

THERMALLY STABLE FLUOROCARBONS

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FINAL REPORT

(1 December 1969 to 31 November 1970)

March 1971

by

Richard W. Anderson
and
Hughie R. Frick

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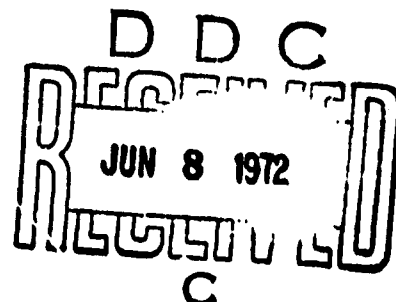
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polymers

fluorosulfonate

fluoroalkoxide

fluoroketone

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FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, on Navy Contract NOOC19-70-C-0284, "Thermally Stable Fluoropolymers". This work was sponsored and administered by Naval Air Systems Command, Department of the Navy, Washington, D. C. 20360.

This report represents the work performed on this contract for the period 1 December 1969 to 31 November 1970, and is being submitted as the Final Progress Report as part of the contract commitment.

Management direction at Dow was under G. F. Mackenzie, Technical Manager of the Organic Product Department Laboratory. Dr. R. W. Anderson is the principal investigator, assisted by H. R. Frick.

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ABSTRACT

The preparation of thermally stable fluoropolymers was investigated using three approaches, each based on the synthesis of a different type of fluorocarbon alkoxide monomer. Two of these alkoxides were prepared by the reaction of potassium fluoride with bis(fluorosulfonate) compounds. One alkoxide is extremely stable, whereas the other is formed only as a transient intermediate. Neither polymerized with perfluorocyclobutene. A prototype of the third type of monomer was prepared, but it too failed to react with perfluorocyclobutene. Results indicate that the reactivity of perfluorinated alkoxides is extremely sensitive to structure.

I. INTRODUCTION

The purpose of this research is to synthesize polymers as candidate elastomer sealants, gaskets and flexible coatings with a thermal stability approaching 1000°F., an operating temperature of at least 600°F., and outstanding chemical stability. More specifically, the program involves the synthesis and evaluation of perfluoroalicyclic compounds containing multiple perfluorinated cyclobutane and cyclobutene rings connected by oxygen, or perfluoroalkyl chains containing oxygen.

Perfluorocarbons as a class of compounds are known to have a very high degree of thermal stability. Among the most stable perfluorocarbons is the alicyclic compound perfluorocyclobutane, which has a reported stability of >1240°F.¹ Perfluorocyclobutene undergoes rearrangement, but not decomposition, at about 900°F. at reduced pressure.

The thermal stability studies on perfluoroalicyclic compounds indicate that perfluorinated cyclobutane groups are stable at temperatures >1000°F. using isoceniscope tests. Due to experimental difficulties, no precise decomposition temperature could be ob-

tained; however, it was found that $\boxed{\text{F}} \boxed{\text{F}} \boxed{\text{F}}$ is as thermally stable as other perfluorinated alicyclic compounds evaluated (1000°F.).

Polymers of the type $\left[\boxed{\text{F}} \right]_n$ have been prepared in this labora-

tory under Navy Contract Nr. N00019-68-C-0174, but these were not elastomeric. To allow flexibility necessary for an elastomer while maintaining thermal stability of the system, these cyclic groups must be connected by groups such as oxygen, or perfluoroalkyl chains containing oxygen. Saturation of the above polymer with fluorine also increased its flexibility.

Fluorocarbon fluids containing ether linkages have shown stability to over 700°F., do not form sludge or tar even in air, and are highly fire resistant and LOX compatible². A fluorocarbon

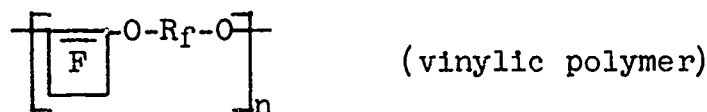
vinyl ether, $1-\text{C}_3\text{F}_7\text{O}-\boxed{\text{F}}$, was prepared in this laboratory and found to be stable to about 700°F.³

Thus, from these data, it appears that polymers of the general structure —(F)—X, where (F) is perfluorinated cyclobutane or cyclobutene, or a mixture thereof, and X is oxygen, or a perfluorinated carbon chain containing an ether oxygen, would have excellent chemical and oxidative stability, low flammability, and elastomeric properties when crosslinked.

II. DISCUSSION

A. INTRODUCTION

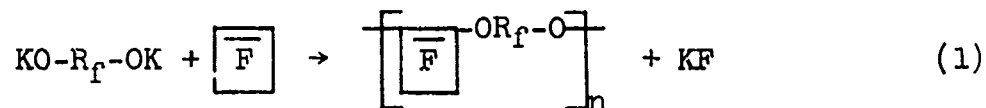
The following two general types of polymers were considered:



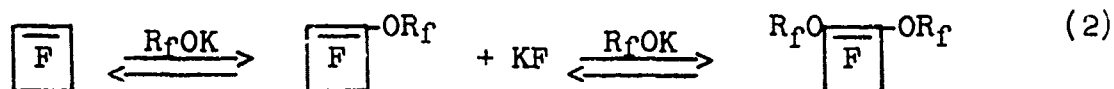
where $\text{R}_f = \text{---}\boxed{\text{F}}\text{---}\boxed{\text{F}}\text{---}$, $\text{---}\boxed{\text{F}}\text{---}$, or $\text{---}\underset{\text{R}'_f}{\text{C}}\text{F}(\text{CF}_2)_x\underset{\text{R}'_f}{\text{C}}\text{F---}$, and $\text{R}'_f = \text{CF}_3$ or C_2F_5 .

Most of the effort was concentrated on attempts to prepare the vinyllic polymer where $\text{R}_f = \text{---}\boxed{\text{F}}\text{---}$ and $\text{---}\boxed{\text{F}}\text{---}\boxed{\text{F}}\text{---}$

The following equation represents the formation of these vinyllic polymers:



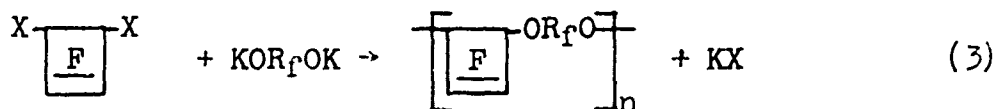
This displacement of vinyllic fluorine has been studied in detail in this laboratory using monofunctional material and has been shown to be an equilibrium at 95°C.,^{4,5} i.e.,



When R_f is 1- C_3F_7 , about 50 percent perfluorocyclobutene, 45 percent monosubstituted product, and 5 percent disubstituted product comprise the equilibrium mixture; but when R_f is cyclic C_4F_7 the equilibrium mixture consists of only a trace of perfluorocyclobutene, 30 percent monosubstituted product and 70 percent disubstituted product. However, at 55°C. with cyclic C_4F_7 , a nearly quantitative conversion to disubstituted product

is obtained, apparently because the reverse reactions are extremely slow at this temperature. Thus, perfluorinated cyclic dialkoxides were considered excellent monomers for preparing thermally and chemically stable polymers.

The proposed preparation of the allylic polymers is illustrated in the following equation:



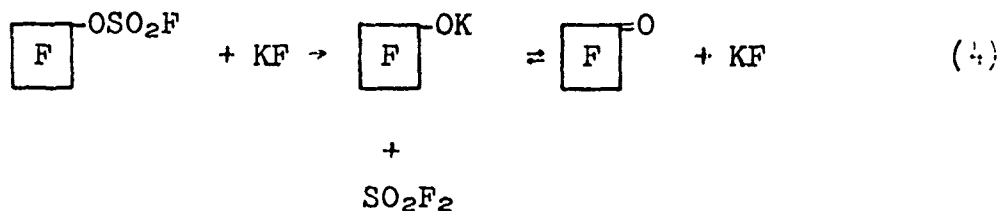
where X is Cl, Br or I, R_f is $-\boxed{\text{F}}-\boxed{\text{F}}-$, $-\boxed{\text{F}}-$, or $-\text{CF}(\text{CF}_2)_x\text{CF}-$ and R'_f is CF_3 or C_2F_5 .
 $\begin{array}{c} | \\ \text{R}'_f \\ | \\ \text{R}'_f \end{array}$

Displacement of allylic halogen is known to be a facile process when the nucleophile is a halide anion⁵, and alkoxides should behave in a manner analogous to halide ions, i.e., displace allylic halogens more rapidly than they displace vinylic fluorine.

Since the perfluorinated dialkoxide monomers were not known, it was necessary to synthesize them. Therefore, the research program fell logically into three areas, each dealing with the preparation and attempted polymerization of a monomer; perfluorinated cyclobutane dialkoxide, perfluorinated bicyclobutenyl dialkoxide, and perfluorinated linear dialkoxides.

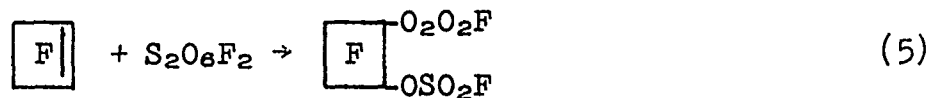
B. PREPARATION AND ATTEMPTED POLYMERIZATION OF PERFLUORINATED CYCLOBUTANE DIALKOXIDE, $\boxed{\text{F}}\begin{array}{l} \text{OK} \\ \text{OK} \end{array}$ (MONOMER I)

Since perfluorocyclobutyl fluorosulfonate compounds can be readily transformed into alkoxides and ketones^{5,6,7,8}, e.g.,

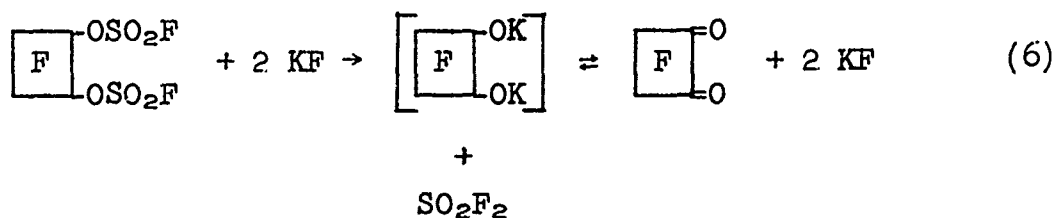


this general method of preparing Monomer I was applied. This reaction sequence began with the slow vapor phase addition of

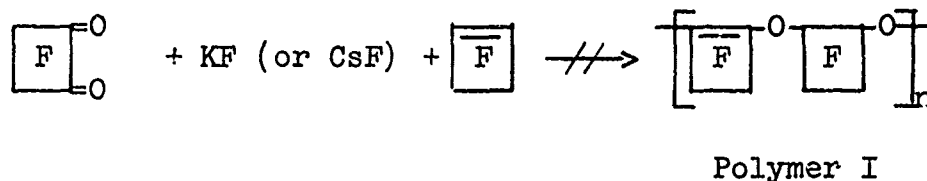
$S_2O_6F_2$ to perfluorocyclobutene, which produced a very energetic reaction and a quantitative yield of perfluoro-1,2-bis(fluoro-sulfonato)cyclobutane, i.e.,



The structure of the product was proven by elemental analysis and NMR spectroscopy. Treatment of this compound with KF resulted in previously reported⁹, blue perfluorocyclobutane-1,2-dione, obtained from the loss of KF from the dialkoxide, i.e.,



The formation of a carbonyl compound from an alkoxide is known to be an equilibrium reaction, the position varying greatly with the type of carbonyl compound¹⁰. Monoketones exist primarily as the alkoxide at $<100^\circ C$. The copolymerization of perfluorocyclobutane-1,2-dione in the presence of alkali metal fluoride with perfluorocyclobutene was unsuccessful, i.e.,



Neither the dianion, $\boxed{F} \begin{matrix} O^- \\ O^- \end{matrix}$, nor the monoanion, $\boxed{F} \begin{matrix} O^- \\ O \end{matrix}$, are stable

when the diketone is treated with cesium fluoride or potassium fluoride under a variety of temperature and solvent conditions. No methyl ether was obtained with methyl iodide in the presence of KF, and methyl iodide is usually very reactive with fluorinated alkoxides, even at mild temperatures³. Attempts to trap the alkoxide by treating the bisfluorosulfonate with potassium fluoride in the presence of methyl iodide or perfluorocyclobutene were also unsuccessful. Apparently the conversion to the diketone

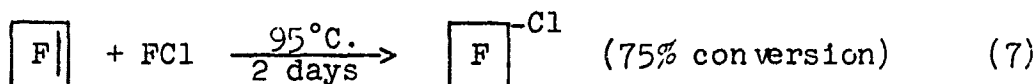
from the bisfluorosulfonate passes very rapidly and irreversibly through the dialkoxide. Thus, the chemical reactivity of this, diketone is not at all like the reactivity of the corresponding monoketone. Because of this lack of reactivity of the diketone no further attempts were made to prepare a vinylic polymer from it, and consequently no attempt was made to prepare an allylic polymer.

C. PREPARATION AND ATTEMPTED POLYMERIZATION OF PERFLUORINATED BICYCLOBUTENYL DIALKOXIDE, (MONOMER II)



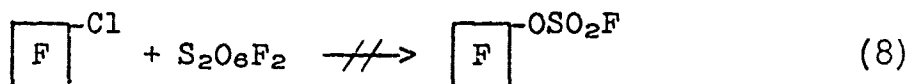
Four general approaches were attempted before a method for preparing Monomer II was found. They all involve introducing the $-\text{SO}_3\text{F}$ group into a molecule in such a way that difunctionality results.

The first method was the attempted replacement of a halogen by a fluorosulfonate group. To prepare material for this type of approach, the addition of FX to perfluorocyclobutene was studied. It was found that with heating FCl adds to the double bond of perfluorocyclobutene to give about 75% conversion to perfluorocyclobutyl chloride, i.e.,

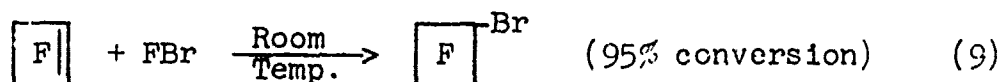


At 65°C . the reaction is much slower. The product was identified from its boiling point (21°C .; lit. 23°C .¹¹) and from its mass spectrum.

Attempts to displace the chlorine by a fluorosulfonate group, as described in the literature^{7,12} for other chlorinated compounds, failed, e.g.,



Attempted reactions at room temperature, at 95°C ., or by irradiation with ultraviolet light were unsuccessful, and displacement with BrSO_3F under similar conditions also failed. Since bromine should be more readily displaced, the corresponding bromo derivative was prepared, i.e.,

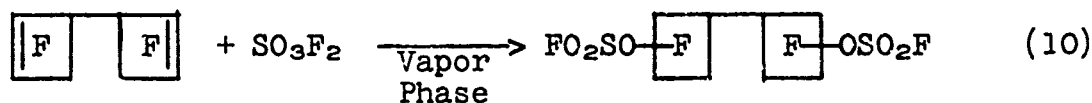


This reaction proceeded nicely at room temperature to give a 95% conversion of perfluorocyclobutyl bromide, which was identified by its mass spectrum and elemental analysis.

Again no replacement of the Br by an $-SO_3F$ group was obtained using both $S_2O_8F_2$ and $BrSO_3F$. Thus, this approach was discontinued without attempting reactions with difunctional perfluorobi-

2-cyclobutenyl, $\boxed{F} \text{---} \boxed{F}$.

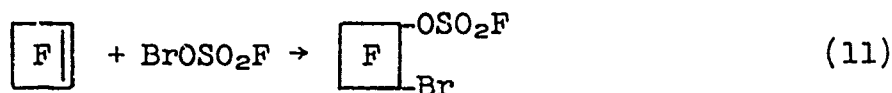
A second approach to preparing $KO \text{---} \boxed{F} \text{---} \boxed{F} \text{---} OK$, Monomer II, was the direct addition of a fluorosulfonate group to perfluorobi-2-cyclobutenyl, i.e.,



This type of addition is quantitative with perfluorocyclobutene⁶. However, in this case the reaction was very energetic and a tarry product was produced which could not be identified. No further attempts were made to pursue this course.

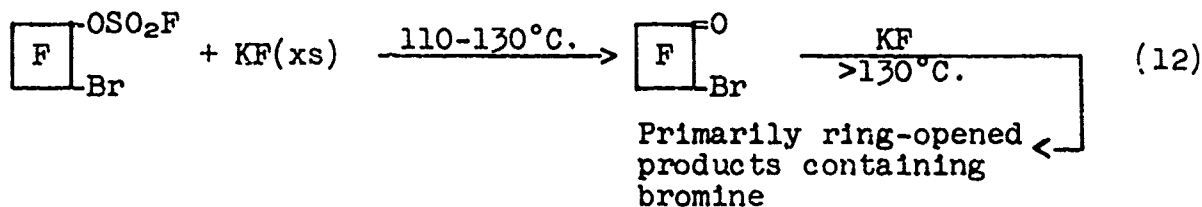
At this point it was felt that introduction of a $-SO_3F$ group by addition of a less reactive reagent such as $BrSO_3F$ should be possible. However, replacement of the bromine by fluorine would be desirable.

Bromine fluorosulfonate is known to add to fluorinated olefins⁷, including perfluorocyclobutene⁶, so some of this product was prepared, viz.,

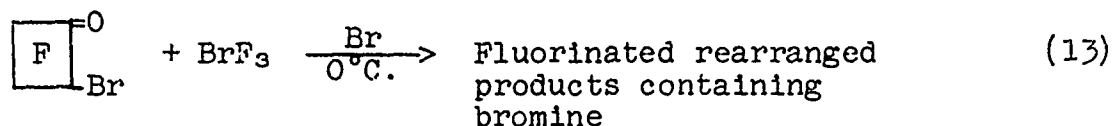


Attempts were made to demonstrate that the bromine could be removed from the addition product before analogous reactions were run using perfluorobi-2-cyclobutenyl.

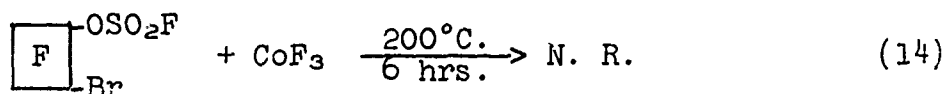
Reaction with KF gave the bromoketone with liberation of SO_2F_2 , but further heating at increased temperature gave a ring-opened product which still contained bromine, i.e.,



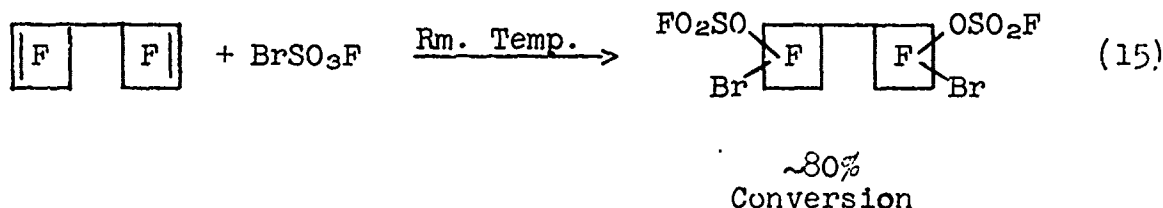
Since BrF_3 is known in many cases^{1,3} to be an effective agent to replace bromine with fluorine, BrF_3 was reacted with perfluoro-2-bromocyclobutanone. However, a mixture of products resulted, most of which contained bromine and had structures rearranged such that a cyclobutane ring no longer existed i.e.,



The removal of a bromine atom from a sample of perfluoro-2-fluorosulfonatecyclobutyl bromide with cobalt trifluoride also was unsuccessful, i.e.,

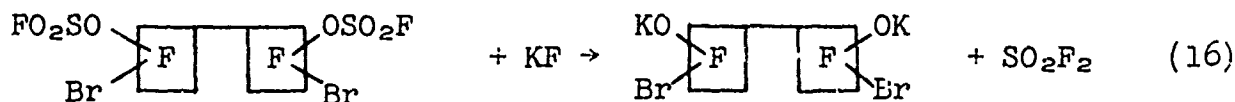


These reactions demonstrate that the bromine in these systems is strongly attached; thus, a polymer prepared from a monomer containing bromine should have good chemical stability. A precursor of a monomer of this nature was prepared by the following reaction:



The high conversion in this reaction is confirmation of the postulate that BrSO_3F should react more controllably than FSO_3F with perfluorobi-2-cyclobutenyl. The NMR analysis of the product of Reaction (15) is consistent with the assigned general structure.

The conversion of the fluorosulfonate groups to alkoxide groups i.e.,

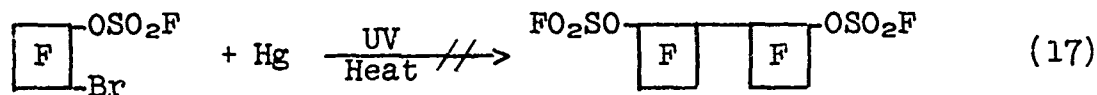


should produce a molecule which would have, in addition to numerous optical isomers, about 45 positional isomers. Thus, any polymer containing units of this nature should be quite amorphous. No attempt was made to carry out Reaction (16) due to higher priority in preparing the fully fluorinated material.

Because of the extreme chemical stability of the brominated materials, no further attempts were made to displace bromine with fluorine.

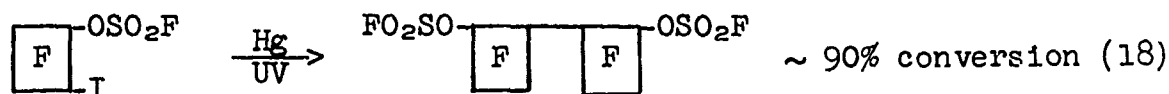
The fourth approach to preparing Monomer II by coupling of a perhalogenated cyclobutyl fluorosulfonate was found to be quite successful. However, only one member of this family of compounds couples to give desired product.

An attempt to couple rings by the following reaction gave no product.



However, under similar conditions the bromoketone $\begin{array}{|c|} \hline \text{F} \\ \hline \text{O} \\ \hline \text{Br} \\ \hline \end{array}$, will couple; and mass spectral analysis indicated the product was an isomer of the above compound, but NMR analysis was not consistent with the desired structure. The exact structure was not determined.

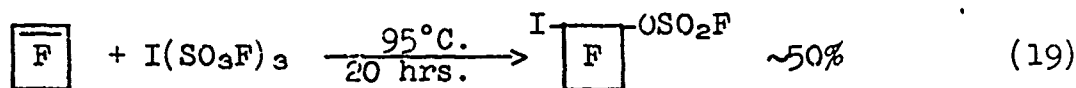
Coupling using an iodofluorosulfonate successfully produced perfluoro-2,2'-bis(fluorosulfonato)bicyclobutyl i.e.,



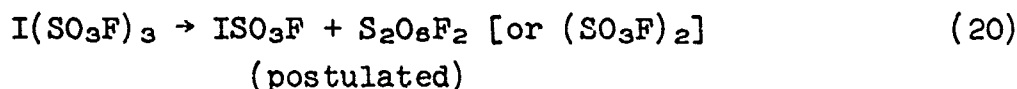
The product was confirmed by NMR and infrared analysis.

Production of enough of this bisfluorosulfonate for subsequent reactions was hampered by the relatively poor conversion in

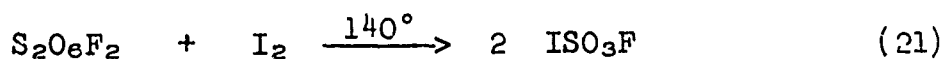
making $\begin{array}{|c|} \hline \text{I} \\ \hline \text{F} \\ \hline \text{OSO}_3\text{F} \\ \hline \end{array}$. As a result, a better method for producing perfluoro-2-iodocyclobutyl fluorosulfonate starting material was developed. Since iodine fluorosulfonate exists primarily as $\text{I}(\text{SO}_3\text{F})_3$ ¹⁴ (ISO_3F has never been isolated), the addition to perfluorocyclobutene was quite slow i.e.,



By heating the reaction mixture to about 114°C. $\text{I}(\text{SO}_3\text{F})_3$ breaks down as follows¹⁴:

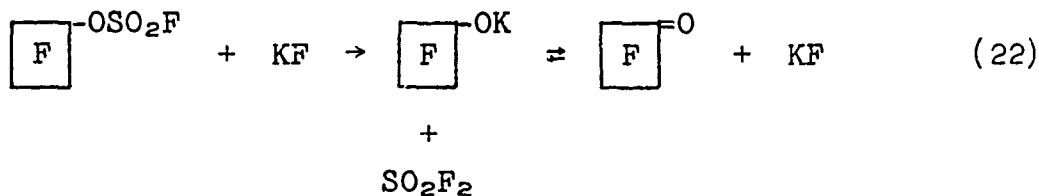


Since $S_2O_6F_2$ reacts violently with perfluorocyclobutene [Reaction (5)], it was postulated that an excess of iodine must be present to convert it to iodine fluorosulfonate, i.e.,

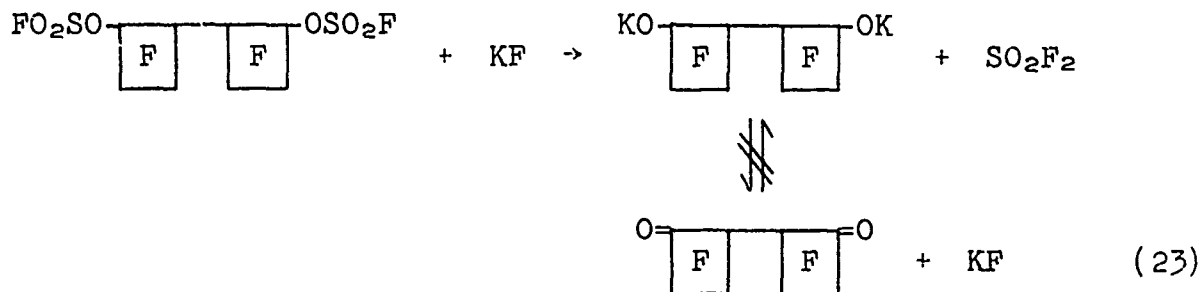


Under these conditions the iodocyclobutyl fluorosulfonate was prepared in about 85% conversion in about two hours [Reaction (19)].

Perfluorocyclobutyl fluorosulfonate in the absence of solvent reacts with KF at about 100°C . to produce perfluorocyclobutoxide⁶ and SO_2F_2 . This alkoxide is in equilibrium with perfluorocyclobutanone and KF, and the ketone can be removed as a vapor, i.e.,

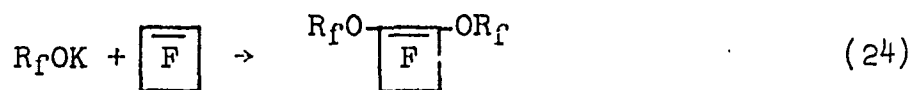


A similar type of reaction has been attempted with the bisfluorosulfonate, i.e.,

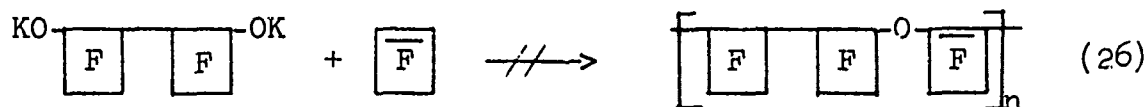


Without solvent no reaction occurred at 125°C ., but when acetonitrile was added as a solvent a quantitative amount of SO_2F_2 was evolved at room temperature in a short time. However, heating produced no ketone. Removal of SO_2F_2 and solvent from the reactor left a solid material with an increase in weight corresponding to a stoichiometric amount of alkoxide.

A two-year study in this laboratory³ of fluorocarbon alkoxides revealed that generally secondary potassium alkoxides undergo a number of reactions. Among them, the following two reactions were observed:



When these types of reactions were attempted with $\text{KO}-\boxed{F}-\boxed{F}-\text{OK}$ as the R_fOK , no desirable reaction resulted, even at elevated temperatures. Reactions with perfluorocyclobutene is the polymerization reaction, i.e.,

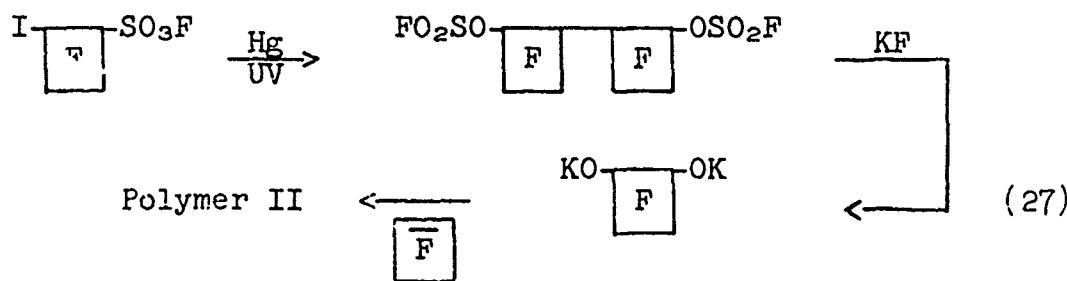


Polymer II

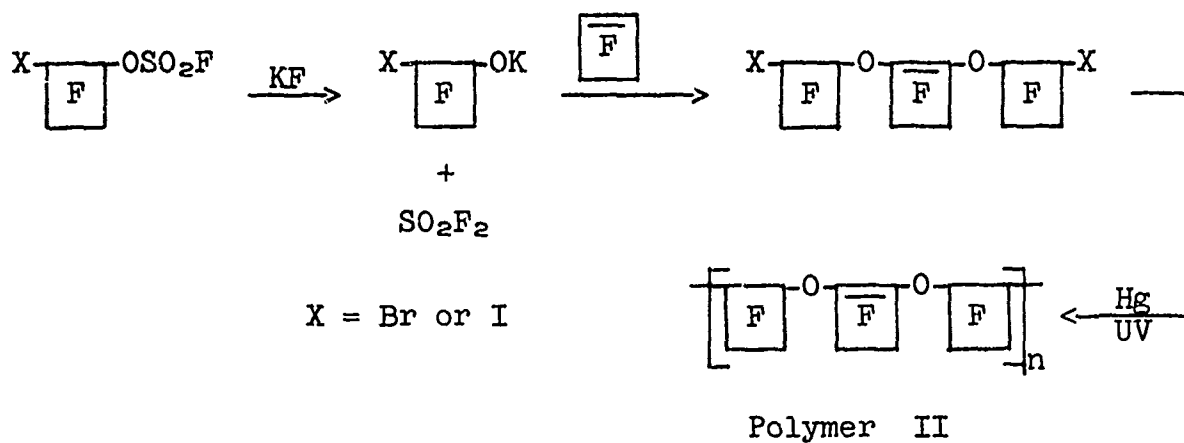
Some high boiling material of unknown structure containing both carbon-fluorine and carbon-hydrogen bonds was obtained, but this material probably was the result of traces of water in the solvent, which was discovered later. Repeating the experiment using re-dried solvent produced no reaction. The cesium alkoxide gave essentially the same result.

Thus, it is evident that this perfluorinated bicyclobutyl dialkoxide is amazingly unreactive, especially when compared to potassium perfluorocyclobutoxide, \boxed{F}^{OK} . Because of this lack of reactivity no further attempts were made to prepare a vinylic polymer from this material, and likewise no attempt was made to prepare an allylic polymer.

However, an alternative approach was made to prepare the same polymer by a rearranged reaction sequence. Instead of coupling first to form the bisfluorosulfonate compound (and subsequent alkoxide) and then polymerizing by reacting the alkoxide with perfluorocyclobutene, i.e.,



these steps were reversed, i.e.,

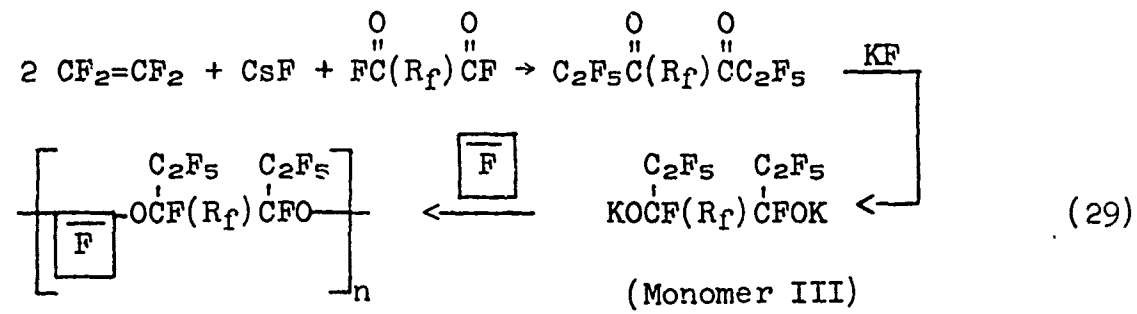


The first step in this sequence proceeded successfully, i.e., both perfluoro-2-iodo- and perfluoro-2-bromocyclobutyl fluorosulfonate were converted by KF to the alkoxide with evolution of the stoichiometric quantity of sulfuryl fluoride. However, addition of these alkoxides to perfluorocyclobutene resulted only in high boiling material having some carbon-hydrogen bonds or in rearranged alkoxide. Work done several years earlier in this laboratory⁶ indicated that this type of alkoxide rearranges at about 100°C., but it was expected that addition to perfluorocyclobutene should be facile enough to prevent extensive decomposition of the alkoxide.

Since this alkoxide, like the perfluorinated cyclobutyl dialkoxide and the perfluorinated bicyclobutyl dialkoxide, did not react with perfluorocyclobutene, no further work was done with this approach.

D. EVALUATION OF THE POLYMERIZATION REACTION TO PREPARE POLYMERS FROM PERFLUORINATED LINEAR DIALKOXIDES

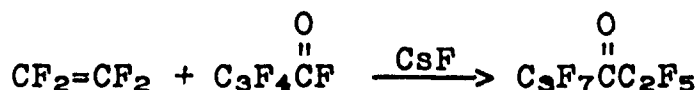
The proposed synthesis of a polymer from this type of monomer is illustrated in the following equation:



Polymer III

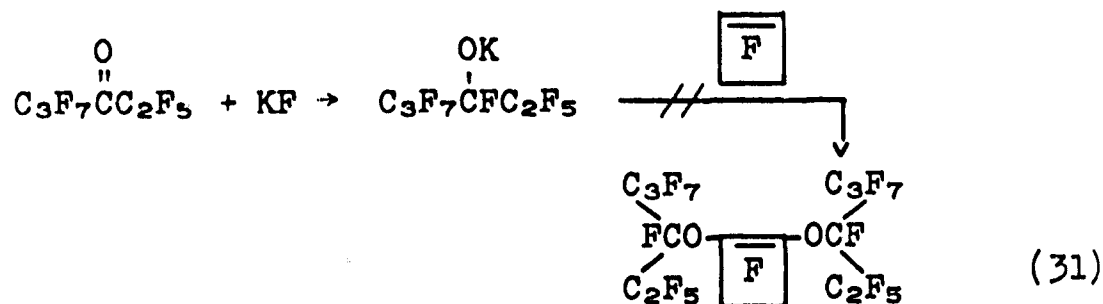
However, before attempting the preparation of Monomer III, analogous monofunctional material was synthesized and its reaction with perfluorocyclobutene studied briefly to evaluate the feasibility of preparing a polymer by the reaction of a linear alkoxide with perfluorocyclobutene.

Perfluoro-3-hexanone, $C_3F_7\overset{O}{\parallel}CC_2F_5$, was synthesized from tetrafluoroethylene and perfluorobutyryl fluoride, i.e.,



Initial attempts with this reaction produced relatively large amounts of CO_2 , $CF_3CF=CF_2$, CF_3CFHCF_3 and CF_2HCF_3 , which indicated that water was probably involved in the reaction. Thus, the diglyme used as the solvent was redried over metallic sodium. As a result, an 81% yield of perfluoro-3-hexanone was obtained from the reaction using dried diglyme.

This monoalkoxide was then treated with perfluorocyclobutene to test the feasibility of preparing a polymer by this type of reaction, i.e.,



The first step in this reaction apparently proceeded as written since the pressure in the reaction vessel dropped and the solid KF disappeared. However, when perfluorocyclobutene was added there was no pressure drop nor other evidence of reaction.

Work-up of the reaction product yielded only perfluorocyclobutene and perfluoro-3-hexanone. Because of the expiration of the contract, no further attempts were made, but it appears that this type of reaction will not produce polymers.

III. SUMMARY AND CONCLUSIONS

The preparation of thermally stable fluoropolymers was investigated using three approaches, each based on the synthesis of a different type of fluorocarbon alkoxide monomer. The following perhalogenated intermediates and potential monomers were among the compounds synthesized and identified:

- (i) Perfluorocyclobutane-1,2-dione (I), prepared from perfluoro-1,2-bis(fluorosulfonato)cyclobutane and potassium fluoride to form the transient dialkoxide and subsequently the diketone.
- (ii) Perfluoro-2-(fluorosulfonato)cyclobutyl bromide, perfluoro-2-bromocyclobutanone, perfluorodibromobis(fluorosulfonato)bicyclobutyl, perfluoro-2-(fluorosulfonato)cyclobutyl iodide, perfluoro-2,2'-bis(fluorosulfonato)bicyclobutyl and dipotassium perfluoro-(bicyclobutyl)-2,2'-diolate, (II).
- (iii) Perfluoro-3-hexanone (III), by the reaction of tetrafluoroethylene and perfluorobutyryl fluoride in the presence of potassium fluoride.

Prototype monofunctional alkoxide reactions indicated that the difunctional Monomers I and II would react with perfluorocyclobutene to form polymers. However, Monomer I did not give a typical alkoxide reaction even when it was generated in the presence of an alkoxide trapping agent. Monomer II also failed to undergo normal alkoxide reactions, but it was sufficiently stable that the corresponding diketone could not be produced by heating. When Monomer prototype III was heated with perfluorocyclobutene and potassium fluoride in an attempted addition reaction, only starting materials were recovered.

From these results it can be concluded that the reactivity of the perfluorinated alkoxides is extremely sensitive to structure, so that the prediction of good reactivity based on analogy was not confirmed. Consequently, the method to be employed for the preparation of thermally stable fluoropolymers containing ether linkages must be changed to other techniques, such as coupling polymerization or vinyl polymerization.

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V. EXPERIMENTAL*

A. PREPARATION OF PERFLUORO-1,2-BIS(FLUOROSULFONATO) CYCLOBUTANE

About 0.0210 mole of $S_2O_6F_2$ was vacuum transferred into a three-liter bulb, and 0.0212 mole of perfluorocyclobutene was added very carefully from a vessel of higher pressure. This reaction is very vigorous, so it was carried out with adequate shielding and with small increments of the cyclobutene. Purification of the reaction mixture consisted of removing the excess perfluorocyclobutene by vacuum transfer, then removing the product from the reaction vessel by pumping through a cold trap. The yield was nearly quantitative. The structure of the product was confirmed by NMR and elemental analysis.

B. REACTION OF PERFLUORO-1,2-BIS(FLUOROSULFONATO) CYCLOBUTANE WITH POTASSIUM FLUORIDE

About 3.0 g. (0.0083 mole) of the bis(fluorosulfonato)cyclobutane was vacuum transferred into a 25-ml. polymer tube containing an excess of potassium fluoride. The reaction mixture was heated up to 125°C., however, at 100°C. SO_2F_2 began to evolve. As the pressure increased in the tube, some of the volatile materials were removed and collected in a cold trap; after about 2.5 hours the reaction was complete. The product was purified by removing SO_2F_2 by vacuum transfer at about -50°C., then vacuum transferring the product at room temperature. The yield was 95%. Infrared analysis confirmed the product was the known perfluorocyclobutane-1,2-dione.

C. PREPARATION OF PERFLUOROCYCLOBUTYL CHLORIDE

Exactly 0.060 mole of perfluorocyclobutene and 0.090 mole of FCl were vacuum transferred into a 60 ml. monel cylinder, and this mixture was allowed to warm to room temperature and then was heated to about 95°C. for 2 days. At the end of this period, the excess FCl was pumped from the reactor, which was maintained at -78°C. The reaction mixture was then warmed to room temperature and the products were vacuum transferred to a glass pressure vessel containing elemental mercury, which reacted to remove chlorine which contaminated the original FCl. The chlorine-free product was then vacuum transferred through a u-trap containing sodium hydroxide pellets, which removed a carbonyl containing impurity. The purified product weighed 4.5 g. (0.04 mole, 73% of theory) and boiled at 21.5°C., which is consistent with the reported¹¹ boiling point. The structure was further confirmed by mass spectral analysis.

*Elemental analysis, infrared spectra, and NMR and mass spectral data are given in the appendix.

D. PREPARATION OF PERFLUOROCYCLOBUTYL BROMIDE

About 10 g. (0.073 mole) of BrF_3 was placed into a monel cylinder containing about 15 g. (0.094 mole) of Br_2 , and the vessel was closed, frozen in liquid nitrogen and evacuated. Then, 14.8 g. (0.091 mole) of perfluorocyclobutene was vacuum transferred into the cylinder, and the reactor was allowed to warm to room temperature. After 3 days at room temperature, no perfluorocyclobutene remained, and the product was vacuum transferred from the reactor into a glass vessel containing mercury, which removed any BrF_3 or Br_2 . About 21.6 g. (0.086 mole; 95% theory) of material boiling at 43°C . was recovered. The structure was confirmed from its mass and IR spectra and elemental analysis.

E. REACTION OF PERFLUOROBIS(2-CYCLOBUTENYL) WITH FLUORINE FLUOROSULFONATE

About 1.09 g. (3.8 mmoles) of perfluorobis(2-cyclobutenyl) was vacuum transferred into a three-liter pyrex bulb, and 0.95 g. (3.0 mmoles) of fluorine fluorosulfonate was added very slowly from a source of greater pressure. The reaction was carefully shielded because the reaction is very vigorous. The white fog which resulted condensed and collected as a liquid in the bottom of the reaction vessel. The product was quite insoluble in Freon solvents and common organic solvents, and no identifiable product was isolated.

F. REACTION OF PERFLUOROBIS(2-CYCLOBUTENYL) WITH BROMINE FLUOROSULFONATE

Bromine fluorosulfonate was prepared by vacuum transferring 3.2 g. (0.016 mole) of $\text{S}_2\text{O}_8\text{F}_2$ into a glass pressure vessel containing 2.9 g. (0.018 mole) of bromine, and allowing the mixture to warm to room temperature where a strongly exothermic reaction occurred. The reactor was then cooled to -196°C . and 6.4 g. (0.022 mole) of perfluorobis(2-cyclobutenyl) was added in 0.5 g. increments. Between incremental additions the reactor was allowed to warm and a reaction occurred at about 0° with a slight exotherm. After addition was complete, the reaction was allowed to stir overnight at room temperature. The reactor was then opened and a small amount of mercury was introduced to remove the excess bromine and any remaining bromine fluorosulfonate. All volatile materials, including the excess olefin, were then removed by vacuum transferring. The high boiling product was extracted from the mercuric salts with Freon-11, which was subsequently removed by distillation. About 8.8 g. (84% of theory) of product was obtained, which was highly purified by preparative scale vapor phase chromatography. The product, a mixture of isomers of perfluorodibromobis(fluorosulfonato)bicyclobutyl was identified from its infrared spectrum and from NMR analysis.

G. PREPARATION OF PERFLUORO-2-(FLUOROSULFONATO)CYCLOBUTYL BROMIDE

About 5.94 g. (0.0298 mole) of bromine fluorosulfonate was prepared as described above. Since the reaction is very vigorous, 4.92 g. (0.0304 mole) of perfluorocyclobutene was added very slowly at room temperature from a vessel of higher pressure. The reaction was then allowed to stir for 3 hours at room temperature, after which the reaction products were vacuum transferred into a glass pressure vessel containing mercury to remove excess bromine and any remaining bromine fluorosulfonate. Vacuum transfer of the slightly impure perfluoro-(2-fluorosulfonato)cyclobutyl bromide to a storage vessel resulted in recovery of 9.8 g. (96% of theory). The infrared spectrum was identical to an infrared spectrum of known perfluoro-2-(fluorosulfonato)cyclobutyl bromide⁶.

H. PREPARATION OF PERFLUORO-2-BROMOCYCLOBUTANONE

About 3.6 g. (0.0105 mole) of perfluoro-2-(fluorosulfonato)cyclobutyl bromide was vacuum transferred into a glass pressure vessel containing 10 g. (0.17 mole) of dry potassium fluoride, and the reaction mixture was heated to 100°C. for 5 hours. The volatile products were vacuum transferred from the reactor and were cooled to -70°C. where the SO_2F_2 was removed, leaving pure perfluoro-2-bromocyclobutanone in a quantitative yield. The infrared spectrum of the product was identical with an infrared spectrum of known perfluoro-2-bromocyclobutanone⁶.

I. PREPARATION OF PERFLUORO-2-(FLUOROSULFONATO)CYCLOBUTYL IODIDE

1. Moderate Conditions

About 10.1 g. (0.051 mole) of $\text{S}_2\text{O}_6\text{F}_2$ was vacuum transferred into a glass pressure vessel containing 13.0 g. (0.054 mole) of iodine. As the mixture was allowed to warm from -196°C. to room temperature an exothermic reaction took place. After standing for 3 hours at room temperature and heating at 95°C. for one hour, the reaction mixture was then cooled to -196°C., and 12.6 g. (0.078 mole) of perfluorocyclobutene was vacuum transferred into the reactor. This mixture was heated at 95°C. for 2 hours, after which the volatile materials were stripped from the reactor and collected in a cold trap. Unreacted perfluorocyclobutene was stripped from this material, and 14.8 g. (0.038 mole; 49% of theory) of perfluoro-2-(fluorosulfonato)cyclobutyl iodide was obtained. Similar results were obtained when the reaction was heated for 72 hours at 95°C. The structure was verified by elemental analysis, infrared spectrum and NMR analysis.

2. Forcing Conditions

About 10.5 g. (0.0530 mole) of $\text{S}_2\text{O}_6\text{F}_2$ was vacuum transferred into a glass pressure vessel containing 13.1 g. (0.0516 mole) of

iodine and allowed to react as described above. Then 16.2 g. (0.103) of perfluorocyclobutene was vacuum transferred into the reactor, and the mixture was heated to 95°C. for one hour. The temperature was then elevated to 135°-140°C. for 16 hours; however, after 3 hours the pressure in the reaction vessel dropped to a constant level. The product was recovered as described above, and 32 g. (0.0825 mole; 80% of theory) was obtained.

J. PREPARATION OF PERFLUORO-2,2'-BIS(FLUOROSULFONATO)BICYCLOBUTYL

About 30.0 g. of mercury, 28.2 g. (0.073 mole) of perfluoro-2-(fluorosulfonato)cyclobutyl iodide and 20 g. of Freon 113 were placed into pyrex pressure vessel under an inert atmosphere. The reactor was closed and irradiated with ultraviolet light as the contents were stirred magnetically. To cool the reactor, a stream of air was directed on the portion of the reactor exposed to the ultraviolet light. Irradiation was carried out for 22 hours, during which time the reactor was opened periodically to scrape solid deposits from the side of the vessel. At the end of the reaction time, the vessel was opened and 25 ml. of Freon 113 was added to aid in extracting the product. The liquid portion was filtered and the solids were extracted with an additional 30 ml. portion of Freon 113 and filtered. This procedure was repeated once again and the Freon from the combined filtrates was removed by distillation on a micro distillation apparatus. About 16.3 g. (0.0312 mole; 86% of theory) of product remained after removal of Freon. The structure of the product was proven by infrared, NMR, mass spectral, and elemental analysis.

K. PREPARATION OF DIPOTASSIUM PERFLUORO[BICYCLOBUTYL]-2,2'-DIOLATE

In an inert atmosphere 6.5 g. (0.0125 mole) of perfluoro-2,2'-bis(fluorosulfonato)bicyclobutane and 3.5 g. (0.065 mole) of potassium fluoride and 4.0 g. of dry acetonitrile were placed into a glass pressure vessel. Gas evolution began almost immediately, and the reactor was allowed to stand at room temperature for 18 hours. All volatile materials were removed from the reactor under vacuum, including the solvent, and the theoretical weight of combined acetonitrile and sulfuryl fluoride was recovered. The weight of the dry material remaining in the reactor was 4.0 g., in addition to the 3.5 g. of KF originally present, the theoretical amount of material which was expected by the formation of the dialkoxide. The structure of the product was inferred based on the evolution of sulfuryl fluoride and the known reactions of organic fluorosulfonato compounds. Addition of acetonitrile and perfluorocyclobutene to this material and heating to 95°C. for 24 hours resulted in a quantitative recovery of perfluorocyclobutene. A similar procedure using cesium fluoride gave essentially the same result. In a separate experiment, only 1 hour was required to liberate the theoretical amount of sulfuryl fluoride from the fluorosulfonato compound.

L. REACTION OF PERFLUORO-2-(FLUOROSULFONATO) CYCLOBUTYL IODIDE WITH POTASSIUM FLUORIDE

About 5.3 g. (0.014 mole) of perfluoro-2-(fluorosulfonato)-cyclobutyl iodide was placed into a glass pressure vessel containing 0.79 g. (0.014 mole) of potassium fluoride in diglyme. All reactants were added under an inert atmosphere. The reaction began immediately, and it was rapid enough that the mixture became warm and turned dark. Within one hour the reaction had ceased and a stoichiometric amount of sulfuryl fluoride was removed from the reactor. About 1.3 g. (0.0080 mole) of perfluorocyclobutene was vacuum transferred into the reactor, and the mixture was stirred at 95°C. for 18 hours. There was no evidence of a decrease in pressure of the reaction mixture, and essentially all of the perfluorocyclobutene was recovered unchanged.

M. PREPARATION OF PERFLUORO-3-HEXANONE

About 7.6 g. (0.034 mole) of perfluorobutyryl fluoride was placed into a glass pressure vessel containing 8.0 g. (0.025 mole) of cesium fluoride in dry diglyme. The reaction mixture was allowed to stir magnetically at room temperature until the pressure in the reactor dropped to about -12 psig. The reactor was then cooled to -196°C., and 3.2 g. (0.032 mole) of tetrafluoroethylene was vacuum transferred into the reactor. The vessel was then warmed to about 95°C., and the pressure was observed to begin to drop. After about 18 hours, the pressure had dropped to about -10 psig, and the reaction was worked up by vacuum transferring about 8.2 g. (76% of theory) of the ketone. The product was identified from its infrared spectrum.

VI. APPENDIX

Table I
Analytical Data for Synthesized Compounds

Compound		%			
		Carbon	Fluorine	Sulfur	Other
$\boxed{\text{F}}-\text{OSO}_2\text{F}$ $\boxed{\text{F}}-\text{OSO}_2\text{F}$	Theory	13.3	42.4	17.8	---
	Found	13.4	42.4	18.0	---
$\boxed{\text{F}}-\text{Br}$	Theory	18.4	50.9	---	30.7 (Br)
	Found	18.3	50.5	---	---
$\text{FO}_2\text{SO}-\boxed{\text{F}}-\boxed{\text{F}}-\text{OSO}_2\text{F}$	Theory	18.4	51.0	12.3	---
	Found	18.4	51.2	12.7	---
$\boxed{\text{F}}-\text{I}$ $\boxed{\text{F}}-\text{OSO}_2\text{F}$	Theory	12.4	34.3	8.3	32.7 (I)
	Found	12.2	31.5	9.8	31.6 (I)

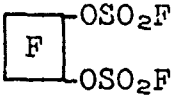
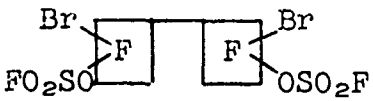

Table II
Mass Spectral Data of Synthesized Compounds

Compound	Ions of Interest*
$\boxed{\text{F}}-\text{Cl}$	$\text{C}_2\text{F}_3\text{Cl}^+$, CF^+ , $\text{C}_3\text{F}_4\text{Cl}^+$, C_2F_4^+ , C_3F_5^+ , C_3F_3^+ , CFCl^+ , CF_2^+ , $\text{C}_3\text{F}_5\text{Cl}^+$, C_4F_7^+
$\boxed{\text{F}}-\text{Br}$	$\text{C}_2\text{F}_3\text{Br}^+$, CF^+ , $\text{C}_3\text{F}_4\text{Br}^+$, C_3F_5^+ , C_2F_4^+ , C_3F_3^+ , C_4F_7^+ , M^+
$\text{FO}_2\text{SO}-\boxed{\text{F}}-\boxed{\text{F}}-\text{OSO}_2\text{F}$	SO_2F^+ , C_2F_4^+ , COF^+ , C_3F_5^+ , CO^+ , $\text{C}_2\text{F}_3\text{O}^+$, $\text{C}_8\text{F}_{11}\text{O}_2^+$, C_3F_3^+ , C_5F_7^+ , $\text{C}_5\text{F}_7\text{O}^+$

*The most intense fragment is listed first, and the others follow in order of decreasing intensity. Some less important fragments have been omitted.

Table III

Fluorine Nuclear Magnetic Resonance Data of
Synthesized Compounds

Compound	Chemical Shifts in ppm*	
	(one isomer)	CF ₂ +125.3 +126.6 CF +134.6 SF - 51.0
(Cis and trans isomers are present in 47% and 53% but are not identified)	(other isomer)	CF ₂ +123.9 127.9 CF +136.6 SF - 51.7
	(Mixture of isomers)	CF ₂ -C-F +180.2 -C-F +138.7 OSO ₂ F +129.4 -C-F +163 Br
	(Cis - trans isomers)	CF ₂ +126.5 -C-F +133.8 OSO ₂ F -C-F +188.0 S-F - 51.2

*Relative to CFCl₃; + = upfield

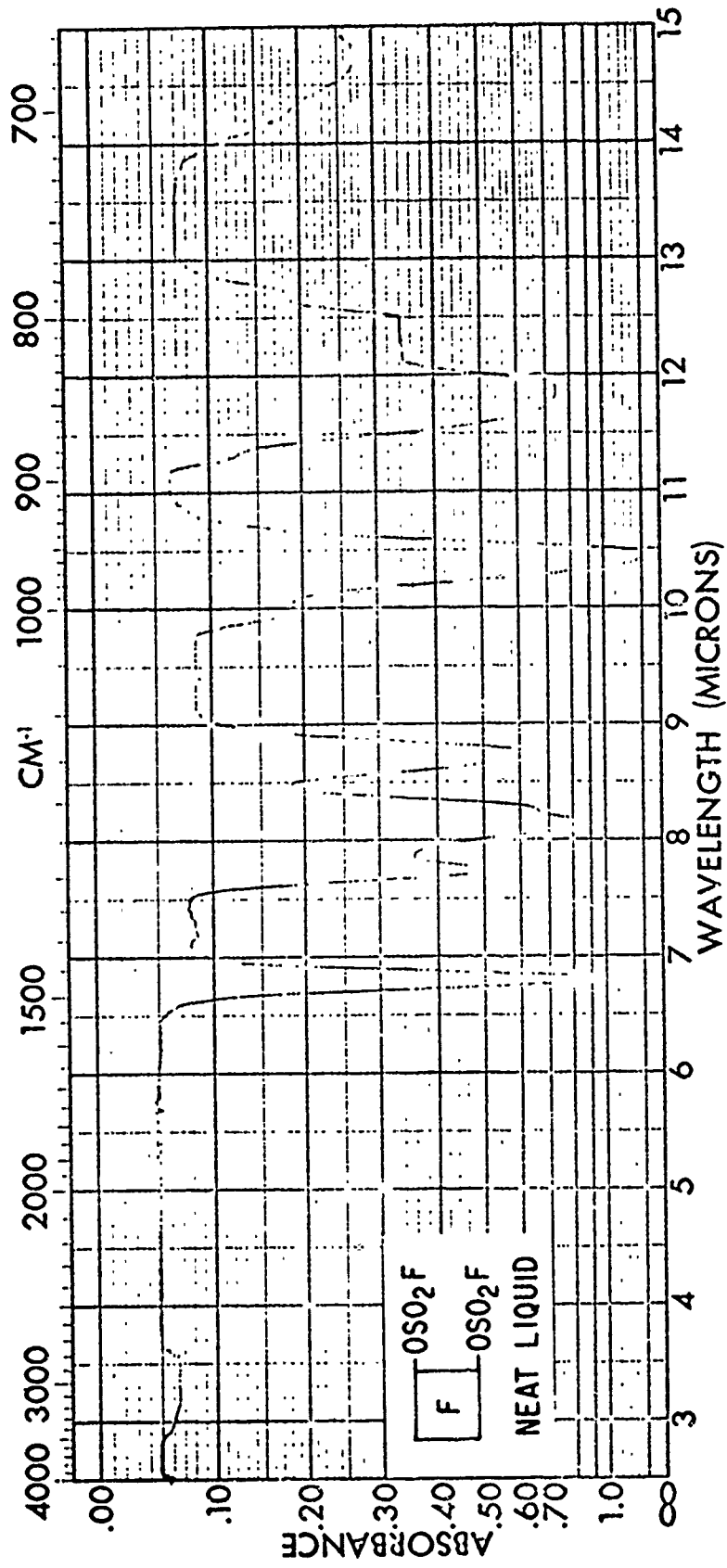


Fig. 1 - Infrared Spectrum of Perfluoro-1,2-bis(fluorosulfonato) cyclobutane

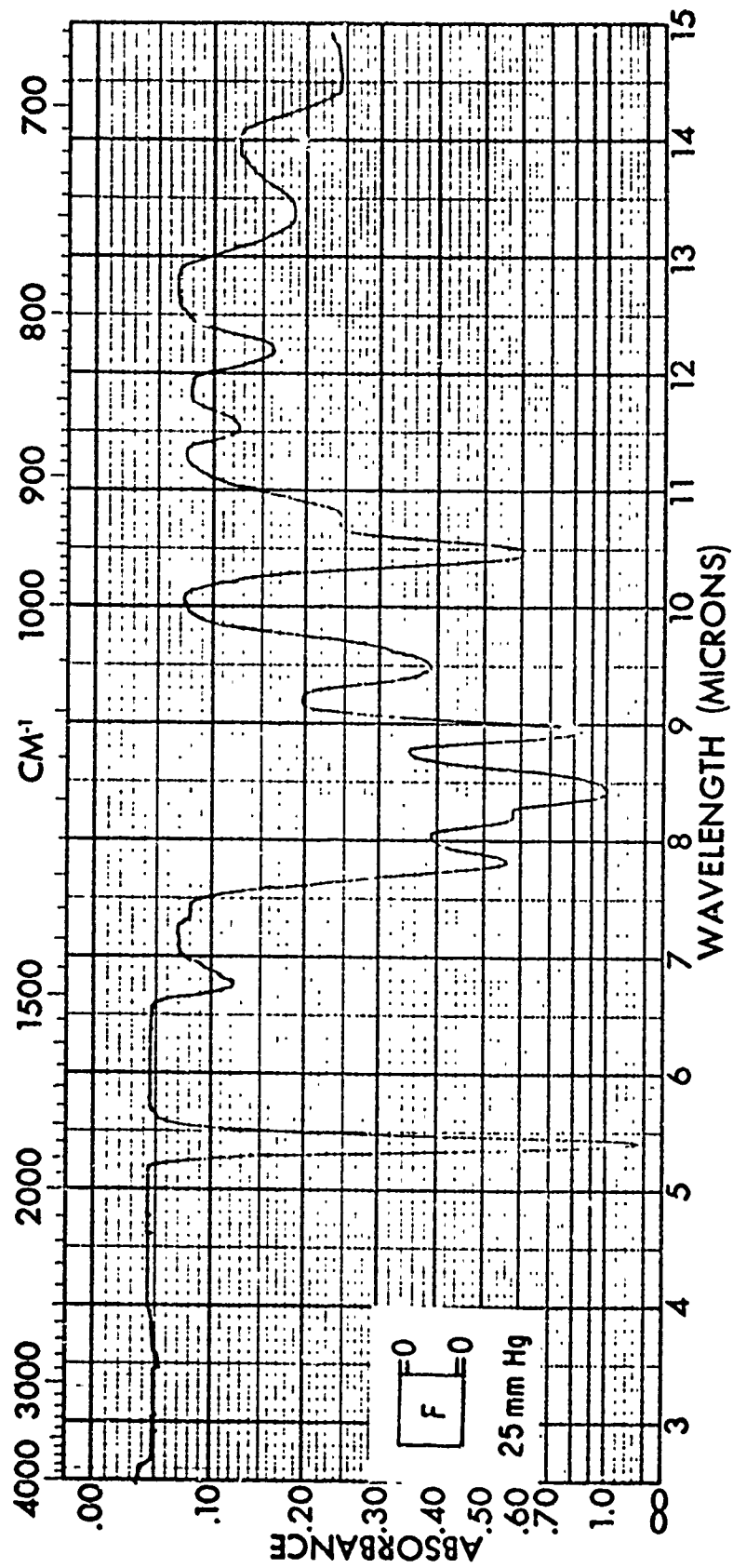


Fig. 2 - Infrared Spectrum of Perfluorocyclobutane-1,2-dione

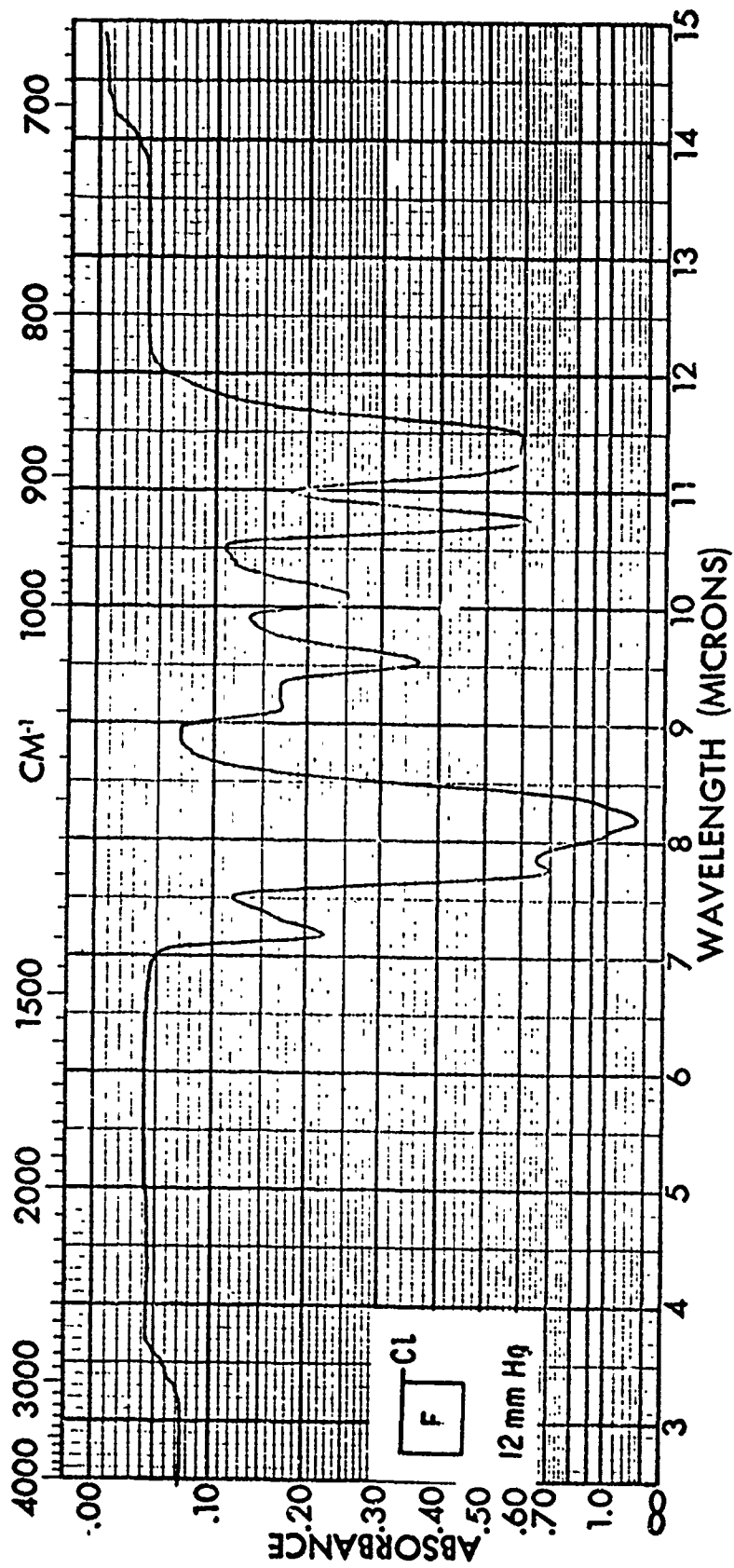


Fig. 3 - Infrared Spectrum of Perfluorocyclobutyl Chloride

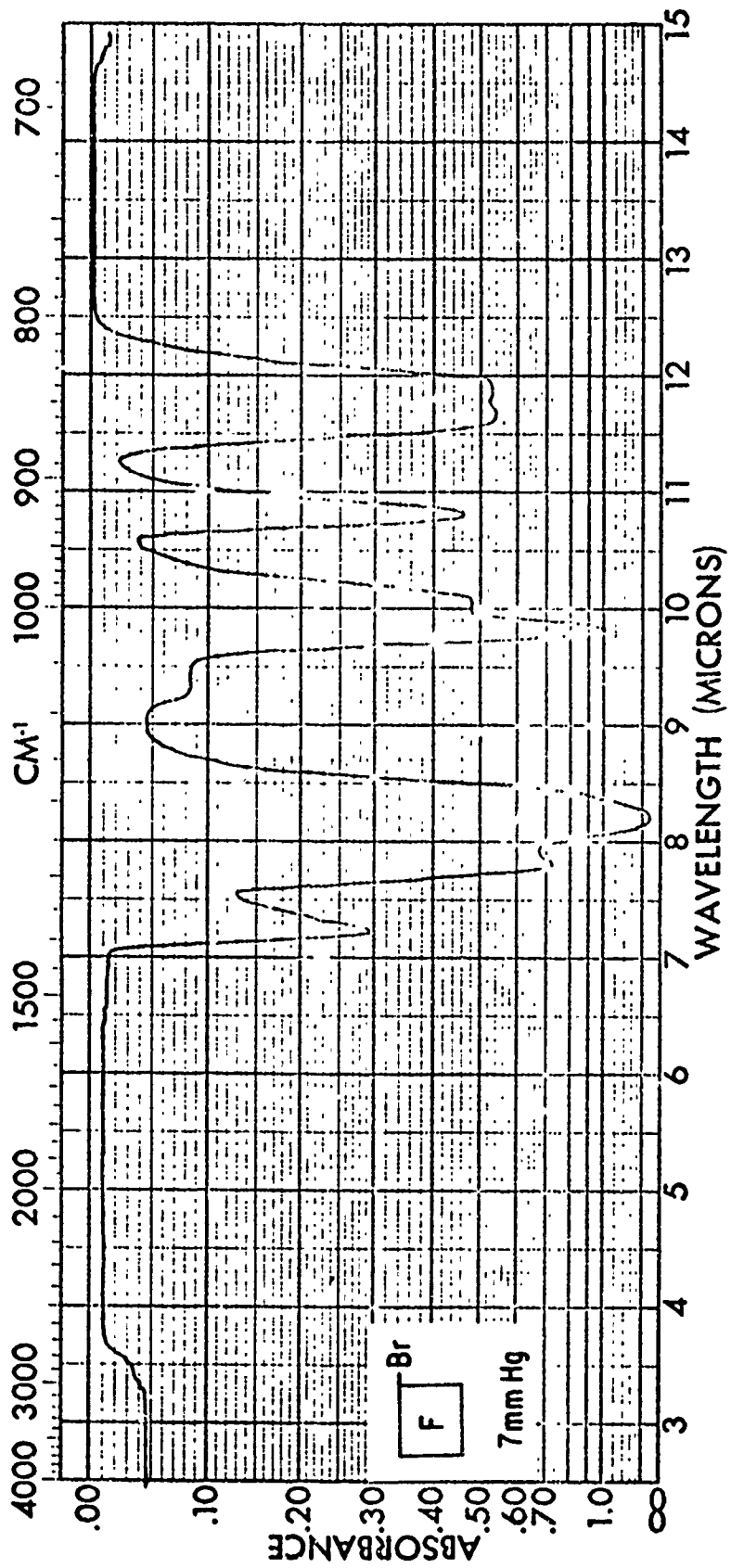


Fig. 4 - Infrared Spectrum of Perfluorocyclobutyl Bromide

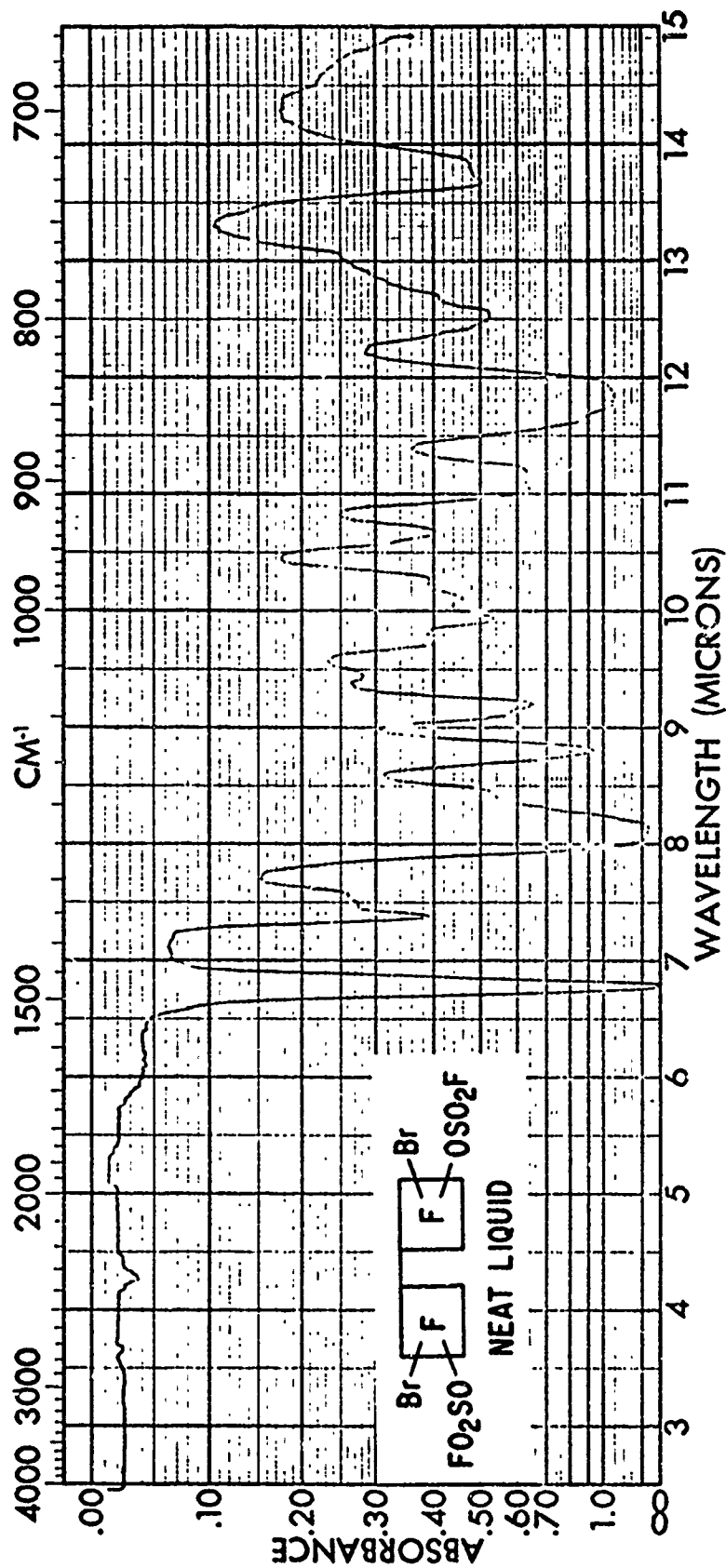


Fig. 5 - Infrared Spectrum of Perfluorodibromobis(fluorosulfonato)bicyclobutyl

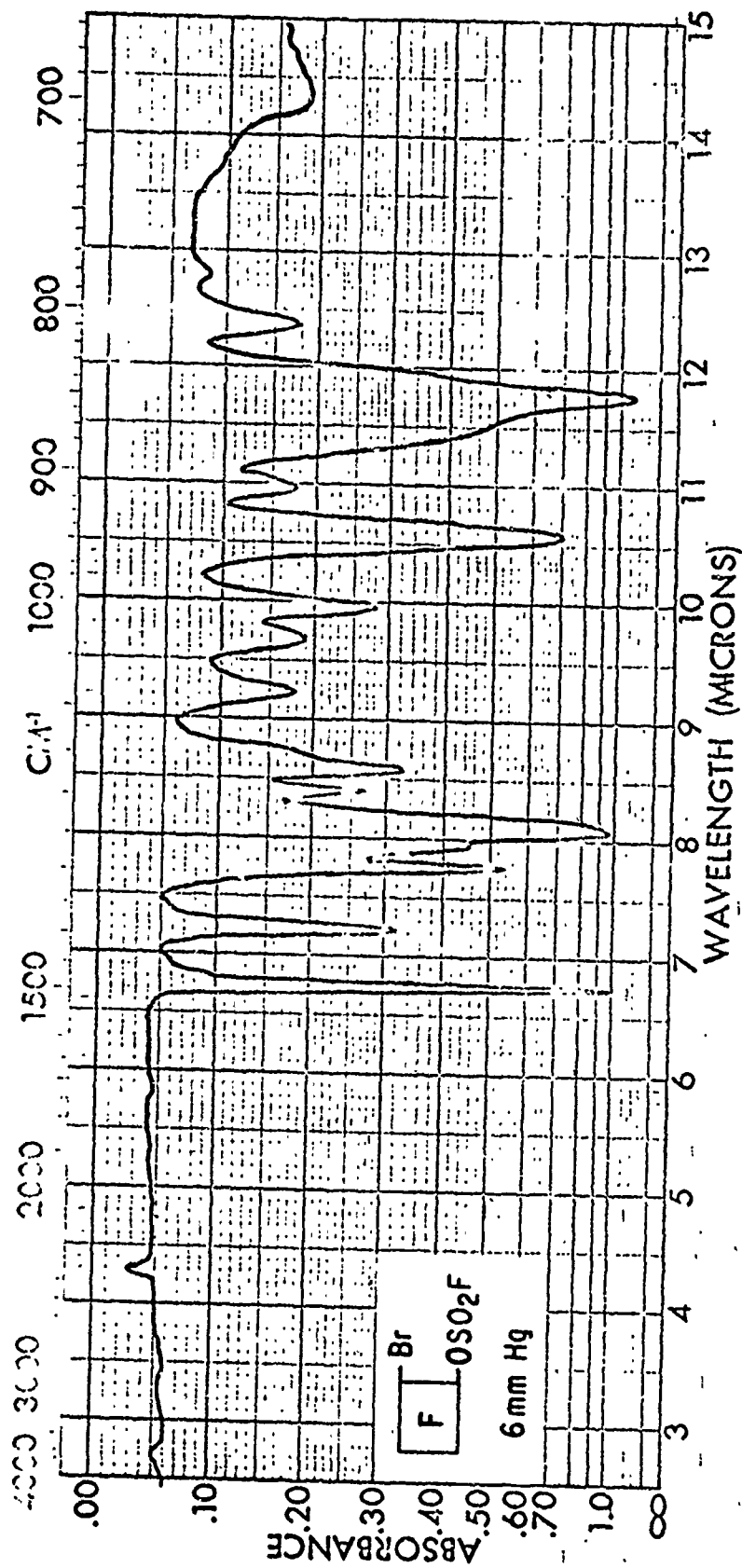


Fig. 6 - Infrared Spectrum of Perfluoro-2-(fluorosulfonato)cyclobutyl Bromide

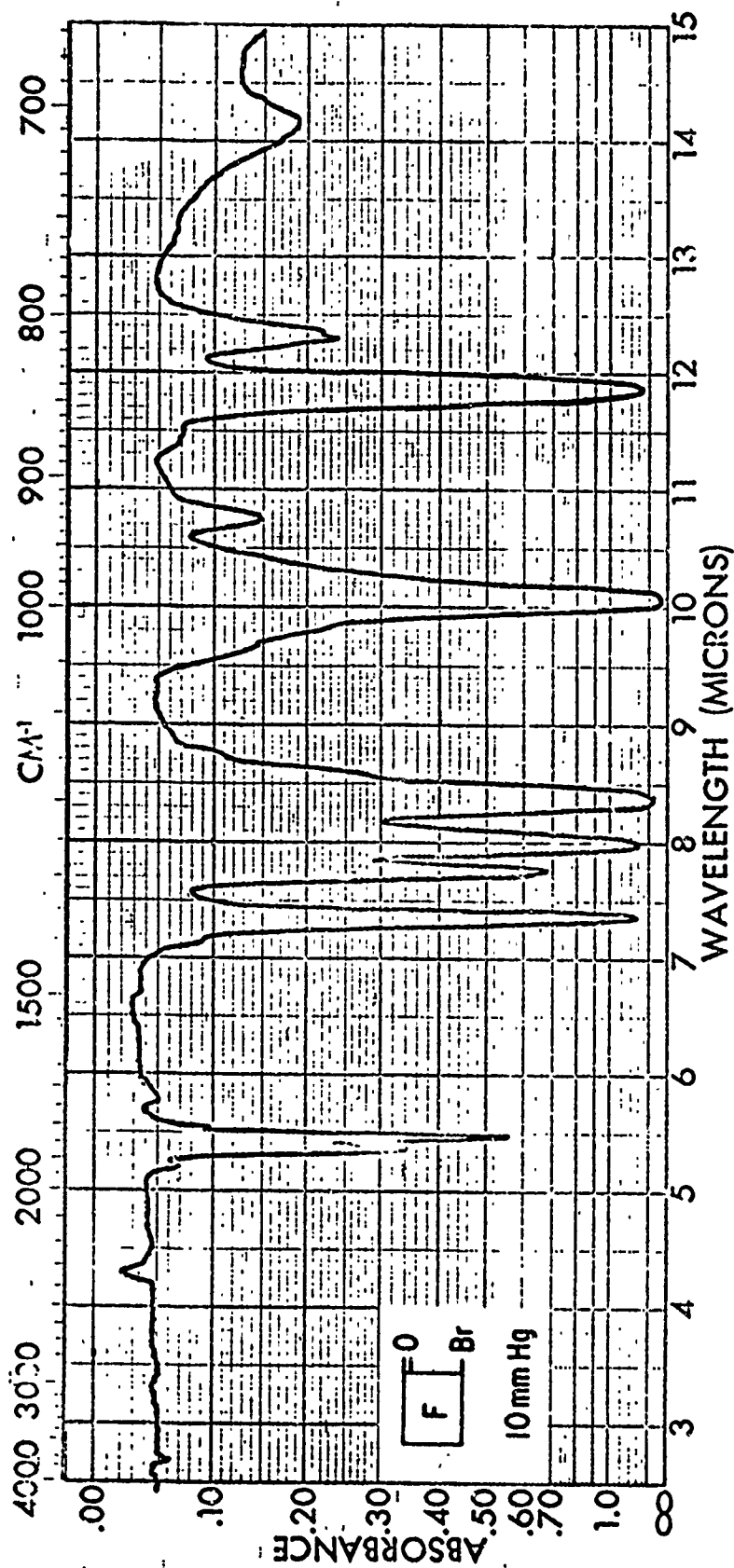


Fig. 7 - Infrared Spectrum of Perfluoro-2-bromocyclobutane

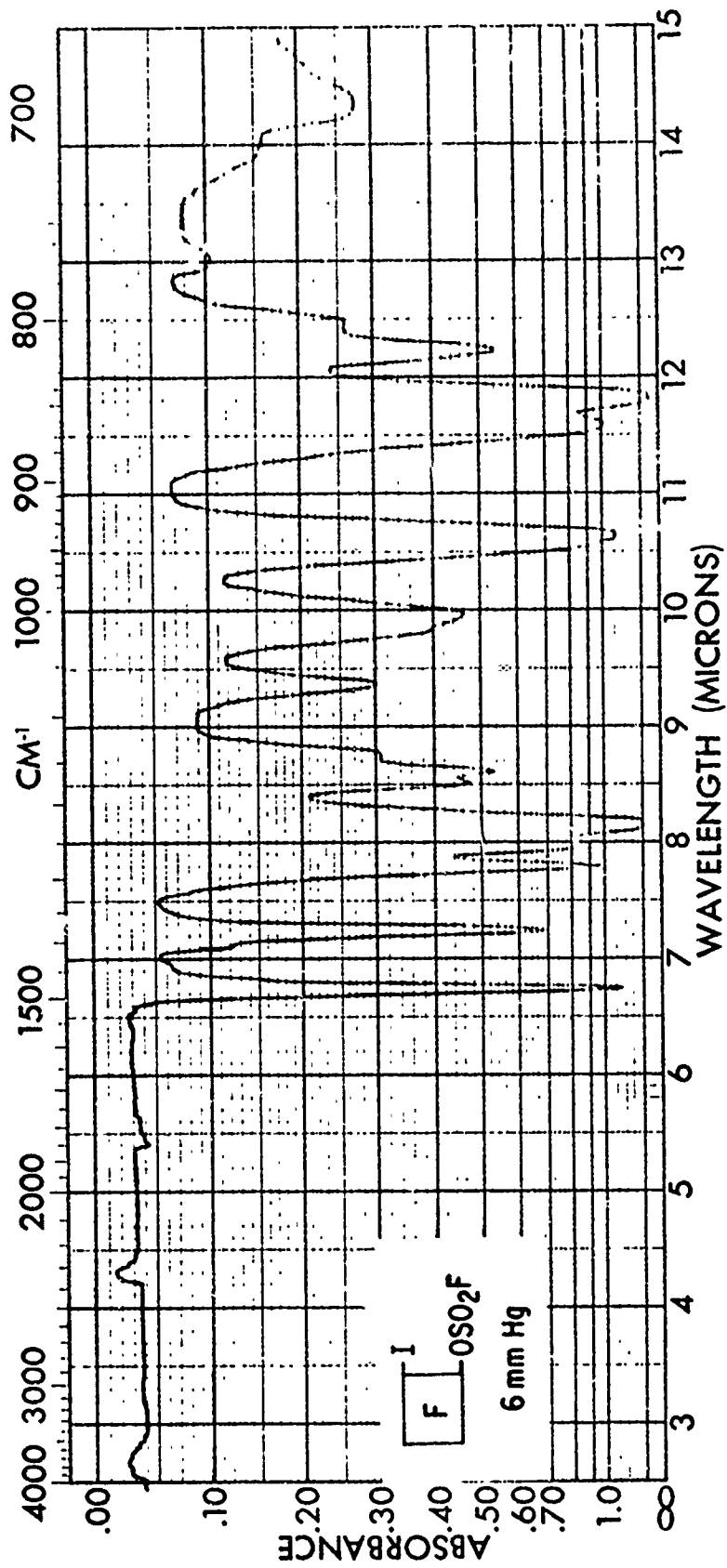


Fig. 2 - Infrared Spectrum of Perfluoro-2-(fluorosulfonato)cyclobutyl Iodine

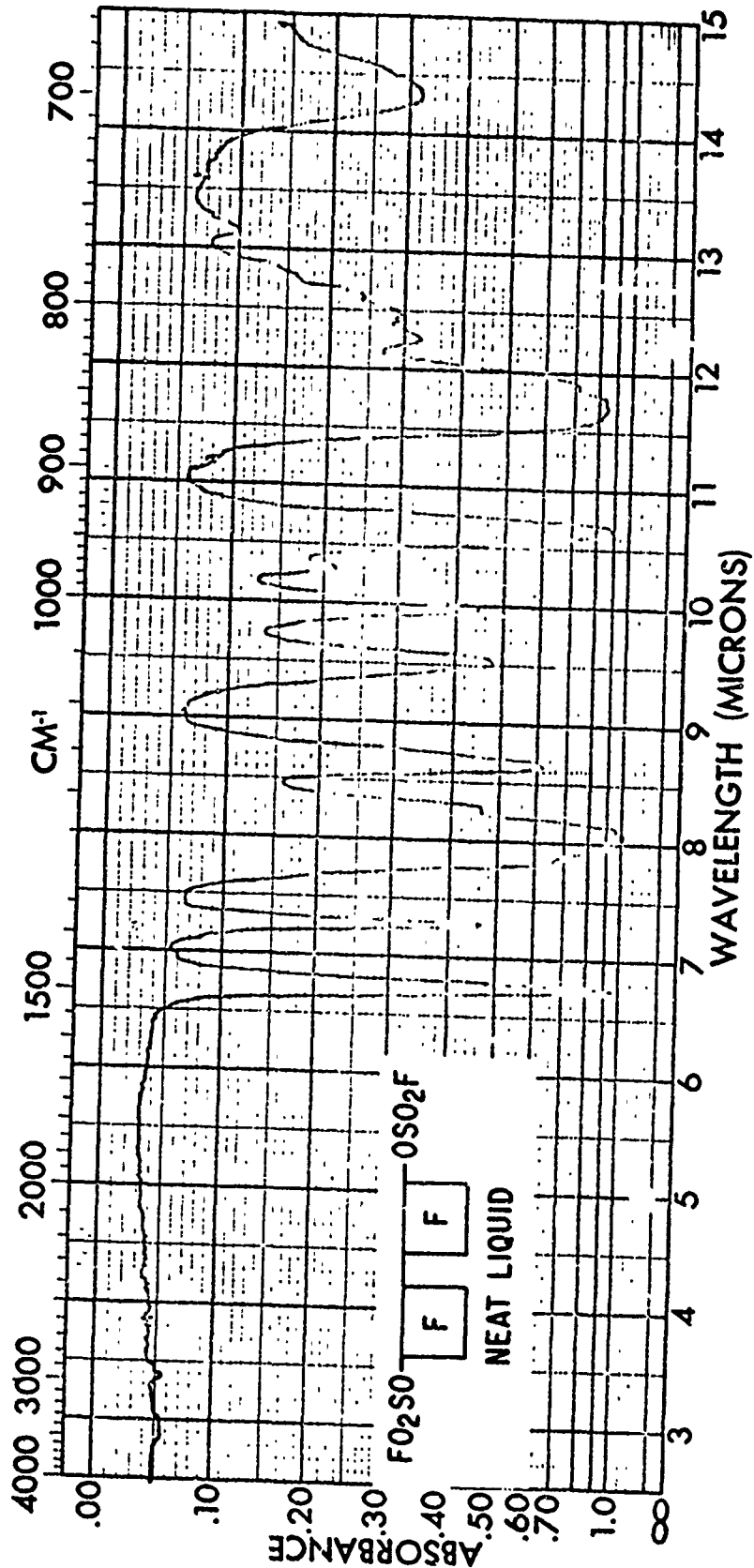


Fig. 9 - Infrared Spectrum of Perfluoro-2,2'-bis(fluorosulfonato)bicyclobutyl

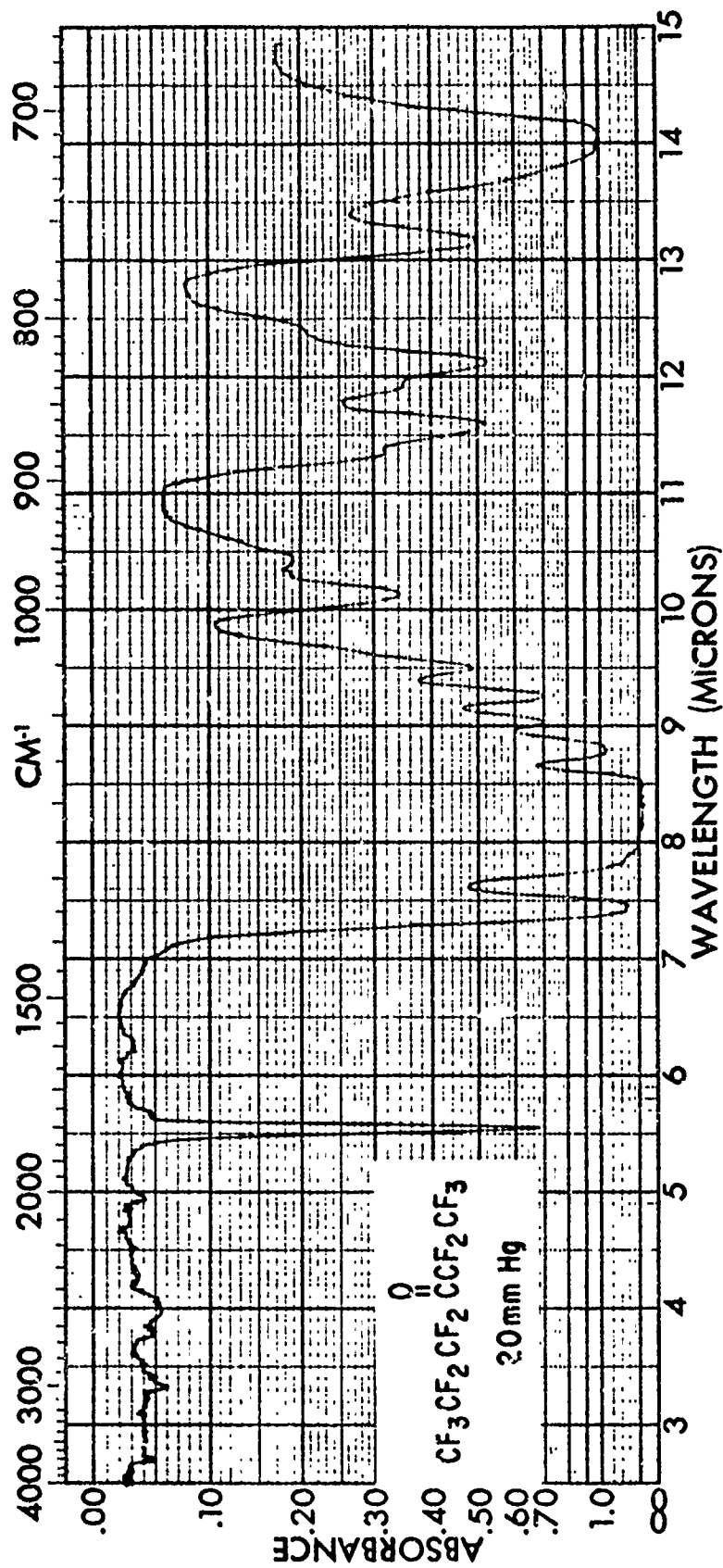


Fig. 10 - Infrared Spectrum of Perfluoro-β-hexane.