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FLUOROAROMATIC CHEMISTRY: SYNTHESIS, PROPERTIES, AND APPLICATIONS OF CERTAIN POLYFLUOROARYLORGANOMETALLIC COMPOUNDS

CHRIST TAMBORSKI

TECHNICAL REPORT AFML-TR-66-405

FEBRUARY 1967

AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FLUOROAROMATIC CHEMISTRY: SYNTHESIS, PROPERTIES, AND APPLICATIONS OF CERTAIN POLYFLUOROARYLORGANOMETALLIC COMPOUNDS

CHRIST TAMBORSKI

FOREWORD

This report was prepared by the Polymer Branch of the Nonmetallic Materials Division. This work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, with Dr. Christ Tamborski acting as project engineer.

This report covers work conducted from June 1964 to June 1966. The manuscript was released by the author in November 1966 for publication as an RTD Technical Report.

The author is indebted to Mr. Edward J. Soloski and Lt. John Ward for the synthesis of the organometallic compounds and Mr. J. Pustinger and J. E. Strobel of Monsanto Research Corporation, Dayton, Ohio, and Lt. R. J. DePasquale of the Polymer Branch for the F^{19} nmr studies.

This work was supported in part by AFML Laboratory Director's Discretionary Funds.

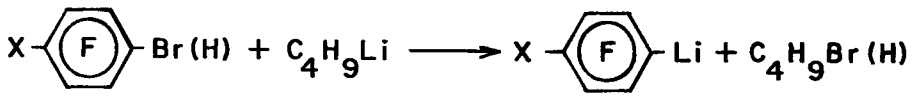
This technical report has been reviewed and is approved.

William E. Gibbs

WILLIAM E. GIBBS
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

Polyfluoroaryllithium and polyfluoroarylmagnesium compounds have been prepared and their chemical reactions studied. These chemical intermediates may be conveniently prepared by either a metal-halogen or metal-hydrogen interconversion reaction. Either Grignards (C_2H_5MgBr) or organolithiums (C_4H_9Li) can be used as the source of the metal. In general, the organolithium-bromine interconversions have been found to be the preferred synthesis route. Organolithium intermediates containing functional groups, e.g., H, F, Cl, CH_3, CF_3 SH, OH, CO_2H (=X) have been prepared by this procedure.



Perfluoroaryllithium intermediates of benzene, biphenyl, and naphthalene have been similarly prepared.

Reactions of certain organolithium intermediates with water, carbon dioxide, sulfur, chlorine, hexafluoroacetone, and metallic halides have been studied. By this procedure numerous difunctional monomeric compounds of perfluoro-benzene, -biphenyl, and -naphthalene can be prepared. Pentafluorophenyllithium or pentafluorophenylmagnesium bromide reacts with various metallic halides of group IV and V elements to yield novel perfluorophenylorganometallic compounds $(C_6F_5)_nM^n$, where M = Si, Ge, Sn, Pb, or P. Reactions with cyclopentadienyl metallic halides yield $(C_5H_5)_2M'(C_6F_5)_2$, where M' = Ti and Zr. Physical and chemical properties of these new pentafluorophenylorganometallic compounds have been studied. In general it has been found that in most instances (except in $(C_6F_5)_4Si$) the presence of a perfluorophenyl group increases the thermal stability of the compound. One other noteworthy feature of these compounds is their enhanced oxidative stability. The presence of fluorine in these compounds increases their vapor pressure considerably. This is evidenced by their ease of sublimation and passage through a vapor phase chromatographic column.

In addition, the polymerization of pentafluorophenyllithium has been studied. This reaction intermediate is stable at -65°. On warming up to room temperature, this compound polymerizes to a polyperfluorophenylene polymer which is believed to be para-oriented. This polymer has unusual and desirable properties. It is insoluble in most organic solvents and is chemically inert to most reagents. Its major thermal decomposition occurs above 700° (centigrade).

Potential applications of certain perfluoroaromatic compounds have been studied. The perfluorophenyltin and phosphorus compounds show excellent anti-oxidant and anti-corrosion activity in certain fluorine-containing high temperature candidate fluids. Tris(pentafluorophenyl)phosphine inhibits the degradation and corrosion of titanium and steel alloys by certain polyperfluoroalkyl ether high temperature operational fluids. Vapor deposition of titanium can be accomplished by the use of bis(cyclopentadienyl)bis(pentafluorophenyl)-titanium. This titanium organometallic has the oxidative and thermal stability requirements necessary in vapor phase deposition technology. High temperature greases have been made utilizing the desirable properties of the polyperfluorophenylene polymer.

TABLE OF CONTENTS

TABLE OF CONTENTS (CONT'D)

TABLE OF CONTENTS (CONT'D)

ILLUSTRATIONS

TABLES

SECTION I

INTRODUCTION

Organometallic compounds (Grignard and organolithium) have been used extensively as intermediates in the preparation of other functional compounds. Thus, to mention only a few, functional groups such as CO_2H, SH, OH, and NH_2 may be conveniently introduced into a chemical structure via such organometallic intermediates.

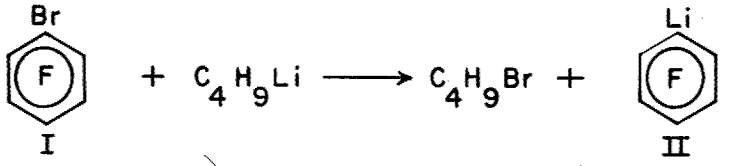
In our continuing study on polyfluoroaromatic compounds we have chosen the utility of the versatile organometallic reagent for: 1.) preparation of mono and difunctional polyfluoroaromatic compounds for model compound and polymer studies, and 2.) synthesis of other organometallic compounds (C_6F_5)-M (M is an element of Group III, IV, or V). In addition to utilizing the organometallic intermediates as a means of preparing other desirable compounds, some of these polyfluoroorganometallic compounds have unique properties of their own, i.e., self polymerization to yield novel thermally stable polymers. In our studies we have prepared and used both the polyfluoroaryl Grignard and polyfluoroaryllithium intermediates. In general, we find that the organolithium reagents are easier to prepare and are more reactive than the organomagnesium reagents. Solvent effect has a pronounced influence in the preparation and subsequent use of these intermediates. Although this solvent effect is not completely understood at this time, it should be kept in mind that the nature of the organometallic and its subsequent reaction may vary from one solvent to another.

SECTION II

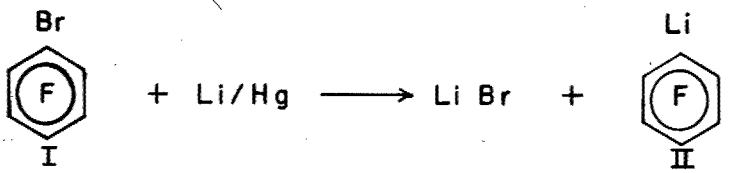
POLYFLUOROARYLLITHIUM COMPOUNDS

Since the aryllithium intermediates are easier to prepare and generally more reactive, most of our research was devoted to the lithium rather than to the magnesium derivatives.

The first synthesis of a perfluoroaryllithium compound was reported by Coe, Stephens, and Tatlow (Reference 1) by two procedures.



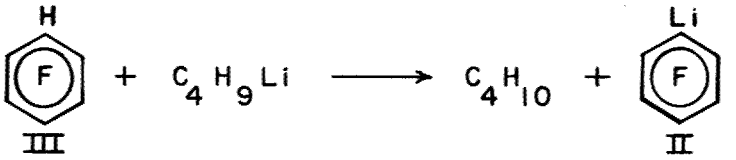
(1)



(2)

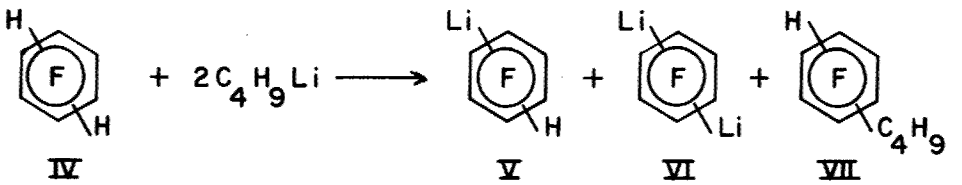
The preparation of II via Equation 1 was the preferred route since it avoided the lithium-mercury amalgam which may be detrimental in subsequent reactions. With a few exceptions, the organolithium intermediate II was reported to undergo typical reactions of an organolithium reagent to yield various monofunctional pentafluorobenzene compounds.

We have recently reported (Reference 2) on a novel synthesis procedure for the preparation of polyfluorophenyllithium and magnesium compounds. The basis of this reaction is the utility of the extremely reactive nature of the proton in hydropolyfluoroaryl compounds. The inductive effect of the multiple fluorine atoms in hydrofluoroaromatic compounds renders the hydrogen acidic. It can thus be expected to undergo acid-base reactions with bases as the organolithium or Grignard reagents.



(3)

Dihydroperfluoroaromatic compounds also undergo acid-base reactions with organolithium reagents, (e.g., butyllithium) to yield mixtures of products indicating mono and dilithium-hydrogen exchange (metalation) and in some cases also alkyl-fluorine exchange (alkylation) reactions.

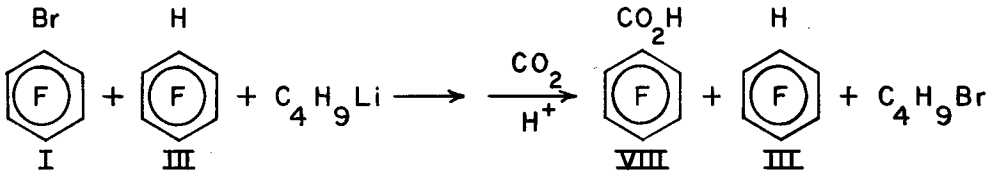


(4)

This reaction of dihydrofluoroaromatic compounds with butyllithium is the subject of our current investigation and will be reported completely at a later date.

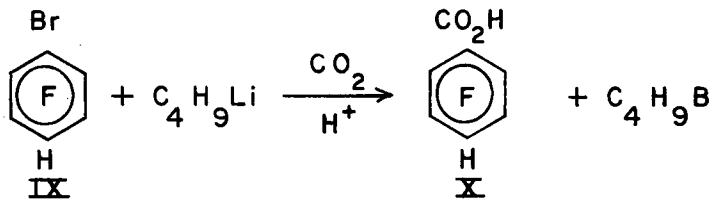
1. Synthesis of Polyfluoroaryllithium Compounds

Our studies on the extension of the lithium-hydrogen and lithium-bromine interconversion has yielded numerous polyfluoroaryllithium compounds. Since both bromine or hydrogen can be replaced by lithium via the interconversion reaction, it was of interest to determine their relative rates of interconversion. A competitive reaction of equimolar quantities of pentafluorobenzene, pentafluorobromobenzene, and butyllithium yielded on carbonation pentafluorobenzoic acid derived only from the pentafluorobromobenzene. Vapor phase chromatographic analysis of the reaction mixture indicated no unreacted pentafluorobromobenzene but did indicate unreacted pentafluorobenzene.



(5)

In a similar manner, equimolar quantities of 2,3,5,6-tetrafluorobromobenzene and butyllithium yielded only the 2,3,5,6-tetrafluorobenzoic acid.



(6)

Both of these examples indicate that the reactivity of the bromine is greater than the hydrogen toward exchange reactions with butyllithium.

We have also examined the reaction media, tetrahydrofuran vs. diethyl ether in the preparation of various fluoroaryllithium compounds. In certain cases where only one reactive site (Br or H) is present per benzene ring, the interchange reactions in tetrahydrofuran or diethyl ether are rapid. If, however, two reactive sites (Br or H) para-oriented are present on one benzene ring, the yields of the organolithium intermediate (mono or dilithio) can be varied and are dependent on solvents and functional group. In the preparation of the organolithium intermediates either mono or dilithio, difficulty has been experienced in producing a single desired specie. The preparations are usually a mixture of two organolithium intermediates with one type predominating. Only in one case, thus far, have the proper conditions been determined which yield only one organolithium specie in high yields (see 1, Table I). It is possible that further studies on variations of solvent, temperature, time, and mode of addition may lead to the preparation of predominantly mono or dilithio species as desired. Table I is a summary of yields of acids formed as a result of the interconversion studies. It can be seen that the use of diethyl ether generally favors mono-interconversion while tetrahydrofuran favors di-interconversion. The availability of these organolithium intermediates should provide a convenient method for preparing various difunctional tetrafluorobenzene compounds.

TABLE I

AVERAGE YIELD OF ACIDS [a] MONO / DI

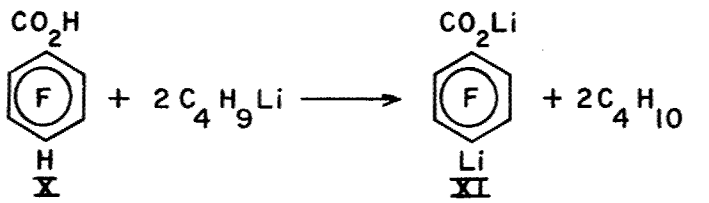
Reactants	Ether	THF
1. p-$Br_2C_6F_4$ + 2n-BuLi	0/52	0/92
2. p-$H_2C_6F_4$ + 2n-BuLi	33/38[b]	7/70[b]
3. p-$Br_2C_6F_4$ + n-BuLi	71/21	51/– [c]
4. p-$H_2C_6F_4$ + n-BuLi	85/2	36/63

(a) Yields reported are on pure products. In general the crude yields were considerably higher. The monoacids could be separated conveniently from the diacids by extraction with petroleum ether (b.p. 90°-120°) in which the diacid is insoluble.

(b) Results originally reported in Reference 2.

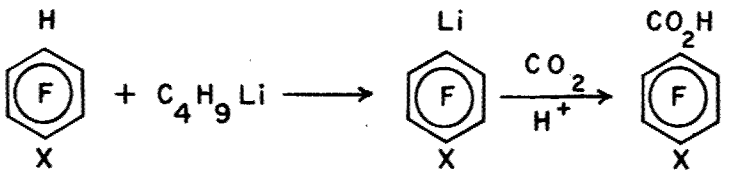
(c) Reaction was hydrolyzed to yield 2,3,5,6-tetrafluorobromobenzene. Since 2,3,5,6-tetrafluorodilithiobenzene on hydrolysis would yield 2,3,5,6-tetrafluorobenzene, no attempt was made to isolate this product resulting from diinterconversion.

The presence of functional groups other than bromine and hydrogen in substituted hydrofluoroaromatic compounds was also investigated. Thus 2,3,5,6-tetrafluorobenzoic acid when allowed to react with two equivalents of butyllithium formed the interesting and useful organometallic intermediate lithium (2,3,5,6-tetrafluoro-4-lithio)-benzoate.



(7)

Thus far it has been shown that the hydrofluoroaromatic compounds having either a fluorine, hydrogen, or carboxy group para to the hydrogen yield organolithium intermediates useful for the synthesis of functionally substituted fluorobenzene compounds.



(8)

X = F, H, CO_2H

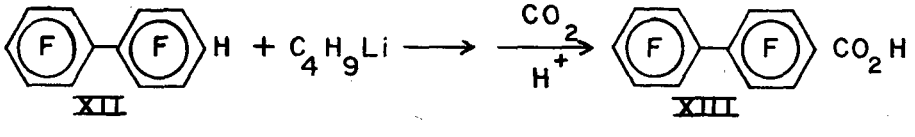
An extension of this type of reaction where X is varied to include a number of substituted hydrofluoroaromatic compounds has been studied and shown to be quite versatile. If X is a group containing an acidic hydrogen, e.g., OH, SH, or NH_2, an equivalent amount of butyllithium must be added to first form the lithium salts of the functional group in addition to the butyllithium necessary to form the aryllithium intermediate. By this general synthesis procedure a wide variety of polyfluorinated arylorganolithium intermediates containing a variety of substituents can be conveniently prepared. Table II shows the various difunctional compounds prepared by this procedure.

TABLE II

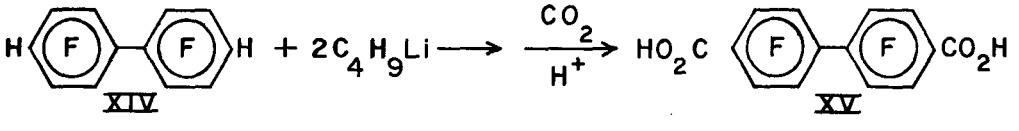
PARA-SUBSTITUTED ACIDS X  CO_2H

X	M.P.	% Yield
OH	154-156	82
NH_2	182-184	37
SH	156-158	77
CH_3	170-171	88
CF_3	110-111	77
p-HC_6F_4	318-320 d.	92
CN	---	0

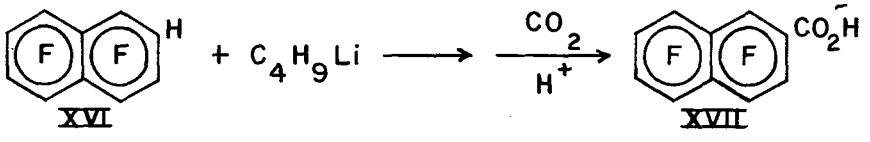
The general reaction of lithium-hydrogen exchange has been studied in other polyfluoroaromatic systems. The hydropolyfluorobiphenyl and naphthyl systems also yield the mono and dilithio intermediates.



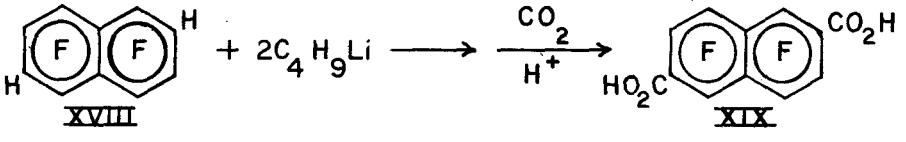
XII XIII (9)



XIV XV (10)



XVI XVII (11)



XVIII XIX (12)

In our studies the organolithium intermediates were generally characterized by carbonation to the acids. The organolithium intermediates, however, can be reacted with other reagents as will be shown subsequently. It, thus, seems likely that these various fluoroaryllithium intermediates discussed above may offer convenient synthesis procedures for a host of mono or difunctional polyfluoroaromatic compounds.

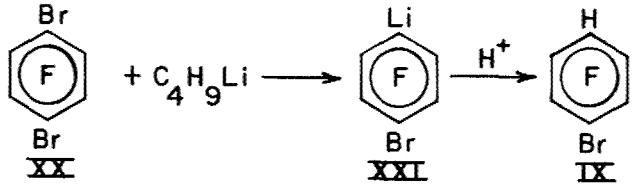
2. Reactions of Polyfluoroaryllithium Compounds

a. Reaction With Carbon Dioxide

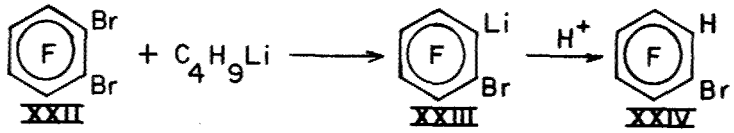
In the synthesis of the various polyfluoroaryllithium compounds, the organlithium intermediate was usually characterized by carbonation to yield the carboxy acids. These reactions have therefore been discussed in the previous section and will not be repeated here.

b. Reaction With Water

Hydrolysis of polyfluoroaryllithium intermediates yields the hydropolyfluoroaromatic compounds. In general, this reaction finds only limited utility since the hydropolyfluoroaromatic compounds are in many instances the source of the organolithium intermediate. There may, however, be certain instances where hydrolysis is useful in yielding desirable hydro compounds. For example, a bromopolyfluoroaromatic may be conveniently reduced to the hydropolyfluoroaromatic.



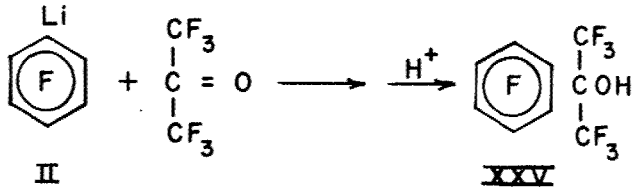
XX XXI IX (13)



XXII XXIII XXIV (14)

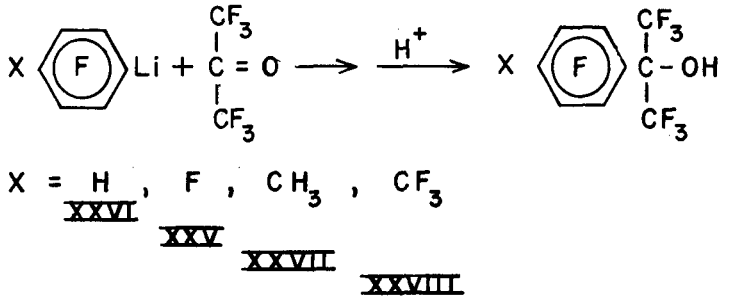
c. Reaction With Hexafluoroacetone

The reaction between pentafluorophenyllithium and hexafluoroacetone was previously reported (Reference 3) to yield the first perfluoroalkylaryl tertiary alcohol.



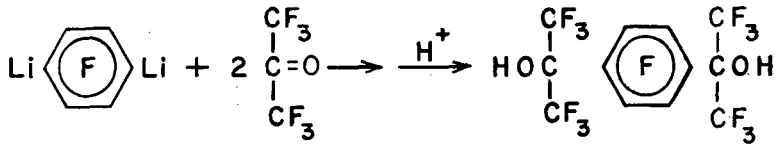
II XXV (15)

This reaction has now been extended to other polyfluoroaryllithium compounds.

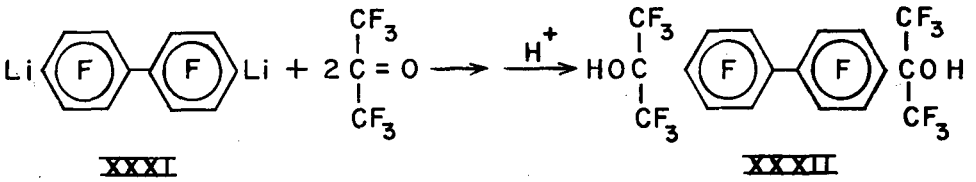


(16)

Similarly the dilithio intermediates yielded the bis-tertiary alcohols.



(17)



(18)

The yields and properties of these alcohols are shown in Table III:

(1) Properties

None of the alcohols prepared in this study exhibited any tendency to form a stable isolable complexes with tetrahydrofuran as was the case with the perfluoro secondary and tertiary alkyl alcohols (Reference 4). However, infrared studies of tetrahydrofuran solutions of the arylalkyl alcohols synthesized in this study indicated hydrogen bonding between the alcohols and the solvent. The same alcohols in a carbon tetrachloride solution, however, indicated unexpectedly two bands in the free OH stretching frequency region (3580-3620 cm^{-1}). Proton magnetic resonance spectrum of XXV Table III at room temperature, however, indicates only one peak for the OH proton. We can determine whether this anomaly is due to chemical exchange between magnetically nonequivalent protons by slowing down the exchange rate. The spectrum of neat XXV was recorded at varying temperatures, and at -36°C the spectrum shows a doublet for the OH proton. More details on the infrared and nuclear magnetic resonance studies of these compounds will be published at a later date.

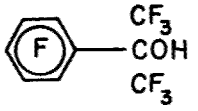
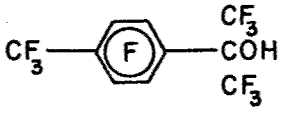
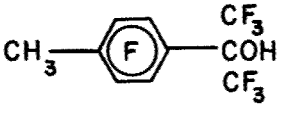
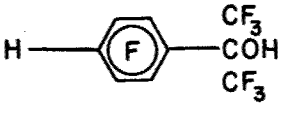
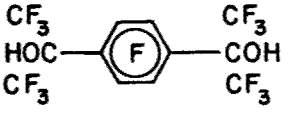
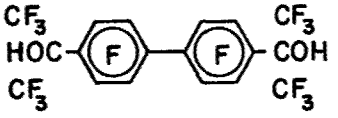
The availability of these tertiary alcohols as well as others which should be capable of synthesis by varying X in Equation 16 (for example X = OH, SH, COOH, etc.) will provide opportunity to study the chemical and physical properties of perfluorotertiary alcohols.

d. Reaction With Metallic And Metalloidal Halides

Organolithium intermediates react with metallic or metalloidal halides to yield the alkyl or aryl substituted product.

TABLE III

PERFLUOROALKYLARYL TERTIARY ALCOHOLS

		B.P.°C	M.P.°C	n_D^T	Yield %
XXV		158 - 160	---	1.3780^{26}	79
XXVIII		103 - 104	---	1.3732^{28}	61
XXVII		193 - 194	---	1.3979^{23}	91
XXVI		161 - 163	---	---	11
XXX		---	94 - 95	---	71
XXXII		---	192 - 193	---	74

$$nRLi + M^nX_n \longrightarrow nLiX + M^n(R)_n$$

R = alkyl or aryl.

The pentafluorophenylithium intermediates likewise react with various halides to yield a variety of pentafluorophenylorganometallic compounds. We have prepared the pentafluorophenyl derivateves of Si, Ge, Sn, Pb, Ti, and Zr by the following reactions:

$$4C_6F_5Li + MCl_4 \longrightarrow (C_6F_5)_4M + 4LiCl$$

M = Si, Ge, Sn

$$4C_6F_5Li + Pb(OCOCH_3)_4 \longrightarrow (C_6F_5)_4Pb + 4LiOCOCH_3$$

$$2C_6F_5Li + (C_5H_5)_2MX_2 \longrightarrow (C_6F_5)_2M(C_5H_5)_2 + 2LiX$$

M = Ti (X=Cl) M = Zr (X = Br)

With the exception of $(C_6F_5)_4Pb$ all the other members of Group IV were easily prepared in ether at -20° to -65° by conventional methods of reacting an organolithium intermediate with a metallic halide. An attempted synthesis of the $(C_6F_5)_4Pb$ compound by the reaction between C_6F_5Li and $PbCl_2$ was unsuccessful.

Table IV summarizes the yields and melting points of the various reaction products.

TABLE IV

PERFLUOROARYL ORGANOMETALLIC COMPOUNDS

		% Yield	M.P.°C
XXXIII	$(C_6F_5)_4Si$	75	245-246
XXXIV	$(C_6F_5)_4Ge$	88	246-247
XXXV	$(C_6F_5)_4Sn$	91	220-221
XXXVI	$(C_6F_5)_4Pb$	16	204-206
XXXVIII	$(C_6F_5)_2Zr(C_5H_5)_2$	27	257
XXXIX	$(C_6F_5)_3P$	57	119-120
XXXVII	$(C_6F_5)_2\ Ti(C_5H_5)_2$	52	228-229

(1) Properties

Many of the prepared pentafluorophenyl derivatives were subjected to the following studies: infrared and vapor phase chromatography analysis, acid and base hydrolysis, thermal stability, and reactions with bromine and lithium.

Infrared Analysis. — The infrared spectra of the pentafluorophenyl derivatives have been recorded on a Perkin-Elmer Model 102 spectrophotometer. The spectra were determined on the sample in KBr pellets and are reported in Table V.

In the hydrogenic series of tetraphenyl group IV elements $(C_6H_5)_4M$, a useful characteristic absorption band for the phenyl-M bond has been reported (Reference 5) as C_6H_5-Si, 9.05μ; C_6H_5-Ge, 9.18μ; C_6H_5-Sn, 9.34μ; and C_6H_5-Pb, 9.45μ. This band has been suggested as due to a phenyl group vibration perturbed by the central atom (M). In the corresponding fluorine series no characteristic bands of a C_6F_5-M bond are apparent. Since the pentafluorophenyl group should have different infrared characteristics from the phenyl group, it is possible that a C_6F_5-M characteristic absorption band lies in the far infrared region of the spectrum. Studies along this line in progress.

Vapor Phase Chromatography. — The presence of a number of pentafluorophenyl groups on a metal or metalloidal atom enhances the volatility of the compound. Many of the $(C_6F_5)_4M$ compounds could be easily sublimed as compared to the hydrogen analogs. In addition, the

TABLE V

INFRARED SPECTRA OF PENTAFLUOROPHENYL COMPOUNDS

	C-F Stretch	Benzene Ring	C_5H_5 Ring	C-H Deformation	C-H Stretch	Others
$(C_6F_5)_4Si$	1379(s) 1292(s) 1140(wsh) 1098(s) 1023(w) 970(s)	1641(m) 1516(s) 1466(s)	---	---	---	
$(C_6F_5)_4Ge$	1411(s) 1313(s) 1140(m) 1106(msh) 1087(s) 1015(w) 970(s)	1671(m) 1539(s) 1479(s)	---	---	---	818(m)
$(C_6F_5)_4Sn$	1378(s) 1281(m) 1137(m) 1087(s) 1077(ssh) 1015(m) 964(s)	1640(m) 1509(s) 1479(s)	---	---	---	803(m)
$(C_6F_5)_4Pb$	1375(s) 1275(m) 1134(w) 1078(s) 1075(msh) 1005(m) 963(s)	1632(m) 1509(s) 1469(s)	---	---	---	782(m)
$(C_5H_5)_2Ti(C_6F_5)_2$	1373(m) 1262(msh) 1252(m) 1055(s) 950(s)	1635(m) 1505(s)	1427(s)	1020(m) 847(sh) 835(s) 827(ssh)	3150(w) 3137(w) 3130(w) 3119(w)	745(m) 1337(m)
$(C_5H_5)_2Zr(C_6F_5)_2$	1363(w) 1260(wsh) 1246(m) 1041(s) 942(s)	1629(m) 1500(s)	1431(s) 1420(s)	1015(m) 827(msh) 804(s) 785(m)	3125(w) 3100(w)	725(s) 1325(w)
$(C_5H_5)_2TiCl_2$	---	---	1435(s)	1011(m) 864(m) 813(s)	3100(m)	---

s = strong
m = medium
w = weak
sh= shoulder

$(C_6F_5)_4Si$, $(C_6F_5)_4Ge$, and $(C_6F_5)_4Sn$ could be analyzed by vapor phase chromatography techniques whereas the hydrogen analogs, under comparable conditions, could not. The $(C_6F_5)_4Pb$ compound under these analytical conditions could not be detected. Since the lead compound has a low order of thermal stability, it is possible that under different analytical conditions, the $(C_6F_5)_4Pb$ could be analyzed by vapor phase chromatography techniques. The retention time for the compounds determined are $(C_6F_5)_4Si$, 2.3 min.; $(C_6F_5)_4Ge$, 3.0 min.; and $(C_6F_5)_4Sn$, 4.1 minutes. Column conditions used isothermal, 275°, 6 ft (1/4 in. O.D.), Apiezon L column on chromasorb P (60-80 mesh), helium flow rate 100 ml/min., F & M 500 instrument (Figure 1).

Hydrolysis. — Hydrolysis of fluoroalkyl-silanes, germanes, and tin compounds have been previously studied. In general, the fluoroalkyl groups attached to these metals can be cleaved under basic hydrolysis conditions. In some cases, hot water alone is sufficient to cleave a perfluoroalkyl group from tin.

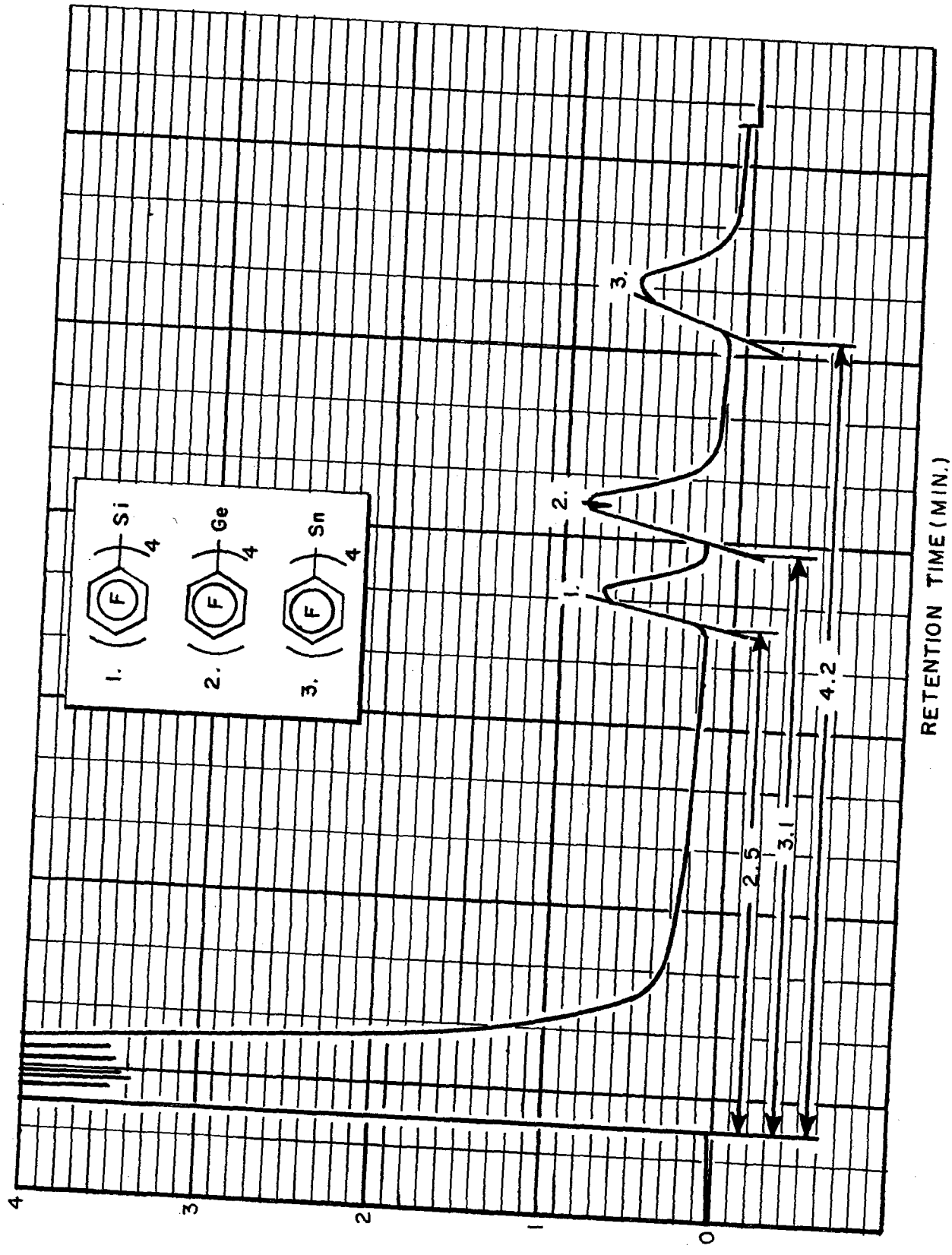


Figure 1. Vapor Phase Chromatography of $(C_6F_5)_4M$ Compounds

Results of our hydrolysis studies on tetra(pentafluorophenyl)-silane, -germane, -tin, and -lead compounds are shown in Table VI. Apparently the pentafluorophenylorganometallic derivatives are more stable to hydrolysis than the perfluoroalkyl compounds. In a heterogeneous acid hydrolysis (6N HCl) medium, the silane, germane, tin, and lead compounds are unaffected at reflux temperature. The silane and germane are also stable to a basic hydrolysis (6N NaOH) in a heterogeneous system at reflux temperature but the tin and lead compounds are hydrolyzed. In a homogeneous hydrolysis (tetrahydrofuran solution) medium under acid and base conditions, the only compound resistant to hydrolysis was the germane whereas the silane, tin, and lead were unstable. There seems to be no apparent reason at this time for the germane to show this anomaly.

The silane can be hydrolyzed at room temperature by wet acetone alone whereas under the same conditions the germane, tin, and lead are unaffected. The hydrolysis studies were carried out by analyzing for one of the expected cleavage products pentafluorobenzene by vapor phase chromatography. No attempt was made to identify any other products of hydrolysis.

TABLE VI

HYDROLYSIS OF PENTAFLUOROPHENYL COMPOUNDS

	Si	Ge	Sn	Pb	Ti*
HCl (6N), reflux 5 hrs	N.R.	N.R.	N.R.	N.R.	
HCl (6N) + THF, reflux 5 hrs	C	N.R.	C	C	
NaOH(10%), reflux 5 hrs	N.R.	N.R.	C	C	
NaOH(10%) + THF, reflux 5 hrs	C	C	C	---	
H_2O-Acetone; R.T., initial	N.R.	N.R.	N.R.	N.R.	
H_2O-Acetone; R.T., 2 days	C	N.R.	N.R.	N.R.	
H_2O-Acetone; R.T., 5 days	C	N.R.	N.R.	N.R.	
H_2O-Acetone; R.T., 26 days	C	N.R.	N.R.	N.R.	
Recovered starting material	0	100%	100%	80%	
NaOH(20%), 100°, 8 days					N.R.
HCl (gas), 150°					C
HCl (aq.) + THF, reflux					C

*data obtained from Reference 6.

N.R. = no reaction, absence of C_6F_5H.
C = cleavage, as indicated by presence of C_6F_5H.
R.T. = room temperature.

Bis(cyclopentadienyl)bis(pentafluorophenyl)titanium has recently been prepared and some of its reactions studied (Reference 6). This compound was stable to basic hydrolysis in a heterogeneous mixture at 100°. Acid hydrolysis in a tetrahydrofuran solution, however, resulted in cleavage of the pentafluorophenyl group.

Thermal Stability. — An indication of thermal stability for the pentafluorophenylorganometallic compounds prepared has been obtained by measuring their decomposition temperatures (Reference 7). Table VII indicates the comparison of the fluorocarbon versus the hydrocarbon derivatives. In earlier studies Wall et al. (Reference 8) qualitatively determined the greater stability of $(C_6H_5)_4Si$ over the $(C_6F_5)_4Si$. As can be seen from the decomposition temperature values, the silicon member of the fluorocarbon series is less thermally stable; however, the other members of the series have equal or increased stability over their hydrocarbon analogs. Recently, Stone et al. (Reference 6) have pyrolyzed bis(cyclopentadienyl)-bis(pentafluorophenyl)titanium in vacuo at 150°. One of the decomposition products identified was bis(cyclopentadienyl)-pentafluorophenyltitanium fluoride. This compound was formed by fluorine migration from a pentafluorophenyl group to the titanium metal, a mode of decomposition characteristic of other fluorocarbon-metal compounds (Reference 9). It is quite conceivable that by an analogous procedure the perfluorophenyl derivatives of the group IV elements decompose in the same fashion.

TABLE VII

RELATIVE THERMAL STABILITIES OF GROUP IV COMPOUNDS

	Decomposition Temperature °C*	
	AR = C_6H_5	AR = C_6F_5
AR_4Si	468	382
AR_4Ge	421	416
AR_4Sn	352	399
AR_4Pb	232	> 260
$AR_2Ti(C_5H_5)_2$	105**	> 260
$AR_2Zr(C_5H_5)_2$	---	256 m.p. (dec.)

* Decomposition temperature defined as the temperature at which the compound decomposes at the rate of 1 mole percent per hour. See Reference 7.

** Reference 6

Reactions of $(C_6F_5)_4M$. — Attempts were made at cleaving a C_6F_5 group from a metal atom with either metallic lithium or bromine. The hydrogenic analogs under similar experimental conditions yield functional compounds according to the following equations:

$$(C_6H_5)_4M + Li \longrightarrow C_6H_5Li + (C_6H_5)_3MLi \quad (19)$$

$M = Si, Ge, Sn\ Pb$

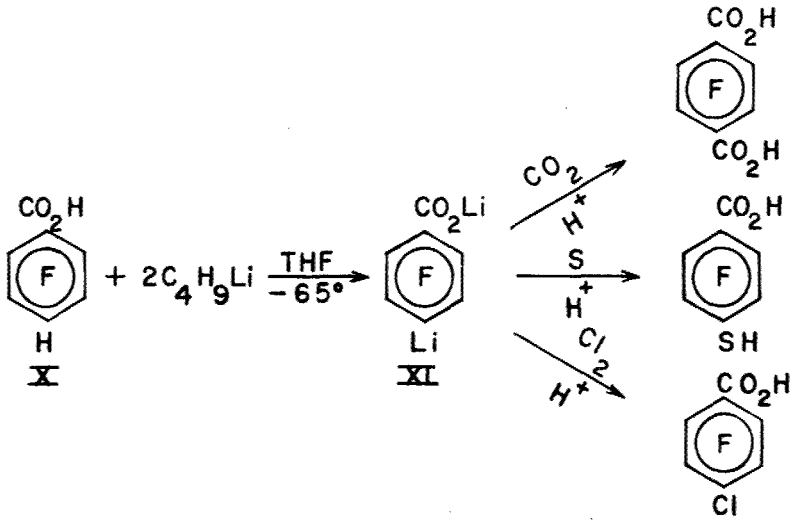
$$(C_6H_5)_4M + Br_2 \longrightarrow C_6H_5Br + (C_6H_5)_3MBr \quad (20)$$

In this manner useful organometallic intermediates can be prepared for the synthesis of other compounds. Unfortunately, the perfluoroaryl analogs (Si, Ge, Sn) do not react with lithium or bromine. This observation may not be too surprising in view of some of the findings of Eaborn (Reference 10) in his studies on rates of cleavage of various substituted aryl silicon compounds. Electron withdrawing groups (e.g., para F and NO_2) retarded cleavage of the phenyl group by electrophilic reagents. The fluorine atoms in the $(C_6F_5)_4M$ compounds would act in a similar manner placing a positive charge on the metal and thus inhibiting an electrophilic attack on the metal atom.

e. Miscellaneous Reactions

The polyfluoroarylorganolithium intermediates may undergo reactions with numerous reagents to give a variety of substituted difunctional compounds. Although the breadth of these reactions have not been investigaged as yet, a few examples carried out will be cited.

Lithium(2,3,5,6-tetrafluoro-4-lithio)-benzoate will react with carbon dioxide, elemental sulfur, and chlorine to yield disubstituted tetrafluorobenzene compounds.



(21)

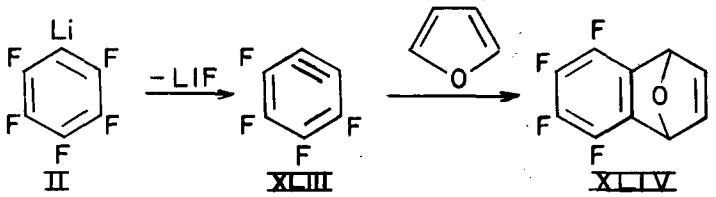
(22)

(23)

Equations 21, 22, and 23 indicate that the fluoroaryllithium intermediates behave as typical aryllithium compounds. There are, however, a few examples where they do not behave similarly. Attempts to react this intermediate with oxygen at temperatures of from -65° to 0° in tetrahydrofuran to yield the 4-hydroxy-2,3,5,6-tetrafluorobenzoic acid were unsuccessful. Only the starting material was recovered.

3. Polymerization of Pentafluorophenyllithium

Pentafluorophenyllithium is a very useful intermediate for synthesis of pentafluorophenyl-containing compounds. Unlike its hydrocarbon analog, it must be used at low temperatures (-65°) due to its instability. In their original preparation of pentafluorophenyllithium, Coe, Stephens, and Tatlow (Reference 1) reported on the stability of this versatile organometallic compound. At 15° (18 hours) in the presence of furan, the organolithium compound decomposed and reacted with the solvent to yield products which indicated the possibility of benzyne formation.

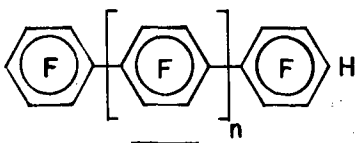


II XLIII XLIV (24)

The formation of the epoxide indicates a potential decomposition path for the pentafluorophenyllithium compound. These investigators also mentioned the formation of highly intractable organic material in the preparation of the organolithium compound at temperatures above -20°. No definite products were isolated from the decomposition of an ether solution of the organolithium intermediate.

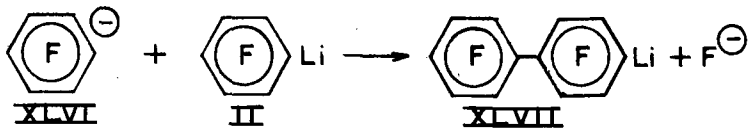
In our work on the preparation and reactions of pentafluorophenyllithium, we too have studied the stability of the organometallic compound. In general, the organolithium compound was found to be much more reactive than the pentafluorophenylmagnesium bromide. The reactions of pentafluorophenyllithium were fast both in ether and tetrahydrofuran solvents. On warming up from -65° to room temperature the organolithium compound decomposes quantitatively to a high melting intractable material. Characterization of this compound was hampered by its lack of solubility in various solvents. We have, however, speculated on its composition and suggest primarily a para-oriented perfluoropolyphenylene structure based on the following:

(a) The analogous perfluoro Grignard reagent, C_6F_5MgBr, in its reactions with metallic halides, yields a series of oligomeric byproducts which are para-oriented (Section III, 1.a.).



XLV

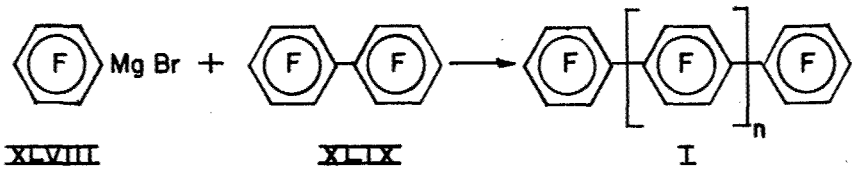
(b) The pentafluorophenyl anion is a good nucleophile and should be able to react in the following fashion.



XLVI II XLVII (25)

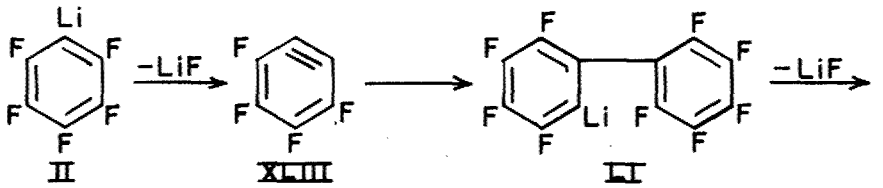
Repetition of this process would yield a para-oriented product.

(c) Studies (Reference 11) on the decomposition of C_6F_5MgBr in the presence of decafluorobiphenyl produce para-oriented products.

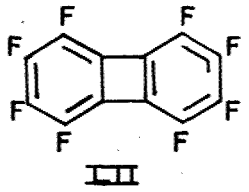


XLVIII XLIX I (26)

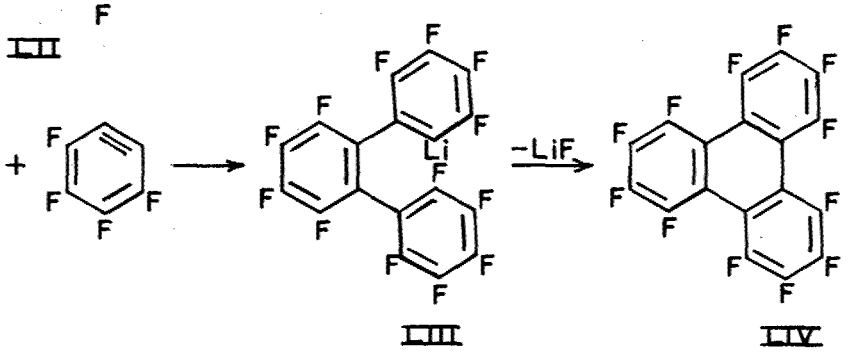
(d) Benzyne formation, which could yield an ortho-oriented polymer, does not play a major role in decomposition. If this were the case then low molecular weight products, e.g., biphenylene (LII) or triphenylene (LIV) would be found.



II XLIII LI (27)



LII



LIII LIV (28)

Since neither LII nor LIV were identified in the decomposition products, it is not likely that ortho-oriented polymeric materials are present to a large extent. The ortho configuration would also provide considerable steric strain to such a polymer structure.

Further studies by various analytical methods, e.g., nuclear magnetic resonance and perhaps X-ray analysis would be required to fully characterize the polymer.

Thermal stability studies via thermogravimetric analysis on perfluoropolyphenylene polymer indicate a high order of stability (Figure 2). Continuing studies on improving the solubility of a polyperfluorophenylene polymer are in progress.

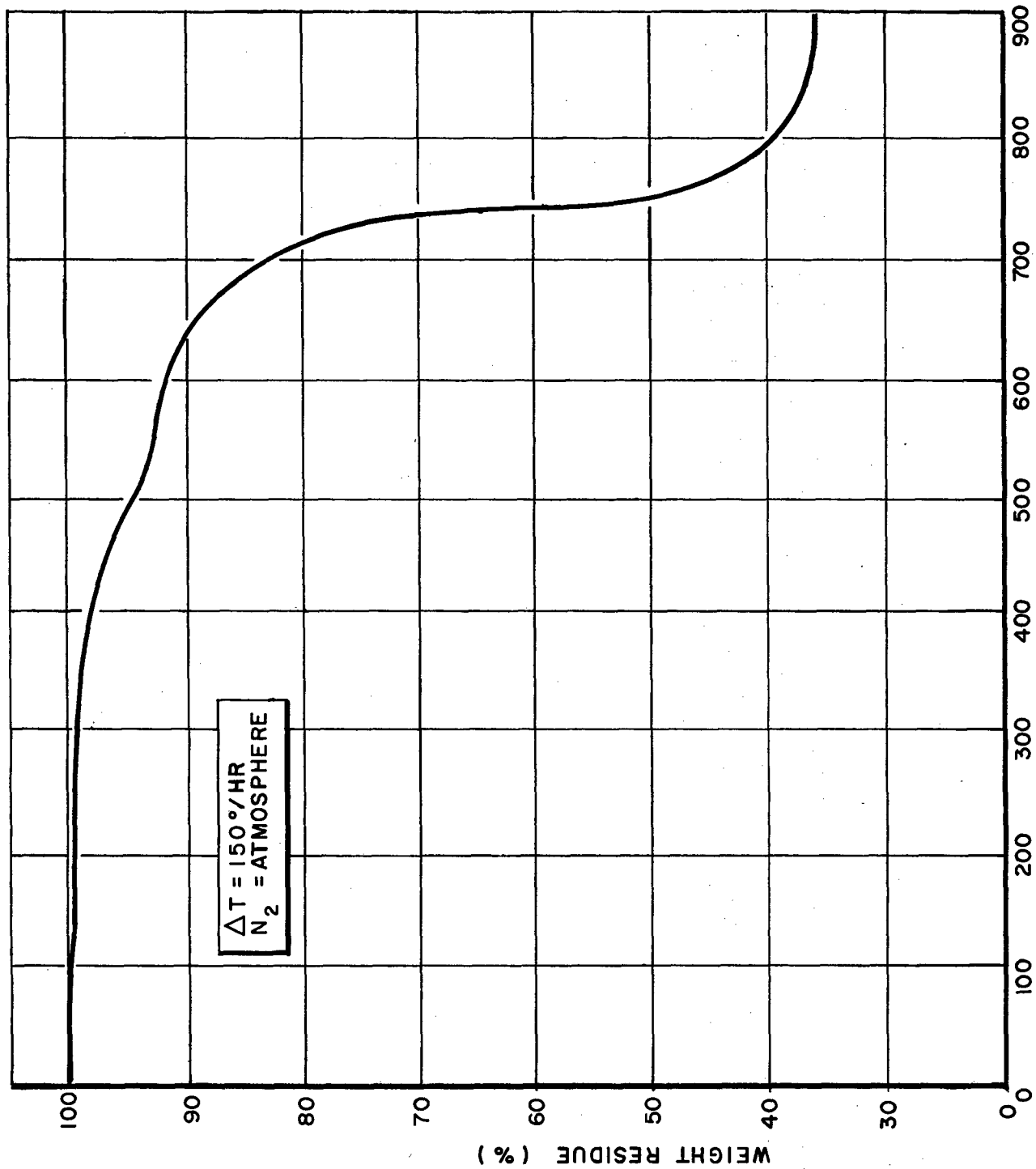


Figure 2. Thermogravimetric Analysis of Perfluoropolyphenylene Polymer

SECTION III

POLYFLUOROARYLMAGNESIUM COMPOUNDS

In 1959 the synthesis of the perfluorophenylmagnesium compound was reported by Wall, Donadio, and Pummer (Reference 8). This perfluorinated phenyl Grignard was prepared by the conventional procedure:

$$C_6F_5Br + Mg \longrightarrow C_6F_5MgBr \qquad (29)$$

Discovery of this Grignard, which preceded the pentafluorophenyllithium intermediate, made possible the synthesis of a variety of pentafluorophenyl-substituted compounds. In most instances the Grignard reacted in the typical fashion of a hydrocarbon Grignard. Of particular interest was the reaction with various halides to yield new

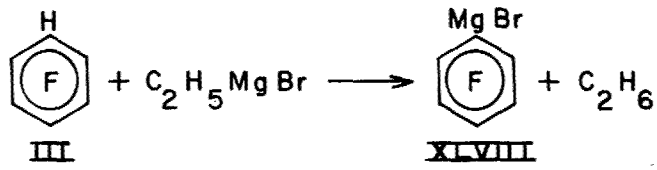
$$4C_6F_5MgBr + SiCl_4 \longrightarrow (C_6F_5)_4Si + 4MgClBr \qquad (30)$$

$$3C_6F_5MgBr + PCl_3 \longrightarrow (C_6F_5)_3P + 3MgClBr \qquad (31)$$

pentafluorophenyl-substituted organometallic compounds. Since its discovery the pentafluorophenylmagnesium bromide has been used extensively for synthesis of various pentafluorophenyl-containing compounds.

1. Synthesis of Polyfluorophenylmagnesium Compounds

In addition to the conventional synthesis of the Grignard (Equation 29) we have recently reported on an improved synthesis for the Grignard in a manner similar to the procedure we use for the preparation of the organolithium intermediates.



III XLVIII (32)

The reaction can be extended to dihydropolyfluoroaromatic compounds to yield mono and dilithiated organometallics. In addition, alkylated products were also identified. The reaction of the Grignard with various dihydropolyfluoroaromatic compounds is not completely understood at this time and requires further investigation. Some preliminary observations indicate that the degree of metalation is a function of solvent (hexane, ether, tetrahydrofuran) as well as the relative position of the two hydrogen atoms on the aromatic ring. This phase of metalation is currently under investigation and will be reported at a later date.

a. Reactions With Carbon Dioxide, Metallic, and Metalloidal Halides

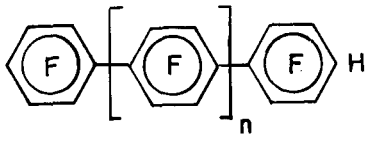
The pentafluorophenylmagnesium bromide undergoes similar reactions to the pentafluorophenyllithium reagent. In most cases it appears that the difference which exists between the two organometallics may be in the degree to which they react with other compounds. As for example, the Grignard, when carbonated, generally produces a lower yield of acid than the organolithium reagent. Likewise, the reactions of the Grignard with various metallic halides produces the pentafluoroorganometallic derivatives in lower yield than the organolithium reagent (Table VIII).

TABLE VIII

YIELDS OF $(C_6F_5)_4M$ COMPOUNDS

	% Product From	
	C_6F_5Li	C_6F_5MgBr
$(C_6F_5)_4Si$	75	69
$(C_6F_5)_4Ge$	88	72
$(C_6F_5)_4Sn$	91	14
$(C_6F_5)_4Pb$	15	1-3

The lower yields of products from the Grignard reagent may possibly be due to an alternate reaction that the Grignard can undergo. For example, in the reaction between the Grignard and silicon tetrachloride, germanium tetrachloride, and tin tetrachloride, side products were obtained in all instances. Only the side products from the silicon tetrachloride were examined in detail in our present studies, although the others were of similar nature, as indicated by vapor phase chromatographic analysis. After the desired tetra(pentafluorophenyl)silane was separated by filtration (see experimental) the solvent soluble material was analyzed by vapor phase chromatography and shown to be a mixture of many components. Although it was a complex mixture there were three major components which accounted for approximately ninety percent of the material. The percent area concentration of the three components decreased as the molecular weight of the component increased. These major components could be separated on an alumina column using petroleum ether (60°-90°) as the eluent. Characterization of these major components indicated a series of oligomers of the following structure:

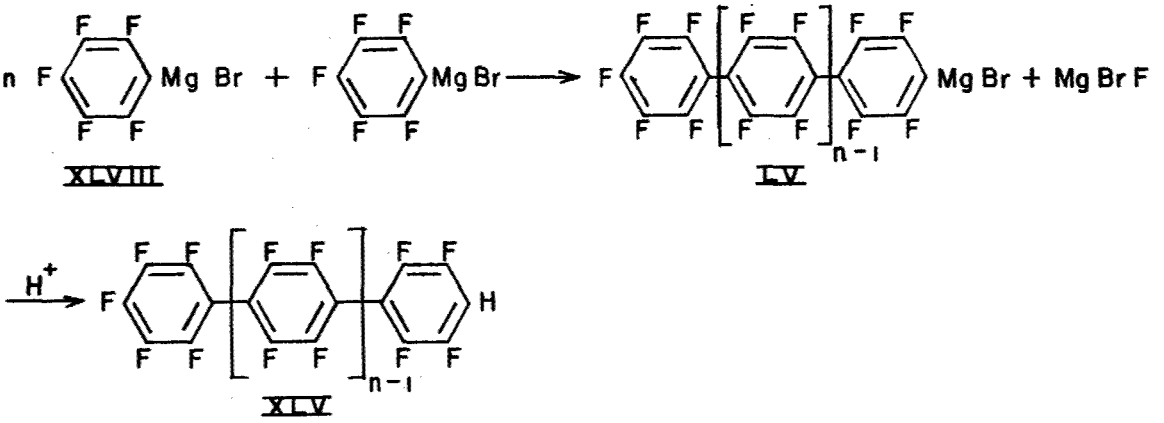


n = 0, 1, 2

When the reaction was repeated under similar conditions, except in the absence of the silicon tetrachloride, there were no indications of any side products. Pentafluorophenylmagnesium bromide in tetrahydrofuran is quite stable at 0°. Only after 55 hours was there any sign of initial decomposition (as determined by vapor phase chromatography) of the Grignard.

It appears, therefore, that the greater quantity of side products obtained from the Grignard and metallic halide reaction may be due to an increased rate of Grignard decomposition in the reaction mixture.

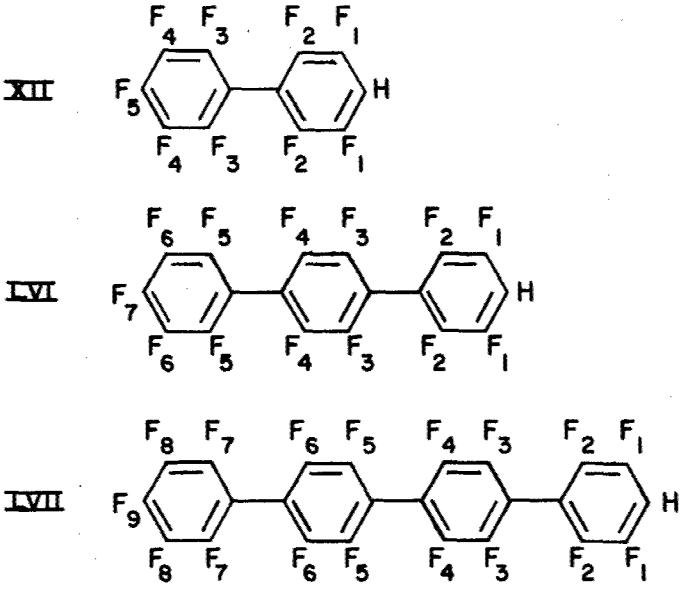
It is quite possible that the Grignard decomposes by several mechanisms. For example (Reference 12), the Grignard may form a tetrafluorobenzyne $\left[C_6F_4^{=}\right]$ intermediate which can then react with a number of different species in the reaction media. It is more likely, in our case, however, that the Grignard reacts with the para fluorine of another Grignard molecule. This repeating process would then account for the oligomeric products isolated.



XLVIII LV XLV (33)

The physical properties and characterization of the products are shown in Table IX. For comparison reasons, there are also included a few related structures.

F^{19} and H^1 Nuclear Magnetic Resonance:



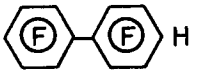
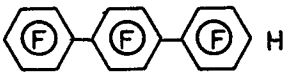
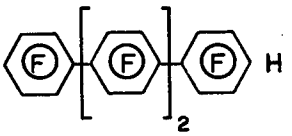
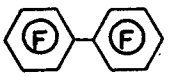
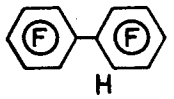
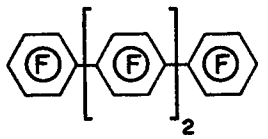
The F^{19} spectra were recorded on a Varian Associates V-4300B spectrometer at 40 Mc/s with trifluoroacetic acid as an external standard (Table X).

The H^1 spectra were recorded on a Varian A60 spectrometer. The spectra of XII and LVI exhibited a first order triplet of triplets centered at 7.6 ± 0.1 ppm with characteristic ortho and meta fluorine-hydrogen coupling constants (References 15 and 16) (J_{F_1H} = 10.1 ± 0.1 cps, J_{F_2H} = 7.8 ± 0.1 cps). This observed pattern confirms the para orientation of the protons. Tetramethylsilane was used as the internal standard for XII. The spectrum of LVI was obtained by using a dimethylacetamide solution (20% by weight) at 100°. The protons of the CH_3-C=O of the solvent were used as a reference point.

It is interesting to note that the reactivity of the pentafluorophenylmagnesium bromide may change by altering the solvent media. In early published research on carbonation studies

TABLE IX

POLYFLUOROAROMATIC COMPOUNDS

		M.P. (Uncor.)	Analysis Calc. / Found			M.W. Calc. / Found
			C	H	F	
XII		81-82[a]	45.59 / 45.80	0.32 / 0.67	54.09 / 54.27	316 / 305
LVI		176-177	46.56 / 46.22	0.23 / 0.16	53.20 / 53.87	464 / 450
LVII		210-211	47.07 / 46.76	0.18 / 0.03	52.75 / 52.72	612 / 596
XLIX		70[b]				
XLVIII		42-43[c]				
LIX		193-194[d]				
LX		233-234[d]				

(a) Prepared by an alternate method, m.p. 82-83
(b) Reference 13
(c) Reference 14
(d) Reference 11

TABLE X

F^{19} NUCLEAR MAGNETIC RESONANCE

Compound	F atom	ppm[c]	Multiplicity[a]	Integrated Peak Area
XII	$F_1F_2F_3$	+ 60.3	m	6
	F_4	+ 83.6	m	2
	F_5	+ 72.9	t($J_{F_4F_5}$ = ~20 cps)	1
LVI	$F_1F_2F_3F_4F_5$	+ 62.3	m	10
	F_6	+ 86.4	m	2
	F_7	+ 75.5	t($J_{F_6F_7}$ = ~20 cps)	1
LVII	$F_1F_2F_3F_4F_5F_6F_7$	+ 62.8	m	b
	F_8	+ 83.2	m	–
	F_9	+ 74.0	t($J_{F_8F_9}$ = ~ 20 cps)	–

(a) m = multiplet, t = triplet.

(b) Concentration was too low to obtain a good integration.

(c) Trifluoroacetic acid as external standard.

of the pentafluorophenylmagnesium bromide in diethyl ether, very poor (0 to < 10%) yields of acid were reported. We have found that by altering the solvent to tetrahydrofuran, yields as high as 85 percent acid were realized. Current studies in various laboratories on the constitution of the Grignard have shown that the composition is affected by many factors (solvent, concentration, purity, temperature, etc.). It is quite possible that in our studies on varying the solvent of the pentafluorophenylmagnesium bromide (and thus possibly varying the composition or perhaps only the rate of reaction), we have found a means of altering the reaction or scope of the pentafluorophenylmagnesium bromide reagent for synthesis purposes. Studies along these lines are currently in progress.

SECTION IV

APPLICATIONS OF PERFLUOROAROMATIC COMPOUNDS

The availability of the perfluoroaromatic compounds discussed in this report made possible for the first time the evaluation of the properties and potential applications of these materials. The specific unique properties that these materials have, in many instances, find applicability where their hydrocarbon analogs have failed.

Many of the evaluations are still in progress and only a few representative examples will be cited here. The complete evaluation data for the various applications is beyond the scope of this report. Such data, however, when completed, can be found in technical reports issued by the various groups performing the evaluation.

1. Perfluorophenylorganometallics as Antioxidants

With the advent of new high performance gas turbine engines, an increasing demand for lubricating materials capable of withstanding severe oxidative degradation at high temperatures for long periods of time is required. Two new classes of lubricating fluids, polyfluoroalkoxy-substituted triazines and phosphonitriles are adequate; however, at temperatures of 246°-260° (475°-500°F) severe oxidative degradation of the fluid takes place. Incorporation of approximately 0.5 percent by weight of tetra(pentafluorophenyl)tin into the base fluid practically eliminates the oxidative degradation of the fluids at temperatures of 260°(500°F) and above. Very little if any, bulk property changes occur in the fluids after oxidation exposure at 260° (500°F). (See Table XI; also, Reference 17.)

TABLE XI

OXIDATION TEST ON ELO-65-27 BASE FLUID

Fluid	Fluid Loss %	% Viscosity Change 100°F	Neut. No. Increase Mg KOH/g	Remarks
ELO-65-27 Base Fluid*	8.30	---	---	Orange-red fluid, became glasslike solid upon cooling to room temperature.
ELO-65-27 with 0.5 wt % $(C_6F_5)_4Sn$	11.0	+ 22.0	0.1	Slightly yellowed fluid.
ELO-65-27 with 0.5 wt % $(C_6F_5)_3P$	79.7	---	---	Orange-red fluid became glasslike solid upon cooling to room temperature.

Micro-Oxidation Test Conditions: 475°F, 24-hr duration, 20 liters/hr airflow, no metals.

* 2-(1,1,7-tri-H-perfluoroheptyloxy)-4,6-bis(1,1,5-tri-H-perfluoropentyloxy)-S-triazine.

2. Perfluoroaromatic Compounds as Antioxidation-Corrosion Agents

Another new class of high temperature candidate fluids are the polyperfluoroalkyl ethers. These fluids have demonstrated potential high temperature utility except for their pronounced tendency to attack metals (titanium and ferrous metals) at 260° (500°F) and above. The metal surfaces are so badly corroded that proper operation of this fluid in the presence of these metals is impossible.

This corrosion problem in these promising high temperature operational fluids has been solved by the incorporation of small quantities (~ 0.5% or less by weight) of tris(pentafluorophenyl)phosphine into the neat fluid. Such a formulation renders the fluid operational, without corrosion to the metal, up to 315° (600°F).

Although the tris(pentafluorophenyl)phosphine is the best inhibiting agent, other members of the group IV elements, e.g., tetra(pentafluorophenyl)-silane, -germane, and -tin also have comparable inhibiting properties. (See Table XII, also Reference 18.)

TABLE XII

COMPATIBILITY OF FORMULATED ELO-64-20 WITH TITANIUM ALLOYS

Additives in ELO-64-20*	% Fluid Loss	% Δ Visc. at 100°F	Δ Neut. No., mgKOH/g	Δ wt (mg/cm^2) and Appearance of Metals		Remarks
				Titanium (4% Al-4% Mn)	Titanium (6% Al-4% V)	
None	6.6	-15.0	0.0	-0.26 Mod. corr., Smooth dark Gray finish	+0.20 Lt. corr., Smooth dark Gray finish	Fluid appearance unchanged. White film formed on O-C tube. Rubber stopper at top of tube blackened.
0.5 wt.% Perfluorotriphenylphosphine	1.0	1.0	0.0	+0.07 Dark tarn., Some graying**	+0.06 Dark tarn., Some bluing	Fluid appearance unchanged. Much additive sublimed early in test.

Micro O-C test conditions: 20 ml sample, 600°F, 24 hours, one-liter/hr dry air, overboard, two metal specimens.

* ELO-64-20 = polyperfluoroalkyl ether.

** Some light corrosion beginning to occur.

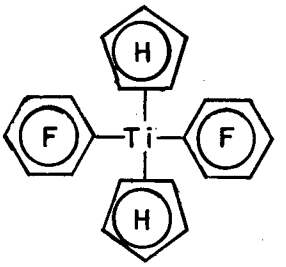
3. Perfluoroorganometallic Compounds For Vapor Deposition of Metals

Certain organometallic compounds can be heated to their decomposition temperature to effect a separation of the metal in relatively pure form. Advantage has been taken of this fact to provide for the plating or deposition of a selected metal on a surface. Such a deposition has been generally referred to as "vapor deposition."

The availability of suitable organometallic compounds has been limited by the low volatility and the low stability toward oxygen of many of the organometallic compounds which might otherwise be useful. This is particularly true of the organometallic compounds of the transition

elements, e.g., titanium. Many organometallic compounds of the transition metals decompose at relatively low temperatures and at temperatures which are very near their vaporization temperatures. Such compounds are difficult to handle because of their tendency to deposit metal in the vapor deposition apparatus on surfaces other than the one selected for coating.

Pentafluorophenyl groups on transition elements increase their thermal and oxidative properties. In addition, the high fluorine content renders them easily volatile (Section II, 2.d. (1), Vapor Phase Chromatography). All of these properties are present in the organometallic compound bis(cyclopentadienyl)bis(pentafluorophenyl)titanium.



LXI

When this compound is exposed to vapor deposition techniques, the best titanium plating so far obtained has been realized (Reference 19).

4. Polyperfluorophenylene Polymers in Grease Application

A grease is generally composed of a base fluid thickened by some high melting inert material.

The new high temperature stable polyperfluoroalkyl ether fluids makes the formulation of high temperature, 288°-315° (550°-600°F), operational greases a reality if the necessary thickeners were available. Thus far, the compatability of fluid to thickening agents is very limited. With but one exception only fluorinated thickening agents could be considered.

Polyperfluorophenylene polymers have the necessary physical and chemical properties to render the polyperfluoroalkyl ethers into useful greases. The polyperfluorophenylene polymer is thermally stable, chemically inert, high melting, and has the desired thickening property. Greases prepared from these polymers provide one of the best grease formulations from the polyperfluoroalkyl ether fluids. For example, in the Pope Spindle, bearing performance life at 228° (550°F), 10,000 rpm and 5-lb load was 220 hours (Reference 26).

SECTION V

EXPERIMENTAL

All reactions were accomplished in an atmosphere of dry, oxygen-free nitrogen. All melting points are uncorrected. Tetrahydrofuran was freshly distilled from sodium. Vapor phase chromatographic analyses were performed on an F&M Model-500 gas chromatogram. A 6-ft Apiezon L on Chromasorb P (60-80 mesh) column using helium carrier gas at about 60 ml/min. was used. The temperature was programmed at 5.6°/min.

1. Competitive Reaction of Pentafluorobenzene and Pentafluorobromobenzene With n-Butyllithium

To a solution of pentafluorobenzene (16.8 g, 0.1 mole) and pentafluorobromobenzene (24.7 g, 0.1 mole) in 300 ml of diethyl ether maintained at -65°, was added a solution of n-butyllithium (0.10 mole, 67 ml of a hexane solution) over a period of 2.5 hours. After Color Test IIA was negative, carbon dioxide was passed slowly through the reaction for 1 hour. The mixture was hydrolyzed with 200 ml of 6N hydrochloric acid and phase separated, and the ether layer was dried. A sample of the ether solution was analyzed via vapor phase chromatography. Analysis indicated the presence of pentafluorobenzene and pentafluorobenzoic acid, but no pentafluorobromobenzene. The dried ether layer was aspirated to yield pentafluorobenzoic acid, 19.7 g (93%).

2. 2,3,5,6-Tetrafluorobenzoic Acid from 2,3,5,6-Tetrafluorobromobenzene

n-Butyllithium (65 ml of a hexane solution, 0.1 mole) was added dropwise to a precooled (-65°) solution of 2,3,5,6-tetrafluorobromobenzene (22.90 g, 0.1 mole) in 300 ml anhydrous diethyl ether. Addition of the n-butyllithium required 38 minutes. Thirty minutes after the addition was complete Color Test IIA was negative. The reaction mixture was stirred an additional hour and then carbonated by bubbling carbon dioxide through the reaction. After one hour the reaction mixture was allowed to warm to room temperature, with continued carbonation. The mixture was then hydrolyzed with 200 ml of 6N hydrochloric acid, phase separated, and the organic layer dried over magnesium sulfate. The ether was removed by distillation yielding 13.8 g (71.1%) 2,3,5,6-tetrafluorobenzoic acid, m.p. 152°-154° m.p. 154° Reference 20).

From the petroleum ether insolubles was isolated a trace amount of crude 2,3,5,6-tetrafluoroterephthalic acid, m.p. 271°-275° which was identified by infrared analysis.

3. 2,3,5,6-Tetrafluoroterephthalic Acid from 1,4-Dibromo-2,3,5,6-tetrafluorobenzene

A solution of 1,4-dibromo-2,3,5,6-tetrafluorobenzene (15.4 g, 0.05 mole) in 43 ml of tetrahydrofuran was added, during ten minutes, to a stirred solution of n-butyllithium (0.10 mole, 67 ml of a hexane solution) and 107 ml of tetrahydrofuran maintained at -65°. The stirred mixture was maintained below -65° for 45 minutes. Color Test IIA was negative. Carbon dioxide was passed slowly through the reaction for one hour. The mixture was hydrolyzed with 125 ml of 6 N hydrochloric acid and phase separated. The organic layer was combined with ether extracts of the aqueous layer. The organic layer was extracted with 5-percent sodium carbonate solution. The sodium carbonate solution was acidified with hydrochloric acid. Extraction with ether followed by drying and evaporation of solvent yielded 10.9 g, (92%) of 2,3,5,6-tetrafluoroterephthalic acid, m.p. 276°-278° (m.p. 281°-282°, Reference 21). The infrared spectrum of this material was identical to an authentic sample.

When the above reaction was carried out in diethyl ether, in place of tetrahydrofuran, 2,3,5,6-tetrafluoroterephthalic acid was obtained in a 52-percent yield.

4. 4-Bromo-2,3,5,6-tetrafluorobenzoic Acid

n-Butyllithium (83.8 ml of a hexane solution, 0.129 mole) was added dropwise over a period of two hours, to a precooled solution (-65°) of 1,4-dibromo-2,3,5,6-tetrafluorobenzene (40.0 g, 0.129 mole) in 300 ml of anhydrous diethyl ether. Color Test IIA was negative 10 min. after addition was complete. The mixture was then carbonated by bubbling carbon dioxide through the reaction. The reaction mixture was allowed to warm to room temperature with continued carbonation. When the solution reached room temperature it was hydrolyzed with 300 ml of 6N hydrochloric acid and was phase separated. The acid layer was washed three times with 100 ml aliquots of diethyl ether which were combined with the organic layer and dried over magnesium sulfate. After drying, the ether was removed by distillation yielding 32.95 g of crude material, m.p. 148°-203°. This crude material was slurried with n-hexane. The insoluble material 29.60 g, m.p. 147.5°-212° was filtered. The filtrate was concentrated to yield 0.28 g of crude 4-bromo-2,3,5,6-tetrafluorobenzoic acid, m.p. 137.5°-143°. Distillation of the filtrate yielded 1.90 g of starting material 1,4-dibromo-2,3,5,6-tetrafluorobenzene.

The above n-hexane insolubles 29.60 g, were placed in a Soxhlet extractor and extracted with ligroin (90°-120°). Concentration of the ligroin extracts yielded 23.46 g (70.8%) of 4-bromo-2,3,5,6-tetrafluorobenzoic acid, m.p. 144.5°-145.5°.

Anal. Calcd. for $C_7HF_4O_2Br$:	C, 30.77;	H, 0.37;	F, 27.84;	Br, 29.27.
Found:	C, 31.03;	H, 0.31;	F, 28.27;	Br, 29.21.

The ligroin insoluble material 7.0 g (21.1%), m.p. 277.5°-278.5°, was identified by mixture melting point determination and infrared analysis as 2,3,5,6-tetrafluoroterephthalic acid.

5. 4-Bromo-2,3,5,6-tetrafluorobenzene

n-Butyllithium (100 ml of a hexane solution, 0.15 mole) was added during one hour to a stirred solution of 1,4-dibromo-2,3,5,6-tetrafluorobenzene (46.2 g, 0.15 mole) in 300 ml of tetrahydrofuran maintained at -65°. Immediately after the addition was completed Color Test IIA was negative. After 14 min. the black mixture was washed repeatedly with water and dilute hydrochloric acid. The dried organic layer was distilled on a spinning band column yielding 17.6 g (51%) of 4-bromo-2,3,5,6-tetrafluorobenzene, b.p. 143°-143.5°, n_D^{20} 1.4691.

Anal. Calcd. for C_6HBrF_4:	C, 31.47;	H, 0.44;	Br, 34.90;	F, 33.19.
Found:	C, 31.59;	H, 0.65;	Br, 34.70;	F, 33.01.

By sublimination the pot residue yielded 8.5 g (18%) of unreacted 1,4-dibromo-2,3,5,6-tetrafluorobenzene as characterized by a mixture melting point determination with an authentic sample and by infrared analysis.

6. 2,3,5,6-Tetrafluorobenzoic Acid from 2,3,5,6-Tetrafluorobenzene

n-Butyllithium (65 ml of a hexane solution, 0.1 mole) was added dropwise to a precooled (-65°) solution of 2,3,5,6-tetrafluorobenzene (15.01 g, 0.1 mole) in 300 ml anhydrous diethyl ether. The addition of the n-butyllithium required 65 minutes. Twenty minutes after the addition was complete Color Test IIA was negative. The reaction mixture was stirred an

additional 45 min. and then carbonated by bubbling carbon dioxide through the reaction. After 15 min. the ice bath was removed and the reaction mixture warmed to room temperature, with continued carbonation. The mixture was then hydrolyzed with 300 ml of 6N hydrochloric acid, phase separated, and the organic layer dried over magnesium sulfate. The ether was removed by distillation yielding 18.10 g (93.2%) crude 2,3,5,6-tetrafluorobenzoic acid. The crude acid was placed in a Soxhlet apparatus and extracted using petroleum ether (b.p. 90°-120°). From the solvent was obtained 16.5 g (85.0%) of pure 2,3,5,6-tetrafluorobenzoic acid, m.p. 152° -154° (m. p. 154°, Reference 20). The petroleum ether insolubles afforded 0.45 g (0.0019 mole) of 2,3,5,6-tetrafluoroterephthalic acid, m.p. 273°-276° which was identified by infrared analysis.

When the above reaction was carried out in tetrahydrofuran in place of diethyl ether, 2,3,5,6-tetrafluorobenzoic acid was obtained in 36.0-percent yield in addition to a 63.0-percent yield of 2,3,5,6-tetrafluoroterephthalic acid.

7. 2,3,5,6-Tetrafluoroterephthalic Acid from 2,3,5.6-Tetrafluorobenzoic Acid

A solution of 2,3,5,6-tetrafluorobenzoic acid (19.4 g, 0.1 mole) in 40 ml tetrahydrofuran was added dropwise to a precooled (-65°) solution of n-butyllithium (135 ml of a hexane solution, 0.2 mole) in 270 ml tetrahydrofuran. The addition of the 2,3,5,6-tetrafluorobenzoic acid solution required 15 minutes. Fifteen minutes after the addition was complete Color Test IIA was negative. The reaction mixture was stirred an additional 35 min. and then carbonated by bubbling carbon dioxide through the reaction mixture. After one-half hour the reaction mixture was allowed to warm to room temperature with continued carbonation. The mixture was then hydrolyzed with 300 ml 6N hydrochloric acid, phase separated, and the organic layer dried over magnesium sulfate. The ether was removed by distillation yielding 22.39 g (94.0%) of 2,3,5,6-tetrafluoroterephthalic acid, m.p. 276°-278° (m.p. 281°-282°, Reference 21). A mixture melting point with an authentic sample showed no depression. The infrared spectrum was also identical to an authentic sample.

8. 4-Thiol-2,3,5,6-tetrafluorobenzoic Acid

A solution of 2,3,5,6-tetrafluorobenzoic acid (9.87 g, 0.051 mole) in 30 ml of tetrahydrofuran was added dropwise to a precooled (-65°) solution of n-butyllithium (65 ml of a hexane solution, 0.1 mole) in 200 ml tetrahydrofuran. The addition of the 2,3,5,6-tetrafluorobenzoic acid required 16 minutes. Forty-five minutes after the addition was complete Color Test IIA was negative. After 23 additional minutes, 1.64 g (0.051 mole) of sulfur was added to the reaction mixture causing the color to gradually change to a green and then to a deep yellow. The reaction mixture was stirred an additional 22 hrs. before Color Test I was negative. The mixture was then allowed to warm to room temperature, hydrolyzed with 150 ml 6N hydrochloric acid, phase separated, and the organic layer dried over magnesium sulfate. The ether was removed by distillation and the crude material remaining was recrystallized from petroleum ether (b.p. 90°-120°) yielding 7.50 g (68.7%) of yellow crystalline 4-thiol-2,3,5,6-tetrafluorobenzoic acid, m.p. 155°-157°.

Anal. Calcd. for $C_7H_2F_4O_2S$: C, 37.18; H, 0.89; F, 33.60; S, 14.18.

Found: C, 37.25; H, 0.95; F, 32.75; S, 14.25.

9. 4-Chloro-2,3,5,6-tetrafluorobenzoic Acid

A solution of 2,3,5,6-tetrafluorobenzoic acid (3.88 g, 0.02 mole) in 25 ml of anhydrous diethyl ether was added dropwise to a precooled (-65°) solution of n-butyllithium (26 ml of a hexane solution, 0.04 mole) in 125 ml of anhydrous diethyl ether. Addition of the 2,3,5,6-tetrafluorobenzoic acid required two minutes. Thirty minutes after the addition was complete, Color Test IIA was negative. The reaction mixture was stirred an additional 30 minutes.

Chlorine gas was slowly bubbled below the surface of the reaction while keeping the temperature at -65°. After 30 minutes Color Test I was negative. The addition of chlorine was discontinued and the reaction mixture was allowed to stir for an additional one hour. The reaction was then allowed to warm to room temperature, hydrolyzed by the addition of 150 ml of 6N hydrochloric acid, phase separated, and the organic layer dried over magnesium sulfate. The dried ether solution was distilled to remove the ether solvent. A yellow viscous liquid, 4.3 g remained. This material was added to warm petroleum ether (b.p. 60°-90°) which on cooling yielded the crude product. Another recrystallization from petroleum ether (b.p. 60°-90°) afforded the desired product 4-chloro-2,3,5,6-tetrafluorobenzoic acid, m.p. 128°-130°.

Anal. Calcd. for $C_7HClF_4O_2$: C, 36.79; H, 0.44; F, 33.25; Cl, 15.51.

Found: C, 36.37; H, 0.65; F, 33.09; Cl, 15.15.

10. 4-Hydroxy-2,3,5,6-tetrafluorobenzoic Acid

2,3,5,6-Tetrafluorophenol (16.6 g, 0.1 mole) dissolved in 50 ml of freshly distilled tetrahydrofuran was added dropwise to a precooled (-70°) solution of n-butyllithium (140 ml of a hexane solution, 0.2 mole) in 400 ml tetrahydrofuran. Time of the addition was 15 minutes. Fifteen minutes after the addition was complete Color Test IIA was negative. After an additional 35 min., carbon dioxide was bubbled into the reaction mixture. Forty-five minutes later the cooling bath was removed and the reaction mixture warmed to room temperature with continued carbonation. The mixture was then hydrolyzed with 300 ml 6N HCl, phase separated, and the organic layer dried over sodium sulfate. The solvent was distilled under reduced pressure to yield 17.3 g (82.5%) crude product. Recrystallization of a sample from xylene yielded 4-hydroxy-2,3,5,6-tetrafluorobenzoic acid monohydrate, m.p. 154°-156° (m.p. 157°, Reference 20).

Anal. Calcd. for $C_7H_4F_4O_4$: C, 36.85; H, 1.76; F, 33.31.

Found: C, 37.05; H, 1.80; F, 33.13.

11. 4-Amino-2,3,5,6-tetrafluorobenzoic Acid

2,3,5,6-Tetrafluoraniline (16.5 g, 0.1 mole) dissolved in 35 ml of anhydrous tetrahydrofuran was added dropwise to a precooled (-70°) solution of n-butyllithium (195 ml of a hexane solution, 0.3 mole) in 450 ml tetrahydrofuran. Time of addition was 15 minutes. Three hours after the addition was complete Color Test IIA was negative. Carbon dioxide was then bubbled into the reaction mixture. After 30 min. the cooling bath was removed and the reaction mixture warmed to room temperature with continued carbonation. The mixture was then hydrolyzed with 250 ml of 3N HCl, phase separated, and the organic layer dried over magnesium sulfate. Distillation of the solvent yielded 9.43 g (45.1%) crude product. Recrystallization from benzene yielded 7.72 g (36.9%) pure 4-amino-2,3,5,6-tetrafluorobenzoic acid, m.p. 182°-184° (m.p. 182°, Reference 21).

Anal. Calcd. for $C_7H_3F_4NO_2$: C, 40.21; H, 1.44; F, 36.34; N, 6.69.

Found: C, 40.16; H, 1.54; F, 36.42; N, 6.87.

12. 4-Thiol-2,3,5,6-tetrafluorobenzoic Acid

2,3,5,6-Tetrafluorothiophenol (27.32 g, 0.15 mole) dissolved in 60 ml anhydrous diethyl ether was added dropwise to a precooled (-70°) solution of n-butyllithium (195 ml of a hexane solution, 0.3 mole) in 400 ml diethyl ether. Time of the addition was 34 minutes. Thirty minutes after the addition was complete Color Test IIA was negative. After an additional

30 min., carbon dioxide was bubbled into the reaction mixture. After 30 min. the cooling bath was removed and the reaction mixture warmed to room temperature with continued carbonation. The mixture was then hydrolyzed with 300 ml 6N HCl, phase separated, and the organic layer dried over magnesium sulfate. Distillation of the solvent under reduced pressure afforded 27.8 g (82.0%) crude product. Recrystallization from petroleum ether (b.p. 90°-120°) yielded 26.0 g (76.5%) of yellow crystalline, 4-thiol-2,3,5,6-tetrafluorobenzoic acid, m.p. 156°-158°.

Anal. Calcd. for $C_7H_2F_4O_2S$:	C, 37.18;	H, 0.89;	F, 33.60;	S, 14.18.
Found:	C, 37.33;	H, 0.86;	F, 32.76;	S, 14.74.

13. 4-Methyl-2,3,5,6-tetrafluorobenzoic Acid

n-Butyllithium (162.5 ml of a hexane solution, 0.25 mole) was added dropwise to a precooled (-70°) solution of 2,3,5,6-tetrafluorotoluene (41.0 g, 0.25 mole) in 500 ml of anhydrous diethyl ether. The n-butyllithium was added over a period of 45 minutes. Thirty-five minutes after the addition was complete Color Test IIA was negative. After an additional 30 min. carbon dioxide was bubbled into the reaction mixture. Thirty minutes later the cooling bath was removed and the reaction mixture warmed to room temperature, with continued carbonation. The mixture was then hydrolyzed with 250 ml 6N HCl, phase separated, and the organic layer dried over magnesium sulfate. The ether was distilled under vacuum and yielded 52.0 g of crude product. Recrystallization from benzene yielded 45.7 g (87.8%) of pure 4-methyl-2,3,5,6-tetrafluorobenzoic acid m.p. 169.5°-171° (m.p. 174°, Reference 20).

14. 4-Trifluoromethyl-2,3,5,6-tetrafluorobenzoic Acid

n-Butyllithium (71 ml of a hexane solution, 0.11 mole) was added dropwise to a precooled (-70°) solution of 2,3,5,6-heptafluorotoluene (21.8 g, 0.10 mole) in 200 ml of anhydrous tetrahydrofuran. The temperature was maintained below -60°. The solution was carbonated by bubbling gaseous carbon dioxide through the reaction mixture for one hour. The reaction was allowed to warm up to room temperature with continued carbonation. The mixture was then hydrolyzed with 300 ml of 6N hydrochloric acid. The two phase solution was distilled until only the aqueous phase remained. This solution was cooled, yielding a white precipitate which on recrystallization from benzene afforded 20.3 g (77%) of white crystalline product, m.p. 107.5°-110.5°. The analytical sample, m.p. 110°-111.5° was obtained by an additional recrystallization from benzene (Reference 22).

Anal. Calcd. for $C_8HF_7O_2$:	C, 36.66;	H, 0.38;	F, 50.7.
Found:	C, 36.72;	H, 0.41;	F, 50.6.

15. 2,2',3,3',5,5',6,6'-Octafluorobiphenyl-4,4'-dicarboxylic Acid

A solution of 2,2',3,3',5,5',6,6'-octafluorobiphenyl (28.9 g, 0.1 mole) in 55 ml anhydrous tetrahydrofuran was added dropwise over a period of 18 min., to a precooled (-70°) solution of n-butyllithium (137 ml of a hexane solution, 0.2 mole) in 250 ml anhydrous tetrahydrofuran. Thirty minutes after the addition was complete Color Test IIA was negative. After 30 additional minutes, carbon dioxide was bubbled through the reaction mixture for 0.5 hour. The mixture was then allowed to warm to room temperature with continued carbonation, then hydrolyzed with 250 ml 6N HCl and the resulting mixture phase separated. The aqueous layer was then washed three times with diethyl ether combined with the organic layer and dried over magnesium sulfate. After drying, solvents were removed by aspiration yielding 38.4 g (96.7%) of the desired 2,2',3,3',5,5',6,6'-octafluorobiphenyl-4,4'-dicarboxylic acid,

m.p. 313°-319°. The analytical sample, m.p. 318°-320° (dec.), was obtained by slurrying the above product in boiling ligroin (b.p. 90°-120°) yielding 35.5 g (91.9%).

Anal. Calcd. for $C_{14}H_2F_8O_4$: C, 43.54; H, 0.52; F, 39.36.

Found: C, 43.24; H, 0.62; F, 39.40.

16. Attempted Preparation of 4-Cyano-2,3,5,6-tetrafluorobenzoic Acid

To a cooled (-70°) stirred solution of 2,3,5,6-tetrafluorobenzonitrile (10.0 g, 0.057 mole) dissolved in 220 ml of diethyl ether was added 0.057 mole of n-butyllithium (37 ml of a hexane solution) over a period of one hour. During the addition the color of the reaction mixture changed from pale yellow to amber and finally to brown. Forty-five minutes after the addition was complete Color Test I was positive and Color Test IIA was negative. The reaction was stirred another 45 min. and then carbon dioxide was bubbled in. During carbonation the mixtures' appearance became a much lighter turbid. The mixture was then warmed to room temperature, hydrolyzed with ice, acidified, extracted with diethyl ether, and dried over magnesium sulfate. Distillation of the dried organic layer yielded a pale yellow semisolid. Attempted crystallization from a variety of solvents as well as silica gel chromatographic separation produced no tractable material. Infrared analysis of the crude materials indicated the presence of a nitrile band at 2250 cm^{-1}.

17. 4-Carboxy-nonafluorobiphenyl

n-Butyllithium (0.025 mole, 19 ml of a hexane solution) was added, during 55 min., to a stirred solution of 4-hydro-2,3',3,3',4',5,5',6,6'-nonafluorobiphenyl (7.90 g, 0.025 mole) in 200 ml of anhydrous diethyl ether maintained at -65°. During this time the color changed from pale yellow to deep orange. The stirred mixture was maintained below -60° for two hours during which time the color returned to yellow. Color Test IIA was negative. Carbon dioxide was then bubbled into the reaction mixture for one hour then hydrolyzed with 200 ml of 6N hydrochloric acid and phase separated. Ether extracts of the aqueous layer were combined with the organic layer and dried over $MgSO_4$. Solvent evaporation yielded 9.50 g of crude material. Recrystallization from petroleum ether (b.p. 90°-120°) yielded 6.16 g (68.5%) of 4-carboxy-nonafluorobiphenyl, m.p. 178°-180°.

Anal. Calcd. for $C_{13}HF_9O_2$: C, 43.35; H, 0.28.

Found: C, 42.98: H, 0.22.

When the above reaction was performed using tetrahydrofuran rather than diethyl ether the 4-lithiononafluorobiphenyl intermediate polymerized at these low temperatures.

18. 2-Carboxy-heptafluoronaphthalene

n-Butyllithium (0.0157 mole, 10.2 ml of a hexane solution) was added, during 20 min., to a cooled (-70°) stirred solution of 4.0 g (0.0157 mole) of 2-hydroheptafluoronaphthalene. After 45 min., Color Test IIA was negative. Carbon dioxide was then bubbled into the reaction mixture. Carbonation was continued while the reaction mixture was warmed to room temperature. The mixture was then hydrolyzed with 150 ml 6N hydrochloric acid and phase separated. The extracts of the aqueous layer were combined with the organic layer and dried over $MgSO_4$. Evaporation of the solvent yielded 4.56 g (97.5%) of crude acid. Recrystallization from benzene yielded 4.15 g (88.5%) of pure 2-carboxyheptafluoronaphthalene, m.p. 185°-188°.

Anal. Calcd. for $C_{11}HF_7O_2$: C, 44.32; H, 0.34; F, 44.61.

Found: C, 44.13; H, 0.39; F, 46.20.

19. 2,6-Dicarboxy-hexafluoronaphthalene

A solution of 2,6-dihydro-1,3,4,5,7,8-hexafluoronaphthalene (1.1 g, 0.0046 mole) in 15 ml anhydrous diethyl ether was added, during 18 min., to a stirred solution of n-butyllithium (0.0092 mole, 6 ml of a hexane solution) and 20 ml of anhydrous diethyl ether maintained at -65°. In one hour the viscous, turbid solution had a negative Color Test IIA. Carbon dioxide was then bubbled into the reaction mixture. Carbonation was continued while the reaction mixture was warmed to room temperature. The mixture was then hydrolyzed with 80 ml of 6N hydrochloric acid and phase separated. Ether extracts of the aqueous layer were combined with the organic layer and dried over $MgSO_4$. Solvent evaporation yielded 1.33 g of crude material. Workup yielded 0.78 g (64%) of 2,6-dicarboxy-1,3,4,5,7,8-hexafluoronaphthalic acid, m.p. 274°-278°.

Anal. Calcd. for $C_{12}H_2F_6O_4$: C, 44.46; H, 0.62.

Found: C, 44.18; H, 0.91.

20. Perfluoro-α,α-dimethylbenzyl Alcohol from Pentafluorophenyllithium

Sixty ml of a solution containing 0.077 mole of n-butyllithium in hexane was cooled to -55° and treated with 12.9 g (0.077 mole) of pentafluorobenzene in 40 ml of diethyl ether. The addition required 30 minutes. The reaction was stirred for two hours. An excess of hexafluoroacetone was introduced above the surface of the stirred mixture. The temperature was maintained between -60° and -55° throughout the addition. After the product was warmed to 10° and hydrolyzed with 10-percent H_2SO_4, the organic layer and two 10 ml ether extracts of the aqueous portion were combined and dried over Na_2SO_4. Fractional distillation in two similar experiments gave an average yield of 79 percent of the alcohol boiling at 158°-160°, n_D^{26} 1.3780.

Anal. Calcd. for $C_9HF_{11}O$: C, 32.35; H, 0.30; F, 62.56.

Found: C, 32.62; H, 0.51; F, 62.31.

21. Perfluoro-α,α,p-trimethylbenzyl Alcohol

To a stirred mixture of 20 ml of tetrahydrofuran and 15.8 ml of a hexane solution containing 0.025 mole of butyllithium, which was maintained at -60°, was added a solution of 5.2 g (0.024 mole) of 4-trifluoromethyl-2,3,5,6-tetrafluorobenzene in 10 ml of tetrahydrofuran during 15 minutes. The mixture was stirred 30 minutes. An excess of hexafluoracetone was introduced above the surface of the liquid. After the product was warmed to room temperature, 40 ml of ice water containing 6.0 ml of H_2SO_4 was added, the organic layer was separated, the aqueous layer was extracted twice with ether, and the combined organic layer and extracts were dried over Na_2SO_4. Fractional distillation through a micro-Claisen head gave 5.5 g (61%) of the alcohol boiling at 103°-104°, n_D^{28} 1.3732.

Anal. Calcd. for $C_{10}HF_{13}O$: C, 31.27; H, 0.26; F, 64.30.

Found: C, 31.39; H, 0.40; F, 64.19.

22. 4-Methyl-perfluoro- α,α -dimethylbenzyl Alcohol

This alcohol was prepared in a similar manner to the above trifluoromethyl derivative except that 2,3,5,6-tetrafluorotoluene was used.

An average yield of 91 percent of the alcohol boiling at 193°-194°, n_D^{23} 1.3979, was obtained.

Anal. Calcd. for $C_{10}H_4F_{10}O$: C, 36.38; H, 1.22; F, 57.55.

Found: C, 36.53; H, 1.28; F, 57.90.

23. Perfluoro-1,4-phenylenebis(dimethylcarbinol)

A stirred mixture of 100 ml of tetrahydrofuran and 93 ml of a hexane solution containing 0.148 mole of butyllithium was treated with a solution of 21.7 g (0.071 mole) of dibromo-2,3,5,6-tetrafluorobenzene is 45 ml of tetrahydrofuran at -60°. The addition required 20 minutes. After an excess of hexafluoroacetone was introduced above the surface of the mixture, the product was hydrolyzed with dilute H_2SO_4, the organic layer separated, combined with ether extracts of the aqueous layer, and dried over Na_2SO_4. Evaporation of the solvents and two recrystallizations from petroleum ether (b.p. 60°-90°) gave 24.0 g (71%) of the diol, m.p. 94°-95°.

Anal. Calcd. for $C_{12}H_2F_{16}O_2$: C, 29,89; H, 0.42; F, 63.05.

Found: C, 29.98; H, 0.62; F, 63.00.

24. Perfluoro-4-H- α,α -dimethylbenzyl Alcohol

To a rapidly stirred solution of 21.9 g (0.146 mole) of 1,2,4,5-tetrafluorobenzene in 150 of tetrahydrofuran, which was maintained at -65°, was added during 45 min. 92 ml of a hexane solution containing 0.146 mole of butyllithium. The reaction was stirred two hours. An excess of hexafluoroacetone was introduced above the surface of the liquid. The mixture was warmed to room temperature, hydrolyzed with dilute sulfuric acid, and the organic phase was separated, combined with ether extracts of the aqueous phase, and dried over Na_2SO_4. Evaporation of the solvents and recrystallization of the residue from petroleum ether (b.p. 60°-90°) gave 21.3 g (61% calcd. on the basis of butyllithium) of perfluoro-1,4-phenylenebis-(dimethylcarbinol), m.p. 94°-95°. Evaporation and distillation of the recrystallization liquors gave 4.9 g (11%) of the monosubstituted alcohol boiling at 161°-163°.

Anal. Calcd. for $C_9H_2F_{10}O$: C, 34.19; H, 0.64; F, 60.11.

Found: C, 34.01; H, 0.75; F, 60.00.

25. Perfluoro-4,4'-biphenylenebis(dimethylcarbinol)

A solution of 2,3,5,6,2',3',5',6'-octafluorobiphenyl (20.7 g., 0.07 mole) in 45 ml of tetrahydrofuran was added over 30 min. to a stirred mixture of 100 ml of tetrahydrofuran and 90 ml of a hexane solution containing 0.144 mole of butyllithium at -60°. After one hour an excess of hexafluoroacetone was introduced above the liquid surface. The product was hydrolyzed with dilute sulfuric acid and the organic layer was separated and dried over Na_2SO_4. Evaporation of the solvents and recrystallization from chloroform gave 32.4 g (74%) of the diol, which melted at 192°-193°.

Anal. Calcd. for $C_{18}H_2F_{20}O_2$: C, 35.20; H, 0.33; F, 61.87.

Found: C, 34.83; H, 0.44; F, 62.00.

26. Tetra(pentafluorophenyl)silane

Silicon tetrachloride (4.25 g, 0.025 mole) dissolved in 20 ml of diethyl ether was added to a solution of pentafluorophenyllithium (prepared from 16.8 g, 0.10 mole pentafluorobenzene, 0.10 mole of n-butyllithium and 130 ml of diethyl ether) at -65° over an 8-min. period. After three hours of stirring at -65°, the Color Test I was negative indicating an absence of pentafluorophenyllithium. The reaction mixture was allowed to warm up to room temperature and the precipitate filtered. The filtrate was aspirated to dryness. The crude solid plus the precipitate were combined and recrystallized from hot benzene. From the benzene solution was obtained tetra(pentafluorophenyl)silane (13.0 g, 75% yield), m.p. 245°-246° (m.p. 248°-250°, Reference 8).

Anal. Calcd. for $C_{24}F_{20}Si$: C, 41.40; F, 54.57; Si, 4.03.

Found: C, 41.22; F, 54.39; Si, 4.31.

In a similar manner as described above via the pentafluorophenyllithium intermediate the following compounds were prepared, tetra(pentafluorophenyl)germane, 88.0-percent yield, m.p. 246.5°-247.5° (Reference 23 reported sublimation 224°-230°); tetra(pentafluorophenyl)tin, 91.4-percent yield, m.p. 220°-222° (Reference 24 reported 221°); tetra(pentafluorophenyl)-lead, (prepared from lead tetraacetate and pentafluorophenyllithium), 15.5-percent yield, m.p. 204°-206° (Reference 25 reported 199°-200°).

27. Bis(cyclopentadienyl)bis(pentafluorophenyl)zirconium

Bis(cyclopentadienyl)zirconium dibromide (6.48 g, 0.017 mole) was added directly to pentafluorophenyllithium (prepared from 5.72 g, 0.034 mole pentafluorobenzene, 0.034 mole of n-butyllithium and 100 ml. of diethyl ether) at -65°. The reaction was allowed to warm up to -20° during 3.5 hours. After this warmup period Color Test I was negative, indicating an absence of pentafluorophenyllithium. The white precipitate was filtered and the filtrate aspirated to dryness. The crude material was combined and recrystallized from warm benzene yielding 2.54 g (26.9%) pure bis(cyclopentadienyl)bis(pentafluorophenyl)zirconium, m.p. 257° (dec.) and 1.93 g of unidentified white crystals, m.p. 340°. The product was identified by infrared analysis and elemental analysis.

Anal. Calcd. for $C_{22}H_{10}F_{10}Zr$: C, 47.57; H, 1.81.

Found: C, 47.49; H, 2.74.

28. Bis(cyclopentadienyl)bis(pentafluorophenyl)titanium

Prepared by a similar procedure as described above, 52-percent yield, m.p. 228°-229° (Reference 6 reported 228°-230°).

29. Hydrolysis Studies of $(C_6F_5)_4M$ Compounds

a. HCl (Heterogeneous)

A 5.0 g sample of tetra(pentafluorophenyl)silane, tetra(pentafluorophenyl)germane, tetra-(pentafluorophenyl)tin, and tetra(pentafluorophenyl)lead were individually treated with 6N

HCl (40 ml) under reflux for five hours. On cooling, the starting materials were recovered in each case quantitatively.

b. HCl (in Tetrahydrofuran)

Tetra(pentafluorophenyl)silane (3.0 g) was treated with 6N HCl (40 ml) and tetrahydrofuran (40 ml) for 5 hrs. at reflux temperature. The solution was cooled and extracted with 5-100 ml portions of diethyl ether. Analysis of the dried ether extract by vapor phase chromatography indicated only pentafluorobenzene. Evaporation of the ether extract yielded none of the tetra(pentafluorophenyl)silane.

Tetra(pentafluorophenyl)tin and tetra(pentafluorophenyl)lead were similarly treated with vapor phase chromatography analysis indicating pentafluorobenzene. Tetra(pentafluorophenyl)-germane under the above hydrolysis conditions was resistant to cleavage. The tetra(pentafluorophenyl)germane was recovered quantitatively.

c. NaOH (Heterogeneous)

Tetra(pentafluorophenyl)silane (5.0 g) and tetra(pentafluorophenyl)germane (5.0 g) when individually refluxed for 5 hrs. in NaOH (40 ml, 10% solution) were recovered quantitatively. Tetra(pentafluorophenyl)tin and tetra(pentafluorophenyl)lead when treated under the same hydrolysis conditions indicated by vapor phase chromatography analysis in the presence of pentafluorobenzene.

d. NaOH (in Tetrahydrofuran)

Tetra(pentafluorophenyl)silane (5.0 g), tetra(pentafluorophenyl)germane (5.0 g) and tetra-(pentafluorophenyl)tin (5.0 g) when individually refluxed in NaOH (40 ml, 10% solution) and tetrahydrofuran (40 ml) for 5 hrs. yielded none of the starting material. Vapor phase chromatography analysis indicated pentafluorobenzene.

30. Attempted Cleavage of $(C_6F_5)_4$-M

a. Bromine

A slurry of tetra(pentafluorophenyl)tin (3.93 g, 0.005 mole) in ethylene dibromine (50 ml) was added to a solution of bromine (0.80 g, 0.005 mole) in ethylene bromide (50 ml) plus a catalytic amount of aluminum bromide. After refluxing for 6 hrs. the reaction mixture was cooled to room temperature. The reaction was treated with potassium sulfite solution. The organic layer was washed with water and dried. A sample of this solution was analyzed by vapor phase chromatography, which indicated no pentafluorobromobenzene. After aspirating the solution to dryness, the crude solid material was recrystallized from chloroform-methanol. Tetra(pentafluorophenyl)tin (3.35 g) was recovered in 85.2-percent yield.

In a similar manner as described above, tetra(pentafluorophenyl)silane and tetra(pentafluorophenyl)germane showed no cleavage of the pentafluorophenyl group.

b. Lithium

A paste of tetra(pentafluorophenyl)silane (3.48 g, 0.005 mole) in a few milliliters of tetrahydrofuran and dispersed lithium (0.02 mole) was rapidly stirred for approximately 20 hrs. at room temperature. No apparent reaction took place. The reaction was heated for an additional 8 hrs. without any indication of reaction. To this mixture was added diethyl ether (30 ml) and the Color Test I which was taken was negative indicating no organometallic

formation. The reaction mixture was hydrolyzed, the ether layer was separated and dried over magnesium sulfate. Aspiration of the ether solution left crude tetra(pentafluorophenyl)-silane (3.35 g, 96.2%).

In a similar manner as described above the tetra(pentafluorophenyl)germane and tetra-(pentafluorophenyl)tin showed no apparent reaction with dispersed lithium.

31. Byproducts from the Reaction Between Pentafluorophenylmagnesium Bromide and Silicon Tetrachloride

Pentafluorophenylmagnesium bromide was prepared by adding pentafluorobromobenzene (0.60 moles, 148.2 g) in 50 ml of dry tetrahydrofuran to magnesium turnings (0.60 mole, 14.6 g) suspended in 620 ml of dry tetrahydrofuran at 0°. The addition required 30 minutes. Two hours after the addition, a 10-ml sample was removed, hydrolyzed, dried, and analyzed by vapor phase chromatography. Other than pentafluorobenzene, and unreacted pentafluoro-bromobenzene, no side products were observed. Analysis of the Grignard by titration indicated a 90-percent yield. A solution of silicon tetrachloride (0.135 mole, 22.94 g) in 50 ml of tetrahydrofuran was added over 1 3/4 hr. at 0°. After the addition was complete, the reaction mixture was slowly allowed to come to room temperature. The precipitate, which consisted of the product tetra(pentafluorophenyl)silane (69% yield) and inorganic salts, was filtered. The filtrate was hydrolyzed with dilute hydrochloric acid and extracted three times with diethyl ether. The diethyl ether extracts were dried and distilled to leave 25 g of a solid which consisted of the side products of the reaction. The material was dissolved in petroleum ether (60°-90°) and separated by passing through an alumina (Woelm, neutral grade) column. Petroleum ether (60°-90°) was used as the eluent. Three main fractions were obtained, Compounds XII, LVI, and LVII, which were further recrystallized from petroleum ether (30°-60°). For characterization of compounds, see Table IX.

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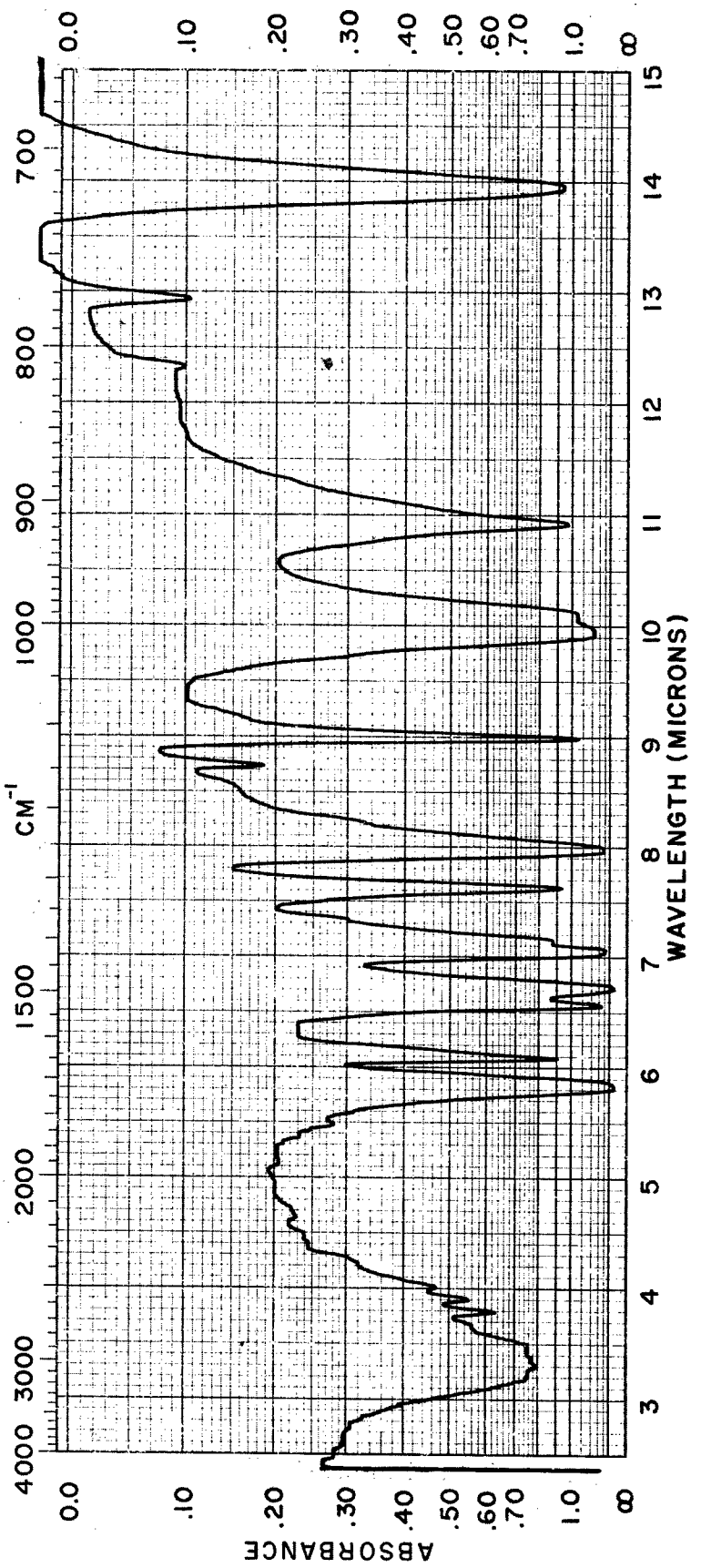

Figure 3. 2,3,4,5,6-Pentafluorobenzoic Acid

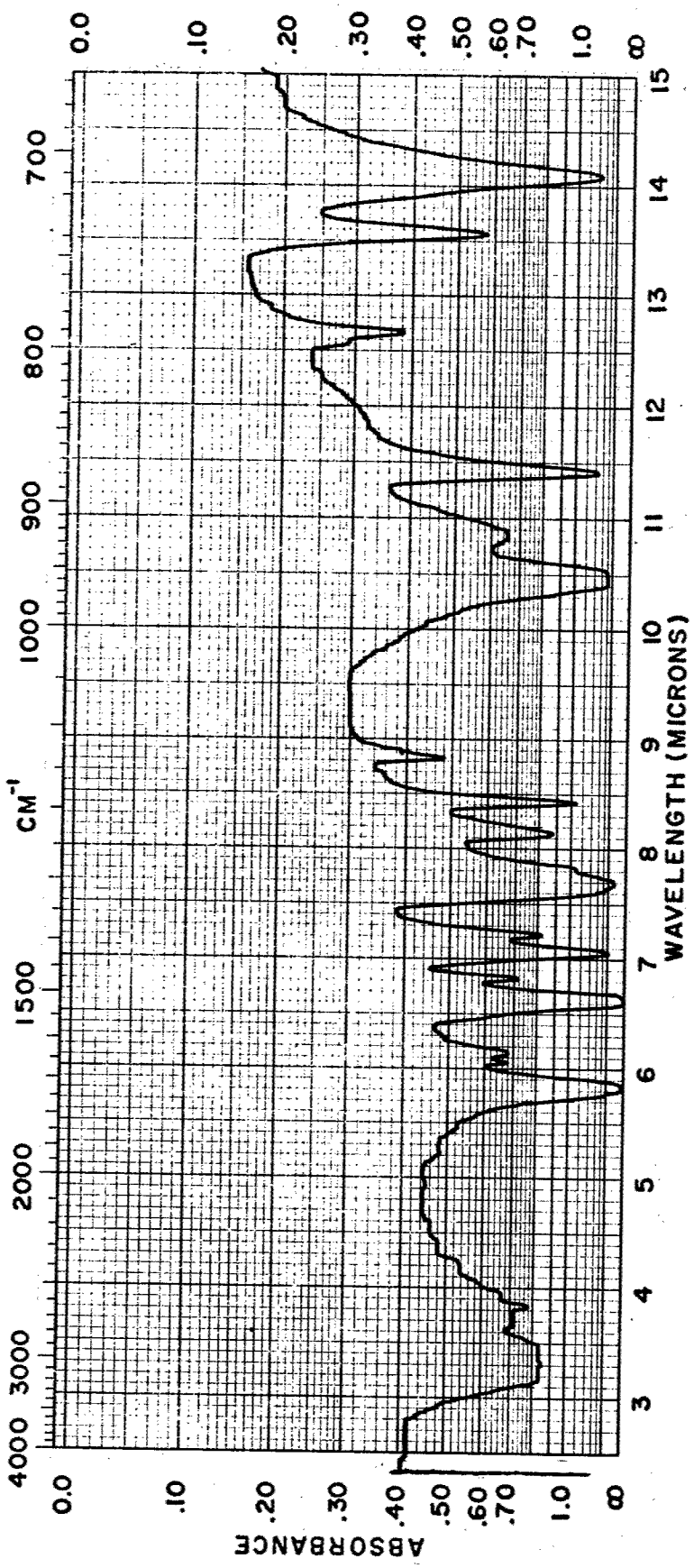

Figure 4. 2,3,5,6-Tetrafluorobenzoic Acid

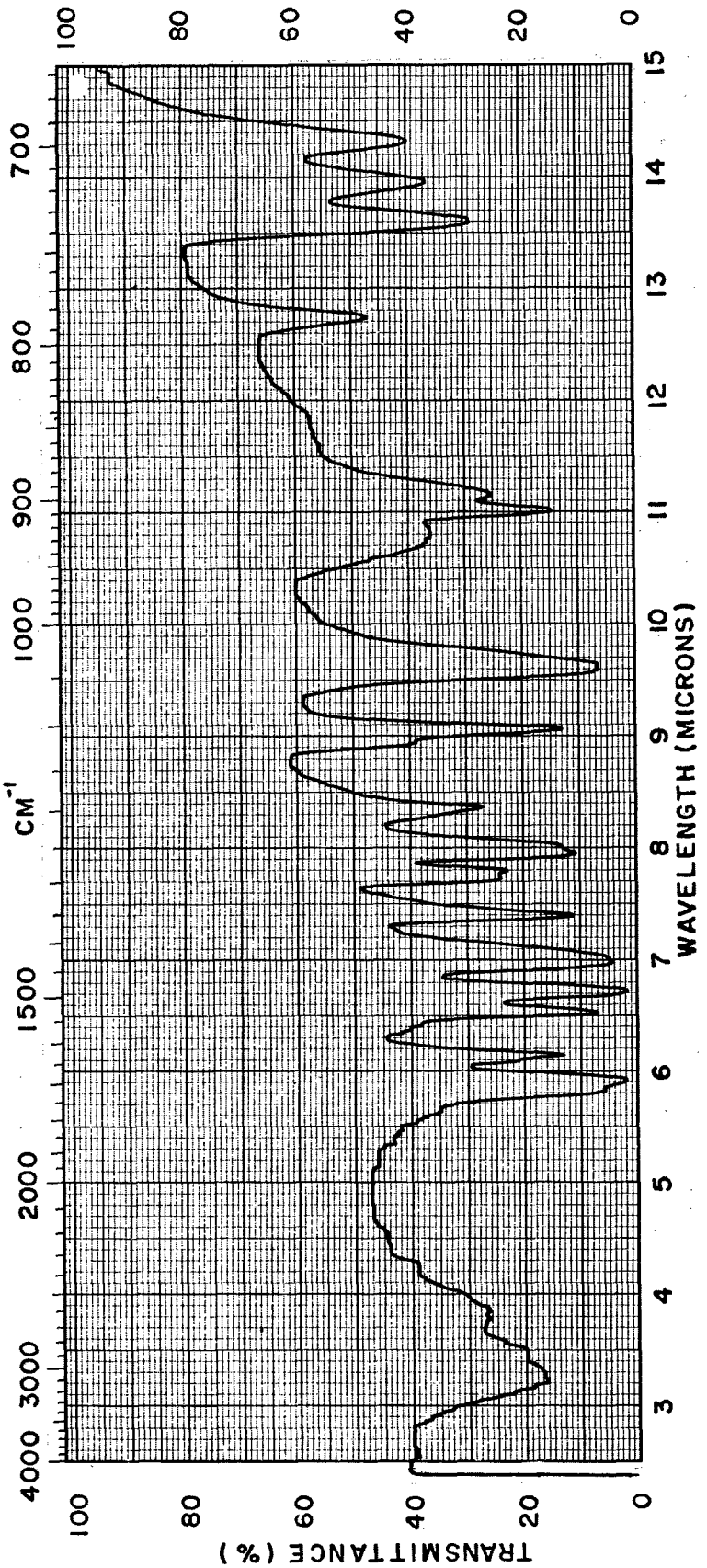

Figure 5. 2,3,4,5-Tetrafluorobenzoic Acid

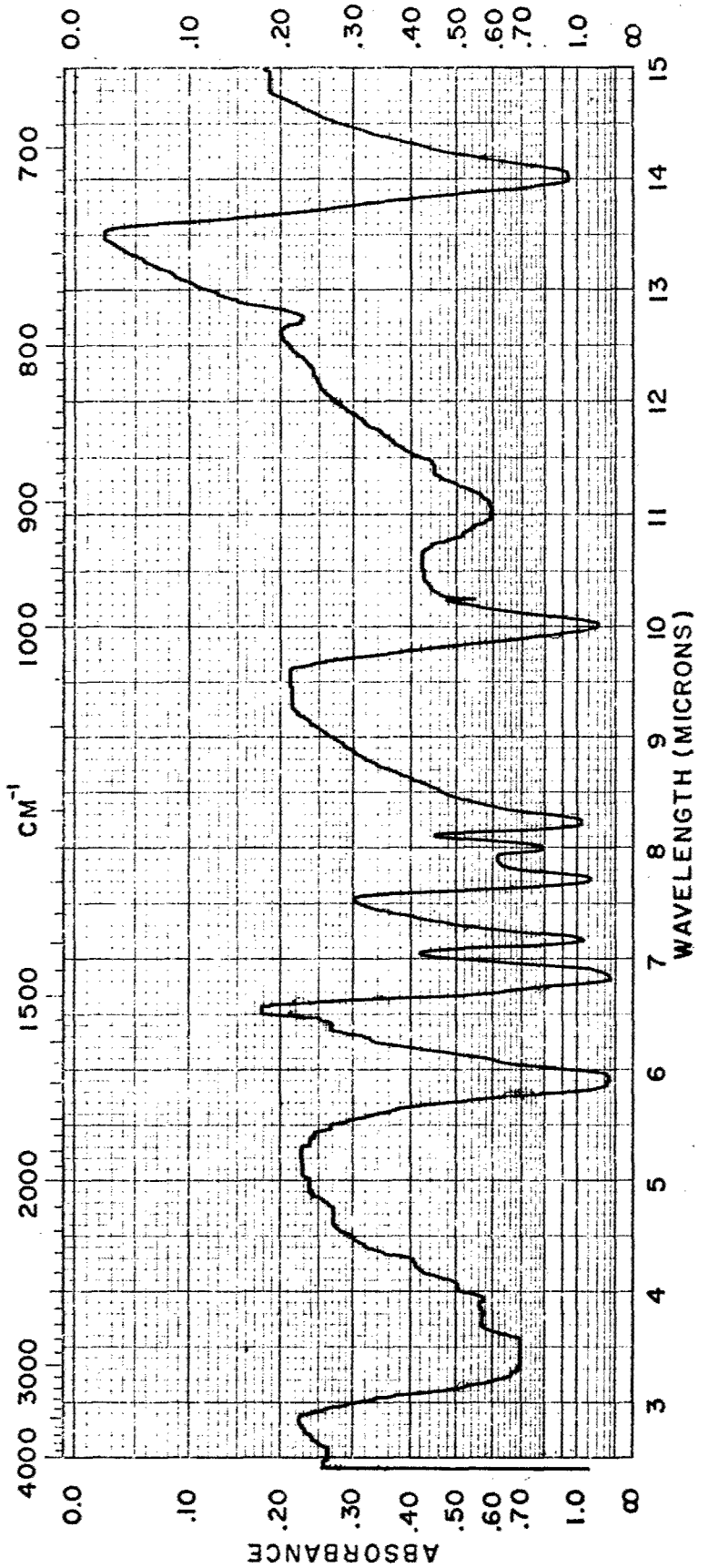

Figure 6. 2,3,5,6-Tetrafluoroterephthalic Acid

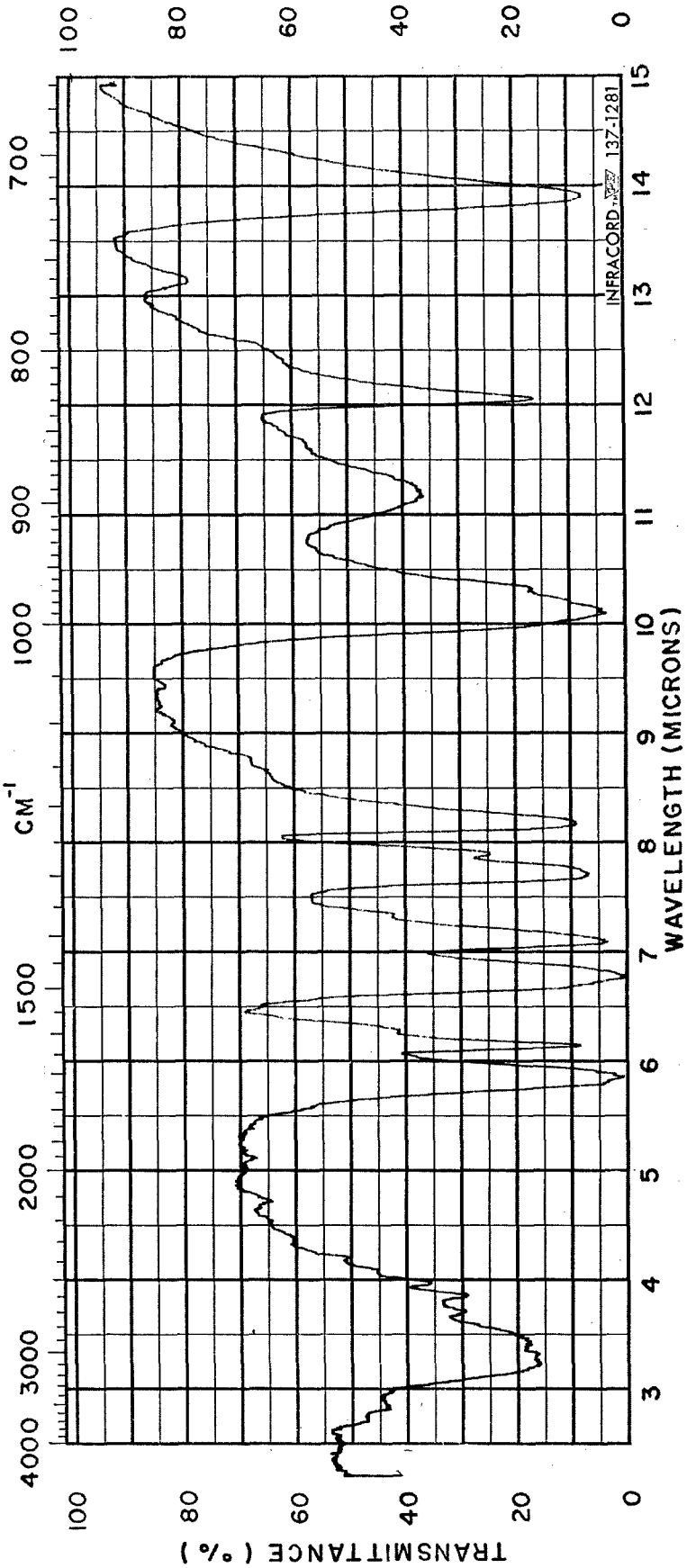

Figure 7. 4-Bromo-2,3,5,6-tetrafluorobenzoic Acid

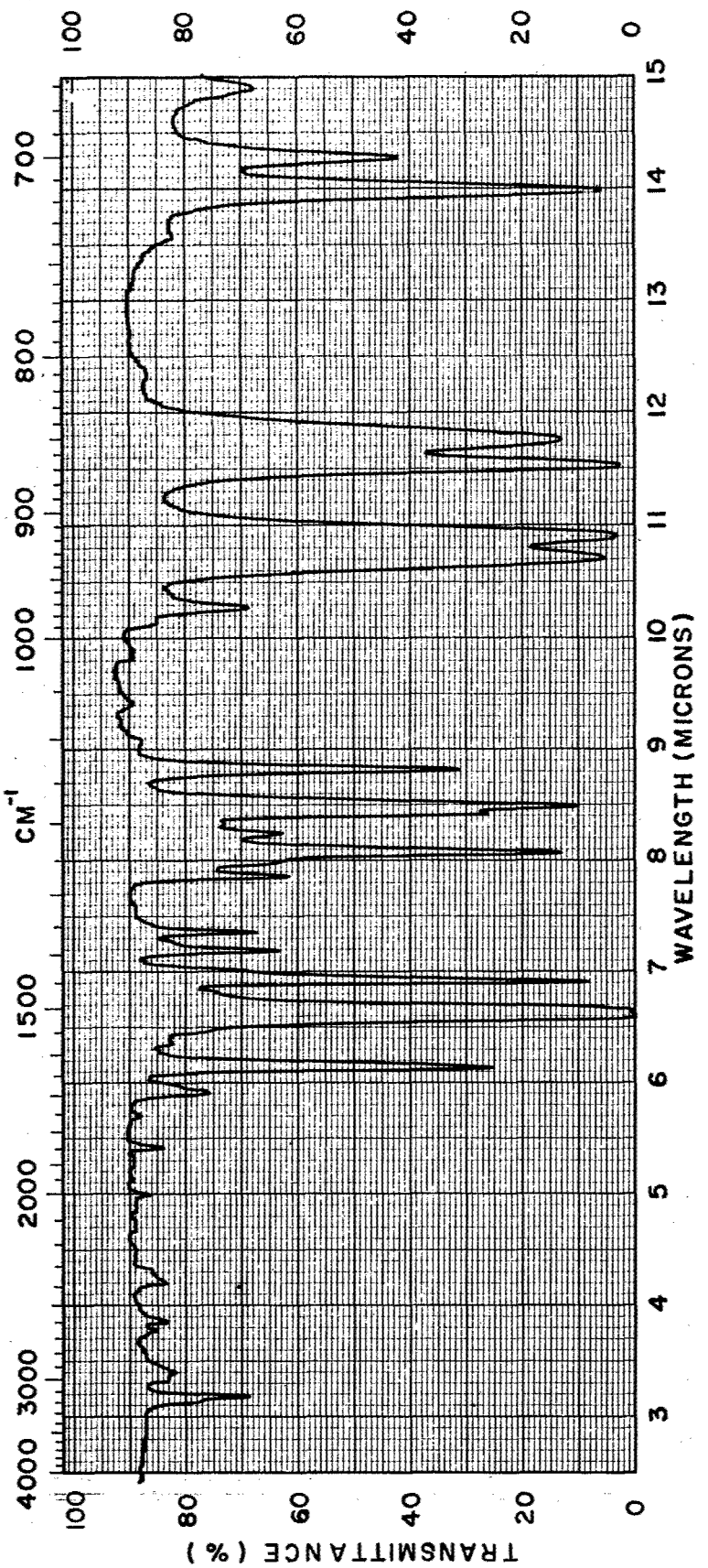

Figure 8. 4-Bromo-2,3,5,6-tetrafluorobenzene

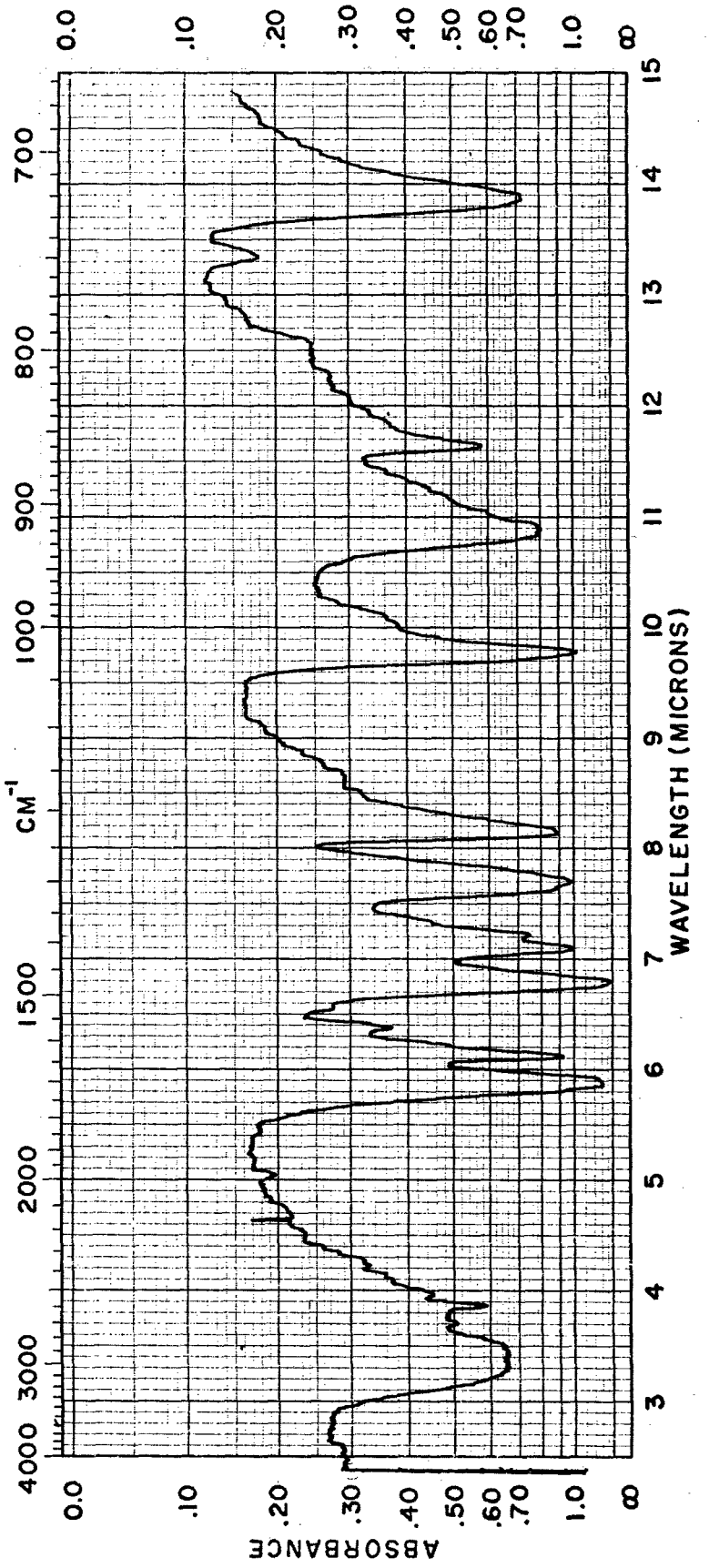

Figure 9. 4-Thiol-2,3,5,6-tetrafluorobenzoic Acid

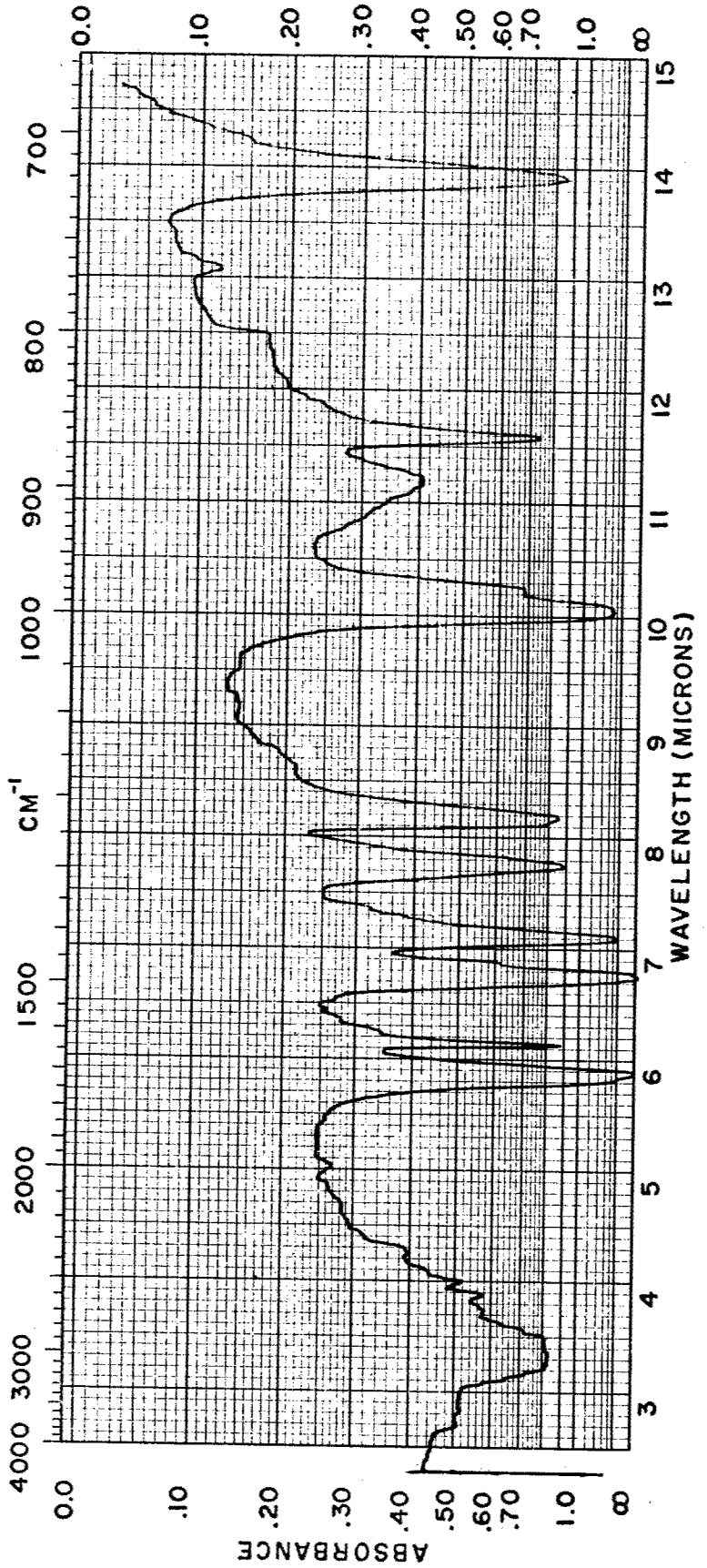

Figure 10. 4-Chloro-2,3,5,6-tetrafluorobenzoic Acid

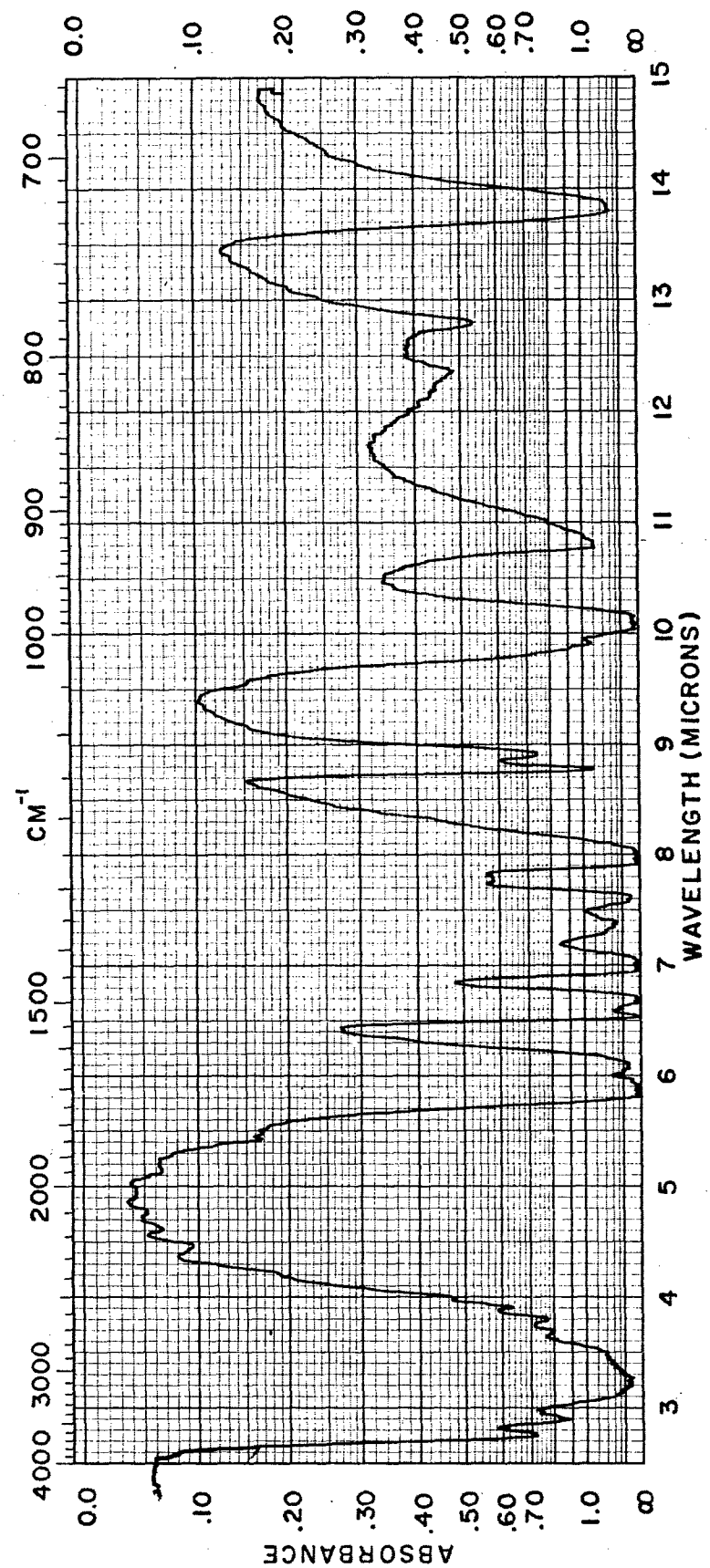

Figure 11. 4-Hydroxy-2,3,5,6-tetrafluorobenzoic Acid

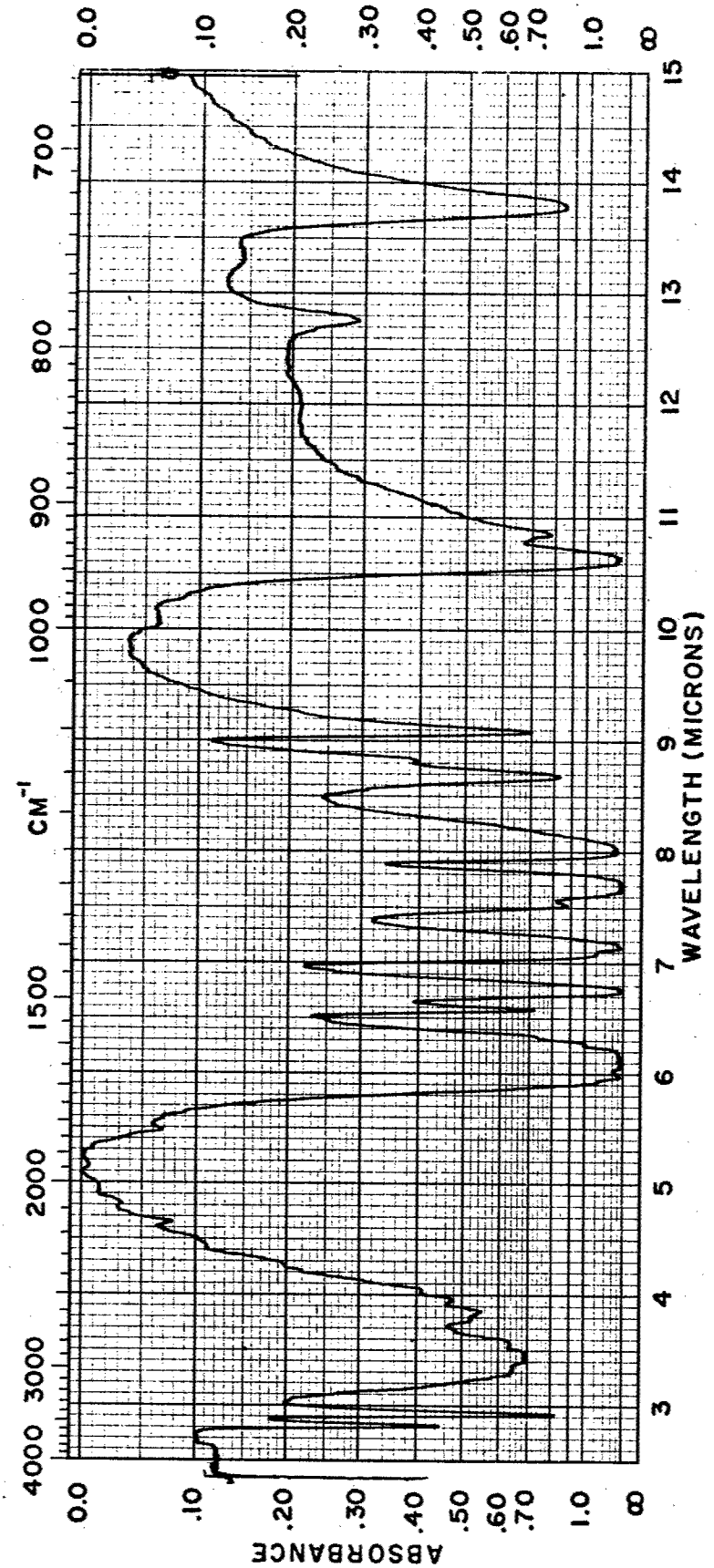

Figure 12. 4-Amino-2,3,5,6-tetrafluorobenzoic Acid

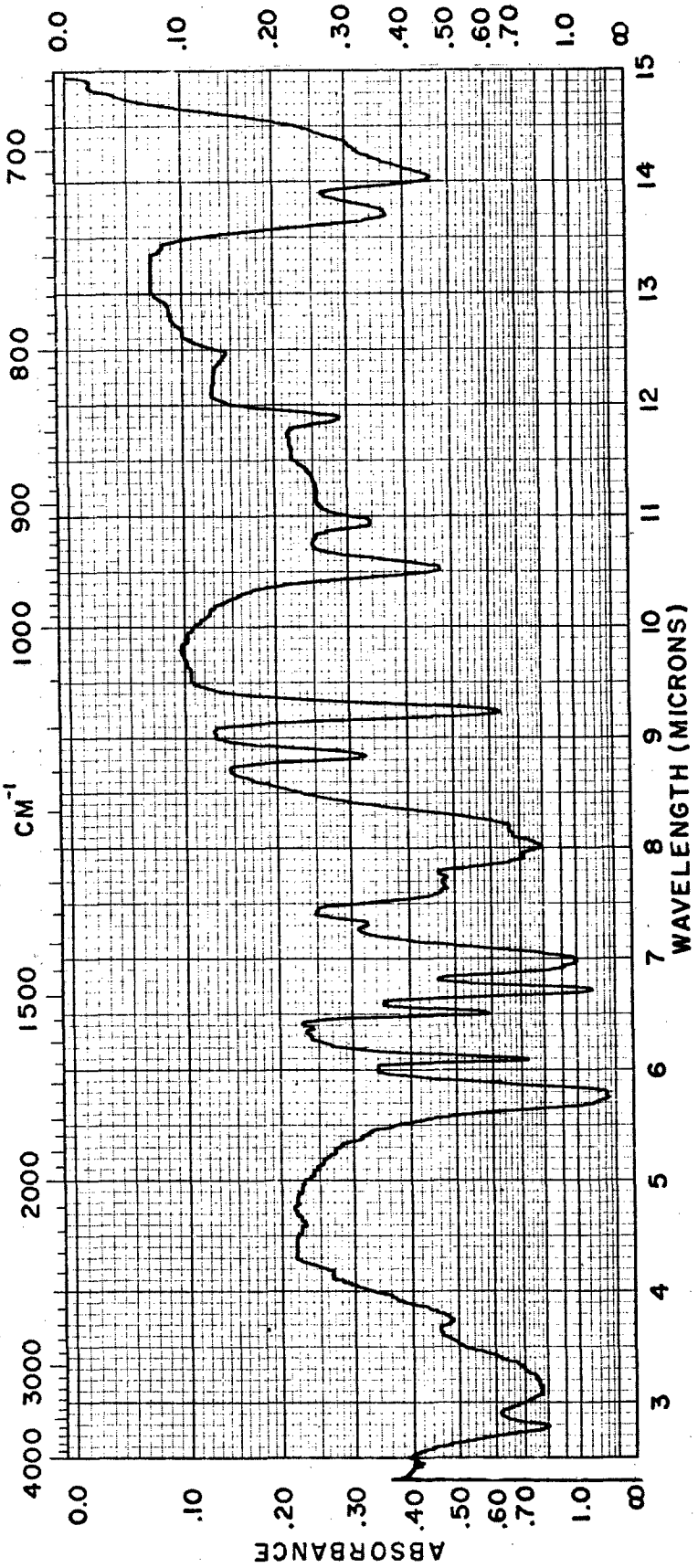

Figure 13. 2,3,4,5-Tetrafluorophthalic Acid

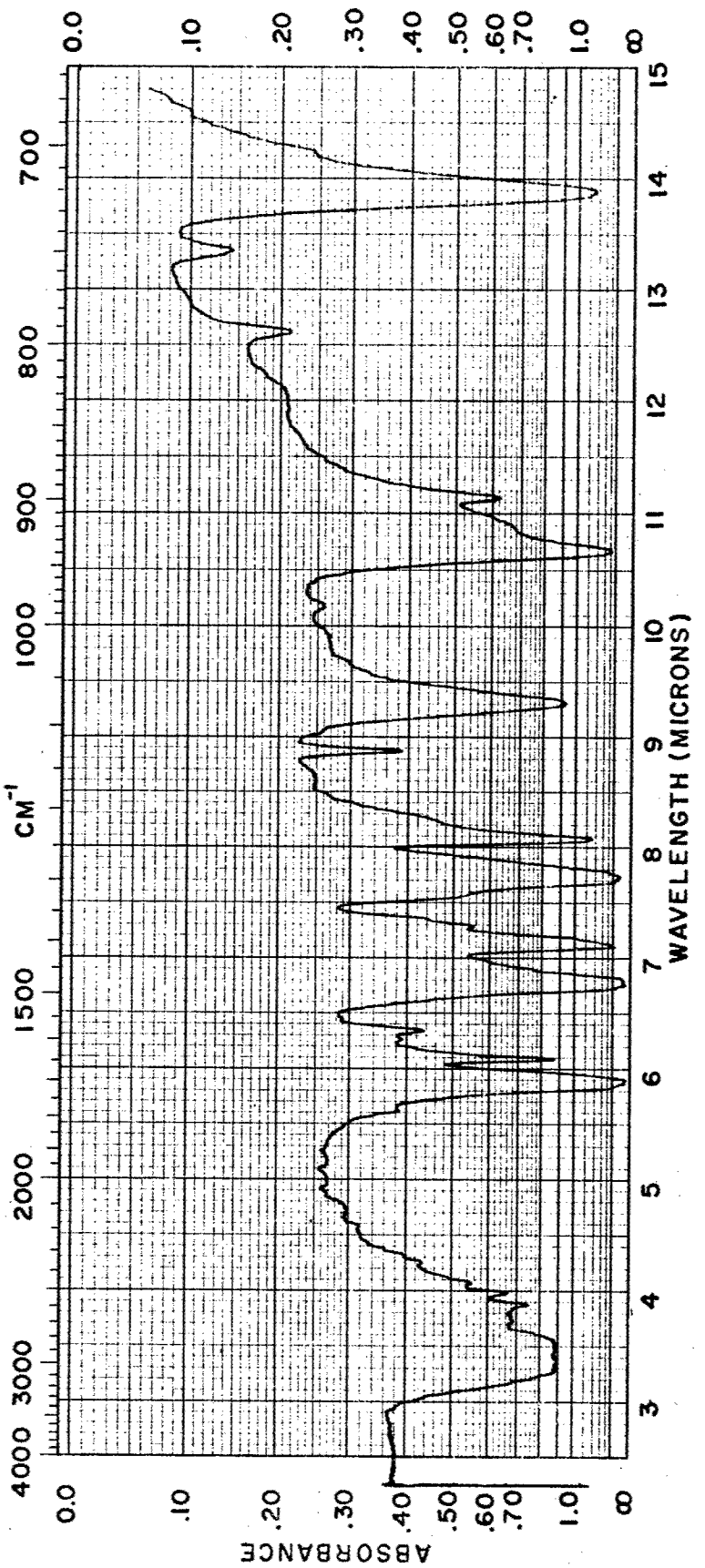

Figure 14. 4-Methyl-2,3,5,6-tetrafluorobenzoic Acid

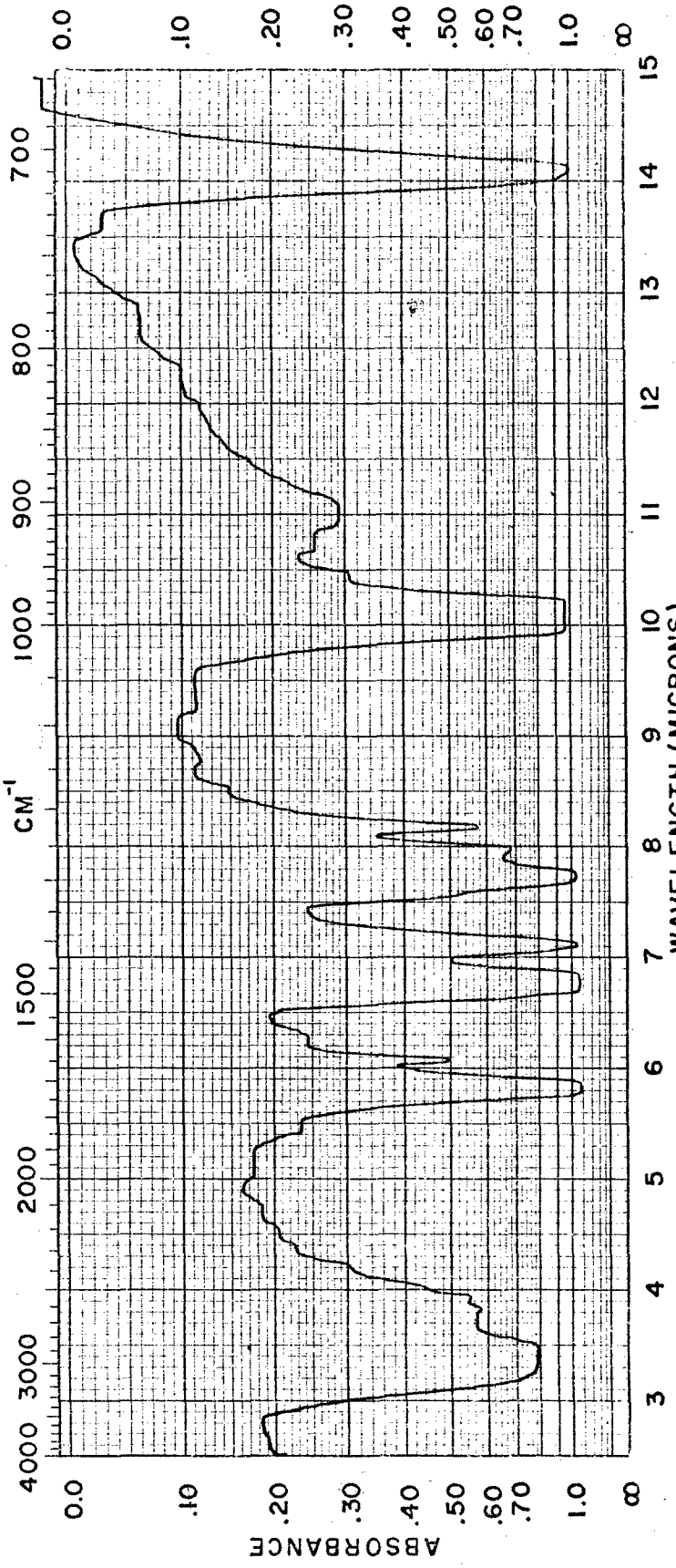

Figure 15. 2,2',3,3',5,5',6,6'-Octafluoro-4,4'-dicarboxylic Acid

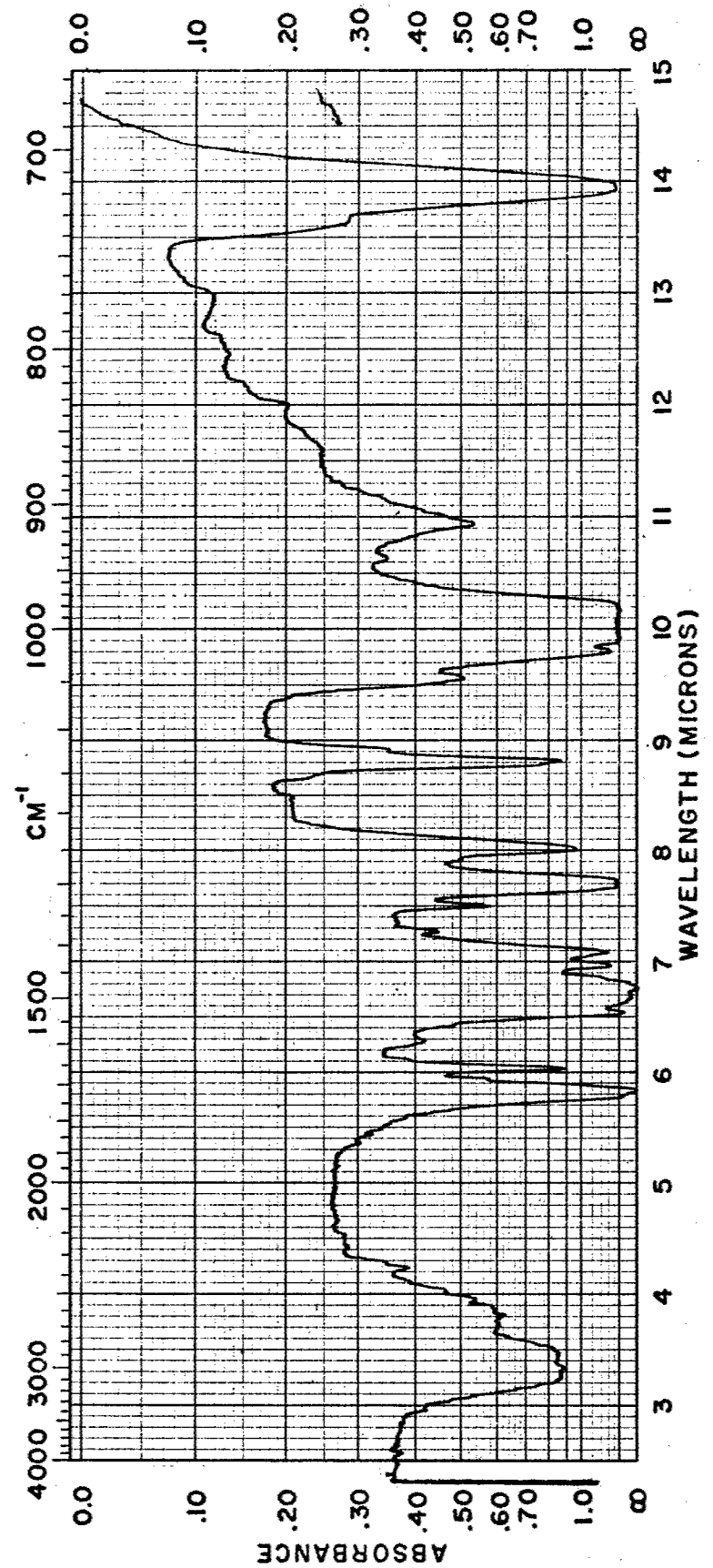

Figure 16. 4-Carboxy-nonafluorobiphenyl

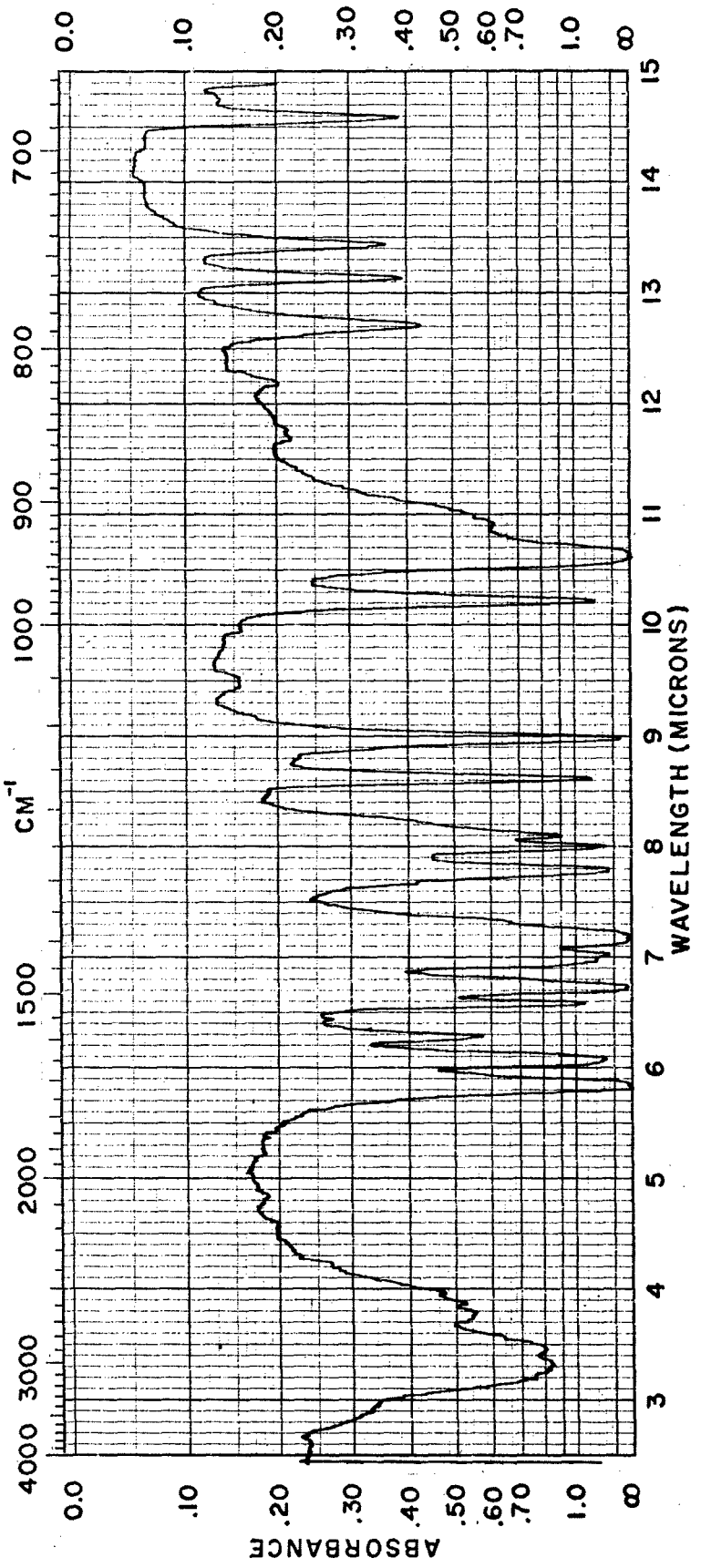

Figure 17. 2-Carboxy-heptafluoronaphthalene

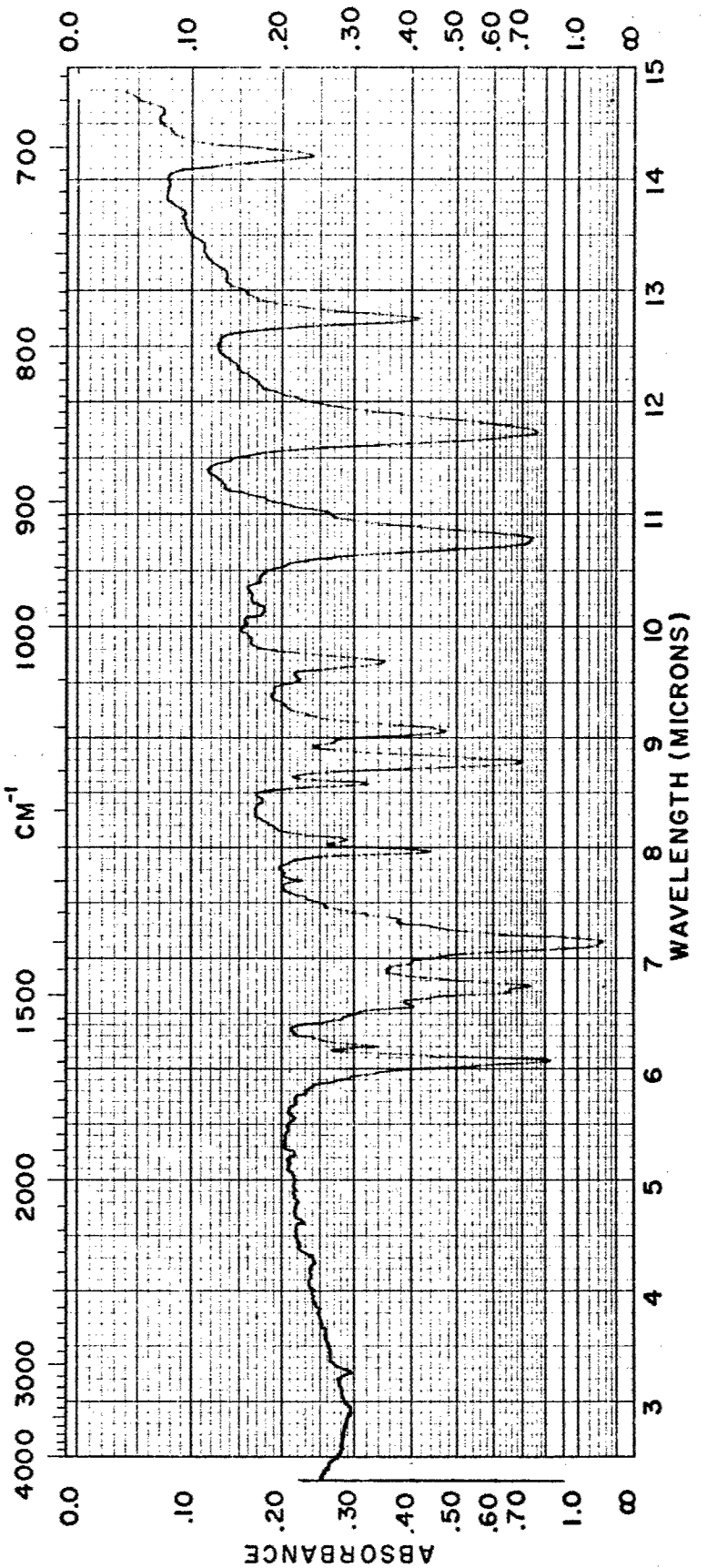

Figure 18. 2-Hydro-heptafluoronaphthalene

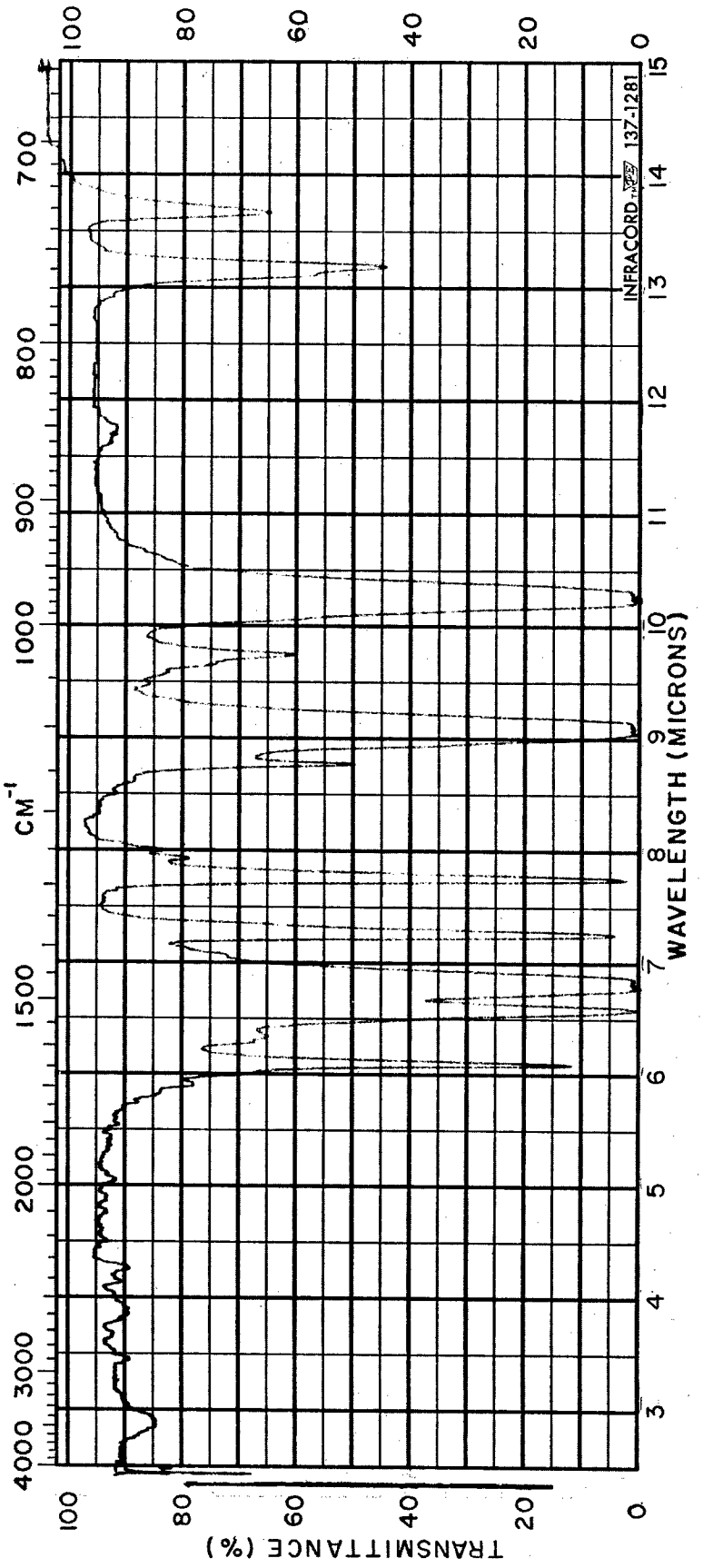

Figure 19. Tetra(pentafluorophenyl)silane

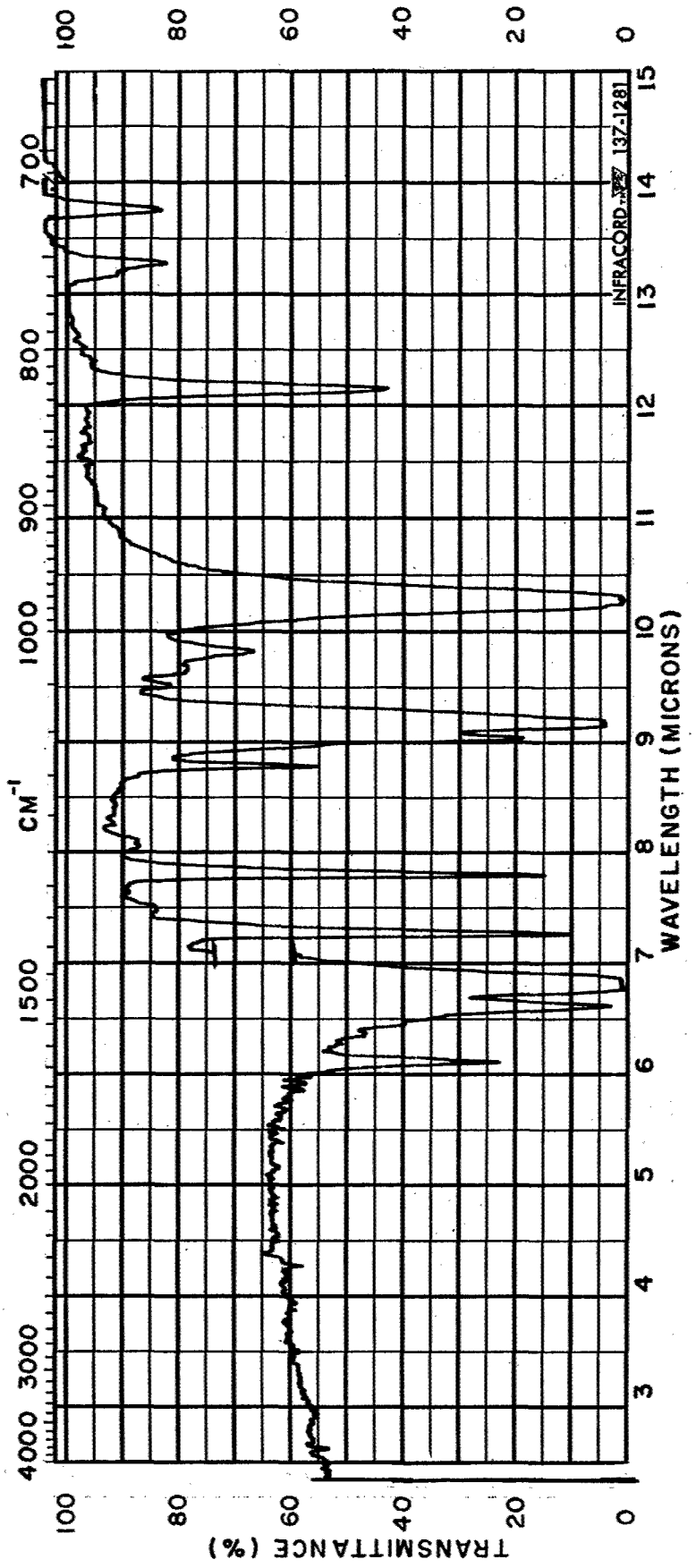

Figure 20. Tetra(pentafluorophenyl)germane

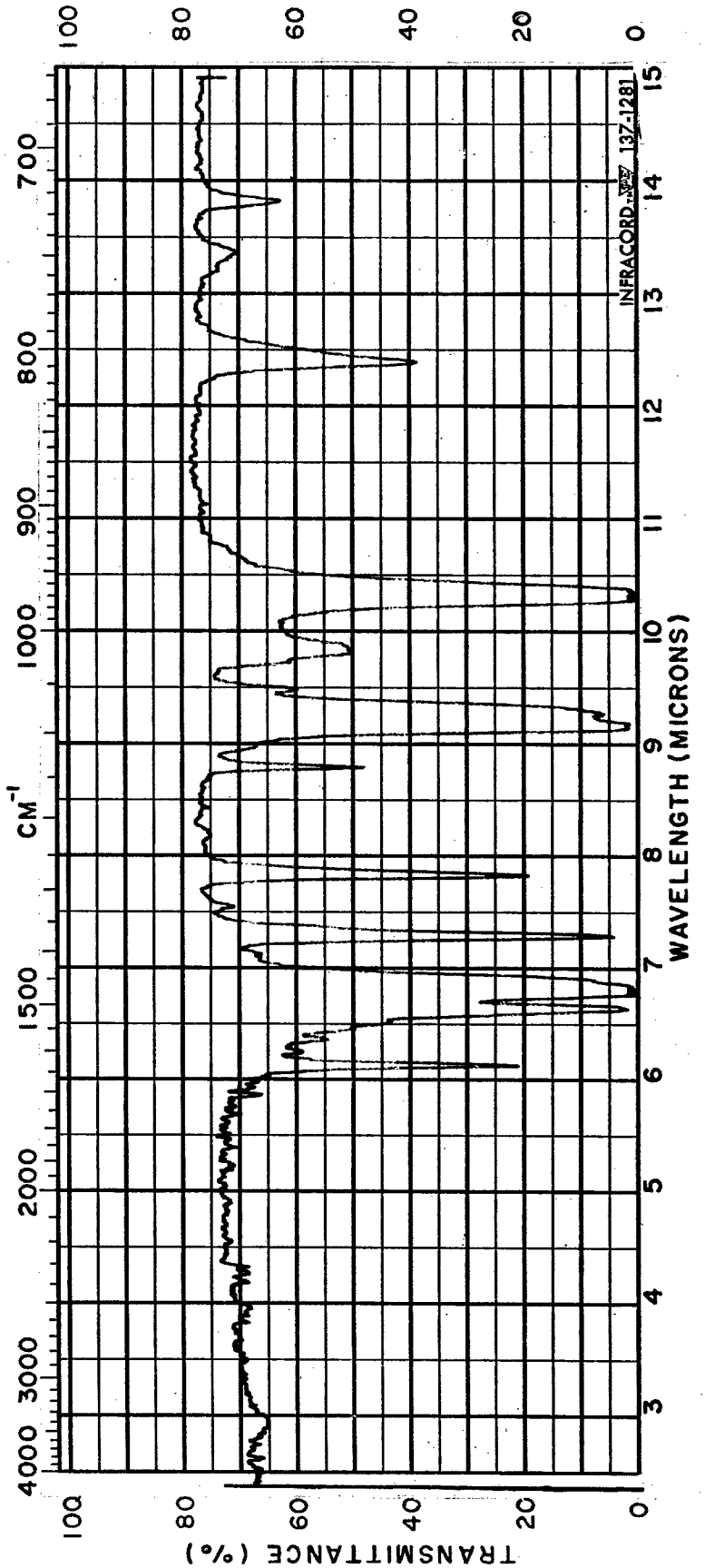

Figure 21. Tetra(pentafluorophenyl)tin

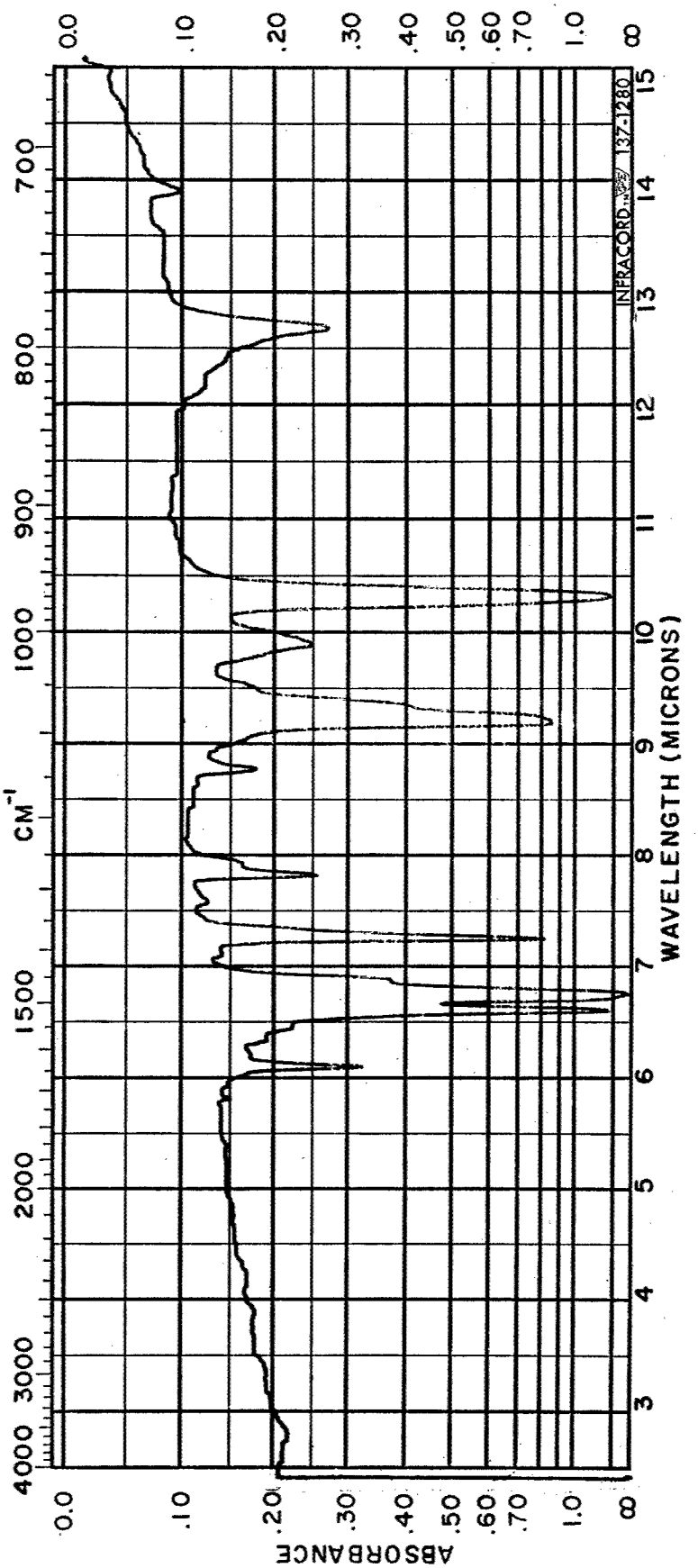

Figure 22. Tetra(pentafluorophenyl)lead

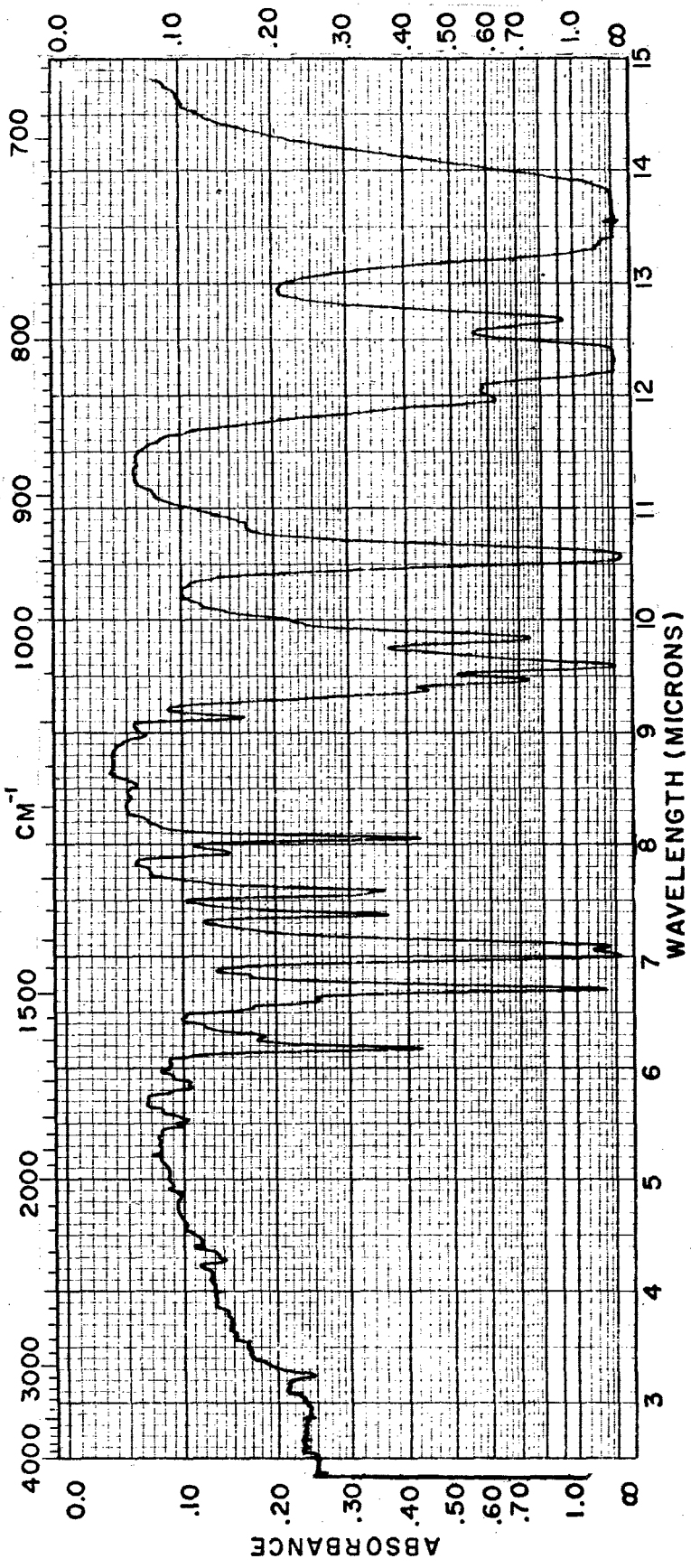

Figure 23. Bis(cyclopentadienyl)bis(pentafluorophenyl)zirconium

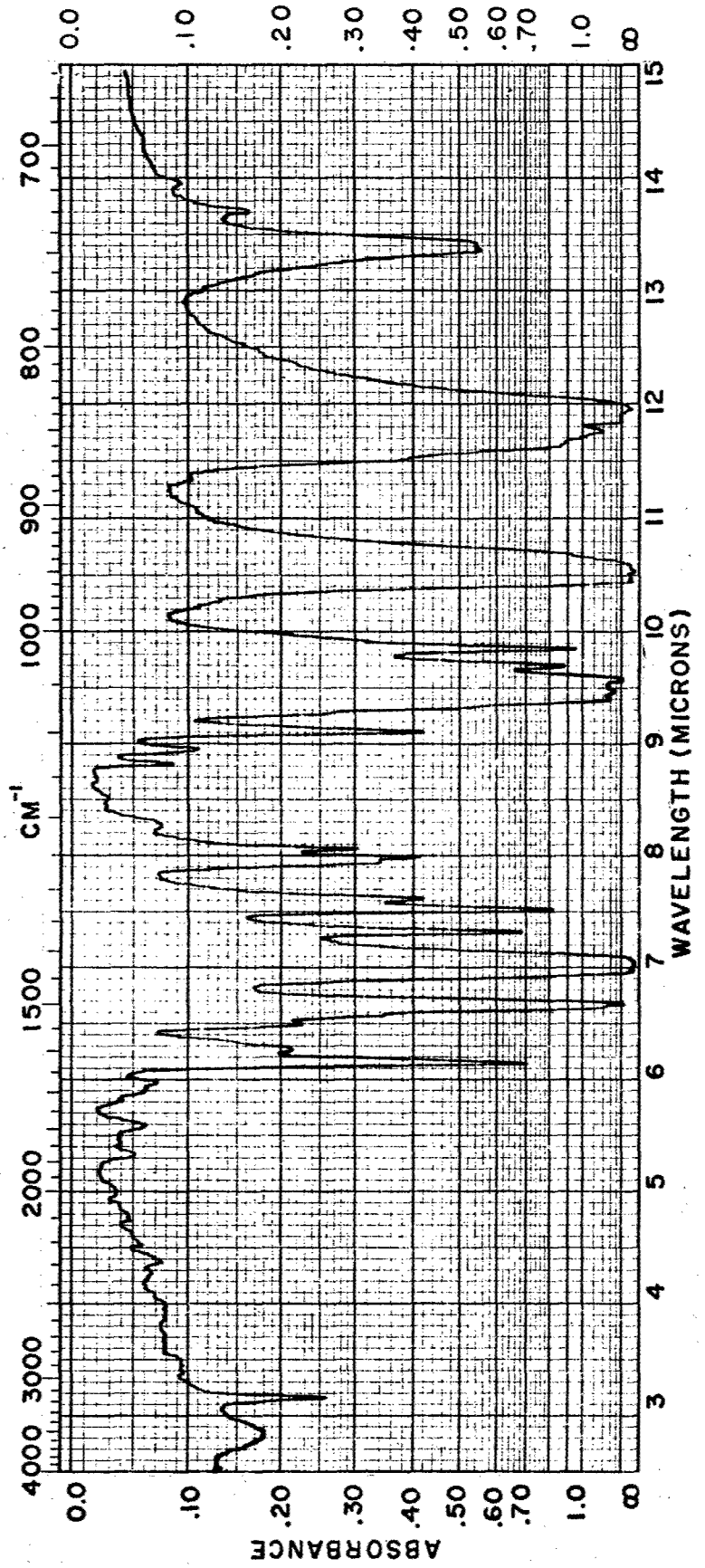

Figure 24. Bis(cyclopentadienyl)bis(pentafluorophenyl)titanium

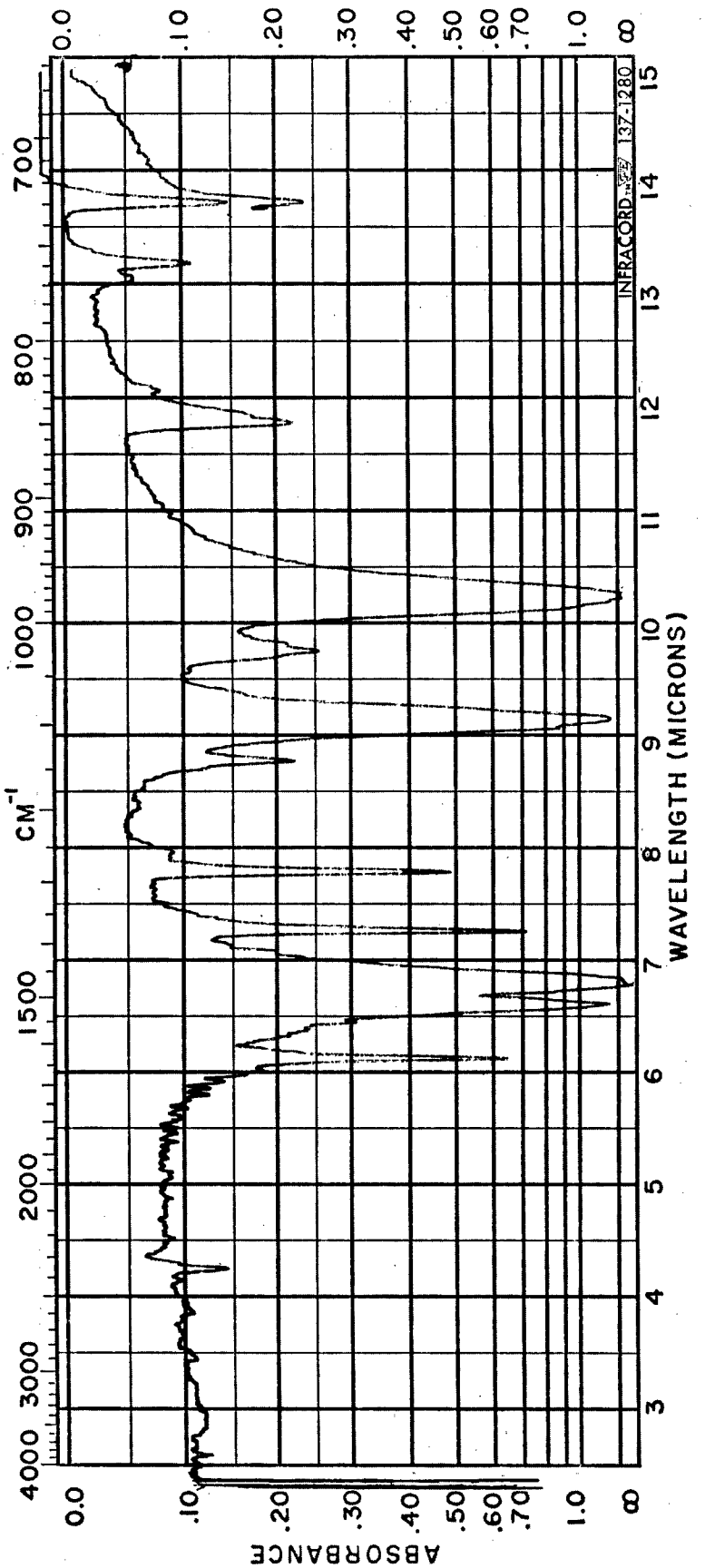

Figure 25. Tri(pentafluorophenyl)phosphine

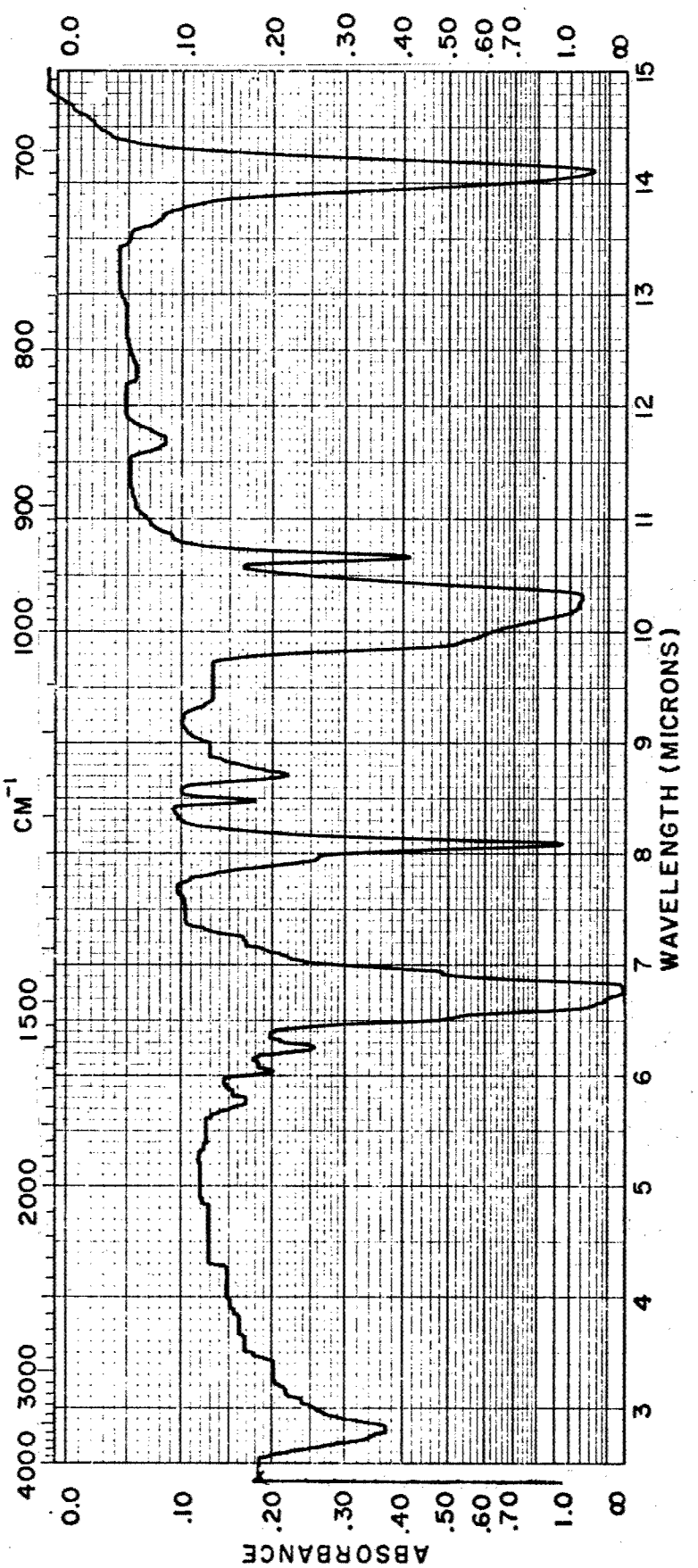

Figure 26. Poly(perfluorophenylene)polymer

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4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
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5. AUTHOR(S) *(Last name, first name, initial)*
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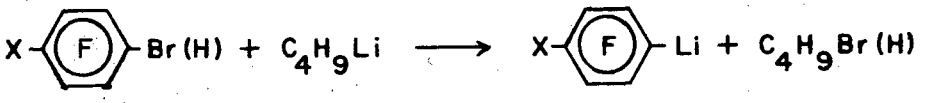
13. ABSTRACT

Polyfluoroaryllithium and polyfluoroarylmagnesium compounds have been prepared and their chemical reactions studied. These chemical intermediates may be conveniently prepared by either a metal-halogen or metal-hydrogen interconversion reaction. Either Grignards (C_2H_5MgBr) or organolithiums (C_4H_9Li) can be used as the source of the metal. In general, the organolithium-bromine interconversions have been found to be the preferred synthesis route. Organolithium intermediates containing functional groups, e.g., H, F, Cl, CH_3, CF_3 SH, OH, CO_2H (=X) have been prepared by this procedure.



Perfluoroaryllithium intermediates of benzene, biphenyl, and naphthalene have been similarly prepared.

Reactions of certain organolithium intermediates with water, carbon dioxide, sulfur, chlorine, hexafluoroacetone, and metallic halides have been studied. By this procedure numerous difunctional monomeric compounds of perfluoro-benzene, -biphenyl, and -naphthalene can be prepared. Pentafluorophenyllithium or pentafluorophenylmagnesium bromide react with various metallic halides of group IV and V elements to yield novel perfluorophenylorganometallic compounds $(C_6F_5)_nM^n$, where M = Si, Ge, Sn, Pb, or P.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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Reactions with cyclopentadienyl metallic halides yield $(C_5H_5)_2M'(C_6F_5)_2$, where M' = Ti and Zr. Physical and chemical properties of these new pentafluorophenylorganometallic compounds have been studied. In general it has been found that in most instances (except in $(C_6F_5)_4Si$) the presence of a perfluorophenyl group increases the thermal stability of the compound. One other noteworthy feature of these compounds is their enhanced oxidative stability. The presence of fluorine in these compounds increases their vapor pressure considerably. This is evidenced by their ease of sublimation and passage through a vapor phase chromatographic column.

In addition, the polymerization of pentafluorophenyllithium has been studied. This reaction intermediate is stable at -65°. On warming up to room temperature, this compound polymerizes to a polyperfluorophenylene polymer which is believed to be para-oriented. This polymer has unusual and desirable properties. It is insoluble in most organic solvents and is chemically inert to most reagents. Its major thermal decomposition occurs above 700° (centigrade).

Potential applications of certain perfluoroaromatic compounds have been studied. The perfluorophenyltin and phosphorus compounds show excellent anti-oxidant and anti-corrosion activity in certain fluorine-containing high temperature candidate fluids. Tris(pentafluorophenyl)phosphine inhibits the degradation and corrosion of titanium and steel alloys by certain polyperfluoroalkyl ether high temperature operational fluids. Vapor deposition of titanium can be accomplished by the use of bis(cyclopentadienyl)bis(pentafluorophenyl)-titanium. This titanium organometallic has the oxidative and thermal stability requirements necessary in vapor phase deposition technology. High temperature greases have been made utilizing the desirable properties of the polyperfluorophenylene polymer.