer. A control experiment demonstrated that the presence of fluoride ion is necessary to observe reaction.



Further attempts to polymerize the spiroepoxide led us to investigate the effect of a crown ether on the fluoride ion initiated polymerization. Since it is well documented[14] that crown ether ligands complex alkali metal cations to such an extent that alkali metal salts can dissolve in organic, nonpolar solvents, an attempt was made to polymerize the spiroepoxide in Freon 113 [$CsOCF(CF_3)_2$ catalyst] containing dicyclohexyl-18-crown-6. After 8 hours at 0-25° no reaction occurred and spiroepoxide was recovered unchanged.

With regard to the attempted fluoride ion initiated polymerization, the spiroepoxide apparently behaves similarly to perfluoroisobutylene oxide[15] in that it is reluctant to undergo homo-oligomerization past the dimer stage at an appreciable rate. Our initial premise that the internal strain in this spiroepoxide would facilitate fluoride ion initiated ring opening seems to be correct -- the spiroepoxide undergoes rapid ring opening at low temperature in the presence of fluoride ion. However, presumably due to a restrictive counteraction of steric factors, oligomerization is minimal past the dimer. This can be rationalized by the following scheme where $k_1 >> k_{-1}$ or $k_1 >> k_2$ or both.



An area of investigation worth pursuing would center around polymerizations based on catalysts other than the alkali metal fluorides, e.g., homogeneous and heterogeneous catalysis using various transition metal complexes. This area is planned for study and will involve the use of a series of fluorinated epoxides.

D. Fluorinated Ether Epoxides

Perfluoroether epoxides, $R_fO\overset{O}{\overset{/\backslash}{CFCF_2}}$, may be interesting intermediates from a practical as well as a theoretical viewpoint. Low DP oligomers of perfluroether epoxides may be useful end products if the appropriate length R_f is chosen. It is documented that an R_fO substituent exerts a similar electronic effect as an F substituent, and sterically more nearly resembles an F substituent than does an R_f substituent. Thus, it is conceivable that the simplest molecule of the series, $CF_3O\overset{O}{\overset{/\backslash}{CF-CF_2}}$, if preparable, may resemble TFEO, which affords high molecular weight material on fluoride ion induced polymerization. This class of epoxide would be of theoretical interest from both thermodynamic and kinetic viewpoints. Does this class of compound undergo unimolecular rearrangement, and if so to an ester or an acid fluoride? What is the center of nucleophilic attack, the α or β carbon atoms; is it regiospecific?

The initial synthetic approach to this class of epoxide centered around the oxidation of fluorovinyl ethers. The vinyl ether chosen for study was prepared from HFPO trimer.

$$C_3F_7O\overset{CF_3}{\overset{|}{C}}FCF_2O\overset{CF_3}{\overset{|}{C}}\overset{O}{\overset{||}{C}}F \;-\; Na_2CO_3 \xrightarrow{150^\circ} C_3F_7O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$$

56%

This vinyl ether was subjected to oxidation by three reagents a) basic H_2O_2, b) O_2/OF_2[16] and c) $O_2/h\nu$. These reactions were followed by infrared. In each instance a band appeared at 6.3μ However, with the first and third reagents, the band was short-lived. The second route, i.e., the oxidation with O_2 and catalytic OF_2 was studied in greater detail (see Table III). To date the

TABLE III

EPOXIDATIONS OF $CF_3CF_2CF_2OC(CF_3)FCF_2OCF{=}CF_2$

Oxidizing Agent	Gram	Temp °C	Time	Phase	% Epoxide	Other Products
H_2O_2 50%	2.2	10	3 hr	liquid	--	an acid (fluorinat
O_2/OF_2 4/1	4.8	0	3 1/2 hr	liquid	∿10	$(HFPO)_2$ acid fluoride, COF_2
O_2/OF_2 20/1	4.3	∿20	20 min	gaseous	∿10	" "
O_2/OF_2 100/1	2.0	∿20	1 hr	gaseous	∿ 5	$(HFPO)_2$, COF_2, no recovered vinyl et
O_2/OF_2 200/1	3.0	-58	30 min	gaseous	∿15	$(HFPO)_2$, COF_2
O_2/OF_2 10/1	13.2	-20	4 hr	liquid	∿20	$(HFPO)_2$, COF_2, recovered vinyl et
O_2/OF_2 20/1	2.8	-40	3 hr	liquid	∿20	$(HFPO)_2$, COF_2
O_2/OF_2 20/1	7.0	-60	5 hr	liquid	∿15	$(HFPO)_2$, COF_2
$O_2/h\nu$	1.6	30	6 hr	gaseous	--	a acid fluoride

epoxide has been prepared in an impure state in ca. 20% yields. The major impurities were found to be the starting vinyl ether and HFPO dimer acid fluoride. The reaction scheme is shown below.

$$\underset{\text{VI}}{C_3F_7OC(CF_3)FCF_2OCF{=}CF_2} + O_2 \xrightarrow{OF_2\ \text{catalyst}}$$

$$\underset{10}{\text{VI}} + \underset{9}{C_3F_7OC(CF_3)F{-}C(O){=}CF} + \underset{5}{C_3F_7OC(CF_3)FCF_2OC(O){-}CF_2} + COF_2$$

The epoxide was characterized by infrared and the ^{19}F-NMR spectrum of the above three-component mixture. In the presence of VI and HFPO dimer, the epoxide decomposes at room temperature (half life ca. 6 hr). GLC analysis

(on-column injection) showed that the epoxide decomposed at the detector (thermal conductivity) liberating carbonyl fluoride and other materials. The crude reaction mixture can be distilled at roughly -10° without appreciable epoxide decomposition, but unfortunately, without further purification. The fact that the epoxide decomposed during an aqueous workup suggests its instability towards strong aqueous acids (R_fCO_2H or HF produced by hydrolysis of acid fluoride impurities). It is encouraging that this class of fluorocarbon epoxide is indeed preparable.

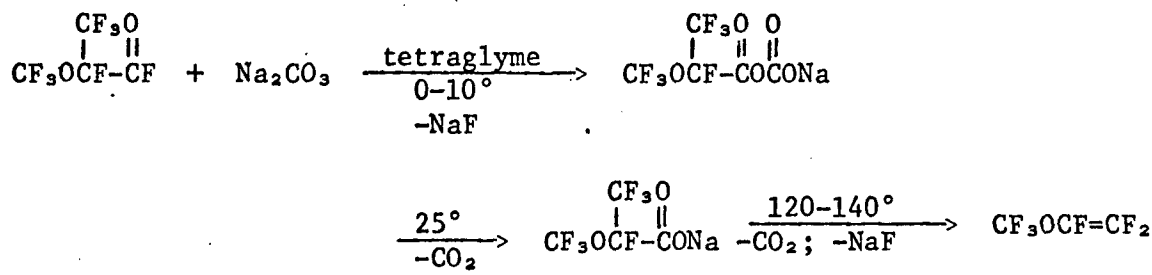
The simplest member of fluorinated epoxy-ethers, $CF_3OC(O)F-CF_2$, would have the greatest interest with regard to polymerization reactions. This compound would be gaseous and probably isolable by methods already proved useful for this epoxy ether's electronically similar analog TFEO. Thus, the precursor of the epoxy ether, perfluoro(methyl vinyl ether), was prepared.

In the first step[17] HFPO and COF_2 were heated at 75° in tetraglyme containing CsF. Low temperature distillation afforded 255 g (>98% purity, 44% yield based on COF_2 consumed) of the desired acid fluoride, bp 5-8°.

$$\text{(excess)}\ COF_2 + CF_3C(O)F-CF_2 \xrightarrow[75^\circ,\ 24\ hr]{CsF,\ tetraglyme} CF_3OCF(CF_3O)-CF + C_2F_5C(O)F$$

An intermediate cut, bp -26 to +5° weighed 83 g and contained 79% of the desired acid fluoride.

The resulting high purity perfluoro(2-methoxy propionyl fluoride) was bubbled into a slurry of Na_2CO_3/tetraglyme at 0-10°. The reaction mixture was then warmed to room temperature until CO_2 evolution ceased, then heated to 120-140°, at which time a perfluoro(methyl vinyl ether)-CO_2 mixture was evolved. Low temperature distillation gave 120 g (>98% purity, 68%) of perfluoro(methyl vinyl ether), bp -26 to -25°.



Attempted oxidation of perfluoro(methyl vinyl ether) was studied (see Table IV). Unlike the ether epoxide derived from HFPO trimer vinyl ether, the epoxide derived from perfluoromethyl vinyl ether is elusive when reactions are run under static conditions. In our hands, using either O_2 or air as oxidant and catalytic amounts of OF_2, Br_2, N_2O_3, or sunlight as initiators, only COF_2 and $CF_3O\overset{O}{\overset{\|}{C}}F$ are formed; little if any epoxide could be detected. Emphasis shifted to the use of a flow system where contact time of reactants can be regulated and products can be removed as formed. Experimentation in such a system (see Experimental) is currently in progress. If the desired epoxyether resists isolation, attempts will be made to prepare a polymer of similar structure by oxidizing perfluoro(methyl vinyl ether) itself by the Montecatini process.[18]

TABLE IV

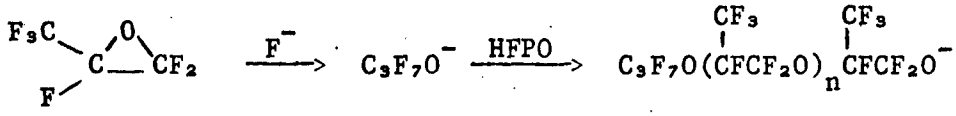
ATTEMPTED OXIDATION OF $CF_3OCF{=}CF_2$*

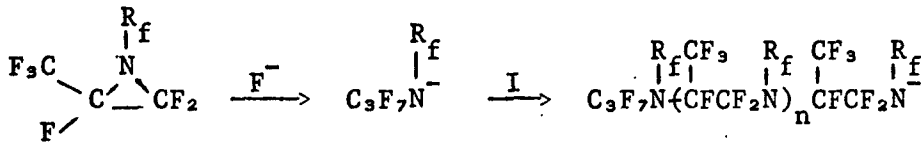
Initiator, Oxidant	Conditions	Product
1. OF_2 (8 mm), O_2 (300 mm)	3-1 flask, -40°	Unreacted ether, COF_2, $CF_3O\overset{O}{\overset{\|\|}{C}}F$
2. OF_2 (8 mm), O_2 (300 mm)	2-1 flask, 10 cc Freon-113, -78° to -40°	No epoxide, decomposition products
3. Br_2 (1 mm), O_2 (300 mm)	1-1 flask, 25°, gradual O_2-Br_2 addition	Trace epoxide, mostly decomposition
4. ''	0°	''
5. Br_2 (1 mm), Air (700 mm)	1-1 flask, 25°	''
6. N_2O_3 (<1 mm), Air (400 mm)	1-1 flask, sunlight	No epoxide
7. Air (600 mm)	1-1 flask, sunlight	Decomposition, no epoxide
8. Br_2, air	Flow system, hν	Unreacted starting material, no products

*Roughly 1 g of ether charged throughout.

E. Perfluoro-N-alkylaziridines

To the best of our knowledge perfluorinated N-alkyl aziridines[19] are unknown. This class of compound may be of interest by analogy to fluorinated epoxides, i.e., perfluorinated three-membered ring nitrogen heterocyclics may be polymerized via fluoride ion catalysis.

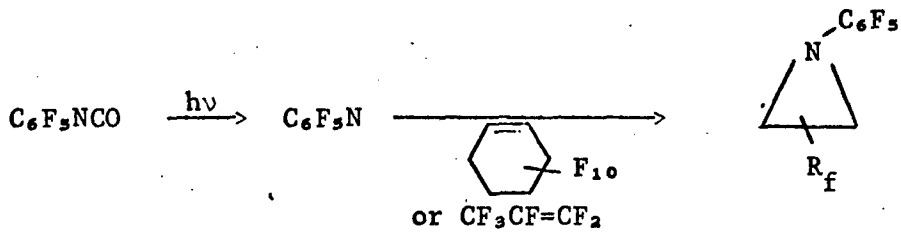




Since a fluorinated nitrogen anion should have different properties than a fluoroalkoxide (greater stability, different chain transfer properties, etc.) there is a distinct possibility that high molecular weight perfluorinated poly tertiary amines could result.

There are several approaches to the preparation of perfluoro-aziridines, for example, addition of nitrene across a C=C, addition of carbene across a C=N, or a synthetic route involving reported aziridines.

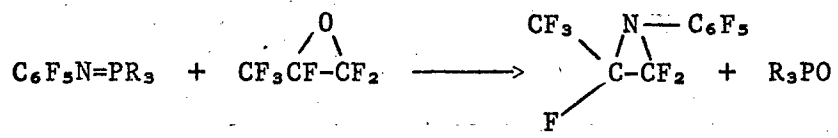
Initially we attempted the addition of a nitrene formed by photolysis of an isocyanate across a fluorinated olefin.



Photolysis with a 450 watt Hanovia lamp for 18 hour gave no evidence of nitrene formation.

The accessibility of fluorinated isocyanates seemed to merit further attempts to use this class of compound as a precursor to a fully fluorinated N-alkylaziridine. Our experience with fluorinated isocyanates suggested the following route.

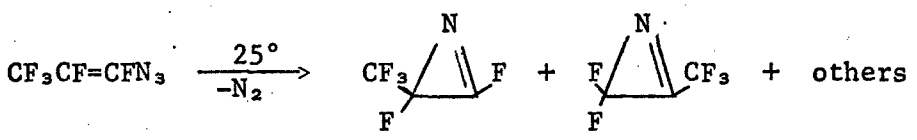
$$C_6F_5NCO + R_3P{\rightarrow}O \xrightarrow{-CO_2} C_6F_5N{=}PR_3$$



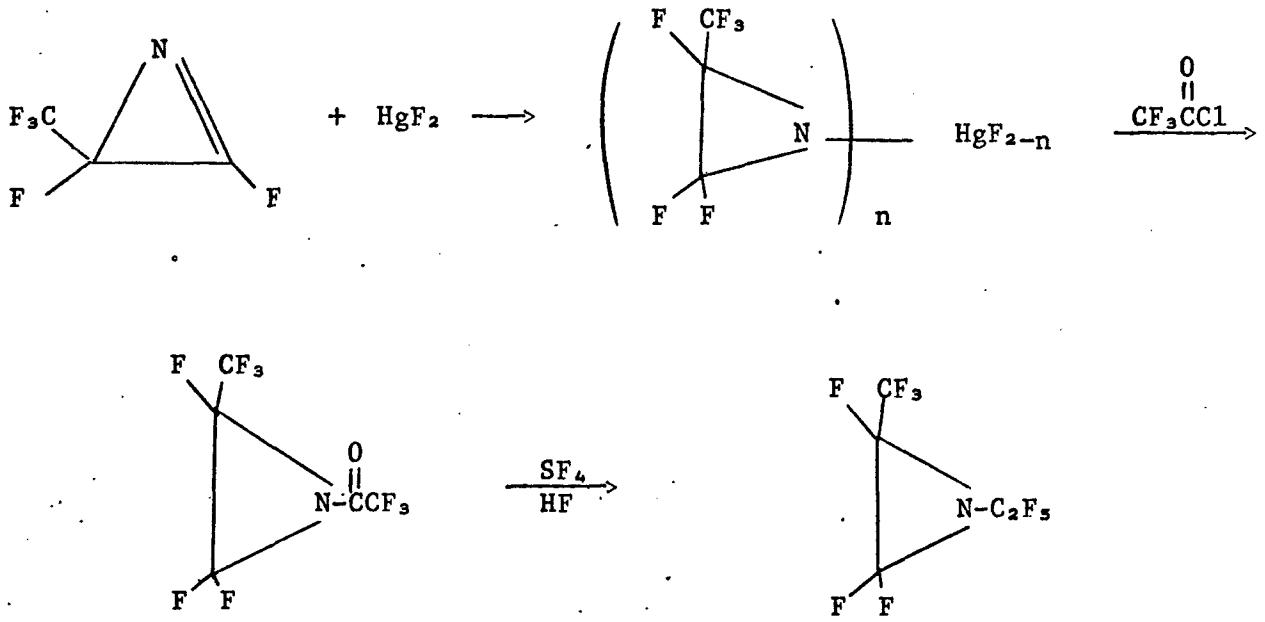
The <u>in situ</u> preparation of the phosphine imine proceeded as shown judging from infrared. Reaction between this material and HFPO at 100° gave a mixture of products containing phosphine oxide and two major components in the estimated boiling range of the aziridine. At this time, judging from the anticipated difficulty that would be encountered in separating these components, it was decided to pursue an alternate route to this class of compound.

Work was then initiated on the reported[20] azirine synthesis as shown below.

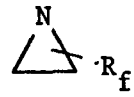
$$NaN_3 + H_2SO_4 \xrightarrow{Et_2O} HN_3 \xrightarrow[0°]{Et_3N} Et_3\overset{+}{N}H\overset{-}{N_3} \xrightarrow[\sim 10°]{CF_3CF{=}CF_2}$$



The proposed scheme to an aziridine is as follows

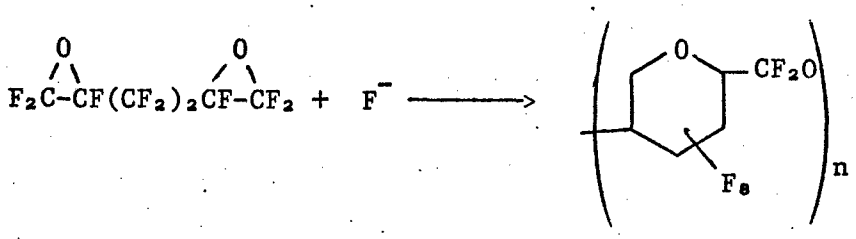


The azirine is reported to be unstable to nucleophiles and accordingly should be stored at -78° in glass. The crude azirine contained $CF_3CF{=}CF_2$ and $CF_3CFHCF_2N_3$ impurities and was used without purification for the subsequent steps.

The azirine does not react with HgF_2 below -20°; however, at 25° reaction proceeded to yield a pasty material which was directly treated with trifluoroacetyl chloride. A product suspected to be the amide was a major component in the product mixture (∿50%). The amide, thus far characterized by infrared ($\overset{O}{\overset{\|}{C}}$ at 5.55μ, a  R_f band[4] at 6.75μ), is thermally stable, stable enough to be isolated by GLC. Work in this area is continuing.

F. Perfluoro Bis-Epoxides

The bis-epoxide derived from 1,5-perfluorohexadiene could conceivably be cyclopolymerized by fluoride ion in solution.



Perfluorohexadiene, the precursor to the bis-epoxide, has been reported[21] to be prepared in low yields in a rather lengthy procedure. An alternate synthesis to the diene involves the preparation of 1,6-diiodo-perfluorohexane. The preparation of this latter compound is underway.

$$CF_2CF_2 + I_2 \xrightarrow{\sim 200^\circ} I(CF_2CF_2)_nI$$

$$I(CF_2CF_2)_3I \xrightarrow[\text{Apply vacuum}]{\text{RMgX, } -50^\circ} F_2C{=}CF(CF_2)_2CF{=}CF_2 \ (?)$$

III. EXPERIMENTAL

A. Solvent Studies

1. Oligomerization of HFPO

Anhydrous cesium fluoride (20.0 g, 0.131 mole, dried at 250°/1 mm overnight) was added to diglyme (100 ml) and the solution stirred magnetically. The solution was frozen in a LOX bath, then evacuated. The mixture was then thawed and cooled with an ice bath. HFPO (1725 g, 10.4 moles) was added, keeping a positive epoxide pressure of 3 psig on the system. The addition was moderated so that the temperature of the reaction did not exceed ca. 40°. The addition was complete after 2.5 hr. The fluorocarbon layer was phase separated (1650 g), then distilled. The following fractions were collected.

B.P. °C	Pressure (mm)	Wt. (g)	Comments
54-58	760	131.3	dimer
60-115	760	13.7	mixture dimer, trimer
115-118	760	337.0	trimer
118-130	760	1.5	--
40-59	0.8-25	389.2	tetramer
Residue		?	Pentamer saved

2. Reaction Between HFPO Dimer and Methoxytriglycol

The HFPO dimer acid fluoride (87.6 g, 0.264 mole) and methoxytriglycol (anhydrous, 43.2 g, 0.264 mole) were charged into a 300-ml stainless steel autoclave and heated with rocking at 80°/15 hr. The clave was cooled and aspirated to remove residual HF; then its contents were distilled. The ester was collected; B.P. 78-80°/0.25 mm, 82.8 (69%).

Anal. Calcd for $C_{13}H_{15}F_{11}O_6$: C, 32.77; H, 3.15
Found: C, 32.48; H, 3.23

3. Reaction Between HFPO Trimer and Methoxytriglycol

In a similar experiment, the trimer of HFPO (81.0 g, 0.127 mole) and methoxytriglycol (27.4 g, 0.167 mole) afforded 57.7 g (72%) of ester, B.P. 97-104°/0.2-0.3 mm.

Anal. Calcd. for $C_{16}H_{15}F_{17}O_7$: C, 30.67; H, 2.4
Found: C, 30.01; H, 2.55.

4. Reaction Between HFPO Tetramer and Methoxytriglycol

In a similar experiment HFPO tetramer (97.4 g, 0.146 mole) and methoxytriglycol (23.9 g, 0.146 mole) afforded 96.8 g (85%) of ester, B.P. 125°/0.1 mm.

Anal. Calcd for $C_{19}H_{15}F_{23}O_8$: C, 28.4; H, 1.9.
Found: C, 28.7; H, 1.9

5. General HFPO Oligomerization Procedure

Cesium fluoride (0.5 g) was placed in a flask and heated at 250° (1 mm) overnight. The flask was cooled and solvent [diglyme (7 ml) or I (10 g)] was added along with Freon E4 (0.5 g). Hexafluoropropylene oxide (3.0 g) was introduced through an acetone-dry ice condenser. The reaction temperature was moderated by external heating or cooling according to Table 1. Samples were periodically withdrawn and analyzed by GLC.

B. Fluorinated Spiroepoxides - Preparation

1. Preparation of $C_3F_7O(\overset{CF_3}{\overset{|}{C}}FCF_2O)_2CF{=}CF_2$ (II)

In a nitrogen atmosphere anhydrous Na_2CO_3 (50.0 g, 0.472 mole) was placed in a flask. Dry tetraglyme (200 ml) was added and the slurry stirred at room temperature. Hexafluoropropylene oxide tetramer acid fluoride (139 g, 0.204 mole) was added dropwise to the mixture. At the completion of the addition the flask was heated to 150° for 0.5 hr, then allowed to cool. The contents were poured into water (1 liter) and the fluorocarbon layer (105.5 g) separated. The aqueous solution was extracted with Freon 113 (3 x 50 ml) and the extracts combined with the fluorocarbon layer. This solution was dried with $MgSO_4$ and distilled. The fraction boiling at 58-62°/22 (67.6 g, 55%) was shown to be >98% pure by GLC.

2. Reaction Between II and Dichlorodifluoroethylene

Trial experiments indicated that the reaction between stoichiometric amounts of the olfefins afforded both homodimers as well as a product suspected to be the codimer. This suggested the use of excess $CCl_2=CF_2$ in a large scale experiment to avoid the consumption of II in a homodimerization reaction.

The vinyl ether II (23.0 g, 0.0384 mole) and dichlorodifluoroethylene (46.5 g, 0.35 mole) were charged into a 300-ml autoclave equipped with a 3000 psi bursting disc. The autoclave was heated at 190°, pressure at temperature was 275 psig. After 24 hrs at 190°, pressure at temperature was 60 psig. The autoclave was cooled and unreacted $CCl_2=CF_2$ was transferred at 12 mm (17.5 g was recovered). The remaining oil weighed 47.5 g and consisted of three materials (GLC) in the ratio of 21:6:7. The first two are $CCl_2=CF_2$ dimer and II, respectively, the last is the desired product, III. Distillation afforded 5.5 g of recovered starting material and 11.2 g of III b.p. 86°/1 mm (based on 17.5 g of II, 52%).

Anal. Calcd for $C_{13}Cl_2F_{24}O_3$: C, 21.1
Found: C, 21.0

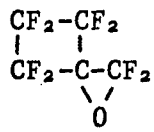
3. Attempted Hydrolysis of III

a. A 50-ml, 3-neck flask was equipped with a magnetic stirrer, a reflux condenser, a thermometer, and a gas outlet backed by a LOX trap. The cyclobutane derivative (III, 6.5 g), 30 cc of 30% fuming sulfuric acid and catalytic amounts of the mercuric salts ($HgSO_4$; Hg_2SO_4) were stirred together. The material was heated to 93°C for 16 hr and then cooled to room temperature. The SO_3 was removed at full vacuum and the flask was then heated to 60°C under full vacuum to remove the product. There was collected 6.0 g of colorless liquid which was shown to be the unreacted starting material.

b. The cyclobutane, III (6.0 g), was placed in a 50-ml, 3-necked flask equipped as described above along with 30 cc of 30% fuming sulfuric acid and catalytic amounts of $HgSO_4$ and Hg_2SO_4. The reactants were heated to 120°C (reflux) for 16 hrs and the products removed as previously described. Unreacted cyclobutane (5.4 g) was collected.

c. An 80-cc stainless steel autoclave was charged with III (5.4 g), 30 cc of 30% fuming sulfuric acid, and catalytic amounts of mercuric and mercurous sulfate. The system was sealed and heated to 145°C for 60 hrs. After being cooled to room temperature the products were removed with a syringe and the SO_3 removed under full vacuum. The products were then distilled out under full vacuum at 60°C to give ∿3.6 g of unreacted cyclobutane. This material was then placed in a glass ampoule along with 10 cc of 30% fuming sulfuric acid. The ampoule was sealed and heated to 185°C for 80 hrs then cooled to ambient temperature (27°C). Two layers were observed in the reactor; the upper layer was removed and found to be 1.8 g of unreacted cyclobutane derivative. No further products were found.

4. <u>Initial Preparation of</u>



A 30-cc stainless steel pressure reactor was equipped with a 1000 psi gauge and checked for leaks. The perfluorocyclobutanone (1.0 g) was condensed into the reactor along with 1.5 g of hexafluoropropylene epoxide. The reactor was heated to 165°C for 16 hr with little or no reaction taking place. The material was then heated to 200°C for ∿60 hr and the perfluorocyclobutanone peak disappeared by GLC (35% PFOX at room temperature) and a higher boiling fraction appeared. A prep IR of the new compound was consistent with the expected spiro-epoxide.

The reaction was repeated on a larger scale. PFCB (14.3 g, 0.8 mole) and HFPO (19 g, 0.114 mole) were transferred to a 300-ml stainless steel autoclave which was heated to 200-220° (P at temp. = 650 psig). After 48 hr the pressure was 600 psig. The clave was cooled and its contents transferred to a flask; 29.6 g of volatiles were obtained. GLC showed a preponderence of CF_3COF as well as traces of PFCB and HFPO. Seven major products were observed in a 30:9:18:7:7:9:18 ratio. This material was fractionated into three portions: CF_3COF (∿90%, 10.2 g) a middle cut (BP ∿25°, 4.0 g, contains ∿75% of the first of the seven products), and a liquid fraction (11.4 g, contains the seven components). GLC-mass spec and ^{19}F NMR of the compounds are shown in the appendix.

5. Preparation of Methyl Trifluorovinyl Ether

A series of attempted preparations of the titled compound were run; only the procedure that was developed is presented for economy of space.

A 3-l stainless steel autoclave equipped with a 2800 psi bursting disc was evacuated. Sodium methoxide (255 g, 5.1 mole) was added to a 1-liter flask in a dry bag. Then dioxane (freshly distilled from Na, 900 ml) was added.[22] The mixture was shaken to a free-flowing slurry and charged into the autoclave by suction. The contents of the autoclave were cooled to -183° when TFE (430 g, 4.3 moles) was condensed into the system. The autoclave was allowed to warm to room temperature with rocking; after 20 hr the pressure was <100 psig. The contents of the autoclave were condensed into a 2-liter flask in vacuo and distilled through a 3' vacuum jacketed, glass packed column. The following fractions were collected.

Fraction	B.P.	Wt.	Composition
I	-79°	∿20.0 g	TFE
II	+9°	30.5 g	>96% $MeOCF{=}CF_2$
III	10-11°	173.5 g	>98% $MeOCF{=}CF_2$
IV	12-14°	16.0 g	>96% $MeOCF{=}CF_2$
Bottoms		293.8 g	Mixture $MeOCF_2CF_2H$ + $(MeO)_2C{=}CF_2$ (?) + dioxane

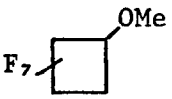
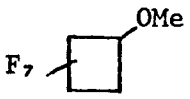
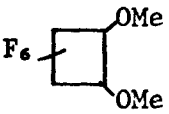
The 200 g of methyl trifluorovinyl ether obtained corresponds to a 46% yield based on TFE.

When this reaction is repeated using freshly purchased NaOMe yields in excess of 70% are obtained.

6. Preparation of Methyl Perfluorocyclobutyl Ether

Four reactions between methyl trifluorovinyl ether and TFE were run on ca. 0.1 mole scale without mishap. The cyclobutyl ether was obtained in an average of 70% yield. The reaction was then scaled up according to the following procedure.

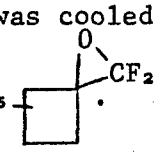
A 1.4-liter stainless steel autoclave was equipped with a 3000 psi bursting-disc and charged with phenothiazine (0.2 g), dipentene (3 ml), methyl trifluorovinyl ether (95 g, 0.85 mole), and TFE (212 g, 2.12 mole) in vacuo at LOX temperature. The autoclave was allowed to warm to 20° overnight with rocking (P = 200 psig). The clave was heated to 100° (P = 580 psig), 125° (P = 700 psig), and 150° (P = 1050 psig) over a 5 hr period. The autoclave was rocked at 150° until the pressure decreased to 900 psig then heated to 165° and rocked at temperature for 17 hours. At that time the pressure was 400 psig. The vessel was allowed to cool to 25°, then the contents were transferred to a flask cooled in LOX at <1 mm. The flask was allowed to warm to room temperature at atmospheric pressure; the volatiles were distilled through a 1' glass packed column and collected in a trap cooled with LOX. The volatiles consisted primarily of perfluorocyclobutane and were discarded. The residue (151.0 g) was carefully distilled and the following fractions collected.

Fraction	B.P.	Wt. g	Composition by GLC
I	50-53°	5.0	~93%  $CH_3OCF_2CF_2H$ (minor)
II	54-57	105	~98% 
III	57-58	4.5	"
Bottoms		22.2	Major component probably 
Trap			Perfluorocyclobutane

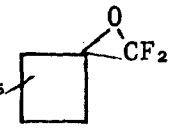
7. Conversion of Methyl Perfluorocyclobutyl Ether to Perfluorocyclobutanone

A 200-ml capacity 14'' x 1'' O.D. (3/32'' ID) glass ampoule was charged with degassed concentrated H_2SO_4 (60 ml) and methyl perfluorocyclobutane (37.0 g, 0.183 mole). The tube was sealed *in vacuo* and placed and rocked in an oil bath at 175° for 3 hr. At this time the homogeneous, amber solution was allowed to cool, frozen at LOX temperature, opened, and allowed to warm slowly to room temperature. During the warming SiF_4 was liberated. The H_2SO_4 solution of perfluorocyclobutanone hydrate was transferred into a 500-ml flask equipped with a solid addition funnel and Vigreaux distillation column. A low temperature reflux condenser cooled with ice water was placed on the top of the distillation column. P_2O_5 (powder, 100 cc volume) was slowly added to this mixture through the solid addition funnel at such a rate that the internal temperature did not exceed 40°. The resulting mixture was then heated; at *ca.* 60° perfluorocyclobutanone distilled from the mixture (efficient stirring is necessary to prevent frothing) and collected. There was obtained 24.7 g of the ketone (theory 31 g, 80% yield) , b.p. ∿0°C.

8. Reaction Between Perfluorocyclobutanone and HFPO in Glass Ampoules (Small Scale)

Perfluorocyclobutanone (1.0 g, 5.6 mmoles) and HFPO (1.86 g, 11.2 mmoles) were charged and sealed in a 25-ml glass ampoule. The ampoule was then heated at 180° for 8 hr (under these conditions there is no apparent liquid phase). The ampoule was cooled and opened. GLC analysis showed only three products CF_3COF, c-C_3F_6, and  . Traces (<2%) of HFPO and perfluorocyclobutanone remained. GLC yield estimates are in excess of 90%. This reaction was repeated using perfluorocyclobutanone (2.0 g, 11.2 mmoles) and HFPO (0.93 g, 5.6 moles) under the same conditions and gave essentially the same yield of the spiroepoxide. In this case, unreacted fluorinated ketone remained and considerably less c-C_3F_6 was observed.

Lastly, the reaction was run in a glass ampoule under essentially the same conditions that were used in a previous reaction in stainless steel; i.e., cyclobutanone (1.0 g, 5.6 mmoles) and HFPO (1.3 g, 8.0 mmoles) were heated at 200° for 48 hr in a 25-ml glass ampoule. The yield of spiroepoxide obtained in this reaction was essentially the same as the yields obtained above.

9. Preparation of F_6  (Scale Up)

Three 200-ml capacity 1'' OD, 3/32'' ID glass ampoules were charged with perfluorocyclobutanone (ca. 9 g) and HFPO (ca. 15 g) in vacuo (total 46.9 g, 0.28 mole, of HFPO and 27.4 g, 0.154 mole, perfluorocyclobutanone). The tubes were sealed and completely submerged in an oil bath maintained at 180 $\pm$1° for 8 hr. The contents of the tube were transferred to a flask (in vacuo), weighed (73.7 g) and distilled. The following fractions were collected.

B.P.	Wt.	Composition
-64 to +17	74.0 g	$CF_3\overset{O}{\overset{\|\|}{C}}F$, C_3F_6, spiroepoxide (~
		Trace of HFPO and PFCB
18 -21°	27.8 g	>98% spiroepoxide

The yield of spiroepoxide was 80% (27.8 g, theory 35 g).

10. Preparation of Trimethyl Trifluoromethyl Tin

Hexamethylditin (85 g, 0.25 mole) and trifluoromethyl iodide (202 g, 1.04 mole) were charged into a 300-ml stainless steel autoclave and heated at 75° for 5 days. The contents of the autoclave were transferred to a flask at <1 mm and distilled to yield 190 g of CF_3I (6% conversion) and 11.4 g of crude distillate, B.P. 90-110°. The latter was redistilled B.P. 103-104° (6.3 g, ~92% one component, 40% yield). A semi-solid residue (54.0 g) was left in the autoclave.

11. Reaction Between Me_3SnCF_3 and Perfluorocyclobutanone

The titled tin compound (1.3 g, 5.6 mmoles) and perfluorocyclobutonone (1.0 g, 5.6 mmoles) were sealed in a 25-ml glass ampoule and heated at 150°/ 20 hr. At this time two phases -- a white solid and dark liquid -- were observed. A combination of GLC-infrared analysis indicated that spiroepoxide was not a dominant product. Four products were detected in the ratio of 1:6:1:2, all of which had similar retention times to the spiroepoxide.

C. Reactions of the Spiroepoxide

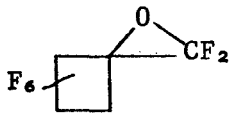
1. Fluoride Ion Catalyzed Reaction of the Spiroepoxide

a. A stock solution of $CsOCF(CF_3)_3$ was prepared by adding $(CF_3)_2CO$ (2.3 g) to anhydrous tetraglyme (100 ml) containing CsF (initially heated at 250°/<1 mm, overnight). The ketone was absorbed into the tetraglyme in vacuo at 25°. The resulting solution contained 0.136 mmoles of alkoxide/ml. A portion of this solution (0.32 ml, $\sim 4 \times 10^{-5}$ mole) was added to anhydrous tetraglyme. The resulting solution was cooled to 0° and stirred while the spiroepoxide (1.5 g, 6.6 mmoles) was added over a 10 min interval. The solution became cloudy then formed a puddle of fluorocarbon. After stirring at 0° for 1 hr, IR revealed complete consumption of the spiroepoxide; GLC showed two products in an 18:1 ratio. The major component was removed from the mixture in vacuo at 0°; there was obtained 1.1 g of this material which was characterized as perfluorocyclobutanoyl fluoride by IR, NMR, and mass spec. This minor component is suspected to be dimer acid fluoride.

b. The reaction was repeated using CsF as initiator (~10 mg) in tetraglyme (1 ml) at -20°. Under these conditions higher oligomers were observed; the ratio of the rearranged acid fluoride to presumed dimer, trimer and tetramer were 8:4:1 trace. The dimer was isolated and characterized by ^{19}F-NMR.

c. The reaction was repeated using diglyme without an added source of fluoride ion in a control experiment. The spiroepoxide was added and the solution slowly warmed from -50° to 0° and maintained at 0° for 6 hr. GLC and IR showed that the spiroepoxide was completely stable under these conditions. These ether solvents do not initiate rearrangement.

d. Freon-113 (3 ml) and dicyclohexyl-18-crown-6 (0.1 g) were stirred together at 25° when a tetraglyme solution of $CsOCF(CF_3)_2$ (0.1 ml, $\sim 10^{-5}$ moles of Cs^+) was added. The solution was stirred and cooled to -20° when



(1.2 g, 5.3 mmoles) was introduced into the solution. After stirring for 2 hr at -20°, IR and GLC indicated that spiroepoxide was not consumed. The solution was allowed to warm to 25° and maintained at that temperature for 18 hr. GLC and IR showed no product, only unreacted spiroepoxide.

2. Reaction Between Spiroepoxide and $(\phi O)_3P$

The spiroepoxide (1.1 g, 4.5 mmoles) and $(\phi O)_3P$ (1.36 g, 4.4 mmoles) were placed in a Fischer-Porter tube and heated at 60°/18 hr. There was no visible reaction. The tube was then heated at 150°/18 hr at which time a red resin solidified in the tube. There were essentially no volatiles left unreacted (trace of spiroepoxide and SiF_4). The red resin (2.3 g) was slightly tacky and unstable to moisture. It liberated phenol when exposed to the air.

The reaction was repeated using 0.1 g $(\phi O)_3P$ and 1.1 g of the spiroepoxide. There was recovered 89% spiroepoxide; a dark resin was formed in the bottom of the tube. It appears that the spiroepoxide and $(\phi O)_3P$ react stoichmetrically to give the resin.

Various reactions of the spiroepoxide are shown in Table II.

D. Fluorinated Ether Epoxides

1. The Preparation of $CF_3CF_2CF_2O\overset{\overset{CF_3}{|}}{C}FCF_2OCF{=}CF_2$

A 1-l, 3-neck flask was equipped with a magnetic stirring bar, a thermometer, and a gas take-off. Sodium carbonate (117 g, 1.10 moles) was dried overnight at 200°C under full vacuum. The following morning the flask was cooled to ambient temperature, and with a dry N_2 sweep the system was equipped with an ice water condenser and a dropping funnel. Tetraglyme (200 cc) was added and the $CF_3CF_2CF_2O\overset{\overset{CF_3}{|}}{C}FCF_2O\overset{\overset{CF_3}{|}}{C}F{-}\overset{\overset{O}{\|}}{C}F$ (200 g, 0.40 moles) was added slowly via the dropping funnel with vigorous stirring. There was a slow exotherm to ∿60°C with the evolution of CO_2; when the evolution had subsided the mixture was heated to 120°C for 30 min. The mixture was cooled to room temperature and poured into a liter of water. The organic layer was separated, dried, and distilled to give 48 g of the desired $CF_3CF_2CF_2O\overset{\overset{CF_3}{|}}{C}FCF_2OCF{=}CF_2$: 60 g of higher boiling material (dimeric) remained.

The preparation of vinyl ether was again carried out under modified conditions to increase the yield of the desired product. Sodium carbonate (100 g) was dried under full vacuum at 200°C for 16 hr in a 1-l, 3-neck

flask equipped with a thermometer, a magnetic stirring bar and a gas take-off. After cooling to room temperature the system was equipped with a condenser and a dropping funnel. Tetraglyme (200 cc) was added and stirred vigorously as the HFPO trimer acid fluoride (218 g, 0.438 mole) was added dropwise. There was a slow exotherm to 70°C while CO_2 evolved from the mixture.

After the exotherm subsided a full vacuum was applied to the system, and the flask was heated to 100° over a 2-hr period. The products were collected in a series of traps -78°C, -196°C, and -196°C. The CO_2 which evolved was collected in the -196°C trap while the desired product was collected in the -78°C trap. There was collected 145 g of material which was distilled to give 101 g of the desired vinyl ether (56% yield) along with 32 g of a higher boiling material.

2. <u>Epoxidation of $CF_3CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$ Using 50% H_2O_2</u>

A 25-cc, 3-neck flask was equipped with a magnetic stirring bar, a reflux condenser, a thermometer, and a stopper. The $CF_3CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$ (2.16 g, 5 mmoles) was added to 10 cc of 10% Na_2CO_3 solution and the stopper replaced by a dropping funnel. H_2O_2 (50%, 5 cc) was added over a 20 minute period and there was an exotherm to 35°C. The flask was then cooled to 10°C and stirred for 3 hr with samples taken 3 times during the 3-hr period. An IR spectrum showed an epoxide band (6.3μ) and a distinctive $\overset{F}{\overset{|}{C}}{=}O$ band which later shifted to an acid carbonyl. The following morning the organic layer had disappeared and there remained only a solid (no epoxide band).

3. <u>Epoxidation of $CF_3CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$ Using O_2/OF_2</u>

a. A 25-ml, 3-neck flask was equipped with a gas inlet below the surface of the liquid and ice water condenser backed by a LOX trap, a magnetic stirring bar, and a thermometer. The $CF_3CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$ (4.8 g, 10 mmoles) was added to the flask and stirred while a 4/1 mixture of O_2/OF_2 introduced. After 2 min. there was an exotherm which was contained by cooling (ice bath). After 3.5 hr IR analysis indicated some acid fluoride and a small amount of material with a peak at 6.3μ which was attributed to the epoxide functional group.

b. A dilution of the OF_2 was suggested from the above results. Therefore a 3-l, 3-neck flask was equipped with a gas inlet, a magnetic stirring

bar, and a septum before being evacuated to a full vacuum. The flask was cooled to -10°C in an ice bath and 700 mm O_2 along with 40 mm OF_2 were added. The vinyl ether ($CF_3CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$, 4.3 g) was added with a syringe and there was an immediate exotherm. A sample was taken and showed by IR to contain $\overset{O}{\overset{\|}{C}}$-F and a small band at 6.3μ attributed to the epoxide. GLC showed two major peaks, one of the acid fluoride and supposedly the epoxide (on 15% PFOX on column injection). After standing at ambient temperature for 24 hr however the IR spectra showed no adsorption at 6.3μ, indicating the decomposition of the epoxide.

c. A 3-l, 3-neck flask was fitted with a magnetic stirring bar, a gas inlet, and a septum. The flask was evacuated to full vacuum and 2.0 g $CF_3CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$ was added via a syringe. The O_2 was pressured in at 700 mm followed by OF_2 (7 mm pressure). Following an immediate reaction the gases were condensed and the liquid removed. An IR spectrum showed predominently acid fluoride with a trace of epoxide. There was virtually no recovered starting vinyl ether.

d. A 3-l, 3-neck flask was equipped with a magnetic stirring bar, a gas inlet, a thermometer, and a septum. After being evacuated to full vacuum, 700 mm of dry O_2 was allowed to expand into the system along with 4 mm of OF_2. The flask was cooled to ∿58°C before the $CF_3CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$ (3.0 g) was added via a syringe. The liquid was stirred for 30 min before a sample was taken which showed no unreacted vinyl ether but a small absorption at 6.3μ with a majority of the material containing acid fluoride functional groups.

e. The vinyl ether ($CF_3F_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$, 13.2 g) was placed in a 50 cc flask which was equipped with a magnetic stirrer, a reflux condenser, a thermometer, a gas inlet below the surface of the liquid and backed up by a LOX trap. The flask was cooled to -25°, then the O_2 was bubbled in at a 10 to 1 ratio to the OF_2 for 4 hr. There was some evidence for the formation of the epoxide (6.3μ absorption in the IR), however, there was also degradation to the dimer acid fluoride. After 4 hr the reaction was stopped. According

to NMR the products consisted of a mixture of the starting vinyl ether, acid fluoride, and the epoxide (ratio 10:9:5). The infrared of the crude mixture is shown in the Appendix.

f. A 50-cc, 3-neck flask was equipped with a magnetic stirring bar, a gas inlet below the surface of the liquid, a thermometer, and a condenser backed by a -196°C trap.

The $CF_3CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$ (2.8 g) was added along with 10 cc of Freon-113; the resulting solution was cooled to ∿-40°C. The O_2 and OF_2 mixture was bubbled in over a 3 hr period. There was both epoxidation and degradation to the acid fluoride as indicated by IR analysis.

g. A 25-ml, 3-neck flask was equipped with a magnetic stirring bar, a gas inlet below the surface of the liquid, a septum, a thermometer, and a condenser backed by a LOX trap. The vinyl ether $CF_3CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$ (5.0 cc) was added and the flask cooled to ∿60°C before the oxygen and OF_2 were introduced. Over a 5-hr period the O_2/OF_2 ratio of 20/1 was bubbled in with very little reaction taking place. There was a small absorption of the $\overset{O}{\overset{||}{C}}$-F but mostly there was recovered vinyl ether. There seems to be degradation to the acid fluoride even at very low temperatures and conversion.

4. <u>Epoxidation of $CF_2CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$ with O_2 and Sunlight</u>

A 1-l vycor flask was evacuated before being pressured to 600 mm with dry oxygen. Then 1.6 g of $CF_3CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2$ was introduced into the system. The flask was placed in the sunlight for 3 hr and an IR of the overgas showed the presence of an acid fluoride, the vinyl ether, and a small amount of an epoxide.

5. <u>Preparation of Perfluoro(2-methoxypropionyl fluoride)</u>

Cesium fluoride (250 g, 1.65 moles) was placed in a 3-liter stainless steel autoclave and heated at 200°/1 mm for 48 hr. Tetraglyme (anhydrous, 600 ml) was then transferred by suction into the evacuated autoclave. Then carbonyl

fluoride (544 g, 8.25 moles) and HFPO (664 g, 4 moles) were condensed into the vessel. The contents were heated to 75° for 20 hr; pressure at temperature was 1200 psig. The contents were transferred into a 1-liter flask in vacuo, and the liquid was distilled through a 2'-glass packed silver-lined column. The following fractions were collected.

Fraction	B.P., °C	Wt., g	Purity
I	-92 to -90	325	95% COF_2
II	-32 to -30	355	97% C_2F_5COF
III	-26 to + 5°	83.1	79% $CF_3OCF(CF_3O)=CF$
IV	+5 to +8°	251	>98% $CF_3OCF(CF_3O)=CF$
V	7-8°	4	"
Bottoms		36	HFPO Oligomers
Trap		74.2	∿90% COF_2
Total		1158	

Fractions IV and V were combined (255 g, theory - 586 g based on 167 g of COF_2 consumed, 44% yield).

6. Preparation of Perfluoro(methyl vinyl ether)

Sodium carbonate (calcined, 254 g, 2.4 moles) was heated in a flask at 250°/1 mm overnight. Then tetraglyme (anhydrous, 400 ml) was added and the slurry stirred. The above acid fluoride (249 g, 1.07 moles) was bubbled through the mixture while maintaining an internal temperature of 0-10°. The acid fluoride was recondensed into the system with an acetone/dry-ice condenser. At the completion of the acid fluoride addition (3 hr) the mixture was allowed to warm to room temperature. The carbon dioxide that evolved was trapped at LOX temperature. After 16 hr at room temperature the condensed CO_2 (containing some acid fluoride) was bubbled through the reaction mixture to consume unreacted acid fluoride. There was obtained 34.7 g of CO_2 which contained ∿3% acid fluoride (by infrared). The reaction mixture was gradually heated; at 120° gas was evolved and collected in a LOX trap. Heating was maintained

at 120-140° for 2.5 hr. Care must be taken to prevent frothing. The $CF_3OCF{=}CF_2/CO_2$ mixture was transferred to an acetone/dry-ice bath and the majority of the CO_2 was allowed to escape and was collected (27.5 g, CO_2, ∿95% purity). The crude vinyl ether (155 g) was then distilled. The following fractions were collected.

Fraction	B.P., °C	Wt., g	Purity
I	-26 to -25°	114	>98% $CF_3OCF{=}CF_2$
II	-25 to -22°	6	"
Bottoms		15.1	$CF_3OCF(CF_3)CF{=}CFOCF_3$ (cis and trans)
Trap		17.2	>98% CO_2
Total		152.3	

Fractions I and II were combined (120 g, 178 g, 68% yield).

7. Epoxidation of CF_3-O-CF=CF_2

a. A 3-l flask was equipped with a magnetic stirring bar, a thermometer, and a gas inlet before being evacuated to full vacuum. The CF_3-O-CF=CF_2 (5.0 g) was condensed into the flask at -40°C while the O_2 and OF_2 (500 mm, 8 mm, respectively) were pressured in. The reaction was carried out at -45°C and initially there appeared a small epoxide band which disappeared after 1.5 hours. After 3 hr a gas sample IR revealed only the starting vinyl ether, COF_2, and what appears to be CF_3-O-$\overset{\overset{\displaystyle O}{\|}}{C}$-F.

b. A 2-l, 3-neck flask was equipped with a thermometer, a magnetic stirring bar, and a gas inlet before being evacuated to full vacuum. Freon-113 (10 cc) was added and the flask was cooled to -78°C before the CF_3-O-CF=CF_2 was condensed in. Dry N_2 was admitted to 250 mm before O_2 (300 mm) and OF_2 (3 mm) were added. After 30 min at -78°C no epoxide had formed so the flask was warmed to -40°C for one hour. After this period of time infrared showed an acid fluoride peak, but no peak corresponding to an epoxide.

c. A 1-l Vycor flask was equipped with a magnetic stirring bar and a gas inlet before being evacuated to full vacuum. The CF_3-O-CF=CF_2 was added (1.52 g) along with Br_2 (∿1 mm) and O_2 (∿300 mm). After about one minute there was an explosion which sheared the stopcock from the vacuum system.

After re-evacuation the reaction was repeated and the O_2 and Br_2 were added in increments over a 1-hr period. An IR was taken every 15 minutes and an epoxide band did appear along with a strong acid fluoride absorption. After sitting overnight the epoxide band had disappeared and there was CO_2 in the flask.

d. A 1-liter Vycor flask was equipped with a magnetic stirring bar and a gas inlet and was evacuated to full vacuum. The flask was cooled to 0°C in an ice bath before the CF_3-O-CF=CF_2 (1.52 g) along with O_2 and Br_2 (300 mm and 3 mm, respectively) were added. After 15 minutes there remained no unreacted CF_3-O-CF=CF_2 by IR analysis and all that was remaining was COF_2 and what appeared to be the fluoro formate $CF_3O\overset{\overset{O}{\|}}{C}F$.

e. A 1-liter Vycor flask was evacuated and charged with $CF_3OCF{=}CF_2$ (100 mm). Pressure was then increased to near atmospheric with a stream of dry air which had been passed over a reservoir of Br_2. After ∿5 seconds, a cloudy swirl developed and this was immediately followed by a sudden pressure surge sufficient to vigorously dislodge the flask stopper. The flask was quickly restoppered and an infrared spectrum indicated that $-\overset{\overset{O}{\|}}{C}F$ and CF_2O were formed, but there was no absorption in the 6.2μ region which is characteristic of $R_fO-\underset{\underset{F}{|}}{\overset{\overset{O}{/\backslash}}{C}}-CF_2$.

f. A 1-liter Vycor flask was evacuated and charged with $CF_3OCF{=}CF_2$ (60 mm). It was then pressured to 60 mm with dry air. After 5 minutes an infrared of this mixture showed only unreacted $CF_3OCF{=}CF_2$. The flask was then placed in sunlight for 4 hours and at this time infrared showed the presence of an acid fluoride with no indication of an epoxide.

g. A 1-liter Vycor flask was evacuated and charged with $CF_3OCF{=}CF_2$ (100 mm) and 450 mm of dry air containing 1/10,000 parts of N_2O_3. After 5 minutes an infrared spectrum of the mixture showed only starting material. The flask was then placed in sunlight for one hour and another infrared spectrum was made. Again, only starting material was present. After an additional two hours in sunlight the mixture gave an infrared spectrum which showed the presence of $-\overset{\overset{O}{\|}}{C}F$ but no $-\overset{\overset{O}{/\backslash}}{C-C}-$.

h. A large test tube with a side arm was fitted with a magnetic stirring bar and a rubber stopper with two gas inlet tubes. The reactor was charged with ∿75 ml of Freon E5 and the gas inlet tubes were adjusted so that they extended to within 1/8'' of the stirring bar. One of the gas inlet tubes was connected to a 1-liter flask charged with a mixture of $CF_3OCF{=}CF_2$ (100 mm) and air (660 mm). The other was connected to a 1-liter flask charged with a mixture of Br_2 and air. This second flask was charged by introducing several drops of Br_2 into the flask and stoppering it when it had completely volatilized. The pressure in the flask was then reduced to 380 mm followed by recharging to atmospheric pressure with air. This process was repeated twice again before the flask was connected to the reactor.

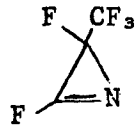
The side arm of the test tube-reactor opened above the liquid level of the Freon E5. This side arm was vented through a -183° trap to a vacuum manifold. A full vacuum was applied to the system, and the E5 was stirred as it was irradiated with a Hanovia u.v. utility lamp. The $CF_3OCF{=}CF_2$/air and Br_2/air mixtures were then bubbled through during a 3-hr period. An infrared spectrum of the product mixture showed only unreacted starting material.

The reaction was repeated under the same conditions with similar results.

E. Perfluoro N-alkylaziridines

1. Attempted Preparation of a Fluorinated Aziridine

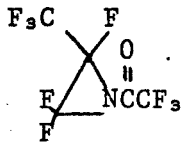
Trioctyl phosphine oxide (10.7 g, 0.028 mole) was placed in a flask and heated to a melt (50°). Then pentafluorophenyl isocyanate (5.8 g, 0.028 mole) was added dropwise maintaining an internal temperature of 60-80°. Gas was evolved throughout the addition. After 1 hr the addition was complete; the mixture solidified on cooling, mp 40-41° (crude $R_3P{=}NC_6F_5$, see Appendix). The solid was dissolved in 15 ml of Freon 113 and charged into a 80-ml stainless steel autoclave. The autoclave was cooled, charged with HFPO (4.6 g, 0.028 mole), then allowed to warm to 25°, P=7 psig. The vessel was heated to 120° for 16 hr. On cooling to 25° there was no pressure on the gauge. The autoclave was opened and 1.7 g of HFPO was condensed into a trap. The contents were transferred to a flask and distilled to remove the Freon 113. Full vacuum was applied to the flask and with gentle heating 2.2 g of a yellow liquid was collected. GLC showed this material to contain two major components in a 6:5 ratio. Examination of the crude reaction product both before and after removal of the yellow liquid verified the presence of trioctyl phosphine oxide.

2. Preparation of 

An ethereal solution of hydrazoic acid was prepared by dissolving sodium azide (120 g) in water (400 ml) and adding Et_2O (400 ml). Then sulfuric acid (98% 120 ml) was gradually added to the stirred mixture at such a rate that Et_2O/HN_3 gently distilled. This distillate was collected in a flask containing 400 ml Et_2O and maintained at 0°. After the completion of the addition the reaction mixture was gently warmed (∿60°C) until no more distillate could be obtained. Roughly 700 ml of distillate was collected and subsequently dried over $CaCl_2$.

Triethylamine (50 g) was dissolved in 400 ml of anhydrous ether. The resulting solution was stirred and cooled to 0° while the above solution of HN_3/Et_3O (700 ml) was added cautiously without agitation. A white precipitate formed during the addition. This precipitate, $HNEt_3N_3$ is presumably explosive and consequently was manipulated as little as possible. The ether was removed in vacuo (∿50 to 10 mm) until a dry, off-white salt was obtained.

The above salt was dissolved in 400 ml of sym-tetrachloroethane (anhydrous) and the solution was cooled to ca -10° and mechanically stirred while perfluoropropylene was bubbled through. The olefin (80 g) was added during a 2 hr period. The reaction is mildly exothermic and was cooled externally to maintain an internal temperature of -10 to -5°. Then the solution was washed with 0.5 N HCl (200 ml) (gas, presumably $CF_3CF{=}CF_2$ containing NH_3 was evolved) and H_2O (200 ml), consecutively, at 0°. The organic layer was phase separated and dried over $MgSO_4$. This solution, containing $CF_3CF{=}CFN_3$ (yellow liquid at -78°), was allowed to warm to 25° in a flask equipped with an ice water cooled condenser backed up by an acetone dry-ice trap and a LOX trap, respectively. Four liters of gas were evolved in ∿5 hr. The contents in the trap cooled to -78° were transferred to a glass storage ampoule at -20° and stored at -78°. There was obtained 15 g of a yellow liquid which contained as a major component (ca 60%) and $CF_3CF{=}CF_2$ and $CF_3CFHCF_2N_3$ as minor components. This material was used in subsequent steps without further purification.

3. Preparation of 

Mercuric fluoride (1.0 g, 4.17 mmoles) was placed in a Fischer-Porter tube and heated at 60°/<1 mm overnight. The tube was cooled at -183° while the crude azirine (transferred in vacuo at -20°, 340 mm, 8.4 mmoles) was introduced. The mixture was allowed to warm with stirring to -78° and maintained at this temperature for 8 hrs; no visible reaction occurred. The mixture was allowed to warm to -20° and maintained at this temperature for 8 hrs; again no visible reaction occurred. The mixture was allowed to maintain 25° and held at that temperature for 18 hr. At this time an orange paste remained. Gas infrared indicated complete consumption of the azirine. Only $CF_3CF{=}CF_2$ and $CF_3CHFCF_2N_3$ were detected in the gas phase. Slight vacuum was applied to the tube to remove the perfluoropropylene and most of the saturated azide. The tube was then cooled to -183° and evacuated while CF_3COCl (300 mm, 7.4 mmoles) was introduced. The mixture was vented at 25° for 18 hr at which time the orange paste had turned into a white solid. From trap to trap fractionation there was obtained 0.5 g CF_3COF (4.8 mmoles), and a mixture (0.7 g) containing $CF_3CFHCF_2N_3$ and what is believed to be the titled amide. GLC of this mixture showed both the azide and the amide (ca 70%). The amide was collected and analyzed by infrared. The infrared spectra of the crude azirine, the azide-amide mixture, and amide are shown in the appendix.

Essentially the same result was obtained by reacting mercuric fluoride with the azirine and trifluoroacetyl chloride combined rather than stepwise.

F. Perfluoro Bis-Epoxides

1. Attempted Synthesis of Decafluorodiiodohexane

A 1.4-l autoclave was charged with $CF_2{=}CF_2$ (300 g, 3.0 moles) and I_2 (254 g, 1 mole) and heated at 160° for 18 hours. The clave was then degassed and opened to give 422 g of a red, liquid product. Distillation of this material showed that it was mostly ICF_2CF_2I (bp = 45°/55 mm). The material was returned to the autoclave and heated an additional 16 hours at 230°. It was again degassed and opened, but this time the product was mostly solid.

2. A 1.4-liter autoclave was charged with $CF_2=CF_2$ (300 g, 3.0 moles) and I_2 (254 g, 1.0 mole) and heated at 160° for 4 hours followed by heating at 230° for 16 hours. The product obtained was again mostly ICF_2CF_2I. This material was returned to the autoclave and an additional 100 g (1.0 mole) of $CF_2=CF_2$ was charged. This material was heated at 230° for an additional 16 hours. Distillation of the product gave mostly ICF_2CF_2I and $I(CF_2CF_2)_2I$ with a small amount (<50 g) of the desired $I(CF_2CF_2)_3I$. The two lower boiling components were again returned to the autoclave and heated at 230° for 24 hours. After this period of time the product obtained was again a solid.

APPENDIX

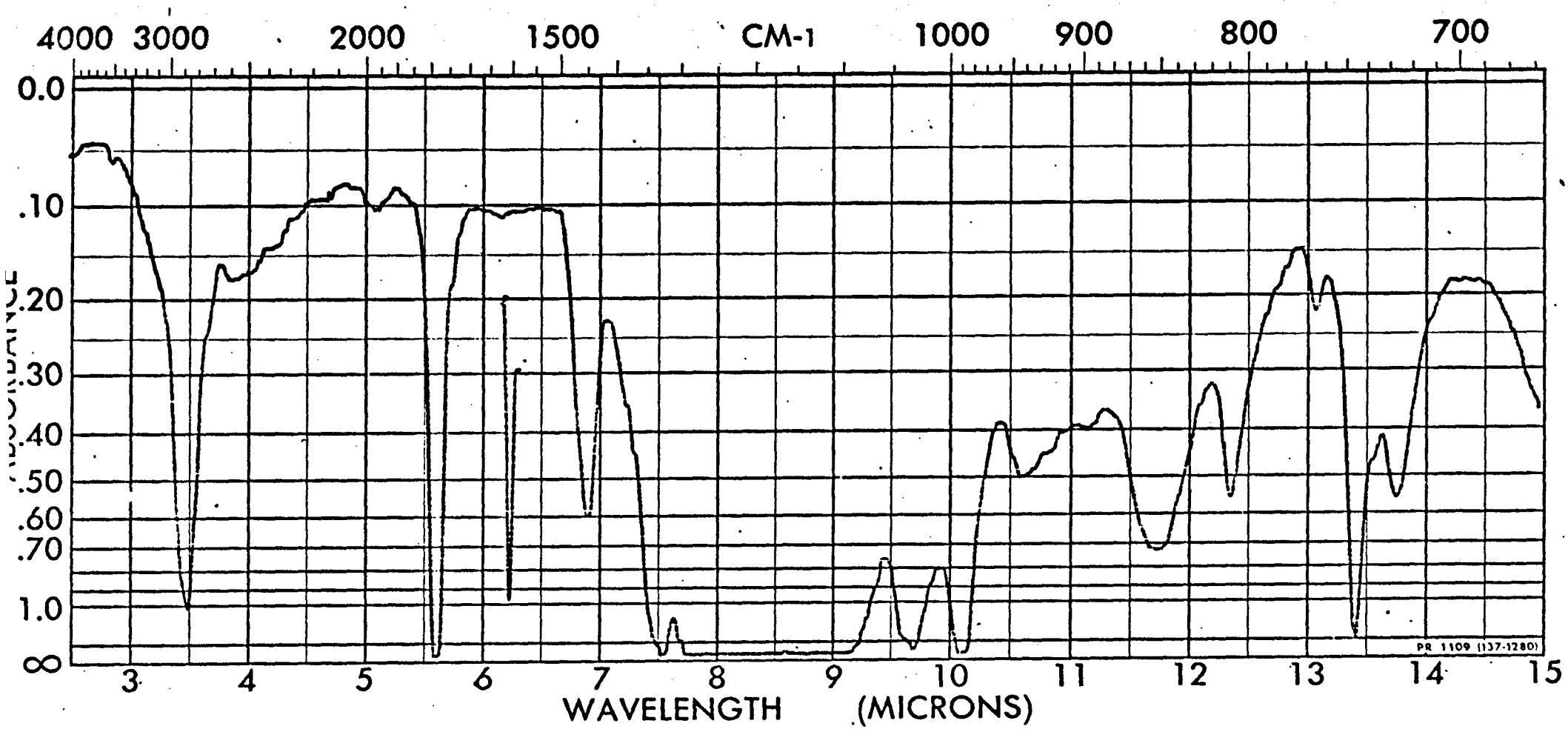


Figure 1

$C_3F_7OC(CF_3)F\overset{O}{\overset{\|}{C}}O(CH_2CH_2O)_3CH_3$

(film)

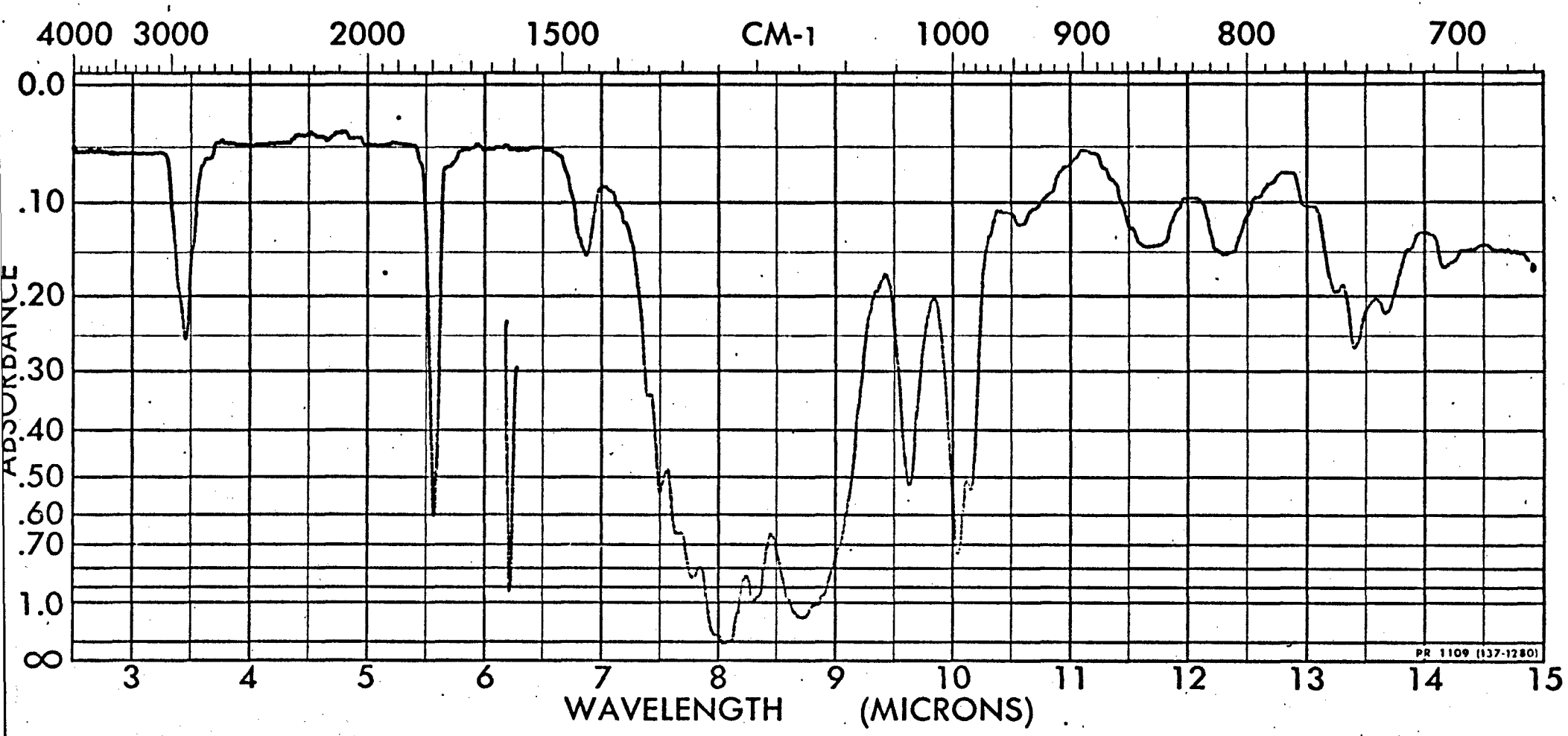


Figure 2

$C_3F_7OC(CF_3)FCF_2OC(CF_3)F\overset{O}{\overset{\|}{C}}O(CH_2CH_2O)_3CH_3$

(film)

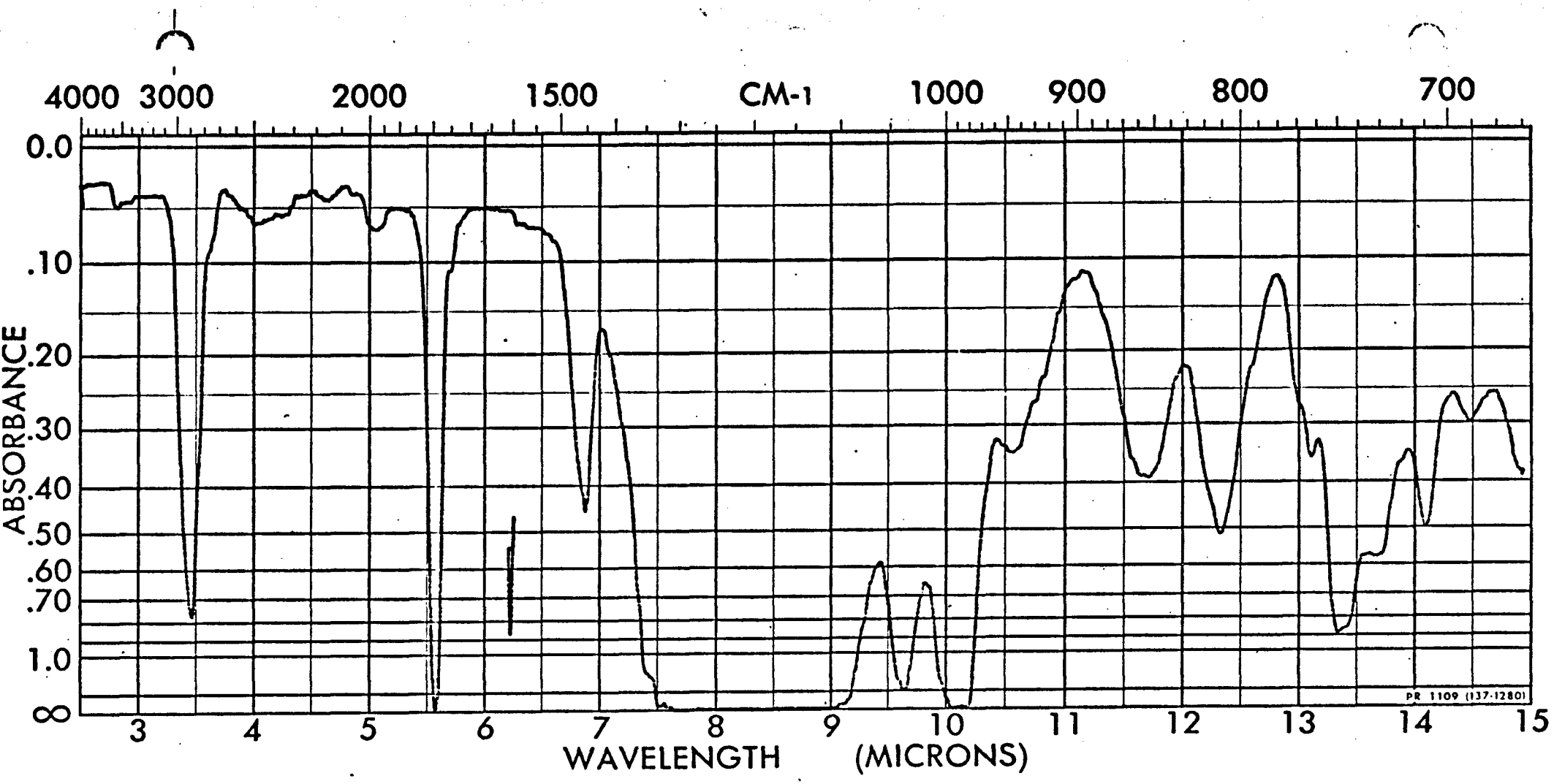


Figure 3

$C_3F_7O[C(CF_3)FCF_2O]_2C(CF_3)F\overset{O}{\overset{\|}{C}}O(CH_2CH_2O)_3CH_3$

(film)

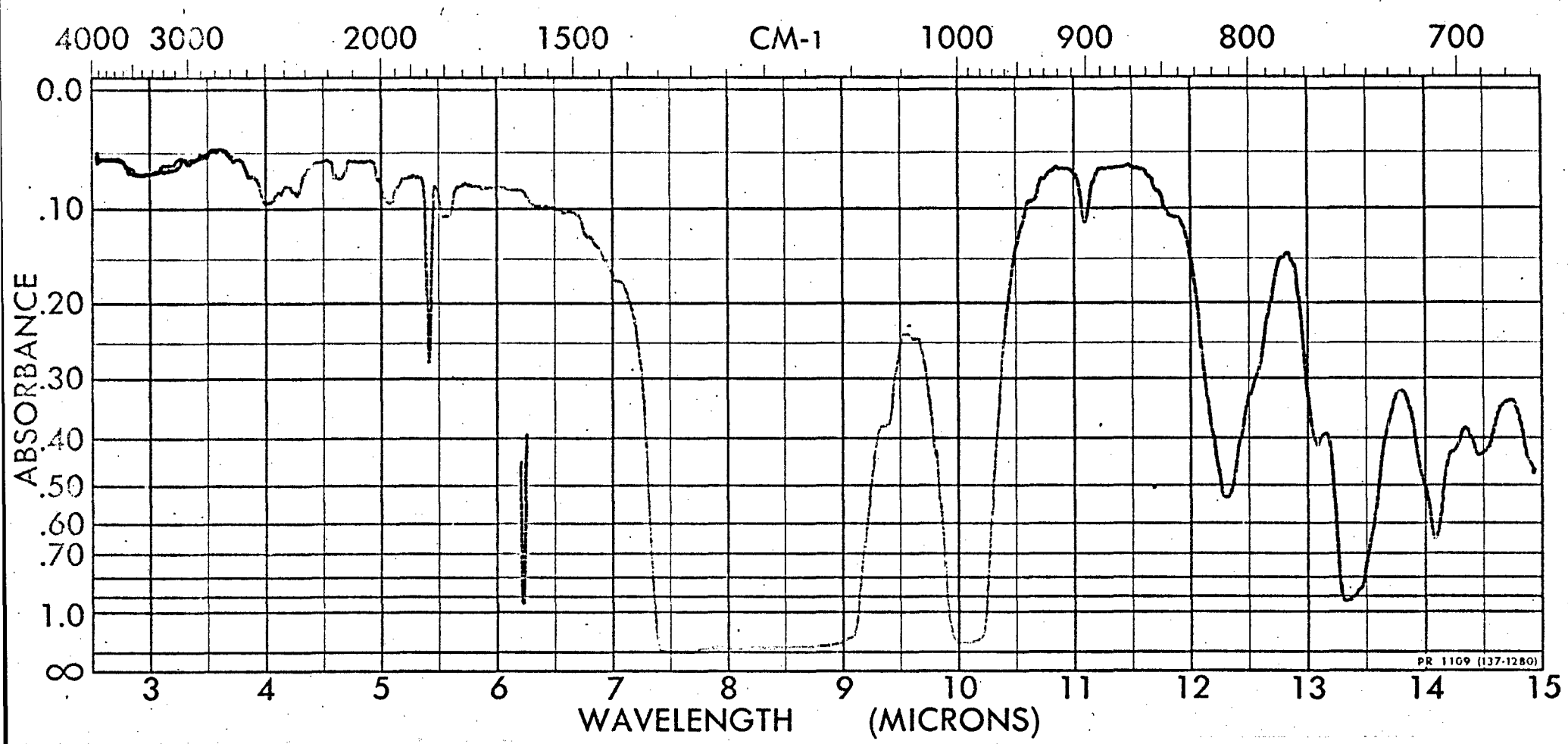


Figure 4

$$C_3F_7O(\overset{\overset{CF_3}{|}}{C}FCF_2O)_2CF{=}CF_2$$

(film)

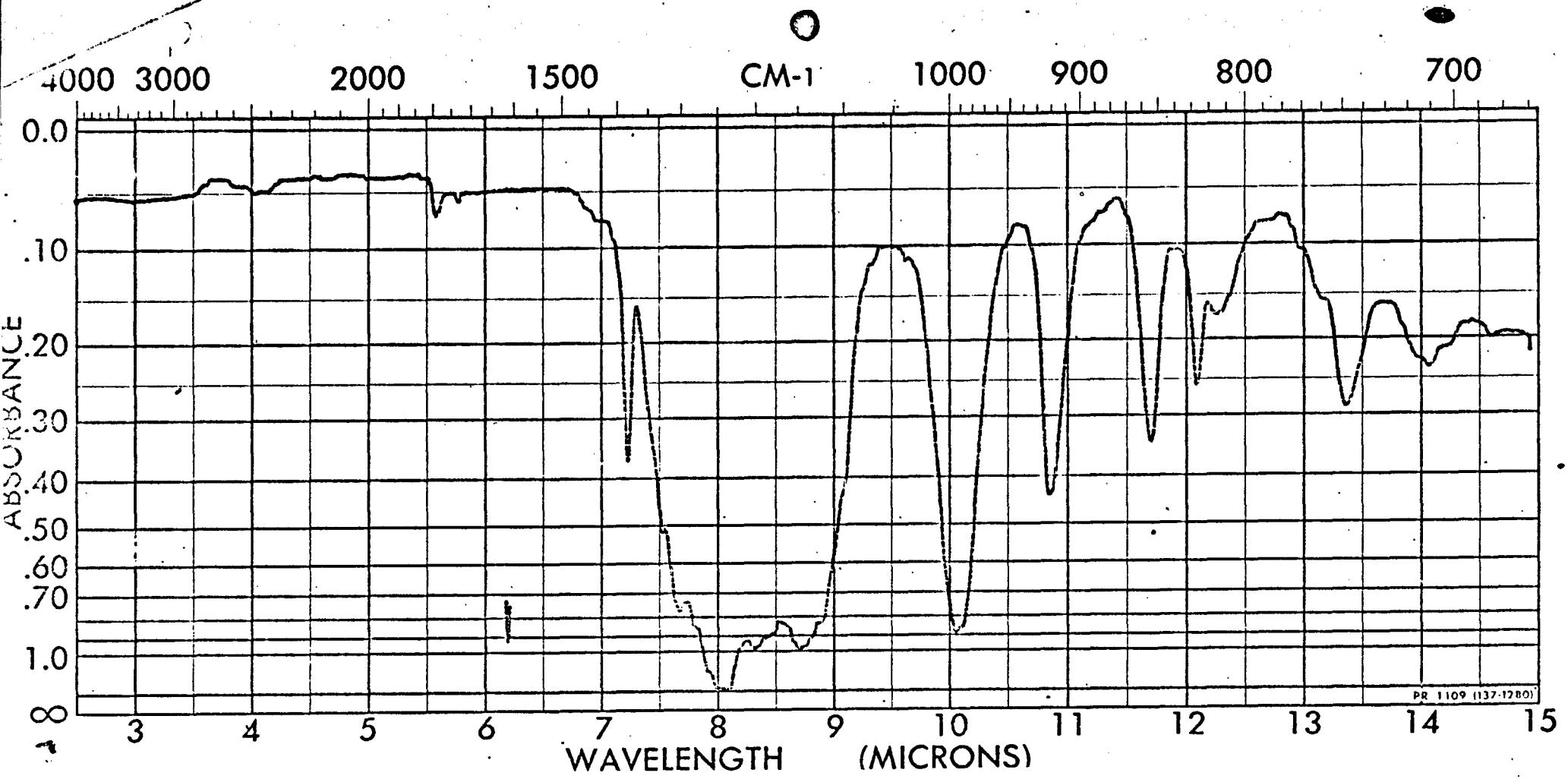


Figure 5

$$C_3F_7O(\overset{\overset{CF_3}{|}}{C}FCF_2O)_2\underset{\underset{Cl_2C}{|}}{CF}-\underset{\underset{CF_2}{|}}{CF_2} \quad + \quad \text{(isomer ?)}$$

(film)

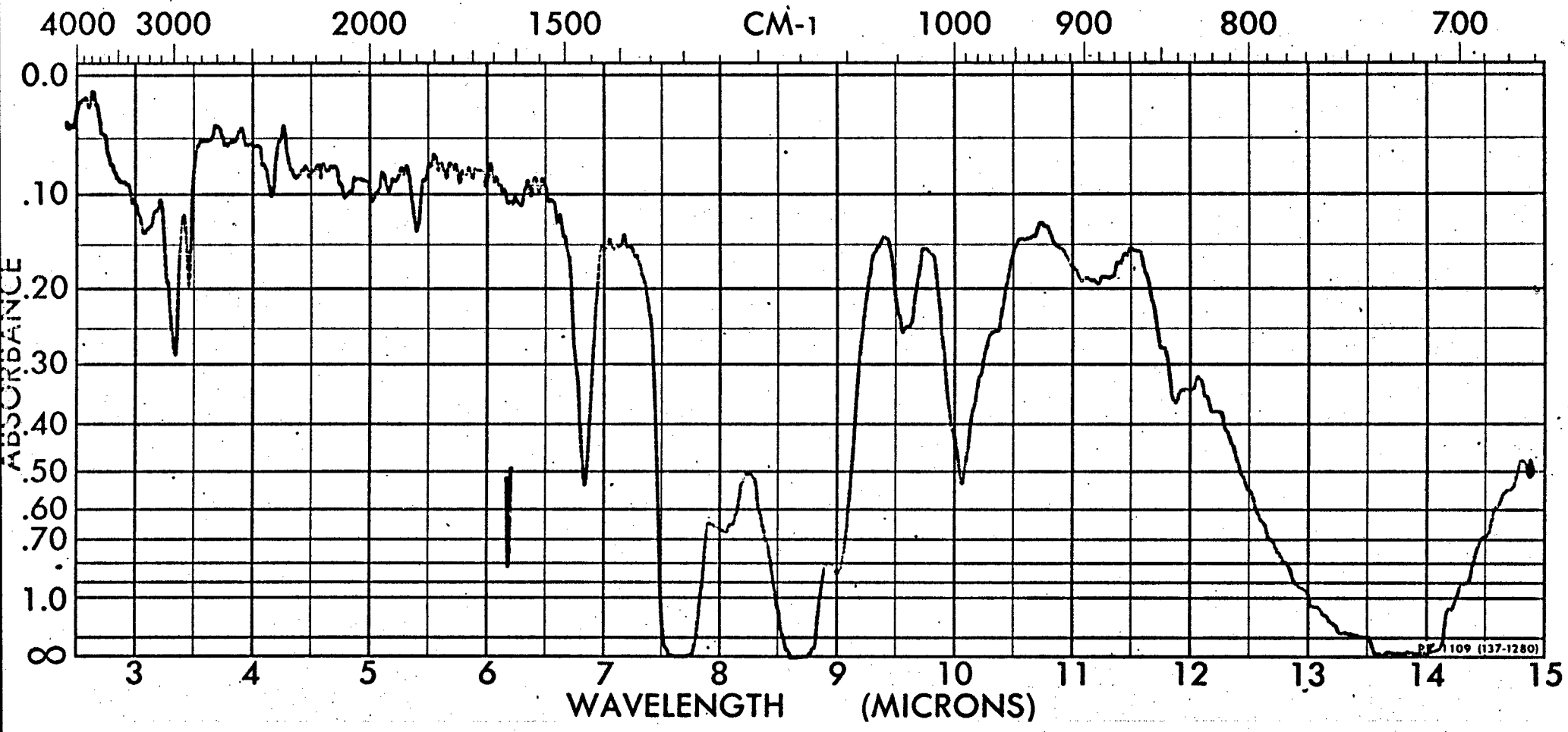


Figure 6

$MeOCF{=}CF_2$
(gas)

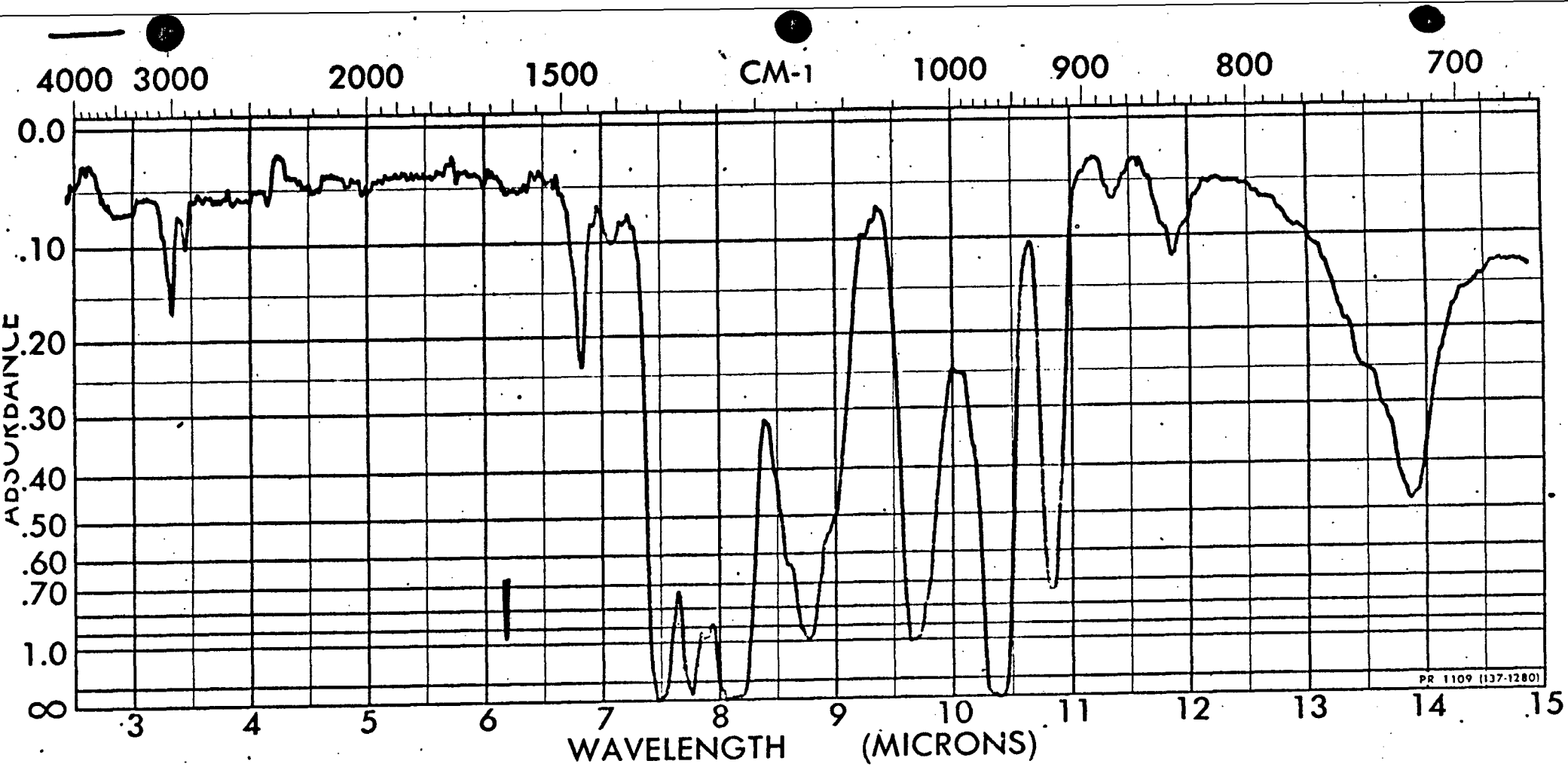
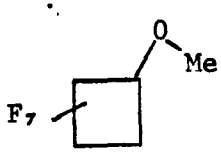

4000 3000 2000 1500 CM-1 1000 900 800 700
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
∞
ABSORBANCE
3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
PR 1109 (137-1280)

Figure 7


O
Me
F7

(gas)

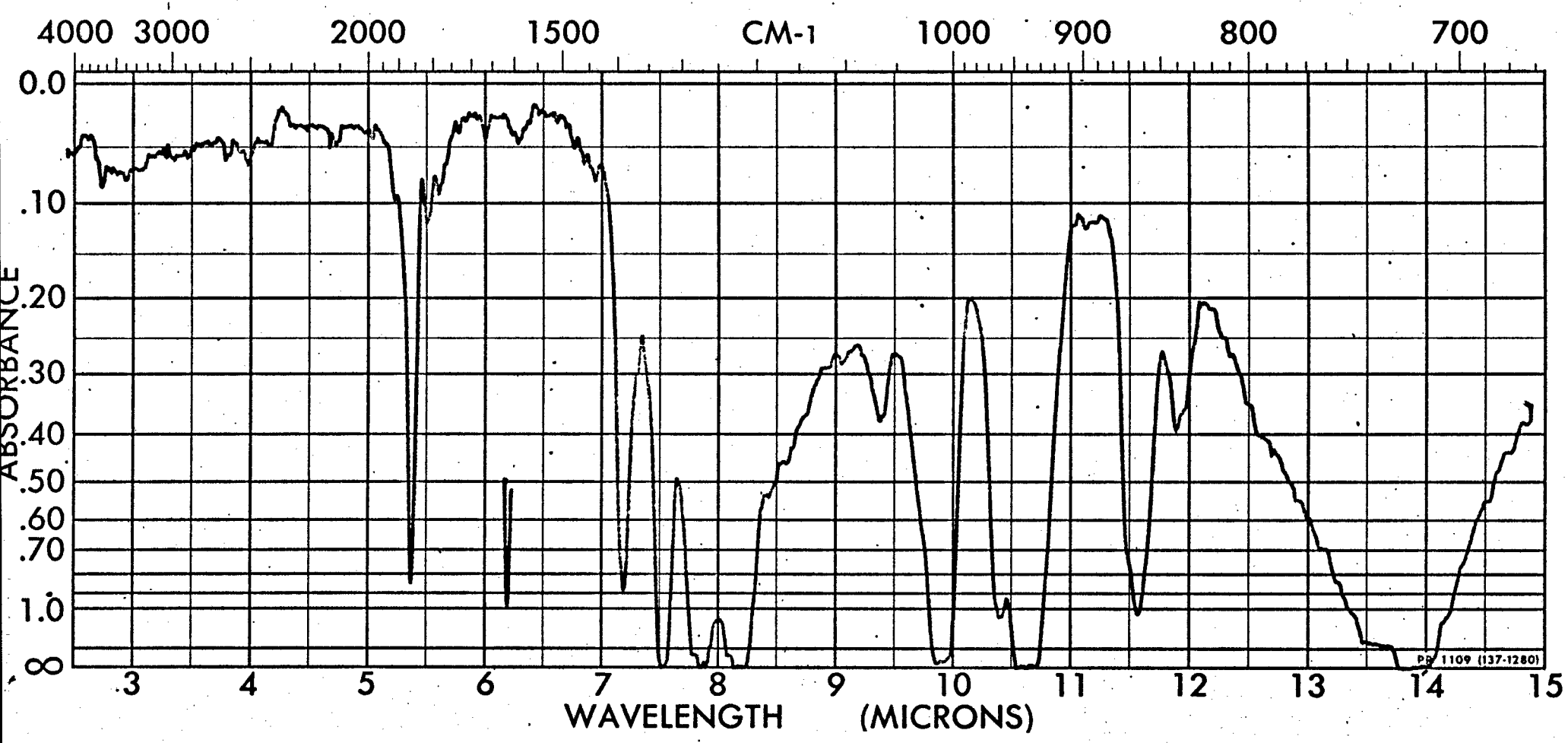
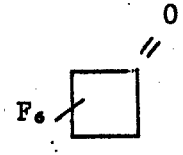

4000 3000 2000 1500 CM-1 1000 900 800 700
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
∞
ABSORBANCE
.3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
PR 1109 (137-1280)

Figure 8


O
F6

(gas)

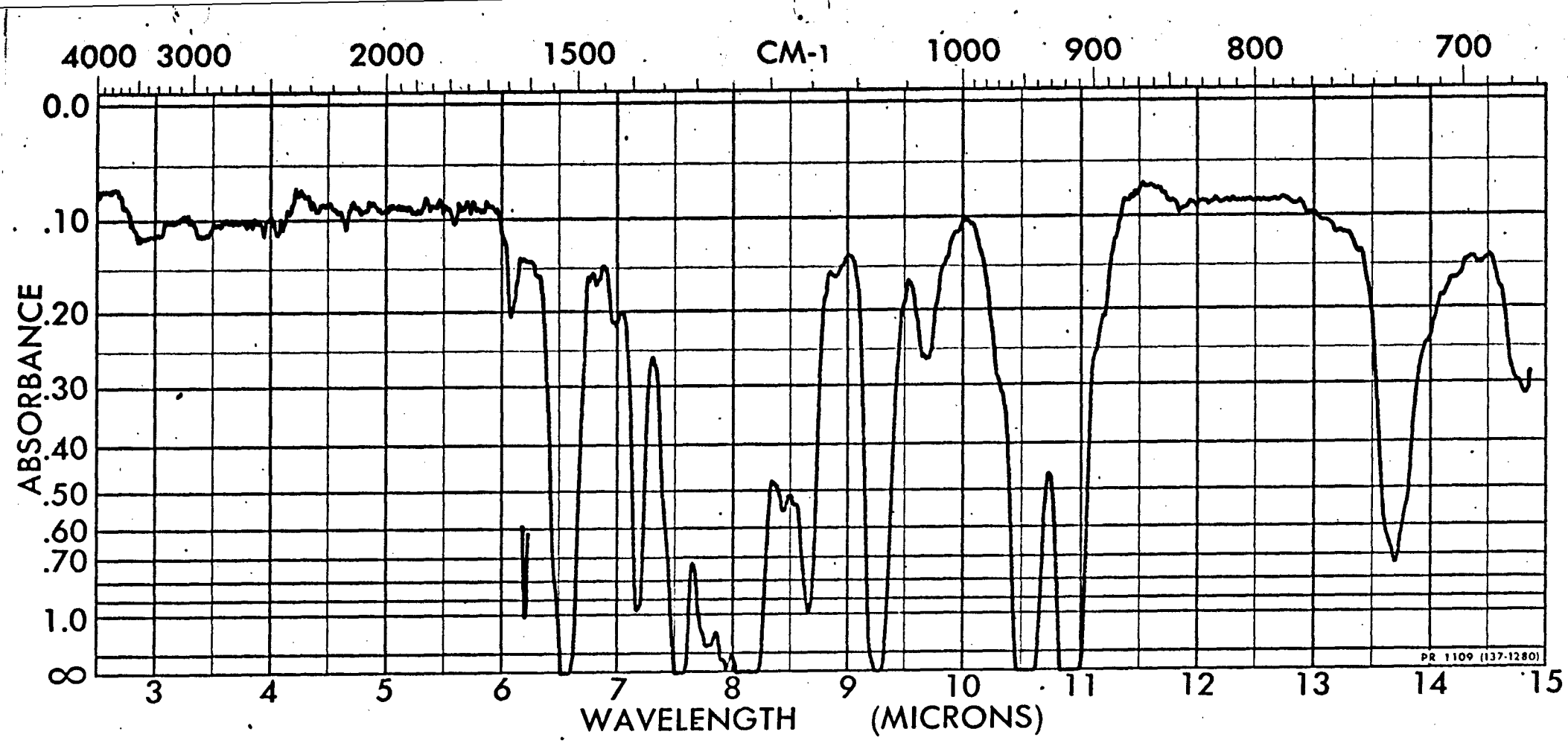
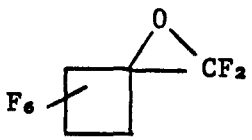

4000 3000 2000 1500 CM-1 1000 900 800 700
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
∞
ABSORBANCE
3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
PR 1109 (137-1280)

Figure 9


O
CF₂
F₆

(gas)

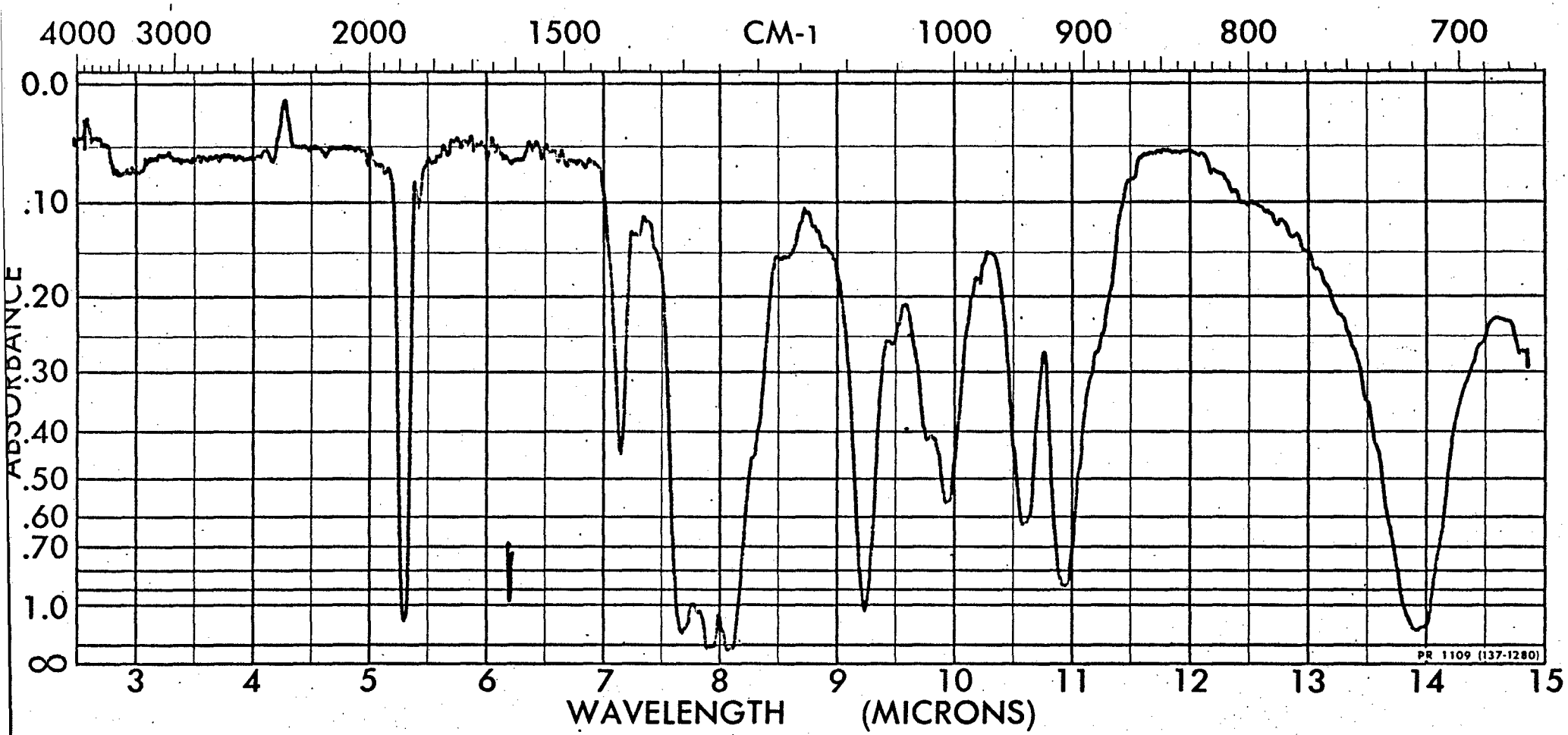
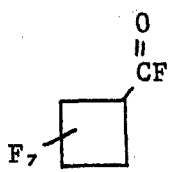


Figure 10



(gas)

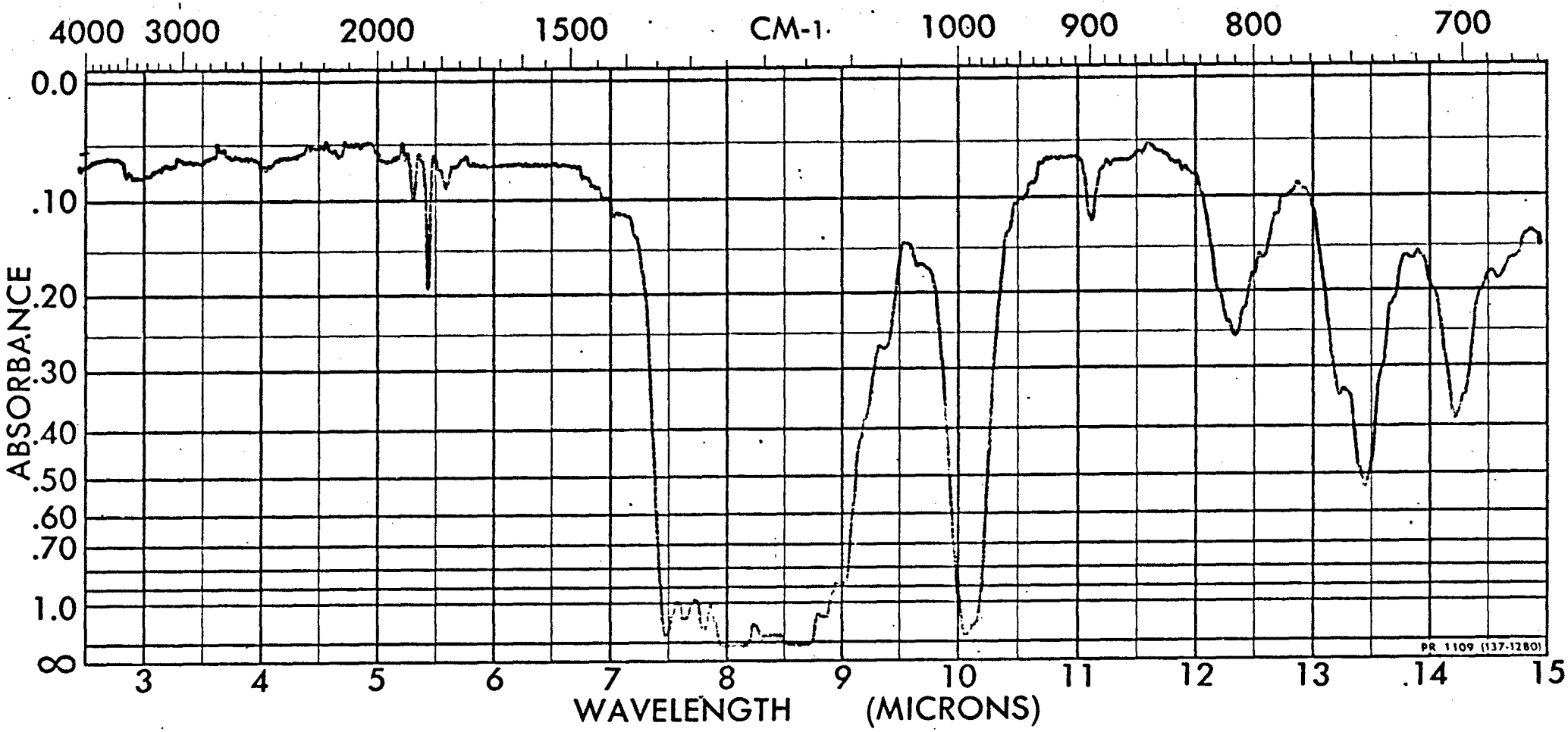


Figure 11

$C_3F_7OCF(CF_3)CF_2OCF{=}CF_2$

(film)

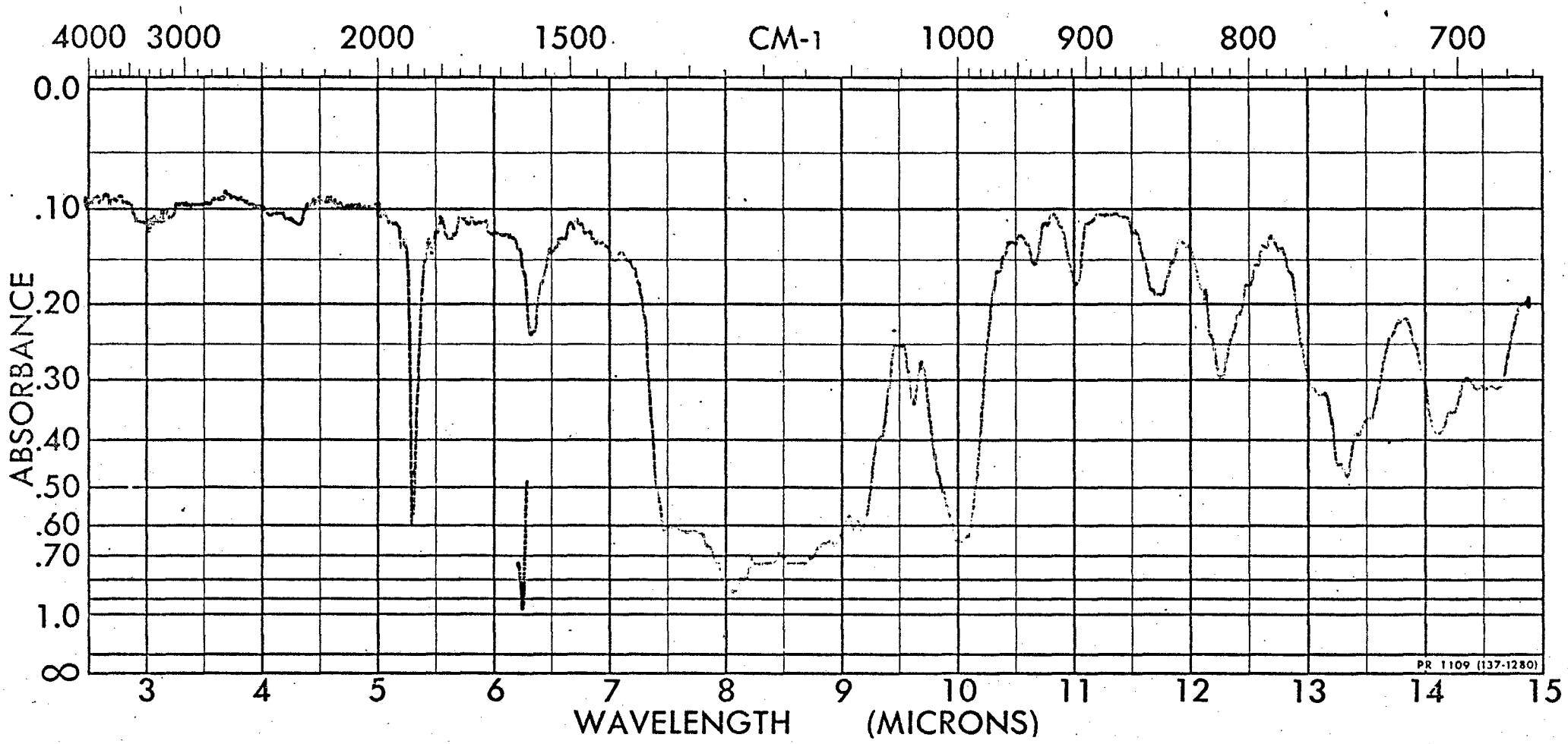


Figure 12

Crude Reaction Mixture $C_3F_7OC(CF_3)FX$

$X = CF_2OCF{=}CF_2$, COF, $CF_2OCF(O)CF_2$

(film)

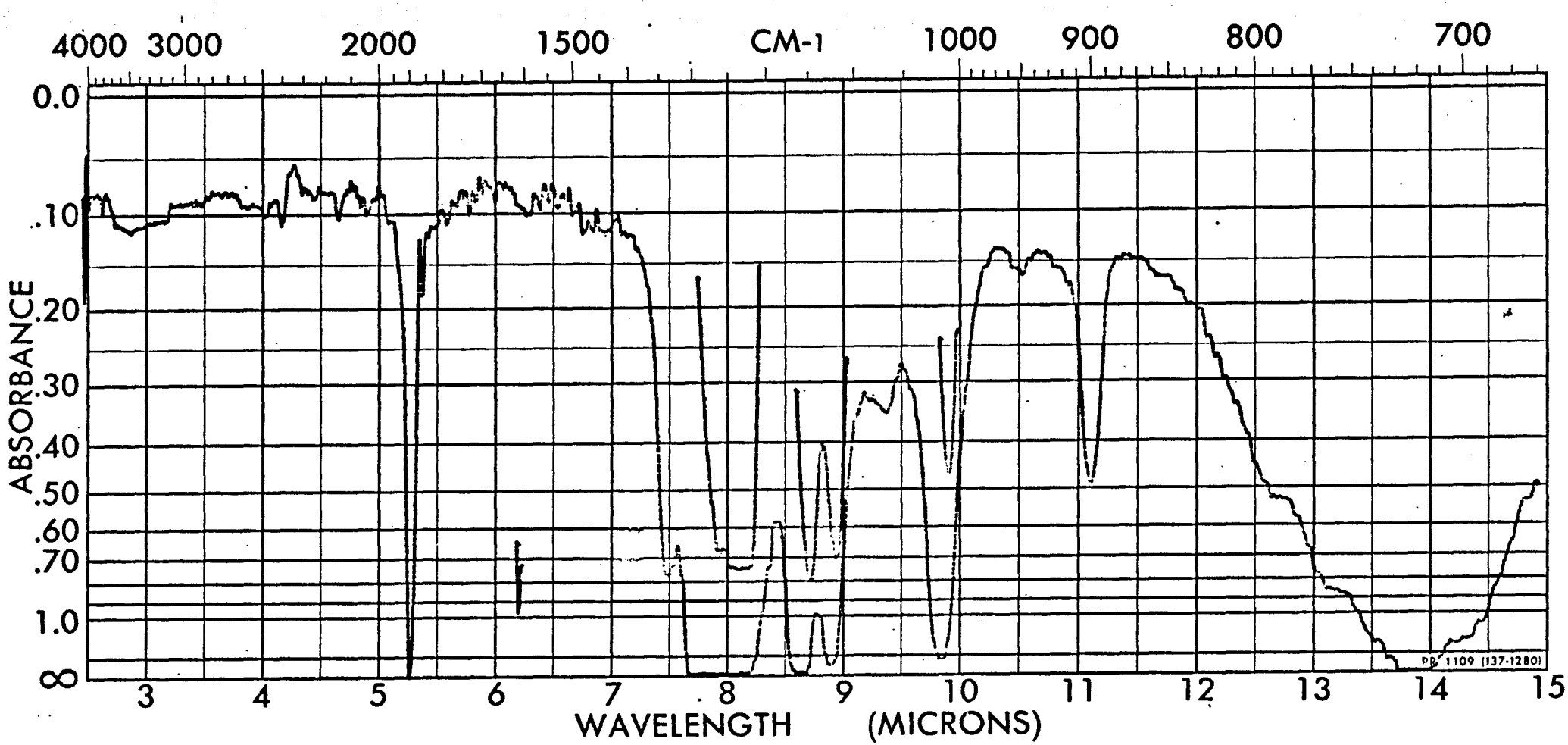


Figure 13

$$\begin{array}{c} CF_3O \\ | \quad\; || \\ CF_3OCF\text{-}CF \end{array}$$

(gas)

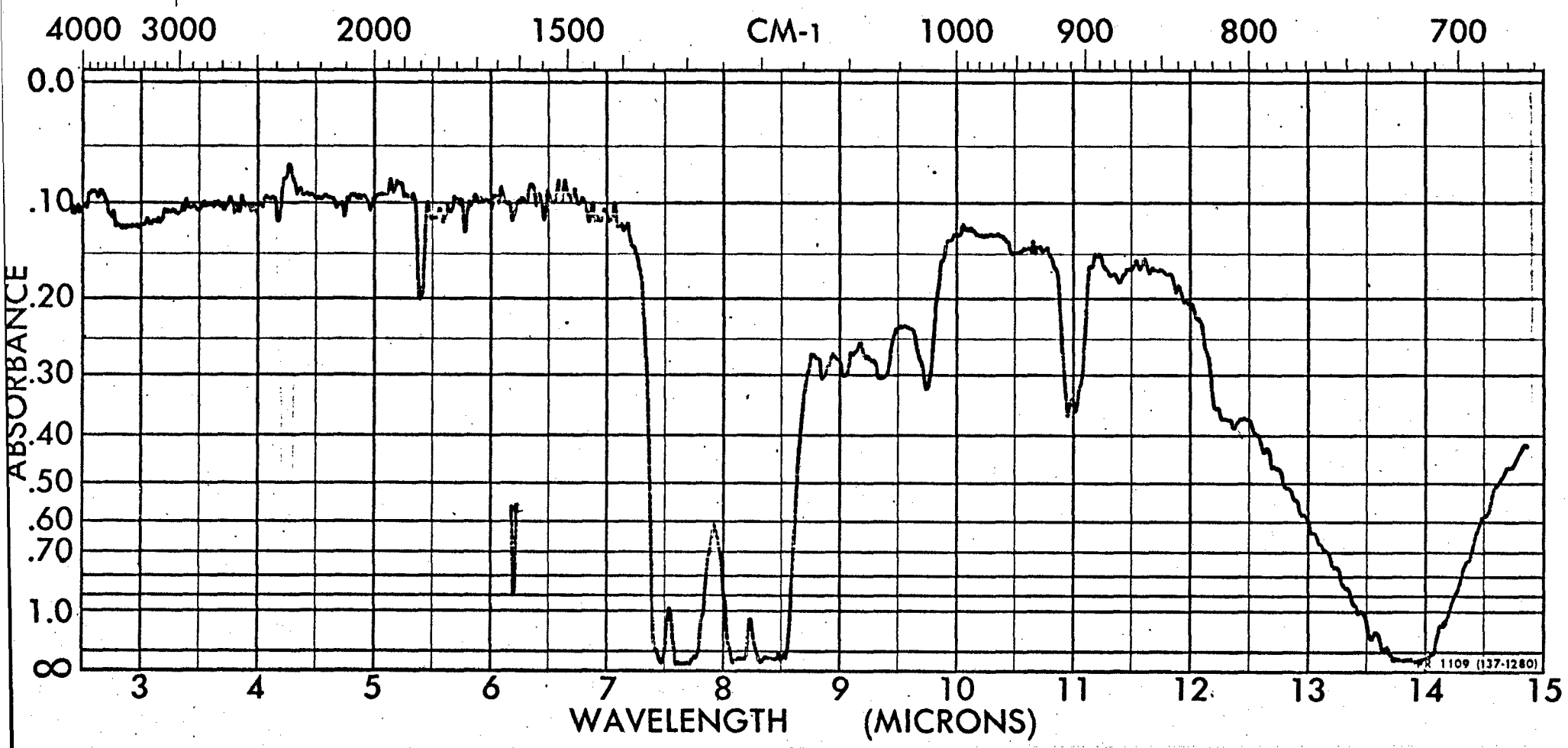


Figure 14

$CF_3OCF{=}CF_2$

(gas)

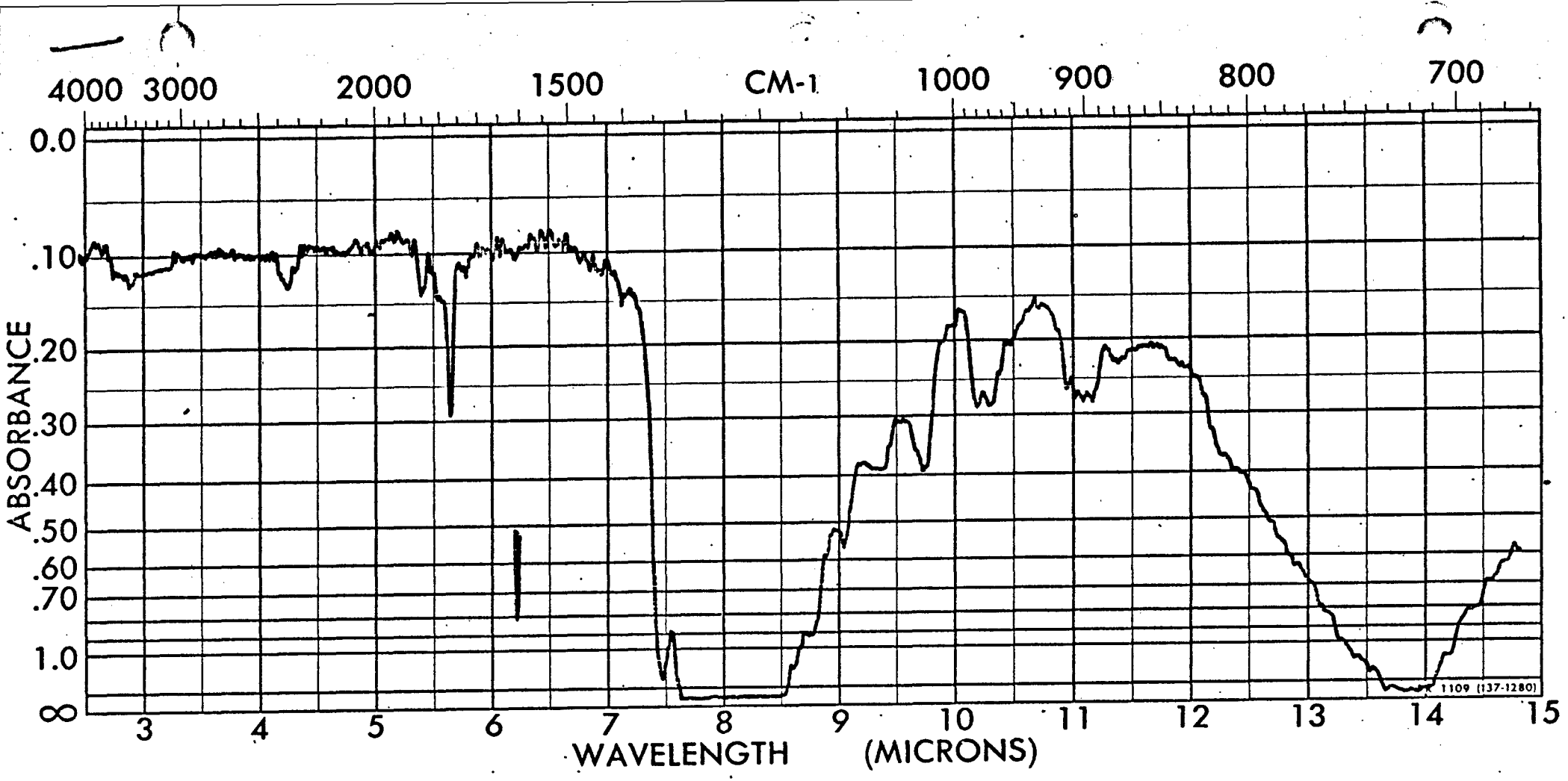


Figure 15

$CF_3OCF{=}CF_2$ dimers

(film)

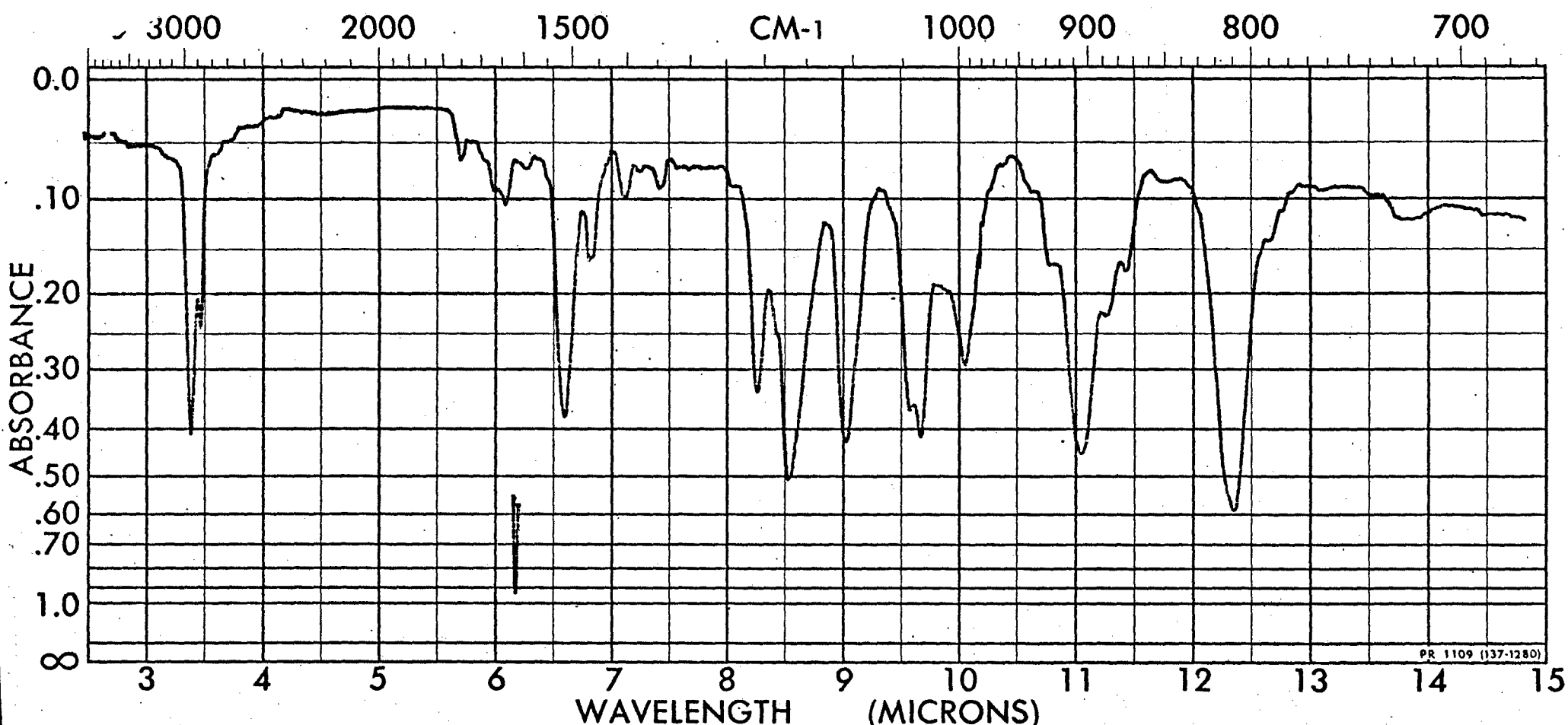


Figure 16

Crude $C_6F_5N{=}P(C_8H_{17})_3$

(gas)

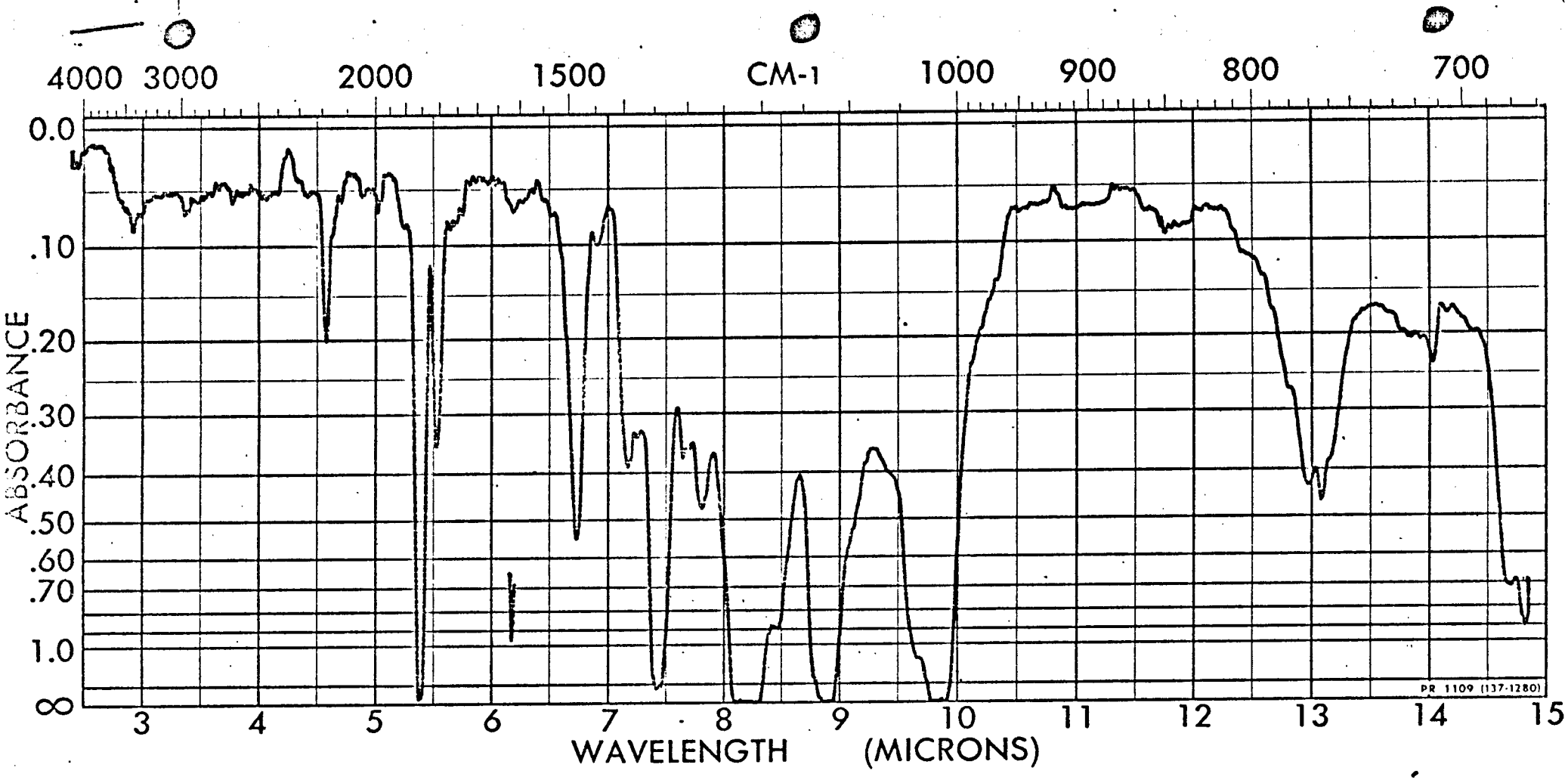
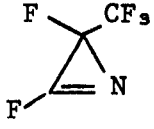


Figure 17

GAS SAMPLE

CRUDE AZIRINE  (5.4, 6.7μ)

$CF_3CF{=}CF_2$ } Impurities

$CF_3CFHCF_2N_3$

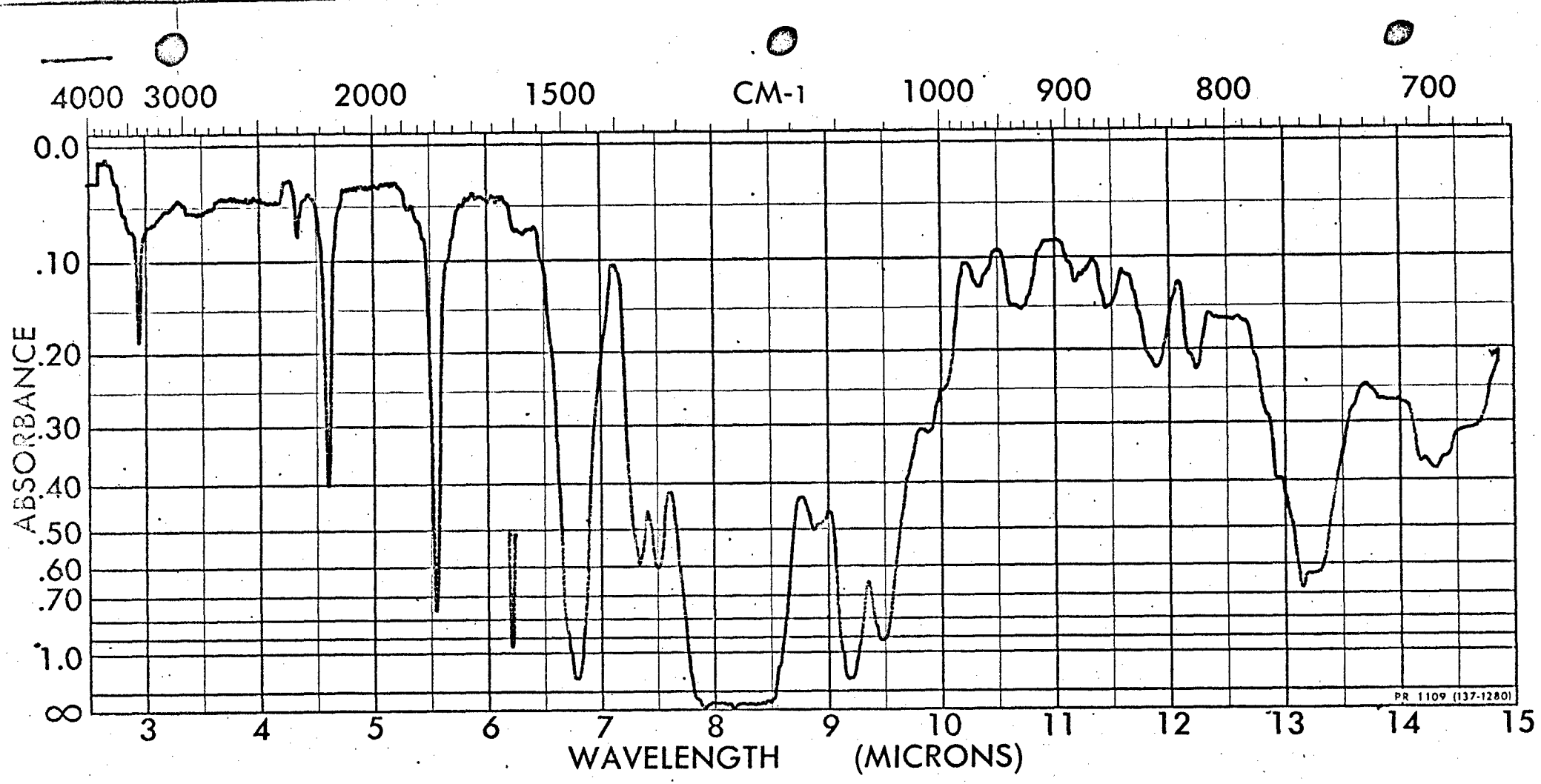
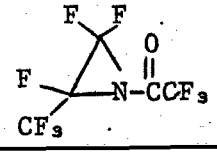


Figure 18

GAS SAMPLE

MIXTURE

$F_3CCFHCF_2N_3$ (2.8, 4.6μ)



(5.55, 6.75μ)

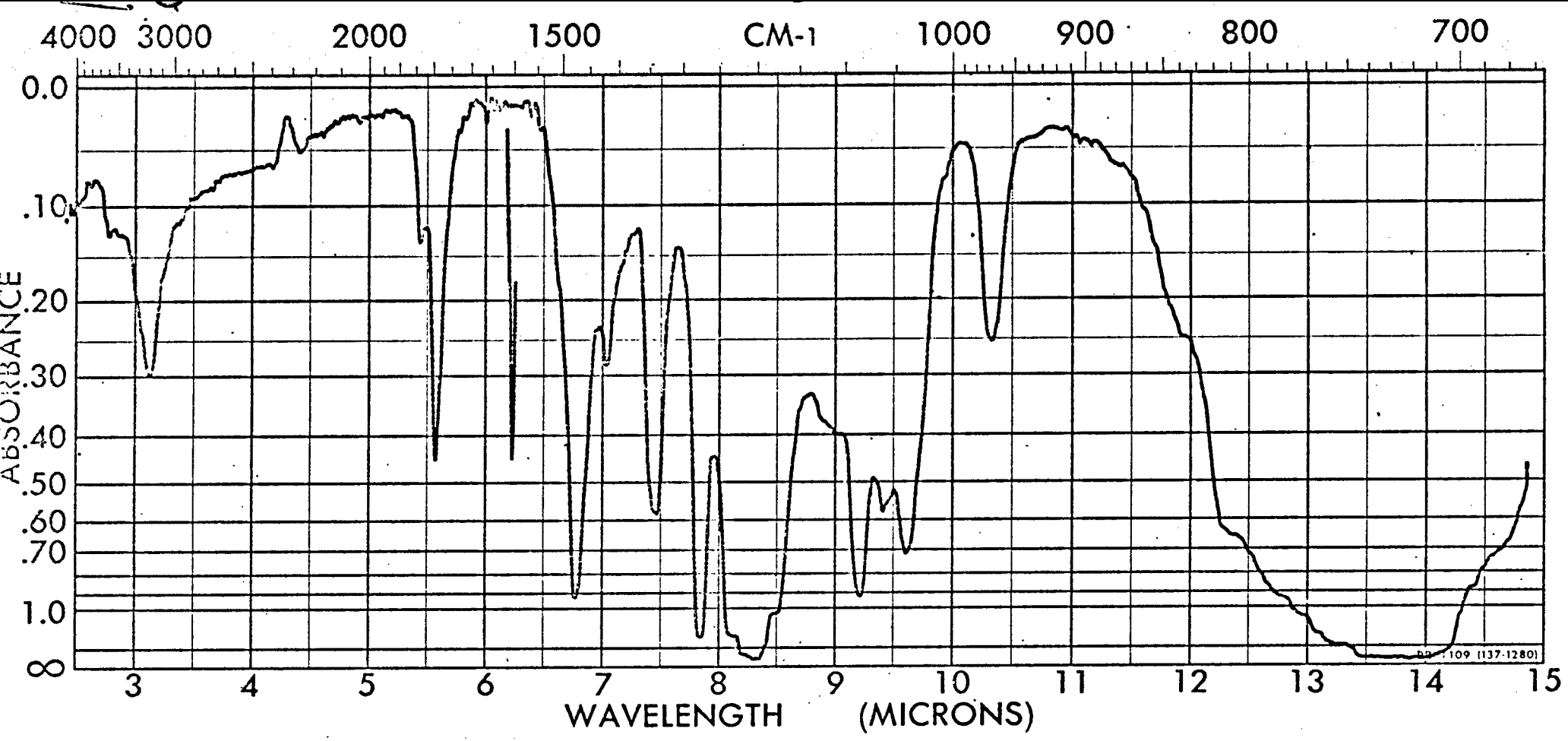
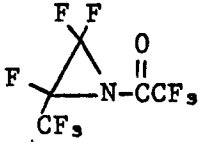


Figure 19

GAS SAMPLE

AMIDE 

COLLECTED BY GLC

3.1μ (cell blank, see next spectrum)

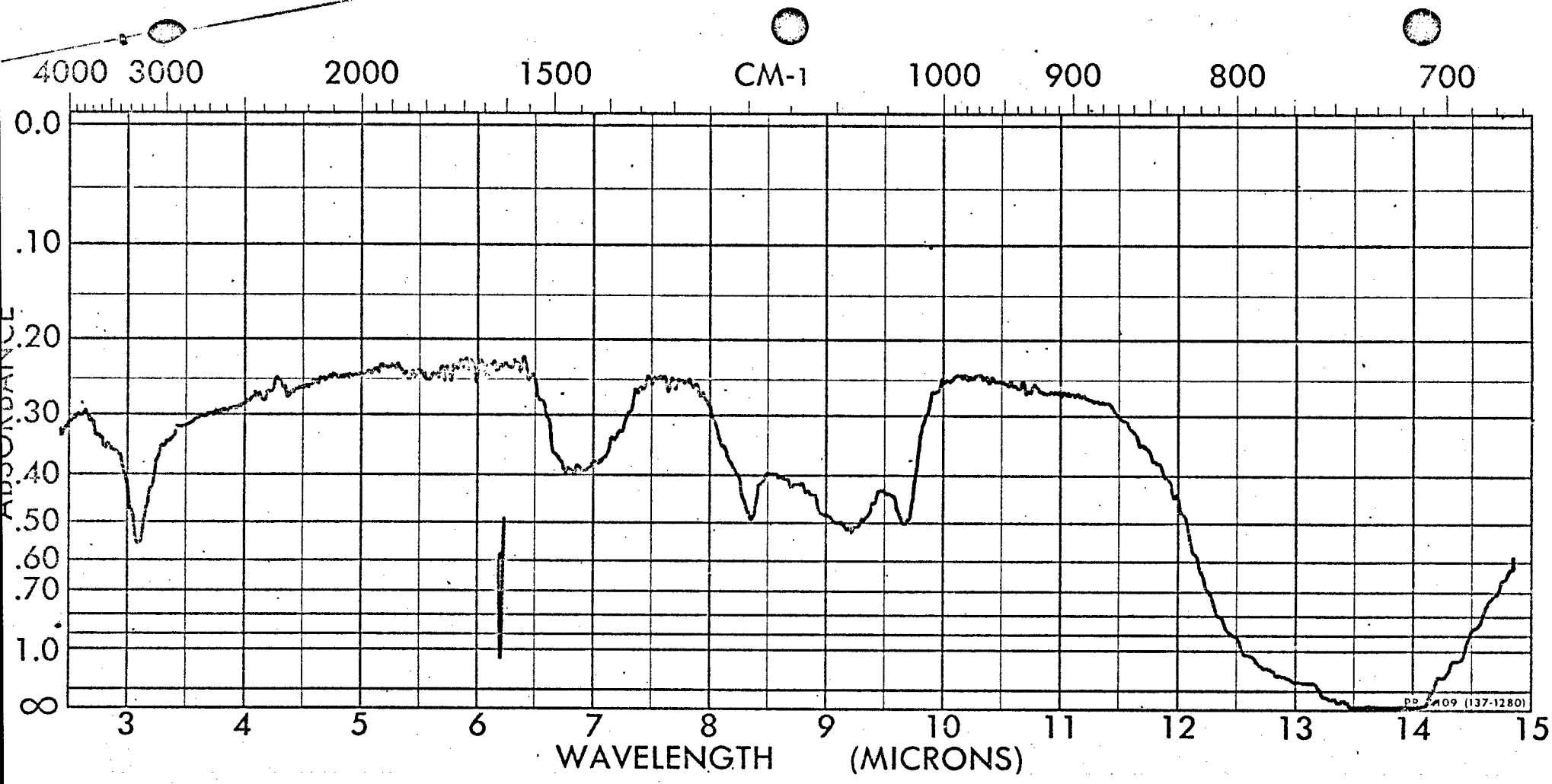


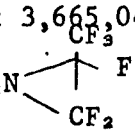
Figure 20

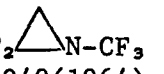
CELL BLANK FOR AMIDE

REFERENCES

1. J. D. Sterling, U. S. Pat. 3,648,112 (February 29, 1972).
2. Yung K. Kim, J. Org. Chem., 32, 3673 (967).
3. Personal communication from D. C. England, duPont.
4. Courtesy of D. C. England.
5. D. C. England, J. Am. Chem. Soc.,83, 2205(1961).
6. S. Dixon, U. S. Pat. 2,917,548(1959).
7. While it was not shown unambiguously, it is suspected that at higher temperature fluoroanions of the type $MeOCF_2CF_2^-$ may abstract protons from ether solvents.
8. These products are not derived from fragments obtained by partial decomposition of perfluorocyclobutanone since this compound is stable up to 300° in glass (see ref. 5) and steel.
9. H. C. Clark and C. J. Willis, J. Am. Chem. Soc., 82, 1888(1960).
10. For recent reviews of properties and polymerization of perfluoroepoxides see: H. S. Eleuterio, J. Macromol. Sci., Chem., A6 (6), 1027(1972); P. Tarrant, C. G. Allison, K. P. Barthold and E. C. Stump, Jr., Fluorine Chemistry Reviews, 5, 77-113(1971).
11. H. Hamberger and R. Huisgen, Chem. Comm., 1690(1971); R. Huisgen, Angew Chem. (Intern. Ed.), 2, 598(1963).
12. R. E. Banks, M. G. Barlow, R. N. Haszeldine, M. K. McCreath, and H. Sutcliffe, J. Chem. Soc., 7209(1965).
13. C. A. Buehler and D. E. Pearson, ''Survey of Organic Synthesis,'' Wiley-Interscience, New York, N. Y., 1970, p. 333.
14. C. O. Pederson and H. K. Frensdorff, Angew. Chem. (International Edit.), 11, 16(1972).
15. K. B. Baucom and R. J. De Pasquale, ''Synthesis of New Elastomeric Polymers and Specialty Chemicals,'' AFML-TR-72-123, Part I, Sept. 1972, pp 92-94; I. L. Knunyants, V. V. Shokina, V. V. Tyuleneva, and T. N. Razumeeva, Bull. Acad. Sci. USSR, Chem, 5, 1133(1972).
16. V. Wienmeyer, U. S. Patent 3,639,429 (1972).
17. C. G. Fritz, E. P. Moore, and S. Selman, U. S. Patent 3,114,778(1963).

18. D. Sianesi and R. Fontanelli, U. S. Patent 3,665,041(1972).

19. A partially fluorinated aziridine, $C_6H_5CH_2N$  , was isolated as a side product in a reaction scheme, see for example W. Carpenter A. Hazmaka, and D. W. Moore, J. Org. Chem., 31, 789(1966);


has also reported, A. L. Logothetis, J. Org. Chem., 29, 3049(1964).

20. C. S. Cleaver and C. G. Krespan, J. Am. Chem. Soc., 87, 3716(1965); R. E. Banks and G. J. Moore, J. Chem. Soc. (C), 2304(1966).

21. J. E. Fearn and J. A. Well, "Polymers of Perfluorohexadiene, Perfluoroheptadiene, and Perfluorooctadiene," NBS Report 8623, February 1965.

22. It seems essential to add the dioxane to the NaOMe; the slurry is free-flowing when prepared in this manner. In one experiment NaOMe was added to the dioxane. The resulting slurry was extremely difficult to charge into the autoclave by suction.

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* PCR, Inc. Gainesville, Florida 32601	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

Perfluorocarbon Epoxides

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Interim 1 April 1972 to 31 March 1973

5. AUTHOR(S) *(First name, middle initial, last name)*

Ralph J. De Pasquale; Calvin D. Padgett; Jerry R. Patton

6. REPORT DATE May 1973	7a. TOTAL NO. OF PAGES 73	7b. NO. OF REFS 22
8a. CONTRACT OR GRANT NO. F33615-72-C-1550 b. PROJECT NO. 7340 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-73-144, Part I 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*	

10. DISTRIBUTION STATEMENT

Distribution limited to U.S. Government agencies only; (test and evaluation). May 1973. Other requests for this document must be referred to the Air Force Materials Laboratory, Nonmetallic Materials Division, Polymer Branch, AFML/MBP, Wright-Patterson Air Force Base, Ohio 45433.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory Air Force Systems Command Wright-Patterson AFB, Ohio 45433

13. ABSTRACT

Potential solvents of the general formula $MeO(CH_2CH_2O)_3\overset{OCF_3}{\overset{\|}{C}}CF(OCF_2\overset{CF_3}{\overset{|}{C}}F)_nF$ were prepared, tested for stability toward fluoride ion, and used as solvents in HFPO oligomerizations. These materials were found to be inferior to the conventional glyme solvents in HFPO oligomerizations. Areas for further investigation were suggested.

Studies directed toward the preparation of a 2.3 spiroepoxide were culminated by the synthesis of perfluoro(1-oxaspiro[2.3]hexane). Considerable effort was spent on obtaining perfluorocyclobutanone, an essential intermediate in the spiroepoxide synthesis. Under the appropriate conditions this fluorinated ketone can be converted to the spiroepoxide in excellent yield. Under specified conditions the attempted preparation of this epoxide leads to the isolation of an unusual series of compounds apparently derived from the spiroepoxide, itself. Attempted polymerization and reactions of the spiroepoxide are discussed.

A new class of compound, a perfluorinated ether epoxide, was prepared by the oxidation of the vinyl ether derived from HFPO trimer. Of the three reagents tested for this oxidation ($O_2/h\nu$, H_2O_2/Na_2CO_3, OF_2/O_2) the OF_2 catalyzed oxidation seemed best. Attempts to extend this reaction to the simplest homolog of this class of epoxide are discussed.

Several approaches leading to the preparation of perfluorinated-N-alkyl aziridines were investigated.

DD FORM 1 NOV 65 1473

Unclassified
Security Classification

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Fluorinated Spiroepoxide						
Fluorinated Ether Epoxides						
Fluoroether Polymers						
Perfluorocyclobutanone						
Perfluoro-N-alkyl Aziridines						
Fluoroepoxide Cycloaddition Reactions						

Security Classification