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Derivatives of Trifluorovinylsulfur Pentafluoride and F-(tert-butyl) Hypochlorite

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Title: Derivatives of Trifluorovinylsulfur Pentafluoride and F-(tert-butyl) Hypochlorite

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Trifluorovinylsulfur pentafluoride dimerizes to $(SF_5CFCF_2)_2$ in the presence of cesium fluoride. Two derivatives of trifluorovinylsulfur pentafluoride, $SF_5CF(CF_3)C(O)F$ and $SF_5CF(CF_3)C(O)NH_2$, were used to prepare the new compounds, $SF_5CF(CF_3)CO_2H$ and $SF_5CF(CF_3)CN$, respectively. The first was prepared by reacting the SF_5-acid fluoride with water, while the second involved the abstraction of water from the SF_5-amide using P_4O_{10}. The attempted preparation of a bis-pentafluorosulfur ketone and a pentafluoro-

sulfur containing acid anhydride were unsuccessful.

Selected transition and post transition metal chlorides and elements undergo oxidative displacement and oxidative addition reactions with F-(tert-butyl) hypochlorite, $(CF_3)_3COCl$, to form new F-(tert-butoxides). Preliminary studies with selected aromatic systems were also carried out.

When $(CF_3)_3COCl$ reacted with $VOCl_3$, the new compound, $VO[OC(CF_3)_3]_3$ was formed. Similarly, $SbCl_5$ reacted with $(CF_3)_3COCl$ to form a white crystalline solid that could not be structurally identified. $(CF_3)_3COCl$, however, did not react with Cu_2Cl_2, UCl_4, $SnCl_4$, or $SiCl_4$ under the reaction conditions employed.

A new preparation of $Ti[OC(CF_3)_3]_4$ was attempted using $(CF_3)_3COH$ and $TiCl_4$, however, no reaction occurred until the base, $(CH_3CH_2)_2NH$, was added. A mixture containing five compounds was formed including the desired $Ti[OC(CF_3)_3]_4$. The major product of the reaction was identified as $(CF_3)_3COH \cdot HN(CH_2CH_3)_2$.

$(CF_3)_3COCl$ was found to be extremely reactive towards the aromatic compounds, benzene and triphenyl phosphine. In one reaction with benzene, over 88 products were separated by gas chromatography.

With the elements, Pb, Te, Bi, S_8, and I_2, the corresponding F-(tert-butoxides), $Pb[OC(CF_3)_3]_2$, $Te[OC(CF_3)_3]_4$, $Bi[OC(CF_3)_3]_3$, $S[OC(CF_3)_3]_4$, and

$I[OC(CF_3)_3]_3$, were formed. With CF_3I, $(CF_3)_3COCl$ forms $CF_3I[OC(CF_3)_3]_2$. Reactions of $(CF_3)_3COCl$ with Br_2, $CoBr_2$, CsBr, and CsI were less fruitful, giving unidentifiable intermediates or products. Si did not react with $(CF_3)_3COCl$ under the reaction conditions used.

Infrared, NMR, and mass spectra are presented in order to support the proposed structures of the new compounds formed.

DERIVATIVES OF
TRIFLUOROVINYLSULFUR PENTAFLUORIDE
AND
F-(TERT-BUTYL) HYPOCHLORITE

by

JO ANN MARIE CANICH

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INTRODUCTION

Trifluorovinylsulfur Pentafluoride

Trifluorovinylsulfur pentafluoride, $SF_5CF=CF_2$, was first prepared in 1961 in an 82% yield, through the dehydrochlorination of 2-chloro-1,2,2-trifluoroethylsulfur pentafluoride (1). It has since been prepared by the dehydrobromination of 2-bromo-1,2,2-trifluoroethylsulfur pentafluoride in a comparable yield of 83% (2). The compound is a clear colorless liquid which boils at 19°C (1). It is stable when heated up to 300°C in Pyrex-glass for up to six hours, however, when subjected to ultraviolet light or γ-radiation, it decomposes via the homolysis of the $C-SF_5$ linkage. Decomposition products include SF_6, S_2F_{10}, SOF_2, SO_2F_2, and SiF_4 (3). In the presence of electrophillic reagents such as $AlCl_3$, trifluorovinylsulfur pentafluoride is unstable. In this case, with prolonged heating, S_2Cl_2, Cl_2, C_2F_6, and SF_4 are formed (4). The infrared spectrum of trifluorovinylsulfur pentafluoride shows absorptions at 1782 (s), 1351 (s), 1246 (s), 1089 (m), 898 (vs), 862 (vs), 706 (m,sh), 702 (m), 698 (m,sh), 657 (m,sh), 654 (m), 650 (m,sh), 618 (m,sh), 614 (m), 610 (m,sh), 573(m), and 536(w) cm^{-1} which include absorptions characteristic of C=C, C-F, and S-F bonds (5). The ^{19}F NMR spectrum is typical of compounds containing the SF_5-group, with the axial SF fluorine showing a nine line pattern with line number six at 69.3 ppm relative to Freon-11. The equatorial SF fluorines are split roughly into a doublet centered at 59.2 ppm. Both axial and equatorial fluorines are further split into multiplets. The resonance of the vinyl fluorine alpha to the SF_5-group is seen at -163.2 ppm, while the Z and E geminal vinyl fluorines are at -99.9 and -100.4 ppm, respectively. These resonances are split approximately into quintets of equally intense doublets. The quintet originates from the coupling between the vinyl and the four equatorial fluorine nuclei, while the doublet splitting arises from the coupling between the vinyl and the single axial fluorine nucleus. Additional splitting is observed (6).

Trifluorovinylsulfur pentafluoride provides a convenient route in the preparation of fluorinated aklylsulfur pentafluoride compounds. For example, in the presence of ultraviolet light, chlorine gas readily adds across the double bond forming, 1,2-dichlorotrifluoroethylsulfur pentafluoride (1):

I-1 $SF_5CF=CF_2 + Cl_2 \longrightarrow SF_5CFClCF_2Cl$

With bromine, 1,2-dibromotrifluoroethylsulfur pentafluoride is formed, but only when the mixture is exposed to light:

I-2 $SF_5CF=CF_2 + Br_2 \longrightarrow SF_5CFBrCF_2Br$

Chlorine, bromine, and trifluorovinylsulfur pentafluoride when heated together give a mixture of compounds including $SF_5CFClCF_2Br$ (13%), $SF_5CFClCF_2Cl$ (1%), $SF_5CFBrCF_2Cl$ (15%), and $SF_5CFBrCF_2Br$ (51%). With hydrogen bromide, products include SF_5CFHCF_2Br (48%) and $SF_5CFBrCF_2Br$ (17.5%). Similarly, trifluoroiodomethane produces a low yield addition product, $SF_5CFICF_2CF_3$ (3). With iodine monofluoride, which is generated _in situ_ from a mixture of iodine and iodine pentafluoride in the presence of aluminum triodide and aluminum metal, trifluorovinylsulfur pentafluoride reacts to form 1-iodotetrafluoroethylsulfur pentafluoride:

I-3 $SF_5CF=CF_2 + (IF) \longrightarrow SF_5CFICF_3$

This compound undergoes reaction with ethylene in the presence of ultraviolet irradiation (4):

I-4 $SF_5CFICF_3 + CH_2=CH_2 \longrightarrow SF_5CF(CF_3)CH_2CH_2I$

The indirect addition of HF (via KF/formamide) to trifluorovinylsulfur pentafluoride forms 1-hydryltetrafluoroethylsulfur pentafluoride (7):

I-5 $SF_5CF=CF_2 + (HF) \longrightarrow SF_5CFHCF_3$

Methanol/sodium methoxide reacts with trifluorovinylsulfur pentafluoride forming 1,2,2-trifluoro-2-methoxyethylsulfur pentafluoride in high yields (3):

I-6 $SF_5CF=CF_2 + CH_3OH \xrightarrow{CH_3ONa} SF_5CFHCF_2OCH_3$

With silver fluoride in the presence of acetonitrile, trifluorovinylsulfur pentafluoride reacts forming 1-pentafluorosulfur-F-ethylsilver with was isolated as the acetonitrile solvate:

I-7 $SF_5CF{=}CF_2 + AgF + CH_3CN \longrightarrow SF_5CFAgCF_3{\cdot}CH_3CN$

This compound was used to prepare five new compounds containing the SF_5-group in addition to several side products:

I-8 $SF_5CFAgCF_3{\cdot}CH_3CN + Br_2 \longrightarrow SF_5CFBrCF_3 + (SF_5CFCF_3)_2$

I-9 $SF_5CFAgCF_3{\cdot}CH_3CN + Cl_2 \longrightarrow SF_5CFClCF_3$

I-10 $SF_5CFAgCF_3{\cdot}CH_3CN + DCl \longrightarrow SF_5CFDCF_3$

I-11 $SF_5CFAgCF_3{\cdot}CH_3CN \xrightarrow{t>50^\circ C} SF_5CF(CF_3)C_2F_5 + (SF_5CFCF_3)_2$

With HX, where X = Cl, Br, OH, or CH_2I, 1-pentafluorosulfur-F-ethylsilver forms 1-hydryltetrafluoroethylsulfur pentafluoride in addition to side products. In the presence of oxygen, the major products formed are SOF_4 and CF_3COF (8, 9).

The reaction of trifluorovinylsulfur pentafluoride with either oxygen or ozone produces the same product, pentafluorosulfuroxydifluoroacetyl fluoride. Side products include SO_2F_2, SOF_2, SF_5OSF_5 and unidentified SF_5-containing species:

I-12 $SF_5CF{=}CF_2 + O_2 \longrightarrow SF_5OCF_2C(O)F$

I-13 $SF_5CF{=}CF_2 + O_3 \longrightarrow SF_5OCF_2C(O)F$

The corresponding acid, amide, and methyl ester of this compound were prepared using water, ammonia, and methanol, respectively (10):

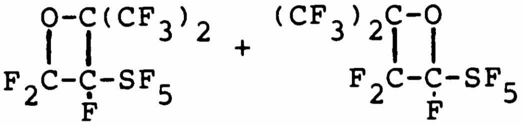
I-14 $SF_5OCF_2C(O)F + H_2O \longrightarrow SF_5OCF_2CO_2H + HF$

I-15 $SF_5OCF_2C(O)F + 2NH_3 \longrightarrow SF_5OCF_2C(O)NH_2 + NH_4F$

I-16 $SF_5OCF_2C(O)F + CH_3OH \longrightarrow SF_5OCF_2CO_2CH_3 + HF$

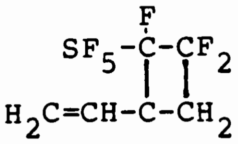
With ultraviolet irradiation, trifluorovinylsulfur pentafluoride reacts with hexafluoroacetone forming 2,2-bis(trifluoromethyl)-3-(pentafluorothio)trifluoro oxetane (major isomer) and 2,2-bis(trifluoromethyl)-4-(pentafluorothio)trifluoro oxetane (minor isomer) (11):

I-17 $2SF_5CF=CF_2 + 2(CF_3)_2CO \longrightarrow$



The cycloaddition between trifluorovinylsulfur pentafluoride and butadiene yields a 1:1 mixture of the cis and trans isomers of 1,1,2-trifluoro-2-pentafluorothio-3-vinylcyclobutane (3):

I-18 $SF_5CF=CF_2 + CH_2=CHCH=CH_2 \longrightarrow$



Trifluorovinylsulfur pentafluoride reacts with bis(trifluoromethyl) peroxide when heated or irradiated with ultraviolet light to give 1,2-bis(trifluoromethoxy) perfluoroethylsulfur pentafluoride. Under similar conditions, it reacts with bis(pentafluorosulfur) peroxide giving 1-pentafluorosulfuroxy-2-pentafluorosulfur perfluoroethane. In both reactions, trace amounts of higher telomers are also formed (12):

I-19 $SF_5CF=CF_2 + CF_3OOCF_3 \longrightarrow SF_5CF(OCF_3)CF_2OCF_3$

I-20 $SF_5CF=CF_2 + SF_5OOSF_5 \longrightarrow SF_5CF_2CF_2OSF_5 + SOF_4$

With tetrafluoroethylene, trifluorovinylsulfur pentafluoride polymerizes in the presence of a free radical initiator, forming a copolymer containing repeating units of both olefins (13). Similarly, vinylidene fluoride reacts with trifluorosulfur pentafluoride to form a copolymer of perfluorovinylsulfur pentafluoride and vinylidene fluoride (3):

I-21 $SF_5CF{=}CF_2 + CF_2{=}CF_2 \longrightarrow [-(CF_2CF_2)_x{\cdot}CF_2CF(SF_5)-]_y$

I-22 $SF_5CF{=}CF_2 + CH_2{=}CF_2 \longrightarrow [-(CH_2CF_2)_x{\cdot}CF_2CF(SF_5)-]_y$

More recent work focuses on the reaction of carbonyl fluoride with trifluorovinylsulfur pentafluoride in the presence of a cesium fluoride catalyst and acetonitrile:

I-23 $SF_5CF{=}CF_2 + COF_2 \longrightarrow SF_5CF(CF_3)C(O)F$

In addition, the corresponding amide and methyl ester have been prepared from this compound (14):

I-24 $SF_5CF(CF_3)C(O)F + 2NH_3 \longrightarrow SF_5CF(CF_3)C(O)NH_2 + NH_4F$

I-25 $SF_5CF(CF_3)C(O)F + CH_3OH \longrightarrow SF_5CF(CF_3)CO_2CH_3 + HF$

It is the purpose of this work to prepare new SF_5-compounds using trifluorovinylsulfur pentafluoride and derivatives thereof. The reactions investigated are summarized in Table I. It is expected that the new SF_5-compounds prepared will provide the basis for further study with regard to the properties, and current uses of compounds containing the SF_5-group. Some of these properties include high dielectric strength, unusual chemical and thermal stability, and biological activity. For example, the high dielectric strength and stability of sulfur hexafluoride allows for its

TABLE I

REACTIONS DISCUSSED IN CHAPTER III

$2SF_5CF{=}CF_2 \xrightarrow{CsF} (SF_5CFCF_2)_2$*

$SF_5CF(CF_3)C(O)F + H_2O \longrightarrow SF_5CF(CF_3)CO_2H$* $+ H_2O$

$SF_5CF(CF_3)CO_2H + P_4O_{10} \longrightarrow SF_5CHFCF_3 + ?$

$SF_5CF(CF_3)C(O)NH_2 + P_4O_{10} \longrightarrow SF_5CF(CF_3)CN$* $+ P_4O_{10} \cdot H_2O$

$2SF_5CF{=}CF_2 + COF_2 + KHF_2 \rightarrow SF_5CF(CF_3)C(O)F + SF_5CHFCF_3 + KF$

$SF_5CF(CF_3)C(O)F + SF_5CF{=}CF_2 \xrightarrow{CsF}$

$CF_3CF_2C(O)F + SF_4 + COF_2$ + a polymeric material

---

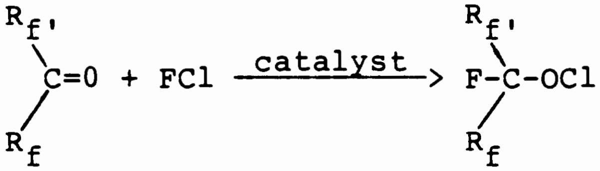
*indicates a new compound

use as an electrical insulator in such things as coaxial cables, high voltage X-ray transformers, and high voltage generators (15). Alone, or as a mixture with sulfur hexafluoride or nitrogen, $SF_5CF{=}CF_2$ can be used as an electrical insulator; it increases the dielectric strength of both mediums (16). Similarly, the addition of SF_5-oxetanes to dielectrics such as sulfur hexafluoride or nitrogen, improves the electrical breakdown strength of the medium (17). The biological activity of $SF_5CF{=}CF_2$, SF_5CFICF_3, and $SF_5CF_2CF_2I$ has given rise to three effective fumigants towards selected insects and insect larvae (18, 19). While these are mildly toxic compounds, S_2F_{10} has been found to be more toxic than phosgene (15). On the more positive side is the biological activity of compounds of the type, $SF_{6-n}(R_f)_n$, which can be used as blood substitutes (20). Many additional examples exist, yet by seeing the diversity of only a few of these, it appears as though the versatility of compounds containing SF_5-groups is almost limitless, especially in consideration of the continued development of new compounds.

F-(tert-butyl) Hypochlorite

F-(tert-butyl) hypochlorite was first prepared by shaking $(CF_3)_3COH$ with ClF at room temperature for a period of 24 hours. An alternate procedure involved reacting the parent alcohol with sodium hydride in diethyl ether to form the sodium salt of F-(tert-butyl) alcohol. The purified salt was reacted with ClF under ambient temperature to form the product in essentially quantitative yield (21). Previous to the formation of F-(tert-butyl) hypochlorite, only primary and secondary perfluoroalkyl hypochlorites had been synthesized, since the reactions involved the addition of ClF across a carbonyl double bond in the presence of a catalyst according to the following equation:

I-26



$$R_{f'}(R_f)C{=}O + FCl \xrightarrow{\text{catalyst}} F\text{-}C(R_{f'})(R_f)\text{-}OCl$$

where $R_{f'}$ = F, CF_3, CF_3, CF_3, and R_f = F, CF_3, F, CF_2Cl. The catalyst was either a metal fluoride, generally CsF, but sometimes KF or RbF (22, 23); a Lewis acid, HF, BF_3, AsF_5, but not PF_5 (24); or the gaseous FNO (25).

F-(tert-butyl) hypochlorite is a clear yellow liquid. The infrared spectrum shows absorptions at 1282 (vs), 1232 (ms), 1190 (mw), 1108 (s), 1003 (s), 983 (s), 788 (w), 758 (m), and 732 (s) cm^{-1} which include absorptions characteristic of C-F, C-O, and O-Cl bonds. The ^{19}F NMR spectrum contains a singlet at -70.1 ppm relative to an internal $CFCl_3$ standard (21). The melting point and boiling point have not been determined due to its hydrolytic instability. Although ordinary alkyl hypochlorites are stable in aqueous media, F-(tert-butyl) hypochlorite reacts with water to form the parent alcohol, $(CF_3)_3COH$. The hydrolytic stability of fluorinated hypochlorites appears to be related to the degree of fluorination in the compound, where the more highly fluorinated compound has a higher degree susceptibility towards hydrolysis. Thus, $(CF_3)_3COCl$ was shown to be the least hydrolytically stable hypochlorite in the following series: $(CF_3)_3COCl < CH_3C(CF_3)_2OCl \sim (CF_3)_2CHOCl < CF_3CH_2OCl \ll (CH_3)_3COCl$ (21). Thermal stability, however, favors the fluorinated hypochlorites over the corresponding alkyl hypochlorites. F-(tert-butyl) hypochlorite shows no tendency to decompose spontaneously at room temperature, and is stable to at least 80°C. At higher temperatures, the compound decomposes to $(CF_3)_2CO$, CF_3Cl, Cl_2, and C_2F_6 (21) according to the following mechanism (23):

I-27 $(CF_3)_3COCl \longrightarrow (CF_3)_3CO\cdot + Cl\cdot$

I-28 $(CF_3)_3CO\cdot \longrightarrow (CF_3)_2CO + CF_3\cdot$

I-29 $CF_3\cdot + Cl\cdot \longrightarrow CF_3Cl$

I-30 $Cl\cdot + Cl\cdot \longrightarrow Cl_2$

I-31 $CF_3\cdot + CF_3\cdot \longrightarrow C_2F_6$

When compared to other fluorinated hypochlorites the order of decreasing thermal stability is: $CF_3OCl > (CF_3)_3COCl \sim CH_3C(CF_3)_2OCl \sim (CF_3)_2CHOCl \sim CF_3CH_2OCl > C_2F_5OCl$ $i\text{-}C_3F_7OCl > SF_5OCl$ (21).

F-(tert-butyl) hypochlorite is a useful reagent in the preparation of F-(tert-butoxides). In many ways, the reaction chemistry is typical of a halogenoid. Like chlorine gas, it is capable of reacting with sulfur dioxide or carbon monoxide; in this case, by inserting the oxide between the O-Cl bond, the corresponding chlorosulfate or chloroformate are formed (21):

I-32 $(CF_3)_3COCl + SO_2 \longrightarrow (CF_3)_3COSO_2Cl$

I-33 $(CF_3)_3COCl + CO \longrightarrow (CF_3)_3COC(O)Cl$

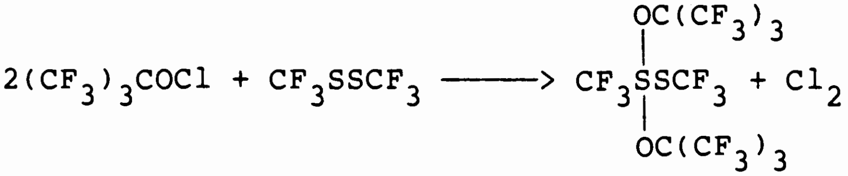
F-(tert-butyl) hypochlorite readily adds to unsaturated systems, forming ethers in near quantitative yields (26):

I-34 $(CF_3)_3COCl + CF_2{=}CF_2 \longrightarrow (CF_3)_3COCF_2CF_2Cl$

I-35 $(CF_3)_3COCl + CH_2{=}CH_2 \longrightarrow (CF_3)_3COCH_2CH_2Cl$

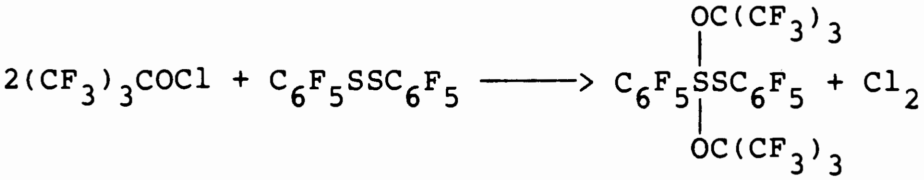
More interesting are its reactions with sulfur compounds where three different reaction modes are possible: oxidative addition, oxidative displacement, or oxidative addition and displacement. Oxidative addition is the only reaction mode possible when CF_3SSCF_3 or $C_6F_5SSC_6F_5$ are reacted with F-(tert-butyl) hypochlorite. With both compounds, however, oxidative addition occurs only at one of the two sulfur atoms leading to the first stable thiosulfuranes in which a four coordinate sulfur (IV) is bonded to a sulfur (II) (27, 28):

I-36



$$2(CF_3)_3COCl + CF_3SSCF_3 \longrightarrow CF_3\underset{\displaystyle OC(CF_3)_3}{\overset{\displaystyle OC(CF_3)_3}{S}}SCF_3 + Cl_2$$

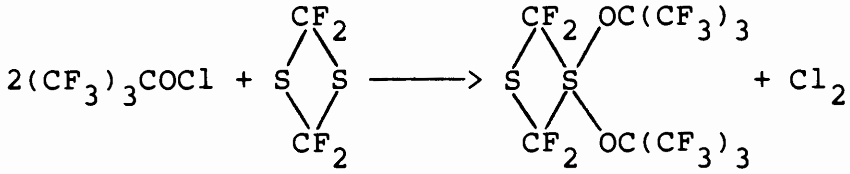
I-37



$$2(CF_3)_3COCl + C_6F_5SSC_6F_5 \longrightarrow C_6F_5\underset{\displaystyle OC(CF_3)_3}{\overset{\displaystyle OC(CF_3)_3}{S}}SC_6F_5 + Cl_2$$

When F-1,3-dithietane reacts with F-(tert-butyl) hypochlorite, again oxidative addition occurs at only one of the two sulfur atoms in the molecule, forming a disubstituted cyclic sulfurane (28):

I-38



With tetrasulfur tetranitride, F-(tert-butyl) hypochlorite oxidatively adds to each of the sulfur atoms with retention of the ring structure, giving tetrathiazyl tetrakis(F-tert-butoxide) (29):

I-39 $4(CF_3)_3COCl + S_4N_4 \longrightarrow N_4S_4[OC(CF_3)_3]_4 + 2Cl_2$

With SCl_2, S_2Cl_2, CS_2, or CCl_3SCl, F-(tert-butyl) hypochlorite oxidatively adds to the sulfur atom, and displaces all other ligands to give tetrakis-F-(tert-butoxy) sulfurane. With CCl_3SCl, $CCl_3OC(CF_3)_3$ is also formed (28):

I-40 $4(CF_3)_3COCl + SCl_2 \longrightarrow S[OC(CF_3)_3]_4 + 3Cl_2$

I-41 $8(CF_3)_3COCl + S_2Cl_2 \longrightarrow 2S[OC(CF_3)_3]_4 + 5Cl_2$

I-42 $(CF_3)_3COCl + CS_2 \longrightarrow S[OC(CF_3)_3]_4$

I-43 $5(CF_3)_3COCl + CCl_3SCl \longrightarrow$

$S[OC(CF_3)_3]_4 + 3Cl_2 + CCl_3OC(CF_3)_3$

One might expect similiar behavior between CCl_3SCl and CF_3SCl, however, when the latter reacts with F-(tert-butyl) hypochlorite, chloro-F-methylbis(F-tert-butoxy) sulfurane is formed instead of the expected tetrakis-F-(tert-butoxy) sulfurane (28):

I-44 $2(CF_3)_3COCl + CF_3SCl \longrightarrow [(CF_3)_3CO]_2SClCF_3 + Cl_2$

CF_3SCl undergoes many reactions which supports the polarity, $CF_3S^{\delta+}Cl^{\delta-}$. Since the chlorine of F-(tert-butyl) hypochlorite has a partial positive charge, e.g. $(CF_3)_3CO^{\delta-}Cl^{\delta+}$, it is believed that the reaction involves initial displacement of the chlorine, followed by the oxidative addition of the hypochlorite to the sulfur atom:

1-45
$$\begin{array}{l} 2(CF_3)_3COCl + CF_3SCl \longrightarrow [(CF_3)_3COSCF_3] + Cl_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad [(CF_3)_3CO]_2SClCF_3 \end{array}$$

While oxidative addition and displacement should be possible when reacting $CF_3S(O)Cl$ with F-(tert-butyl) hypochlorite, only oxidative displacement occurs (28):

I-46 $(CF_3)_3COCl + CF_3S(O)Cl \longrightarrow CF_3S(O)OC(CF_3)_3 + Cl_2$

Oxidative addition does not occur in this case, because of the unavailability of the tightly bound unshared electron pair on the sulfur atom. With SCl_2, CCl_3SCl, and CF_3SCl for example, oxidative addition is more likely, and does occur because of the availability of the two less tightly bound unshared electron pairs. With SF_4, $CF_3S(O)CF_3$, and $CF_3SF_2CF_3$, which all have one unshared electron pair about the sulfur atom, no reaction occurs (28).

F-(tert-butyl) hypolchlorite reacts similiarily with some non-sulfur compounds. With $PClF_4$, PCl_2F_3, and PCl_5, where only oxidative displacement of the chlorine atoms is possible, the expected mono- and di-substituted F-(tert-butoxy) fluorophosphoranes and F-(penta-tert-butoxy) phosphorane are formed (30, 31):

I-47 $(CF_3)_3COCl + PClF_4 \longrightarrow (CF_3)_3COPF_4 + Cl_2$

I-48 $2(CF_3)_3COCl + PCl_2F_3 \longrightarrow [(CF_3)_3CO]_2PF_3 + 2Cl_2$

I-49 $5(CF_3)_3COCl + PCl_5 \longrightarrow P[OC(CF_3)_3]_5 + 5Cl_2$

Interestingly, with phosphoryl trichloride, no reaction occurs. The hydrolysis of F-(penta-tert-butoxy) phosphorane, however, gives the expected product of this reaction (31):

I-50 $3(CF_3)_3COCl + OPCl_3 \not\longrightarrow OP[OC(CF_3)_3]_3 + 3Cl_2$

I-51 $P[OC(CF_3)_3]_5 + H_2O \longrightarrow OP[OC(CF_3)_3]_3 + 2(CF_3)_3COH$

Both oxidative addition and displacement are possible in the reaction between phosphorous trichloride and F-(tert-butyl) hyphochlorite, yet only the latter occurs, forming F-(tri-tert-butoxy) phoshine (31):

I-52 $3(CF_3)_3COCl + PCl_3 \longrightarrow P[OC(CF_3)_3]_3 + 3Cl_2$

With phosphorous trifluoride, the di-substituted F-(tert-butoxy) fluorophosphorane, prepared peviously, is formed. This is the only reported case of the oxidative addition of the hypochlorite to a phosphorous compound (31):

I-53 $2(CF_3)_3COCl + PF_3 \longrightarrow [(CF_3)_3CO]_2PF_3 + Cl_2$

Nitrosyl chloride readily reacts with F-(tert-butyl) hypochlorite forming F-(tert-butyl) nitrite by oxidative dispacement of the chlorine atom (32):

I-54 $(CF_3)_3COCl + NOCl \longrightarrow (CF_3)_3CONO + Cl_2$

This compound was previously prepared in the following manner (33):

I-55 $(CF_3)_2C{=}CF_2 + NOF \longrightarrow (CF_3)_3CN{=}O \xrightarrow[2mo.]{NO_2} (CF_3)_3CONO$

With boron trichloride, oxidative displacement of the chlorine atoms gives F-(tert-butyl) borate (34,35):

I-56 $3(CF_3)_3COCl + BCl_3 \longrightarrow B[OC(CF_3)_3]_3 + 3Cl_2$

F-(tert-butyl) hypochlorite has been found to oxidatively displace the chlorine atoms on both chromyl chloride and titanium tetrachloride (32):

I-57 $2(CF_3)_3COCl + CrO_2Cl_2 \longrightarrow CrO_2[OC(CF_3)_3]_2 + 2Cl_2$

I-58 $4(CF_3)_3COCl + TiCl_4 \longrightarrow Ti[OC(CF_3)_3]_4 + 4Cl_2$

With Vaska's complex, t-$IrCl(CO)(PPh_3)_2$, F-(tert-butyl) hypochlorite reacts to form $Ir[OC(CF_3)_3]_2Cl(CO)L_2$, where L is no longer PPh_3, but rather a complex ligand with $(CF_3)_3CO$- and Cl- groups attached. While F-(tert-butyl) hypochlorite reacts with free carbon monoxide (21), it is interesting to note that the coordinated CO ligand is uneffected by the hypochlorite (32).

F-(tert-butyl) hyporchlorite has also been found to react with mercury metal in the presence of a solvent to form a reactive mercurial:

I-59 $(CF_3)_3COCl + Hg \longrightarrow (CF_3)_3COHgCl$

This mercury salt has been shown to be a useful reagent for the introduction of the F-(tert-butoxy) group into a number of compounds containing a labile halogen. Several reactants and products are listed in Table II (36).

TABLE II

THE REACTIONS OF $(CF_3)_3COHgCl$

Reactants	Products
$(CF_3)_3COHgCl + CH_3I$	$CH_3OC(CF_3)_3$
$(CF_3)_3COHgCl + CF_3SCl$	$CF_3SOC(CF_3)_3$
$(CF_3)_3COHgCl + CF_3C(O)Br$	$CF_3(O)OC(CF_3)_3$
$(CF_3)_3COHgCl + CF_3C(O)SCl$	$CF_3C(O)SOC(CF_3)_3$
$(CF_3)_3COHgCl + (CH_3)_3SiCl$	$(CH_3)_3SiOC(CF_3)_3$
$(CF_3)_3COHgCl + (CH_3)_3SiH$	$(CH_3)_3SiOC(CF_3)_3 + (CF_3)_3COH$
$(CF_3)_3COHgCl + CH_3C(O)Cl$	$CH_3C(O)OC(CF_3)_3$
$(CF_3)_3COHgCl + CNCl$	$(CF_3)_3COCN$

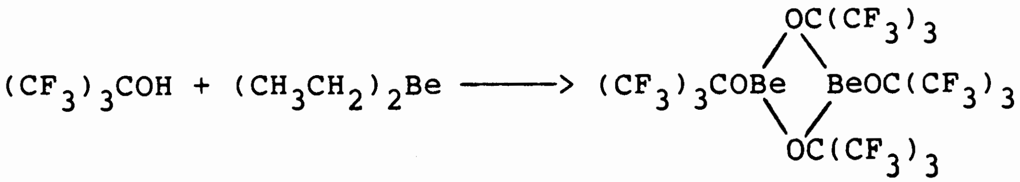
Another method of preparing F-(tert-butoxides) involves direct use of the parent alcohol of F-(tert-butyl) hypochlorite, $(CF_3)_3COH$. The alcohol can be reacted with the appropriate metal, or with a metal hydride in the presence of anhydrous diethyl ether to form the corresponding metal F-(tert-butoxide) (37, 38):

I-60 $(CF_3)_3COH + Na \longrightarrow (CF_3)_3CONa + \frac{1}{2}H_2$

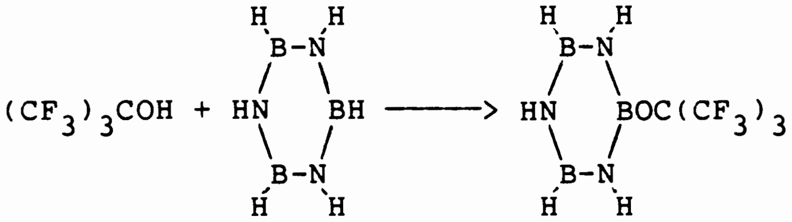
I-61 $(CF_3)_3COH + MH \longrightarrow (CF_3)_3COM + H_2$

$M = Li, Na, K$

With diethyl beryllium, the dimeric bis-F-(tert-butoxy) beryllium is formed in addition to side products (39):

I-62 

The photochemical reaction of borazine with F-(tert-butyl) alcohol gives the mono substituted B-(perfluoro-tert-butoxy) borazine and side products (40):

I-63 

Reaction of the alcohol with dichlorodimethyl silane gives a product formed by the replacement of the labile chlorine atoms by the F-(tert-butoxy) group (41):

I-64 $(CF_3)_3COH + (CH_3)_2SiCl_2 \longrightarrow (CH_3)_2Si[OC(CF_3)_3]_2$

With thionyl chloride, F-(tert-butyl) alcohol is unreactive, however, upon addition of the base, triethylamine, the F-(tert-butyl) alcohol-triethylamine adduct is initially formed, which goes on to react with the thionyl chloride to form bis-F-(tert-butyl) sulfite (42):

I-65 $(CF_3)_3COH + (CH_3CH_2)_3N \longrightarrow (CF_3)_3COH\cdot N(CH_2CH_3)_3$

I-66 $(CF_3)_3COH\cdot N(CH_2CH_3)_3 + SOCl_2 \longrightarrow$

$[(CF_3)_3CO]_2SO + (CH_3CH_2)_3N\cdot HCl$

An alcohol-amine adduct using trimethylamine has also been formed:

I-67 $(CF_3)_3COH + (CH_3)_3N \longrightarrow (CF_3)_3COH\cdot N(CH_3)_3$

This adduct has been reacted with trifluoromethylsulfinyl chloride to give F-(tert-butyl) trifluoromethylsulfinate, which is the same product produced using F-(tert-butyl) hypochlorite instead of the adduct (43):

I-68 $(CF_3)_3COH \cdot N(CH_3)_3 + CF_3S(O)Cl \longrightarrow$

$CF_3S(O)OC(CF_3)_3 + (CH_3)_3N \cdot HCl$

Various rare earth metal chlorides react with F-(tert-butyl) alcohol and ammonia in the presence of diethyl ether to form the following type of complexes in addition to side products (44):

I-69 $(CF_3)_3COH + MCl_3 + NH_3 \longrightarrow M[OC(CF_3)_3]_3 \cdot 3NH_3$

M = Yb, La, Gd, Y

With hexakis(dimethylamido)tungsten (VI) in benzene, a low yield tungsten (VI) alkoxide, $WO[OC(CF_3)_3]_4$, is formed in addition to a new alcohol-amine adduct, $(CF_3)_3COH \cdot HN(CH_3)_2$ (45).

With hexakis(dimethylamido)dimolybdenum in benzene, a hexakis(alkoxy)dimolybdenum complex is formed in low yield (46):

I-70 $4(CF_3)_3COH + Mo_2[N(CH_3)_2]_6 \longrightarrow$

$Mo_2[OC(CF_3)_3]_4[N(CH_3)_2]_2 + 4(CF_3)_3COH \cdot HN(CH_3)_2$

The metal F-(tert-butoxides) have also been used to prepare new F-(tert-butoxides). Unlike F-(tert-butyl) hypochlorite, sodium F-(tert-butoxide) reacts with phosphoryl trichloride to give both F-(tert-butoxy) phosphoryl dichloride and bis-F-(tert-butoxy) phosphoryl chloride (47):

I-71 $3(CF_3)_3CONa + 2OPCl_3 \longrightarrow$

$(CF_3)_3COPOCl_2 + [(CF_3)_3CO]_2POCl + 3NaCl$

The soidium salt has also been reacted with $MoOCl_4$ in dichloromethane, giving fully and partially subsitituted compounds depending on the stoichiometry used:

I-72 $n(CF_3)_3CONa + MoOCl_4 \longrightarrow MoOCl_{4-n}[OC(CF_3)_3]_n + nNaCl$

Of the four possible products, only tris-F-(tert-butoxy) chloro oxo molybdenum (VI), and tetra-F-(tert-butoxy) oxo molybdenum (VI) where isolated (48). Sodium F-(tert-butoxide) also reacts with beryllium chloride in diethyl ether to give a bis-F-(tert-butoxy) beryllium-diethyl ether complex, which is one of the few examples of a three-coordinate monomeric beryllium complex. Ammonia and pyridine complexes can also be formed by reacting the diethyl ether complex with either excess ammonia in hexane, or with excess pyridine (39):

I-73 $2(CF_3)_3CONa + BeCl_2 + (CH_3CH_2)_2O \longrightarrow$

$Be[OC(CF_3)_3]_2{\cdot}O(CH_2CH_3)_2 + 2NaCl$

I-74 $Be[OC(CF_3)_3]_2{\cdot}O(CH_2CH_3)_2 + xs\ NH_3 \longrightarrow$

$Be[OC(CF_3)_3]_2(NH_3)_2 + (CH_3CH_2)_2O$

I-75 $Be[OC(CF_3)_3]_2{\cdot}O(CH_3CH_3)_2 + xs\ C_5H_5N \longrightarrow$

$Be[OC(CF_3)_3]_2(C_5H_5N)_2 + (CH_3CH_2)_2O$

With dichlorine heptoxide in carbon tetrachloride, F-(tert-butyl perchlorate is formed (49):

I-76 $(CF_3)_3CONa + O_3ClOClO_3 \longrightarrow (CF_3)_3COClO_3 + NaClO_4$

Both the sodium and the potassium salts react with chlorine cyanide giving F-(tert-butoxy) cyanide (50):

I-77 $(CF_3)_3COM + ClCN \longrightarrow (CF_3)_3COCN + MCl$ (M = Na,K)

The potassium salt has been shown to react with both peroxydisulfuryl difluoride and nitryl fluoride as shown in the following equations. Side products are also formed (51):

I-78 $(CF_3)_3COK + S_2O_6F_2 \longrightarrow (CF_3)_3COOSO_2F + [(CF_3)_3CO]_2$

I-79 $(CF_3)_3COK + FNO_2 \longrightarrow (CF_3)_3CONO_2 + KF$

Preparation of F-(tert-butoxides) has spanned the past two and a half decades of literature. Application of these compounds have included use as textile-treating agents, monomers, plasticizers, solvents, and surfacants (38, 41, 50). Interestingly, the metal F-(tert-butoxides) are volatile compounds which could have potential use as metal vapor sources and gas transport reagents. Other volatile metal complexes such as β-ketonates are presently being used for this purpose (52).

The preparation of F-(tert-butoxides) from F-(tert-butyl) hypochlorite, has so far been limited to compounds possessing a carbon, sulfur, phosphorus, boron, nitrogen, titanium, chromium, iridium, or mercury atom attached to the F-(tert-butoxy) group. Other starting reagents, as described, have been used to introduce new F-(tert-butoxides) containing elements such as silicon, beryllium, or yttrium, bonded to the F-(tert-butyl) group. It is the purpose of this work to prepare and characterize new F-(tert-butoxides) containing transition metals, post transition metals, metalloids, and new non-metals attached to the F-(tert-butoxy) group, using F-(tert-butyl) hypochlorite. In addition, the reaction of F-(tert-butyl) hypochlorite with elements other than mercury, and with aromatic systems have been investigated. A summary of the reactions studied is given in Table III.

TABLE III

REACTIONS DISCUSSED IN CHAPTER IV

Reactants	Products
$(CF_3)_3COCl + VOCl_3$	$VO[OC(CF_3)_3]_3$
$(CF_3)_3COCl + SbCl_5$	$Sb[OC(CF_3)_3]_xCl_y$
$(CF_3)_3COCl + Cu_2Cl_2$	no reaction occurred
$(CF_3)_3COCl + UCl_4$	no reaction occurred
$(CF_3)_3COCl + SnCl_4$	no reaction occurred
$(CF_3)_3COCl + SiCl_4$	no reaction occurred
$(CF_3)_3COH + TiCl_4$	no reaction occurred
$(CF_3)_3COH + (CH_3CH_2)_2NH$ $+ TiCl_4$	$Ti[OC(CF_3)_3]_{4-n}Cl_n$ $+ (CF_3)_3COH\cdot HN(CH_2CH_3)_2$
$(CF_3)_3COH + (CH_3CH_2)_2NH$	$(CF_3)_3COH\cdot HN(CH_2CH_3)_2$
$Ti[OC(CF_3)_3]_4 + HCl$	$(CF_3)_3COH + [TiCl_4]$
$(CF_3)_3COCl + PPh_3$	*
$(CF_3)_3COCl + C_6H_6$	*
$(CF_3)_3COCl + Pb$	$Pb[OC(CF_3)_3]_2$
$(CF_3)_3COCl + Te$	$Te[OC(CF_3)_3]_4$
$(CF_3)_3COCl + Bi$	$Bi[OC(CF_3)_3]_3$

TABLE III (con't)

Reactants	Products
$(CF_3)_3COCl + Si$	no reaction occurred
$(CF_3)_3COCl + S_8$	$S[OC(CF_3)_3]_4$
$(CF_3)_3COCl + I_2$	$I[OC(CF_3)_3]_3$
$(CF_3)_3COCl + CF_3I$	$CF_3I[OC(CF_3)_3]_2$
$(CF_3)_3COCl + Br_2$	$[(CF_3)_3COBr] \longrightarrow (CF_3)_2CO + CF_3Br$
$(CF_3)_3COCl + CoBr_2$	*
$(CF_3)_3COCl + CsBr$	*
$(CF_3)_3COCl + CsI$	*

* Products not fully characterized.

CHAPTER II

EXPERIMENTAL METHODS

Apparatus

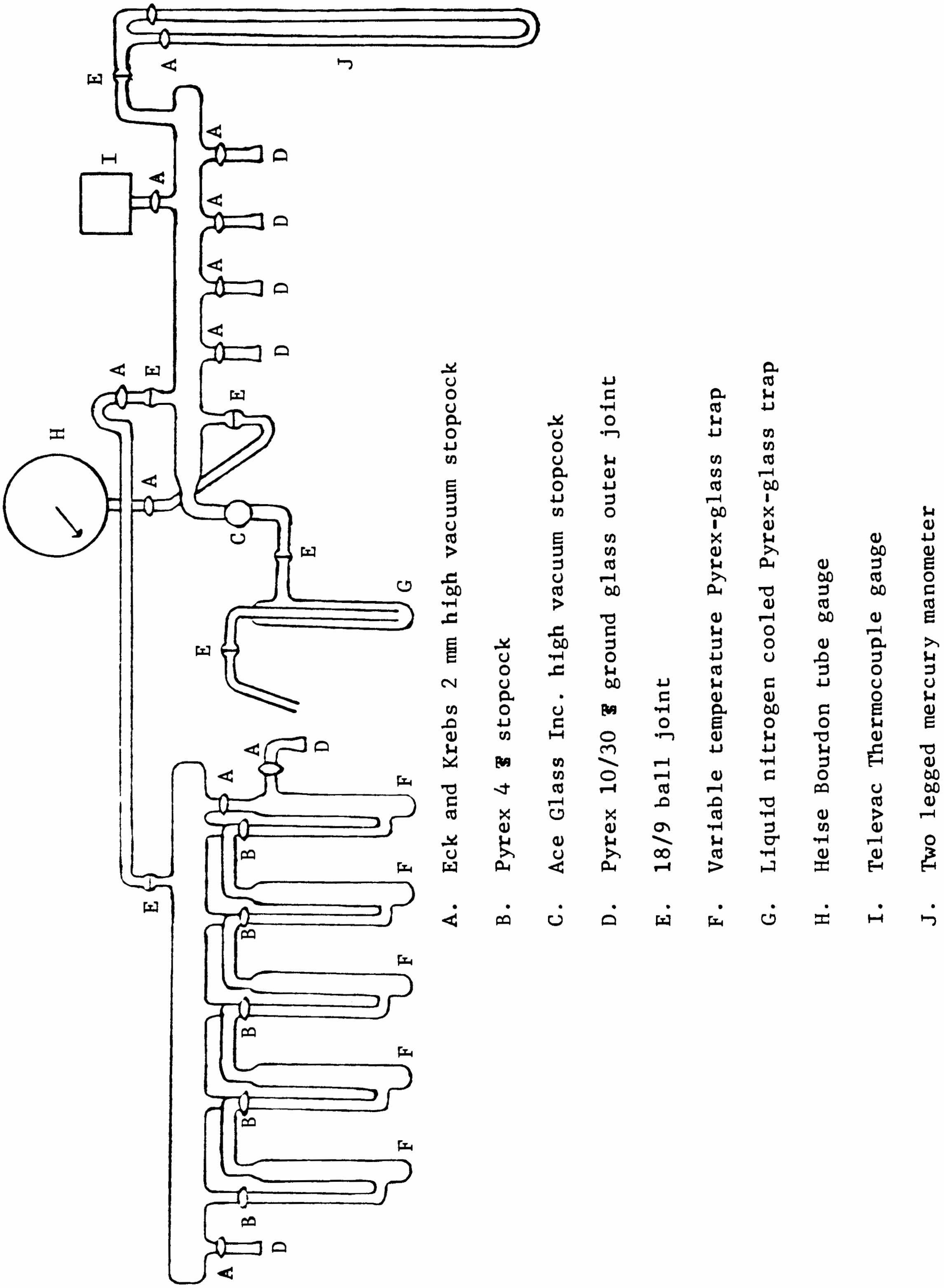
Vacuum System. For the transfer of volatile materials, a vacuum system was used which consisted of a manifold constructed from 18 mm and 12 mm I.D. Pyrex-glass tubing. Connected directly to the manifold were four Eck and Krebs 2 mm high vacuum stopcocks to which Pyrex 10/30 \$ ground glass outer joints were attached. The manifold was evacuated through a liquid nitrogen cooled trap by a Welch Duo-Seal rotary pump. The vacuum was monitored by a Televac Thermo-couple gauge, and was generally maintained between 10^{-3} to 10^{-2} torr. Higher pressures within the manifold, when required, could be measured by a two legged mercury manometer to ±0.1 torr, or by a Heise Bourdon tube gauge to ±1 torr. The manifold was also connected to a trap-to-trap distillation unit consisting of a separate manifold connected to five Pyrex 4 \$ stopcocks which were attached to traps constructed from 14 mm and 8 mm I.D. Pyrex-glass tubing. The traps were also connected in series by additional 8 mm I.D. Pyrex-glass tubing. All joints in the vacuum system were lubricated with either Apiezon-M or

Fluorolube GR-90 grease. An illustration of the vacuum system is shown in Figure 1.

Reaction Vessels. Low pressure reactions were carried out in 50 ml, 75 ml, 100 ml, or 20 ml Pyrex-glass reaction vessels equipped with a Kontes high vacuum Teflon valve and Teflon stirring bar, and tipped with a Pyrex 10/30 $ inner joint for attachment to the vacuum line. High pressure reactions were done in a 75 ml stainless steel Hoke vessel attached to either a Hoke, VWR, or Whitey stainless steel valve or a Whitey brass valve, and tipped with a metal 10/30 $ inner joint. Reactions which were not compatible with either glass or stainless steel, were carried out in a 35 ml Kel-F reaction vessel fitted with a Teflon top attached to a Whitey brass valve and a brass 10/30 $ inner joint.

Vacuum Traps. Vacuum traps were constructed of two concentric Pyrex-glass tubes of 22 mm and 10 mm I.D. The outer tube was connected to a Kontes high vacuum Teflon valve by a piece of 10 mm I.D. Pyrex-glass tubing. The inner tube was connected to another Kontes high vacuum Teflon valve. Both valves were fitted with 10/30 $ inner joints for attachment to the vacuum line or to other vessels.

Dry Box. Air sensitive compounds were handled under an atmosphere of nitrogen in a KSE dry box desiccated with phosphorous pentoxide.



A. Eck and Krebs 2 mm high vacuum stopcock

B. Pyrex 4 ₮ stopcock

C. Ace Glass Inc. high vacuum stopcock

D. Pyrex 10/30 ₮ ground glass outer joint

E. 18/9 ball joint

F. Variable temperature Pyrex-glass trap

G. Liquid nitrogen cooled Pyrex-glass trap

H. Heise Bourdon tube gauge

I. Televac Thermocouple gauge

J. Two legged mercury manometer

Figure 1: Pyrex-glass Vacuum Manifold and Trap-to-trap Distillation Unit.

Physical Methods

Fractional Distillation. Purification of some liquid products was achieved by fractional distillation using a Bantam-Ware (Kontes) distillation apparatus. For distillations carried out under reduced pressure, the apparatus was equipped with a multiple fraction collector head, and was attached to the vacuum line through a trap cooled to -78°C. For distillations performed at atmospheric pressure, the distilling column was exposed to the atmosphere through a cold trap at -78°C which was in turn connected to a calcium chloride drying tube to prevent condensation of water into the cold trap.

Trap-to-trap Distillation. Trap-to-trap distillations were performed by attaching the reaction vessel of the compound to be purified to a series of cold traps under dynamic vacuum. The traps were arranged in order of decreasing temperature, the warmest being attached to the reaction vessel. The chosen temperature of each cold trap was dependent upon the volatility of the components being separated.

Sublimation. Purification of some solids was achieved by sublimation using a conventional Pyrex-glass sublimation unit. The cold finger was cooled by flowing water, and a vacuum was achieved by attachment of the sublimation unit to the vacuum line through a trap cooled to -196°C. A second method of sublimation involved heating the lower end of a Pyrex-glass reaction vessel which was under static vacuum, and allowing the product to sublime onto the cooler, upper portion of the reaction vessel.

Gas Chromatography. The purity of some products was determined by gas chromatography using a Varian 3700 Capillary Chomatograph. A 30 meter SE-54 capillary column having a 0.8 mm O.D. was used. Column temperature and split ratio were adjusted as needed for maximum separation.

Elemental Analysis. Elemental analysis was performed at the University of Idaho, Moscow, or by Beller Microanalytical Laboratories, Göttingen, West Germany.

Analysis of Chlorine Gas. Chlorine gas produced in the F-(tert-butyl) hypochlorite reactions was quantitatively determined by reaction with mercury metal contained in a weighed glass reaction vessel.

Molecular Weights. Molecular weights for liquid phase compounds with sufficient vapor pressure were determined by vapor density method, using a 209.6 ml Pyrex molecular weight bulb equipped with a Kontes high vacuum Teflon stopcock and an inner 10/30 $ ground glass joint.

Melting Points. Melting points of solid phase compounds were determined using sealed capillary tubes in a Mel-Temp apparatus. For samples which were found to sublime up the walls of the capillary tube, the melting point was obtained by totally immersing the sealed tube in an oil bath, where the temperature gradient was minimized by constant stirring and very slow heating. The melting points of selected liquid compounds were determined by immersing the sealed tube in a dry ice/acetone bath contained in a silver-stripped dewar. The bath was allowed to slowly warm until the melting point was observed. Melting point values reported are not corrected for thermometer calibration error.

Infrared Spectra. The infrared spectra were recorded on a Perkin-Elmer 467 spectrophotometer having a range of 4000-250 cm^{-1}. Gaseous samples were contained in a Monel cell equipped with a Whitey brass valve and brass 10/30 § inner joint for attachment to the vacuum line. The cell windows were NaCl, KBr, or AgCl, and the path length of the cell was 8.25 cm. The spectra of non-volatile liquids were obtained neat between NaCl, KBr, or AgCl plates. The spectra of solid samples were obtained neat between NaCl, KBr, or KRS-5 discs, or as potassium bromide pellets. All spectra were calibrated using polystyrene film.

Nuclear Magnetic Resonance Spectra. A Varian Model EM-390 spectrometer operating at 90.0 MHz for proton and 84.67 MHz for fluorine resonances was used to record the nuclear magnetic resonance spectra. Chemical shifts are reported relative to TMS for proton spectra, and Freon-11 for fluorine spectra where downfield resonances are reported as positive values. Trifluoroacetic acid was used as an external standard when required.

Mass Spectra. The mass spectra of compounds containing the SF_5-group were measured with a CEC 21-110 B double focus mass spectrometer fitted with a 6 KV ion accelerator and operated at 70 volts. A Hitachi Perkin-Elmer RMU-6E mass spectrometer at 15 eV was used for the F-(tert-butoxides). Perfluorokerosine was used as an internal standard.

Ultraviolet Spectrum. The ultraviolet spectrum was recorded on a Cary 14 spectrophotometer using a quartz cell having a 1.00 cm path length.

Reagents

Acetonitrile. Analytical reagent grade CH_3CN was purchased from Mallinckrodt and was used after drying over $MgSO_4$ for at least one hour.

Ammonia. Anhydrous NH_3 was purchased from Matheson and was used without further purification.

Antimony Pentachloride. $SbCl_5$ was purchased from Alfa Inorganics and was used without further purification.

Benzene. Spectral grade benzene was purchased from Mallinckrodt and was used without further purification.

Bismuth. Granular bismuth was obtained from Allied Chemical and Dye and was ground prior to use.

Bromine. Analytical reagent grade bromine was purchased from Mallinckrodt and was used without further purification.

Carbon Tetrachloride. Analytical reagent grade

CCl_4 was purchased from Matheson Coleman and Bell, and was used without further purification.

Carbonyl Fluoride. COF_2 was purchased from Peninsular Chem Research and was used without further purification.

Cesium Bromide. CsBr was obtained from Alfa Products and was used without further purification.

Cesium Fluoride. CsF was purchased from either Peninsular Chem Research or Alfa Inorganics, and was dried under vacuum prior to use.

Cesium Iodide. CsI was obtained as an "ultrapure lump" from Alfa Products, and was ground and dried under vacuum prior to use.

Chlorine Monofluoride. ClF was purchased from Pennwalt Chemicals and Equipment Health Products Inc., and was used without further purification.

Cobalt (II) Bromide. $CoBr_2$ was obtained from Alfa Products and was used without further purification.

Copper (I) Chloride. Cu_2Cl_2 was purchased from Johnson Matthey Chemical Limited, and was used without further purification.

Diethylamine. Diethylamine was purchased from Matheson Coleman and Bell, and was used without further purification.

Disulfur Decafluoride. S_2F_{10} was received as a gift from Dr. Meude Tremblay, Centre Canadien de Recherches et Perfectionnement des Armes (CARDE) Quebec, Canada, and was used without further purification.

Freon-11. Freon-11 ($CFCl_3$) was purchased from Dupont and was stored over type 5A molecular sieves prior to use.

F-(tert-butyl) Alcohol. $(CF_3)_3COH$ was purchased from Peninsular Chem Research and was stored over type 5A molecular sieves prior to use.

F-(tert-butyl) Hypochlorite. $(CF_3)_3COCl$ was synthesized by an adaptation of the method used by Young, Anderson, Gould, and Fox (21). $(CF_3)_3COH$ and a slight excess of ClF were condensed into a pretreated stainless steel reaction vessel which was allowed to warm to 0°C and remain there for approximately 15 hours. The contents of the vessel were condensed into a second metal reaction vessel containing an excess amount of CsF. This reaction vessel was shaken frequently while slowly warmed to 0°C. Trap-to-trap distillation was used to separate the $(CF_3)_3COCl$ (-78°C trap) from the unreacted ClF (-196°C trap).

Hydrogen Chloride. Anhydrous HCl was purchased from Matheson and was used without further purification.

Iodine. Iodine was purchased from Mallinckrodt and was ground into finer particles prior to use.

Iodotrifluoromethane. CF_3I was purchased from Peninsular Chem Research and was used without further purification.

Lead. Lead powder (200 mesh) was purchased from

Matheson Coleman and Bell, and was used without further purification.

Mercury. Analytical reagent grade mercury was purchased from Mallinckrodt and was used without further purification.

Molecular Sieves. Type 5A molecular sieves (8-12 mesh beads) were purchased from Matheson Coleman and Bell, and were dryed in an oven at 130°C prior to use.

Nitric Acid. HNO_3 (70.9%) was purchased from Baker and was used without further purification.

Pentafluorosulfur Bromide. SF_5Br was prepared similar to the literature method which involved reacting S_2F_{10} and Br_2 at 138°C (53). A Hoke stainless steel vessel was substituted for a borosilicate glass break-seal tube which allowed the reaction to be carried out at a higher pressure, and in a larger quantity. The heating time was increased from 24 hours to 48 or more hours. SF_5Br was transferred from the reaction vessel at -55°C to -60°C and was used without further purification. Possible contaminants include SF_6, SF_4, S_2F_{10}, and Br_2.

2-Pentafluorosulfur-F-propanamide. $SF_5CF(CF_3)C(O)NH_2$ was prepared by literature method (14). The synthesis involved reacting $SF_5CF(CF_3)C(O)F$ with NH_3 followed by the separation of $SF_5CF(CF_3)C(O)NH_2$ from NH_4F using carbon tetrachloride.

2-Pentafluorosulfur-F-propionyl fluoride. $SF_5CF(CF_3)C(O)F$ was prepared by literature method (14). The preparation involved reacting $SF_5CF{=}CF_2$ with COF_2 in the presence of CsF and acetonitrile. Impurities often included the starting materials, $SF_5CF{=}CF_2$ and COF_2, or the solvent, acetonitrile.

Perfluoro-2-butyltetrahydrofuran. Perfluoro-2-butyltetrahydrofuran was purchased from Peninsular Chem Research and was used without further purification.

Petroleum Ether. Petroleum ether (90-120) was purchased from Mallinckrodt and was used without further purification.

Phosphorous Pentaoxide. P_4O_{10} was purchased from Baker and was dried under vacuum prior to use.

Potassium Bifluoride. KHF_2 was purchased from Research Organic/Inorganic Chemical Corp., and was dried under vacuum prior to use.

Potassium Bromide. Infrared grade KBr was purchased from Mallinckrodt and was stored in an oven at 130°C prior to use.

Potassium Hydroxide. KOH pellets were purchased from Matheson Coleman and Bell, and were ground into powder prior to use.

Silicon. Granular silicon was purchased from Matheson Coleman and Bell, and was ground into a powder prior to use.

Silver Nitrate. $AgNO_3$ was purchased by VWR Scientific and was used without further purification.

Sodium Fluoride. Analytical grade NaF was purchased from Mallinckrodt and was dried under vacuum prior to use.

Sodium Hydroxide. Analytical reagent grade NaOH pellets were purchased from Mallinckrodt and were used without further purification.

Sulfur. Sulfur roll was purchased from VWR Scientific and was ground into powder prior to use.

Tellurium. Powdered tellurium was purchased from Matheson Coleman and Bell, and was used without further purification.

Tetrachlorosilane. $SiCl_4$ was purchased from Peninsular Chem Research and was used without further purification.

Tetramethylsilane. $(CH_3)_4Si$ was purchased from Stohler Isotope Chemicals and was used without further purification.

Tin (IV) Chloride. $SnCl_4$ was purchased from Baker and was used without further purification.

Titanium Tetrachloride. $TiCl_4$ was purchased from Peninsular Chem Research and was used without further purification.

Trifluoroacetic Acid. CF_3CO_2H was obtained from Peninsular Chem Research and was sealed in capillary tubes for use as an external standard for NMR spectra.

Trifluoroethylene. Inhibited $CFH=CF_2$ was obtained from Peninsular Chem Research and was used without further purification.

Trifluorovinylsulfur Pentafluoride. $SF_5CF=CF_2$ was prepared by literature method (2). The synthesis involved reacting SF_5Br with $CFH=CF_2$, to form the adduct, SF_5CHFCH_2Br, which was dehydrohalogenated using KOH in petroleum ether (90-120).

Triphenyl phosphine. PPh_3 was purchased from Matheson Coleman and Bell, and was used without further purification.

Uranium Tetrachloride. UCl_4 was purchased from Research Organic/Inorganic Chemical Corp., and was used without further purification.

Vanadium (V) Oxide Trichloride. $VOCl_3$ was purchased from Alfa Products and was used without further purification.

Water. Distilled water was obtained from the tap, and was boiled for approximately one hour to remove air.

CHAPTER III

SYNTHESIS OF SF_5-COMPOUNDS

Introduction

The use of trifluorovinylsulfur pentafluoride and its derivatives provides a productive method for the preparation of new SF_5-compounds. Since its initial preparation in 1961 (1), many useful compounds have been made from it. Two such compounds, $SF_5CF(CF_3)C(O)F$ and $SF_5CF(CF_3)C(O)NH_2$, have been used in this work. The reported preparation of $SF_5CF(CF_3)C(O)F$ involves the addition of carbonyl fluoride across the double bond of the olefin in the presence of the catalyst, CsF, and a solvent, acetonitrile (14). In the preparation of this compound, it was decided to omit the solvent in hope of simplifying the separation and purification of $SF_5CF(CF_3)C(O)F$. Instead, what was isolated, was the dimer of trifluorovinylsulfur pentafluoride. A second reaction was carried out, where the carbonyl fluoride was also omitted and the dimer was produced again:

III-1 $2SF_5CF{=}CF_2 \xrightarrow{CsF} (SF_5CFCF_2)_2$

The structure of this new compound has not been determined. Interestingly, the infrared spectrum shows no absorption due to the carbon-carbon double bond, however, one is seen in the Raman spectrum at 1705 cm^{-1}. This implies a symmetrical structure for the dimer about the carbon-carbon bond, however, the ^{19}F NMR spectrum indicates otherwise and will be discussed later.

The SF_5-acid fluoride, $SF_5CF(CF_3)C(O)F$, was found to react with water, forming the corresponding SF_5-acid, $SF_5CF(CF_3)CO_2H$. When the reaction was carried out in a stainless steel reaction vessel, in addition to the acid, a green-grey solid was formed. This material is most likely a mixture of SF_5-acid salts, with iron being the major cation. The infrared spectrum of the solid shows absorptions characteristic of S-F, C-F, and C=O bonds. The elemental analysis confirmed the presence of carbon, fluorine, sulfur, and iron, but was not useful in determining the composition of the solid. The ratio of C:S:F from the elemental analysis does not support the presence of all $SF_5CF(CF_3)CO_2$- groups. The possibility of other metals in the solid can not be ruled out.

A second reaction between $SF_5CF(CF_3)C(O)F$ and water was carried out in a Kel-F reaction vessel. Sodium fluoride was used in order to pick up the hydrogen fluoride produced. By not using a metal reaction vessel, the yield of $SF_5CF(CF_3)CO_2H$ was increased from 36% to 52%, and the production of the solid-by-product was eliminated.

III-2 $SF_5CF(CF_3)C(O)F + H_2O \longrightarrow SF_5CF(CF_3)CO_2H + HF$

The titration of the SF5-acid with sodium hydroxide produced the corresponding salt:

III-3 $SF_5CF(CF_3)CO_2H + NaOH \longrightarrow SF_5CF(CF_3)CO_2Na + H_2O$

When the SF_5-acid was reacted with P_4O_{10}, the expected anhydride was not formed, but rather a previously made compound, SF_5CHFCF_3, and a rusty colored solid were produced. The formation of SF_5CHFCF_3 can be rationalized from the decarboxylation of $SF_5CF(CF_3)CO_2H$, however, no carbon dioxide was detected in the infrared spectrum of the volatile materials. This does not refute the formation of carbon dioxide, since it absorbs weakly in the infrared region and because the infrared spectrum was taken at relatively low concentrations. The solid formed was not investigated.

When $SF_5CF(CF_3)C(O)NH_2$ was reacted with P_4O_{10}, the corresponding SF_5-nitrile, $SF_5CF(CF_3)CN$, was formed in a 74% yield:

III-4 $SF_5CF(CF_3)C(O)NH_2 + P_4O_{10} \longrightarrow SF_5CF(CF_3)CN + P_4O_{10}\cdot H_2O$

In an attempt to prepare a SF_5-ketone, trifluorovinylsulfur pentafluoride was reacted with carbonyl fluoride in a 2:1 ratio, and in the presence of potassium bifluoride and acetonitrile. The products formed were identified as SF_5CHFCF_3 and $SF_5CF(CF_3)C(O)F$. In the reported reaction between trifluorovinylsulfur pentafluoride and carbonyl fluoride in the presence of cesium fluoride and acetonitrile, $SF_5CF(CF_3)C(O)F$ was produced. The following mechanism was proposed (14):

III-5 $SF_5CF{=}CF_2 + F^- \longrightarrow SF_5\bar{C}FCF_3$

III-6 $SF_5\bar{C}FCF_3 + COF_2 \longrightarrow SF_5CF(CF_3)C(O)F + F^-$

This same mechanism can explain the products produced in this reaction if an additional step is added:

III-7 $SF_5\bar{C}FCF_3 + KHF_2 \longrightarrow SF_5CHFCF_3 + KF_2^-$

Thus, the net reaction is:

III-8 $2SF_5CF{=}CF_2 + COF_2 + KHF_2 \longrightarrow$

$SF_5CF(CF_3)C(O)F + SF_5CHFCF_3 + KF$

A second attempt to make the SF_5-ketone involved reacting $SF_5CF(CF_3)C(O)F$ with $SF_5CF{=}CF_2$ in the presence of cesium fluoride and acetonitrile. Cesium fluoride was used instead of potassium bifluoride in order to eliminate the production of SF_5CHFCF_3. $SF_5CF(CF_3)C(O)F$ was used directly, instead of generating it in the reaction as done previously. Identified reaction products include $CF_3CF_2C(O)F$, SF_4, and COF_2, in addition to a non-volatile polymeric material which was formed upon transferring the volatile contents in the reaction vessel to a trap at -196°C. The solid material shows infrared absorptions in both the S-F and C-F regions. It is thought that an unstable product (possibly the ketone, $[SF_5CF(CF_3)]_2CO$) was formed and decomposed/polymerized upon vacuum transfer.

Experimental

Preparation of $(SF_5CFCF_2)_2$. In a 75 ml Hoke stainless steel vessel containing 2 mmol of CsF (predried at 100°C for 12 hours), 38 mmol of $SF_5CF{=}CF_2$ was condensed at -196°C.

The olefin was heated at 50°C (2 hr), 80°C (2 hr), and 100°C (2 hr) with frequent shaking (2 minutes during every 15 minute heating stage). The dimer was purified by distillation under reduced pressure; b.p. 38-39°C/24.6 mm Hg; purity, 96% by gas chromatography; yield, 78%; molecular weight, 413 found versus 416 calculated.

Preparation of $SF_5CF(CF_3)CO_2H$. In a 75 ml Hoke stainless steel vessel equipped with a Whitey brass valve, 22 mmol of $SF_5CF(CF_3)C(O)F$ and 6 mmol of H_2O were condensed at -196°C. The vessel was heated at 40°C (5.5 hr); additional H_2O (13 mmol) was added and again the reaction mixture was heated at 40°C (42 hr). The volatile contents of the reaction vessel were transferred into a trap at -196°C. An IR spectrum of the volatiles indicated the absence of both starting materials. The trap contents were purified by distillation under reduced pressure (b.p. 86-88°C/50.5 mm Hg), giving the viscous liquid, $SF_5CF(CF_3)CO_2H$, in a 36% yield. The metal reaction vessel was found to contain 0.4997 gram of a green-grey solid. Other than obtaining an infrared spectrum and an elemental analysis, the solid was not studied further.

In a 35 ml Kel-F vessel equipped with a Teflon top and Whitey brass valve, and containing 31 mmol of NaF, 15 mmol of $SF_5CF(CF_3)C(O)F$ and 17 mmol of H_2O were condensed at -196°C. After heating the vessel from room temperature to 55°C for 11 hours, the volatile materials were pumped away leaving behind a white solid. Heating the solid to 80°C over a 12 hour period, while pumping through a trap cooled to -196°C, resulted in the transfer of the acid into the trap. The product, $SF_5CF(CF_3)CO_2H$, was formed in a 52% yield; b.p. 86-88°C/50.5 mm Hg. The molecular weight of the acid was determined by titration with sodium hydroxide. Thus, 0.5544 gram of the SF_5-acid was titrated to its equivalence point with 5.50 ml of 0.3701 N NaOH, giving a molecular weight of 272; calculated, 272.

Reaction of $SF_5CF(CF_3)CO_2H$ with P_4O_{10}. In a 35 ml Kel-F vessel equipped with a Teflon top and stirring bar, and a Whitey brass valve, 2.58 mmol of dried P_4O_{10} and 3.46 mmol of $SF_5CF(CF_3)CO_2H$ were added. The reaction mixture was heated at 40°C (5.5 hr) and 50°C (4.5 hr). The volatile material in the reaction vessel was transferred into a trap at -196°C and was identified as SF_5CHFCF_3 by its infrared spectrum (7). A rusty colored solid remained in the reaction vessel and was not analyzed.

Preparation of $SF_5CF(CF_3)CN$. $SF_5CF(CF_3)C(O)NH_2$ (12 mmol) and P_4O_{10} (16.5 mmol) were placed together in a 100 ml round bottom flask and then attached to a condenser which was connected to three traps cooled to -19°C, -78°C, and -130°C respectively. The temperature was slowly increased from 20°C to 138°C over a three hour period. Additional P_4O_{10} (12 mmol) was added and the temperature was increased to 152°C over a two hour period. The product, $SF_5CF(CF_3)CN$, collected mainly in the -78°C trap and was formed in a 74% yield; b.p. 39-41°C.

Reaction of $2SF_5CF{=}CF_2$ with COF_2/KHF_2. In a 75 ml Hoke stainless steel vessel equipped with a Whitey stainless steel valve, and containing 3.2 mmol of KHF_2 (predried at 110°C for several months), 61 mmol of $SF_5CF{=}CF_2$, 27.4 mmol COF_2, and 9.7 ml of dried CH_3CN were added. The reaction vessel was heated from 25°C to 105°C over a period of 9 hours, and at 150°C for 11 hours. The volatile materials, SF_5CHFCF_3 and $SF_5CF(CF_3)C(O)F$, were transferred out of the reaction vessel and identified by infrared spectroscopy (7, 14). Unreacted starting materials were also present.

Reaction of $SF_5CF(CF_3)C(O)F$ with $SF_5CF{=}CF_2/CsF$. In a 75 ml Hoke stainless steel vessel equipped with a Whitey valve, and containing 2.4 mmol of CsF (predried at 150°C under vacuum for 5 hr), 21 mmol of $SF_5CF(CF_3)C(O)F$, 21 mmol of $SF_5CF{=}CF_2$, and 7.5 ml of CH_3CN were condensed at -196°C. The reaction vessel was heated at 100°C (8 hr) and at 140°C (20 hr). The volatile contents of the reaction vessel were condensed into a trap at -196°C. Identified volatile products include $CF_3CF_2C(O)F$, SF_4, COF_2 and possibly some SOF_2. No unreacted $SF_5CF{=}CF_2$ or $SF_5CF(CF_3)C(O)F$ were present. In addition, a non-volatile grey polymeric material was found in the trap. Other than obtaining an infrared spectrum, the solid was not further studied.

Elemental Analysis

The data for the elemental analysis is listed in Table IV. There is good agreement between the experimental and calculated values for $(SF_5CFCF_2)_2$, $SF_5CF(CF_3)CO_2H$, and $SF_5CF(CF_3)CN$. As mentioned previously, the results from the elemental analysis for the solid formed in the reaction between $SF_5CF(CF_3)C(O)F$ and H_2O (in a metal reaction vessel) does not support the presence of all $SF_5CF(CF_3)CO_2$-groups. The ratio of C:F:S for this group should be 1.12:5.33:1.00, but instead we find 1.54:6.03:1.00 for this solid.

TABLE IV

ELEMENTAL ANALYSIS FOR SF_5-COMPOUNDS

Compound	Element	Wt.% Calc.	Wt.% Found
$(SF_5CFCF_2)_2$	Carbon	11.54	11.67
	Sulfur	15.38	15.26
	Fluorine	73.08	73.1
$SF_5CF(CF_3)CO_2H$	Carbon	13.24	13.55
	Sulfur	11.78	11.42
	Fluorine	62.84	62.2
	Hydrogen	0.37	0.47
$SF_5CF(CF_3)CN$	Carbon	14.24	14.34
	Sulfur	12.67	12.19
	Fluorine	67.56	68.1
	Nitrogen	5.53	5.43
$SF_5CF(CF_3)CO_2M(?)$	Carbon	-----	12.45
Solid from	Sulfur	-----	8.08
$SF_5CF(CF_3)C(O)F + H_2O$	Fluorine	-----	48.7
	Iron	-----	13.48

Infrared Spectra

The infrared absorptions are tabulated in Table V, and the actual spectra are shown in the Appendix. The common feature of all new compounds is the SF_5-group which reportedly absorbs strongly in the 850-920 cm^{-1} region due to S-F stretching vibrations, and in the 600 cm^{-1} region due to S-F deformation modes (5). The new SF_5-compounds absorb strongly between 838-900 cm^{-1} and at 600 cm^{-1} due to S-F stretching and deformation modes respectively. For polyfluorinated carbon compounds, a whole series of intense bands appear in the 1090-1360 cm^{-1} range due to the strong coupling of the C-F and C-C stretching vibrations. CF_3-groups attached to an alkyl group, characteristically have five strong absorption bands between 1135-1290 cm^{-1} (54). These bands are found between 1122-1280 cm^{-1} for the new SF_5-compounds. The CF_3 deformation modes are generally between 505-608 cm^{-1}, however, may be absent for α-unsaturated compounds (55). Absorption bands are found in this region for all of the new compounds. The carbonyl stretching absorption for the acid, sodium salt, and the uncharacterized (iron?) salt(s) occurs at 1766, 1690, and 1734/1662 cm^{-1} respectively. Carbonyl stretching vibrations in fluorinated carboxylic acids generally occur between 1760-1790 cm^{-1}, while the asymmetric carbonyl stretching of the salts of carboxylic acids occurs between 1680-1700 cm^{-1} (56). The symmetric stretching frequency of the latter

TABLE V

INFRARED ABSORPTION BANDS FOR SF_5-COMPOUNDS

$SF_5CF(CF_3)CO_2Na$	$SF_5CF(CF_3)CO_2H$	$SF_5CF(CF_3)CN$
1690 (s,b)	3100 (m,b)	2260 (m)
1370 (ms)	1766 (s)	1600 (vw)
1306 (m)	1415 (m)	1275 (s)
1272 (s)	1318 (m)	1245 (s)
1226 (s)	1280 (s)	1220 (s)
1186 (s)	1240 (s)	1163 (s)
1144 (ms)	1200 (s)	1052 (s)
1122 (ms)	1160 (s)	955 (w)
1008 (w)	1125 (s)	900 (s)
948 (w)	1014 (m)	850 (s)
872 (s)	880 (s)	790 (m)
838 (s)	843 (s)	735 (s)
816 (w)	812 (m)	713 (m)
788 (m)	760 (w)	687 (m)
744 (m)	714 (w)	600 (s)
662 (ms)	680 (m)	574 (ms)
600 (s)	600 (s)	
570 (s)	576 (s)	

$(SF_5CFCF_2)_2$		$SF_5CF(CF_3)CO_2M$? Solid from $SF_5CF(CF_3)C(O)F + H_2O$	
1325 (s)	890 (s,b)	1734 (s)	1022 (m)
1300 (w)	840 (m)	1662 (s)	966 (w)
1270 (s)	800 (s)	1396 (s)	882 (s,b)
1240 (s)	750 (ms)	1310 (m)	844 (s)
1200 (s)	730 (m)	1276 (s)	828 (m)
1165 (ms)	690 (w)	1230 (s,b)	790 (m)
1135 (s)	660 (s)	1200 (s)	744 (m)
1110 (w,sh)	650 (w)	1158 (s)	668 (m)
1050 (w)	600 (s)	1128 (ms)	600 (ms)
946 (ms)	580 (s)	1042 (w,sh)	578 (m)
930 (s)			

*Refers to the intensity of the absorption where s = strong, ms = medium-strong, m = medium, w = weak, vw = very weak, b = broad, and sh = shoulder. Absorption bands are in units of cm^{-1}.

is in the 1335-1420 cm^{-1} region (57) and is seen at 1370 and 1396 cm^{-1} for the salts of the SF_5-acid. While nitriles commonly absorb near 2250 cm^{-1} (58), the new SF_5-nitrile absorbs at a slightly higher frequency, 2260 cm^{-1}, as expected. The broad absorption band at 3100 cm^{-1} in the spectrum of the SF_5-acid is assigned to the O-H stretching vibration, and is within acceptable limits (59).

Nuclear Magnetic Resonance Spectra

The NMR chemical shifts for $SF_5CF(CF_3)CO_2H$ and $SF_5CF(CF_3)CN$ are listed in Table VI. For comparison purposes, the values for the starting materials, $SF_5CF(CF_3)C(O)F$ and $SF_5CF(CF_3)C(O)NH_2$, are also included (14). Chemical shifts reported for $SF_5CF(CF_3)CO_2H$ correspond to the product produced from the reaction between $SF_5CF(CF_3)C(O)F$ and H_2O in the presence of NaF and in a Kel-F reaction vessel. The NMR spectrum of the product produced from $SF_5CF(CF_3)C(O)F$ and H_2O in a stainless steel reaction vessel gave the same spectrum as the above compound with the exception to further splitting of all resonances into doublets. In the latter case, it is believed that rotomers were produced, however, additional work is needed to confirm this.

The SF_5 fluorine resonance consists of an AB_4 multiplet. The axial SF_5 fluorine has a characteristic nine line pattern with line number six used to report the

TABLE VI

NMR CHEMICAL SHIFTS* for SF_5-COMPOUNDS

	$SF_{(ax)}$	$SF_{4(eq)}$	CF_3	CF	H
$SF_5CF(CF_3)CO_2H$	67.5	55.7	-74.9	-141	10.1
$SF_5CF(CF_3)CN$	63.2	53.3	-76.9	-137.3	
$SF_5CF(CF_3)C(O)F$	64.6	56.3	-75.6	-144.4	
$SF_5CF(CF_3)C(O)NH_2$	69.5	54.3	-71.7	-137.5	7.0, 7.4**

*Fluorine and proton chemical shifts are reported relative to internal $CFCl_3$ and $Si(CH_3)_4$ standards, respectively.

**Band centers for a broad doublet

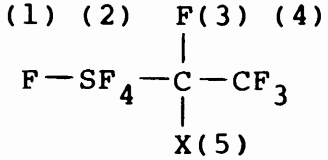
chemical shift value. The equatorial SF_5 fluorines consist of a doublet with each segment further split into six peaks (60). The minimum between the B maxima is reported as its chemical shift value. Chemical shift values for the new compounds are consistent with other compounds containing the $SF_5CF(CF_3)$-group including the SF_5-starting reagents (14). Values for the SF (axial) fluorine are near 65 ppm downfield from Freon-11, while those of the SF_4 (equatorial) fluorines are near 55 ppm. The CF_3-group chemical shift is typically found in the -70 ppm region, while that of the CF fluorine is further upfield at approximately -140 ppm. The proton in $SF_5CF(CF_3)CO_2H$ is found at 10.1 ppm downfield from TMS which is slightly upfield from the typical carboxylic acid proton resonance (61).

The NMR spectra of the SF_5-acid and SF_5-nitrile generally consists of complex multiplets, however, first order coupling constants could be determined in most cases, and are reported in Table VII. The second order $J_{1,2}$ coupling constant is also reported. The values for the starting materials, $SF_5CF(CF_3)C(O)F$ and $SF_5CF(CF_3)C(O)NH_2$, are included for comparison purposes (14).

The second order coupling between the SF (axial) and SF_4 (equatorial) fluorines gives $J_{1,2}$ values of 144 and 146 for the SF_5-acid and SF_5-nitrile, respectively. The reported $J_{1,3}$ coupling is assumed to be due to the SF (axial) to CF (vicinal) coupling which results in the

TABLE VII

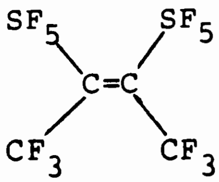
NMR COUPLING CONSTANTS FOR SF_5-COMPOUNDS*

Compound	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$
 $\overset{(1)}{F}-\overset{(2)}{SF_4}-\underset{X(5)}{\overset{F(3)}{C}}-\overset{(4)}{CF_3}$					
X = CO_2H	144	2.8	2.8	12.0	5.6
X = CN	146	4.2	1.7	9.5	9.5
X = C(O)F	135		3.0	12.0	6.0
X = $C(O)NH_2$	144	4.2	5.1	11.3	5.1

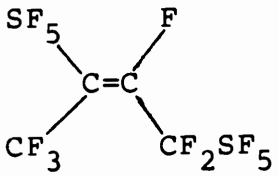
*Detailed analyses of coupling constants were determined in cooperation with Dr. H. F. White of this department.

doubling of the nine line A pattern. Because of the complex splitting of the CF resonance, unambiguous comfirmation of the assignment cannot be made. The CF resonance consists of a poorly resolved 12 or more line pattern for the SF_5-acid, while the spectrum of the SF_5-nitrile gives a quartet ($J_{3,4}$) with each element clearly resolved into a pentet ($J_{2,3}$). The splitting pattern for the CF_3 group is dependent on the relative values of the $J_{2,4}$ and $J_{3,4}$ coupling constants. For the SF_5-acid, where $J_{2,4}$ is larger than $J_{3,4}$, the CF_3 resonance appears as a pentet ($J_{2,4}$) with each element of the pentet split into a doublet ($J_{3,4}$). For the SF_5-nitrile, the coincidental degeneracy of the $J_{2,4}$ and $J_{3,4}$ coupling values gives a well resolved six line pattern. It is interesting to note that the summation of $J_{2,3}$, $J_{2,4}$, and $J_{3,4}$ for the four compounds listed in Table VII is essentially constant (20.9 $\pm$0.5) and suggests a predominant "through bond" coupling mechanism within the $SF_5CF(CF_3)$-group (14).

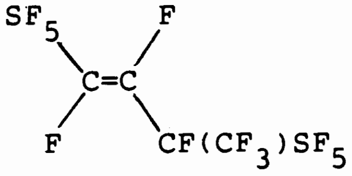
Chemical shift values for the NMR spectrum of the dimer, $(SF_5CFCF_2)_2$, are reported in Table VIII. The NMR spectrum has not been completely analyzed, therefore, the structure(s) of the material is unknown. The presence of the 1705 cm^{-1} band in the Raman spectrum and the single AB_4 pattern of the SF_5-group in the NMR spectrum supports the existence of a symmetrical compound such as:



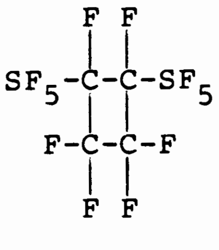
however, the NMR data of the CF_x groups (x = 1, 2, or 3) suggests a much more complicated structure. By analogy with the dimerization of $CF_3CF=CF_2$ (62), the E and Z isomers of the following compounds should have been prepared:



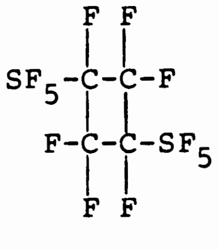
and



however, only one major isomer was separable by gas chromatography (96%). In addition, only one AB_4 pattern is observed in the NMR spectrum, indicating equivalent SF_5-groups which cannot be explained in the above isomers. Assuming the absence of a carbon-carbon double bond, both syn and anti isomers of the following cyclic structures are plausible:



and



In all cases, the SF_5-groups are equivalent, yet once again, the CF_x resonances cannot be explained nor can the band at 1705 cm^{-1} in the Raman spectrum. Consequently, the structure of the dimeric compound has not been determined, however, chemical analysis and molecular weight determinations support the molecular formula of $(SF_5CFCF_2)_2$. Additional work is needed in order to determine the structure(s) of this compound.

TABLE VIII

NMR CHEMICAL SHIFTS FOR $(SF_5CFCF_2)_2$

	(ppm)	Rel. Int.	Splitting
$SF_{(ax)}$	62.8	2	nine line pattern
$SF_{(eq)}$	56.0	8	doublet/multiplet
CF_x*	-12	3	multiplet
	-70	5	nine plus lines
	-82	5	doublet/doublet
	-93	2	doublet/septet
	-107	3	doublet/multiplet
	-110	1	octet

*x = 1, 2, or 3

Mass Spectra

The major mass spectral peaks for $(SF_5CFCF_2)_2$, $SF_5CF(CF_3)CO_2H$, and $SF_5CF(CF_3)CN$ are reported in Table IX. Although no parent peak was found, both $(SF_5CFCF_2)_2$ and $SF_5CF(CF_3)CO_2H$ have a peak corresponding to the parent peak minus a fluorine. Major peaks for the SF_5-acid and SF_5-nitrile include the SF_5^+ and SF_3^+ peaks, while those for

TABLE IX

MASS SPECTRA FOR SF_5-COMPOUNDS

M/e	Rel. Int.	Type	M/e	Rel. Int.	Type
$(SF_5CFCF_2)_2$			81	10	$C_2F_3^+$
63	6	SCF^+	82	3	SF_2C^+
69	22	CF_3^+	89	92	SF_3^+
89	11	SF_3^+	100	65	$C_2F_4^+$
101	21	SF_3C^+	101	26	SF_3C^+
105	4	$C_4F_3^+$	108	2	SF_4^+
113	7	$SF_3C_2^+$	119	5	$C_2F_5^+$
119	100	$C_2F_5^+$			$SFC_3O_2^+$
127	10	SF_5^+	125	5	$SF_3C_3^+$
131	11	$C_3F_5^+$			$C_3F_3O_2^+$
151	71	$SF_5C_2^+$	127	34	SF_5^+
162	10	$C_4F_6^+$	131	5	$C_3F_5^+$
189	3	$SF_7C_2^+$	145	5	$C_3F_4O_2H^+$
251	8	$SF_9C_4^+$	151	3	$SF_5C_2^+$
289	3	$SF_{11}C_4^+$	208	16	$SF_8C_2^+$
397	3	$S_2F_{15}C_4^+$	252	2	$SF_8C_3O_2^+$
$SF_5CF(CF_3)CO_2H$			253	1	$SF_8C_3O_2H^+$
50	6	CF_2^+	$SF_5CF(CF_3)CN$		
51	30	SF^+	31	6	CF^+
63	2	SCF^+	44	2	SC^+/CO_2^+
69	2	CF_3^+	50	2	CF_2^+
		$C_3O_2H^+$	51	2	SF^+
70	5	SF_2	57	3	C_2FN^+

TABLE IX (con't)

M/e	Rel. Int.	Type
58	4	SCN^+
63	2	SCF^+
69	47	CF_3^+
		C_3FN^+
70	7	SF_2^+
		SC_2N^+
76	35	$C_2F_2N^+$
89	65	SF_3^+
		SFC_2N^+
100	3	$C_2F_4^+$
101	3	SF_3C^+
		SC_3FN^+
107	2	$C_3F_3N^+$
108	2	SF_4^+
119	19	$C_2F_5^+$
126	75	$C_3F_4N^+$
127	100	SF_5^+
		$SF_3C_2N^+$
131	3	$C_3F_5^+$
139	3	SF_5C^+
151	10	$SF_5C_2^+$
165	1	$SF_5C_2N^+$

the dimer include $C_2F_5^+$ and $SF_5C_2^+$. The fragmentation patterns are supportive of the structures for both $SF_5CF(CF_3)CO_2H$ and $SF_5CF(CF_3)CN$, however, those for the dimer do not delineate any particular structure.

CHAPTER IV

SYNTHESIS OF F-(TERT-BUTOXIDES)

Introduction

F-(tert-butyl) hypochlorite provides a convenient route in the preparation of F-(tert-butoxides). The reaction mode has been demonstrated in a number of non-metal systems, and includes oxidative addition, oxidative displacement, or a combination of the two (28, 29, 30, 31, 34, 35). The use of F-(tert-butyl) hypochlorite has now been expanded to include reactions with new transition metal chlorides, post transition metal chlorides, various elements, and aromatic systems, in addition to a few miscellaneous reactions.

One of the disadvantages of using F-(tert-butyl) hypochlorite, is its relatively low stability towards oxidizable compounds. In general, reactions must be run at low temperatures in order to limit thermal decomposition of the hypochlorite. Reactions must also be shielded from light, since uv radiation enhances the rate of decomposition of the hypochlorite. Advantages, however, include few reaction side products, $(CF_3)_2CO$, CF_3Cl, Cl_2. All of these substances are easily removed from the product, simply by vacuum transfer, thus leaving in many cases, the desired product in near quantitative yield. A convenient method of monitoring reaction completeness, can be accomplished simply by reacting the side product, chlorine, with mercury.

F-(tert-butyl) hypochlorite was found to react with two metal chlorides. With vanadyl trichloride, the vanadyl complex, $VO[OC(CF_3)_3]_3$, is formed in quantitative yield from the oxidative displacement of the labile chlorine atoms:

IV-1 $3(CF_3)_3COCl + VOCl_3 \longrightarrow VO[OC(CF_3)_3]_3 + 3Cl_2$

When F-(tert-butyl) hypochlorite was added to antimony pentachloride, a white sublimable solid was formed. The solid was found to contain F-(tert-butoxy) groups by ^{19}F NMR (-71.3 and -72.3 ppm), and chlorine atoms by chemical analysis, however, a molecular formula could not be determined. The compound or mixture of compounds is believed to be of the type $SbCl_x[OC(CF_3)_3]_y$.

With Cu_2Cl_2, UCl_4, $SnCl_4$, and $SiCl_4$, no reaction occurred under the reaction conditions employed. In all cases, the hypochlorite was decomposed to $(CF_3)_2CO$ and CF_3Cl.

$Ti[OC(CF_3)_3]_4$ was prepared previously by the reaction of F-(tert-butyl) hypochlorite with titanium tetrachloride (32). An attempt to prepare this compound using the parent alcohol, $(CF_3)_3COH$, in place of the hypochlorite was unsuccessful. However, upon addition of diethylamine, a yellowish white solid was immediately formed. The ^{19}F NMR spectrum of the solid in $CFCl_3$ showed three major resonance bands at -72.7, -74.6, and -76.3 ppm, and two minor ones at -75.2 and -75.6 ppm. The major resonance bands at -74.6 and -76.3 ppm were determined to be $Ti[OC(CF_3)_3]_4$ and $(CF_3)_3COH \cdot HN(CH_2CH_3)_2$, respectively. The latter can be easily prepared in near quantitative yield simply by mixing F-(tert-butyl) alcohol with diethylamine:

IV-2 $(CF_3)_3COH + (CH_3CH_2)_2NH \longrightarrow (CF_3)_3COH \cdot HN(CH_2CH_3)_2$

In order to identify the remaining peaks, believed to be $Ti[OC(CF_3)_3]_{4-n}Cl_n$, where n = 1, 2, or 3, an attempt was made to prepare $Ti[OC(CF_3)_3]_2Cl_2$. When one mole of $Ti[OC(CF_3)_3]_4$ to two moles of HCl were added together, the only identifiable product by ^{19}F NMR was $(CF_3)_3COH$, in addition to the starting titanium complex:

IV-3 $Ti[OC(CF_3)_3]_4 + 4HCl \longrightarrow 4(CF_3)_3COH + (TiCl_4)$

Thus, while F-(tert-butyl) alcohol in the presence of an amine is capable of forming $Ti[OC(CF_3)_3]_4$ in low yield, the use of F-(tert-butyl) hypochlorite forms the compound in near quantitative yield, and with fewer side products.

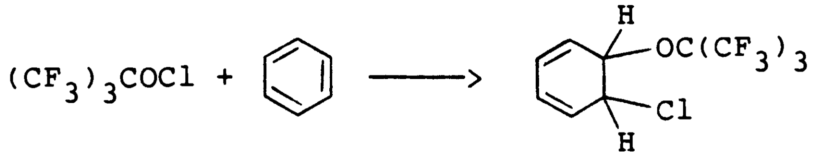
F-(tert-butyl) hypochlorite reportedly reacts not only with the iridium atom in Vaska's complex, but also with the triphenyl phosphine ligands present, forming $Ir[OC(CF_3)_3]_2Cl(CO)L_2$, where L is no longer PPh_3, but rather a ligand complex with $(CF_3)_3CO-$ and Cl- groups attached. The ^{19}F NMR data suggests three F-(tert-butoxy) groups per PPh_3, and two F-(tert-butoxy) groups coordinated to the iridium atom. The ^1H NMR data suggests loss of aromaticity in some of the benzene rings (32). In an attempt to determine more information about L, triphenyl phosphine was reacted with F-(tert-butyl) hypochlorite. The resulting product was a bright yellow viscous liquid showing one broad resonance band in the ^{19}F NMR spectrum (-70.0 ppm), and two broad resonance bands in the ^1H NMR spectrum, one in the aromatic region and the other slightly upfield to it (7.68 and 6.60 ppm). Side products to the reaction included the usual $(CF_3)_2CO$, CF_3Cl, and Cl_2, in addition to the parent alcohol, which suggests that the hypochlorite is capable of abstracting hydrogen atoms from the benzene rings. The chlorine gas produced is more than that expected from the simple oxidative addition of the hypochlorite to the phosphorus (III) atom, although from the data collected, it was impossible to determine the oxidation state of the phosphorus atom. In an effort to simplify the reaction, benzene was reacted with the hypochlorite in a 1 to 7 molar ratio, producing a clear and colorless viscous liquid. The gas chromatograph of this liquid showed an excess of 88 peaks with the major one at 32%. Again, the parent alcohol, $(CF_3)_3COH$, was found as a side product, but interestingly, no Cl_2 gas was produced. The ^{19}F NMR spectrum showed more than seven resonance bands in the $(C\underline{F}_3)_3CO-$ region. The ^1H spectrum showed a total loss of aromaticity by having several resonance bands upfield from the aromatic region

(0.90, 1.28, and from 4.5 to 5.6 ppm). The infrared spectrum supported this, showing no absorptions in the aromatic or alkene regions. A second reaction ran, using a 3.1 to 1 molar ratio of benzene to F-(tert-butyl) hypochlorite, gave similar results, with exception to a very weak C=C absorption in the infrared spectrum. It appears as though two major reaction types are taking place. The first, being the abstraction of the hydrogen atom forming the parent alcohol:

IV-4

and the second, being the addition of the hypochlorite to the benzene ring, where aromaticity is lost:

IV-5



In addition, reactions involving ring opening cannot be ruled out. The combination of these two reactions could easily account for the 88 peaks seen in the gas chromatograph. A further study of the reaction of F-(tert-butyl) hypochlorite with aromatic systems is needed.

F-(tert-butyl) hypochlorite has been found to oxidatively add to the metals, Pb, Te, and Bi:

IV-6 $2(CF_3)_3COCl + Pb \longrightarrow Pb[OC(CF_3)_3]_2 + Cl_2$

IV-7 $4(CF_3)_3COCl + Te \longrightarrow Te[OC(CF_3)_3]_4 + 2Cl_2$

IV-8 $6(CF_3)_3COCl + 2Bi \longrightarrow 2Bi[OC(CF_3)_3]_3 + 3Cl_2$

Silicon, however, did not react with F-(tert-butyl) hypochlorite.

With elemental sulfur, sulfur monochloride and tetrakis-F-(tert-butyl) sulfurane are formed:

IV-9 $8(CF_3)_3COCl + S_8 \longrightarrow 2S[OC(CF_3)_3]_4 + 3S_2Cl_2 + Cl_2$

Tetrakis-F-(tert-butoxy) sulfurane was prepared previously, by reacting SCl_2, S_2Cl_2, CS_2, or CCl_3SCl with the hypochlorite (28). Therefore, the sulfur monochloride produced in this reaction can go on to react with the hypochlorite to form additional tetrakis-F-(tert-butoxy) sulfurane:

IV-10 $8(CF_3)_3COCl + S_2Cl_2 \longrightarrow 2S[OC(CF_3)_3]_4 + 5Cl_2$

F-(tert-butyl) hypochlorite reacts with elemental iodine, forming the orange crystalline solid, tris-F-(tert-butoxy) iodine:

IV-11 $6(CF_3)_3COCl + I_2 \longrightarrow 2I[OC(CF_3)_3]_3 + 3Cl_2$

With CF_3I, the hypochlorite reacts to form a light yellow iodine (III) solid:

IV-12 $2(CF_3)_3COCl + CF_3I \longrightarrow CF_3I[OC(CF_3)_3]_2 + Cl_2$

Reactions of F-(tert-butyl) hypochlorite with compounds containing bromine have been disappointing. With elemental bromine, the hypochlorite gave $(CF_3)_2CO$, CF_3Cl, Cl_2, and CF_3Br. The presence of CF_3Br suggests the possible initial formation of F-(tert-butyl) hypobromite, followed by decomposition into $(CF_3)_3CO$ and CF_3Br.

F-(tert-butyl) hypochlorite reacts with cobalt (II) bromide forming a non-volatile brown solid, which could not be purified; consequently, the solid could not be characterized. The solid contained the F-(tert-butyl) group as determined by ^{19}F NMR, and a halogen, as shown by chemical reaction of the solid with silver nitrate. Presence of the halogen could be due to unreacted starting material. If so, the brown solid formed was probably $Co[OC(CF_3)_3]_2$ in a yield of approximately 90%. Chemical analysis of this material was inconclusive.

Both cesium bromide and cesium iodide behave like "sponges" in the uptake of the hypochlorite. With cesium bromide, a light yellow flakey solid was formed, which produces $(CF_3)_3COH$ when reacted with water. With cesium iodide, a mixture of brown and white solids were formed. An attempted separation of the solids by extraction with Freon-113 was unsuccessful due to decomposition of the solids. Interestingly, the reaction with cesium bromide produced chlorine gas as a side product, whereas the reaction with cesium iodide did not. This suggests the uptake of chlorine atoms in addition to the $(CF_3)_3CO$- group for the reaction with cesium iodide. In both reactions, however, the solids formed could not be identified.

In general, the F-(tert-butoxides) formed are moisture sensitive compounds which decompose giving $(CF_3)_3COH$. Besides forming the alcohol, $VO[OC(CF_3)_3]_3$ rapidly decomposes when exposed to air, forming an orange vanadium oxide, while the antimony compound formed, decomposes to a black solid. The butoxides of lead, tellurium, and bismuth all decompose to give the alcohol and probably the corresponding metal oxides. $I[OC(CF_3)_3]_3$ and $CF_3I[OC(CF_3)_3]_2$ give iodine and the alcohol; the latter also forms CF_3I in the presence of water. The unidentified compounds formed from the reaction of the hypochlorite with $CoBr_2$, CsBr, and CsI are all moisture sensitive, decomposing to the alcohol. Because of the high moisture sensitivity of these compounds, they must be handled in an inert atmosphere, and solvents used must be thoroughly dry.

Experimental

$\underline{VOCl_3 \text{ with } (CF_3)_3COCl}$. To a 75 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar, 0.677 mmol of $VOCl_3$ and 2.73 mmol of $(CF_3)_3COCl$ were added. The reaction mixture was maintained at 0°C (22 hr). After removing the volatile materials under vacuum, 0.670 mmol of the light yellow solid, $VO[OC(CF_3)_3]_3$, was formed in a 99% yield. Separation and analysis of the volatile material found: $(CF_3)_2CO$, CF_3Cl, and Cl_2 (2.05 mmol, theor. 2.03 mmol). The light yellow product sublimes in vacuo at ~60°C to a white crystalline solid; m.p. 62-63°C.

$\underline{SbCl_5 \text{ with } (CF_3)_3COCl}$. To a 150 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, $SbCl_5$ (0.535 mmol) and $(CF_3)_3COCl$ (2.746, 1.368, 1.791, and 1.292 mmol) were added. The reaction vessel was maintained at 0°C for a total of 20 days. Volatile materials at -78°C were periodically removed and analyzed: $(CF_3)_2CO$, CF_3Cl, $(CF_3)_3COH$, Cl_2 (1.688 mmol). A white crystalline solid (0.4250 g) was formed, and was found to sublime from 40-60°C. A qualitative reaction reaction with $AgNO_3/HNO_3$ indicated the presence of chlorine atoms in the solid.

$\underline{Cu_2Cl_2 \text{ with } (CF_3)_3COCl}$. To a 50 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar, 0.448 mmol of Cu_2Cl_2 and 3.847 mmol of $(CF_3)_3COCl$ were added. The reaction mixture was maintained at 0°C (18 hr) and then at room temperature (23 hr). The volatile material contained only $(CF_3)_2CO$ and CF_3Cl. The weight of the solid left behind increased by only 0.0147 gram. The reaction was not studied further.

$\underline{UCl_4 \text{ with } (CF_3)_3COCl}$. To a 200 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, 0.654 mmol of UCl_4 and 3.3 mmol of $(CF_3)_3COCl$ were added. The reaction mixture was warmed to 0°C (120 hr). The volatile material contained $(CF_3)_2CO$ and CF_3Cl. The weight of the solid left behind was essentially unchanged.

$\underline{SnCl_4 \text{ with } (CF_3)_3COCl}$. To a 200 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, 0.422 mmol of $SnCl_4$ and 2.57 mmol of $(CF_3)_3COCl$ were added. The reaction mixture was maintained at 0°C for 9 hours and then at room temperature for 48 hours. No solid product was formed, and in the gas phase, only the

$(CF_3)_3COCl$ decomposition products were observed; $(CF_3)_2CO$ and CF_3Cl.

$\underline{SiCl_4 \text{ with } (CF_3)_3COCl}$. To a 200 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, 0.409 mmol of $SiCl_4$ and 3.3 mmol of $(CF_3)_3COCl$ were added. The reaction mixture was warmed to 0°C (2.5 hr) and then to room temperature. No solid/liquid products were formed, and in the gas phase, only the $(CF_3)_3COCl$ decomposition products were observed; $(CF_3)_2CO$ and CF_3Cl.

$\underline{TiCl_4 \text{ with } (CF_3)_3COH}$. To a 200 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, 0.782 mmol of $TiCl_4$ and 3.573 mmol of $(CF_3)_3COH$ were added. The reaction mixture was maintained at room temperature (18 hr) and then heated to 30-50°C (7.5 hr). No reaction was evident, and an infrared spectrum showed essentially $(CF_3)_3COH$ and the absence of HCl.

$\underline{TiCl_4 \text{ with } (CF_3)_3COH \text{ and } (CH_3CH_2)_2NH}$. To the above reaction mixture, 3.111 mmol of $(CH_3CH_2)_2NH$ was added. A yellowish white solid was formed as the reaction mixture was warmed slowly from -196°C to 0°C. After 20 hours at 0°C, the volatile materials were removed leaving behind 1.1498 grams of a light yellow solid. Since the solid contained several different compounds, studies other than NMR were not undertaken.

$\underline{(CF_3)_3COH \text{ with } (CH_3CH_2)_2NH}$. To a 100 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, 0.66 mmol of $(CF_3)_3COH$ and 7.4 mmol of $(CH_3CH_2)_2NH$ were added. Upon warming to room temperature, a white solid was immediately formed. After 0.75 hour at room temperature, the volatile materials were removed, leaving behind 0.62 mmol of $(CF_3)_3COH \cdot HN(CH_2CH_3)_2$ in a 94% yield. The material sublimes at ∿40°C under vacuum.

$\underline{Ti[OC(CF_3)_3]_4 \text{ with } HCl}$. To a 200 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, 0.235 mmol of $Ti[OC(CF_3)_3]_4$ and 0.466 mmol of HCl were added. After one month at room temperature, the IR of the volatiles in the reaction vessel showed $(CF_3)_3COH$ and the absence of HCl. The ^{19}F NMR spectrum of the solid material gave a resonance band at -74.6 ppm, indicating unreacted $Ti[OC(CF_3)_3]_4$ (32).

$\underline{PPh_3 \text{ with } (CF_3)_3COCl}$. To a 75 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar, 0.517 mmol of PPh_3 and 1.949 mmol $(CF_3)_3COCl$ were added. The reaction was maintained at 0°C (23 hr); an additional 3.842 mmol of $(CF_3)_3COCl$ was added and again the reaction was maintained at 0°C (24 hr). The materials volatile at room temperature were removed under vacuum, leaving 1.0427 grams of a viscous yellow liquid. Separation and analysis of the volatile materials found: $(CF_3)_2CO$, CF_3Cl, $(CF_3)_3COH$, and Cl_2 (1.235 mmol). Other than taking the IR and ^{19}F NMR spectra of the liquid, the reaction was not further studied.

$\underline{C_6H_6}$ with $\underline{(CF_3)_3COCl}$. To a 200 ml Pyrex glass-vessel equipped with a Kontes Teflon valve and Teflon stirring bar, 1.011 mmol of benzene and 4.040 mmol of $(CF_3)_3COCl$ were added. The reaction was maintained at 0°C (22 hr); additional $(CF_3)_3COCl$ (1.994, 1.196 mmol) was added and again the reaction was maintained at 0°C (19 hr), and at room temperature for a total of 22 days. The materials volatile at room temperature were removed under vacuum, leaving 0.7813 gram of a clear and colorless viscous liquid. Separation and analysis of the volatile materials found: $(CF_3)_2CO$, CF_3Cl, $(CF_3)_3COH$ (2.6 mmol), and no Cl_2 or unreacted benzene. The gas chromatograph of the liquid product gave over 88 peaks with the major one at 32%. Other than taking the IR and NMR spectra of the liquid, the reaction was not further studied.

Excess $\underline{C_6H_6}$ with $\underline{(CF_3)_3COCl}$. To a 75 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar, 4.491 mmol of benzene and 1.402 mmol of $(CF_3)_3COCl$ were added. The reaction mixture was held at 0°C for 20 hours prior to removing the volatiles, C_6H_6 and $(CF_3)_3COH$, at room temperature. A clear colorless viscous liquid and a white solid (0.1394 g) were left behind. Other than taking the IR and NMR spectra of the product, the reaction was not further studied.

Pb with $\underline{(CF_3)_3COCl}$. To a 50 ml Pyrex-glass vessel equipped with a Kontes valve and Teflon stirring bar, 0.499

mmol of Pb and 4.50 mmol of $(CF_3)_3COCl$ were added. The reaction mixture was maintained at 0°C (90 hr) and at room temperature (50 hr); an additional 1.63 mmol of $(CF_3)_3COCl$ was added, and again maintained at room temperature (24 hr). The materials volatile at -78°C were periodically removed during this time. The materials volatile at room temperature were removed under vacuum, leaving 0.508 mmol of a light tan solid, $Pb[OC(CF_3)_3]_2$, in a 100% yield. Separation and analysis of the volatile materials found: $(CF_3)_2CO$, CF_3Cl, and Cl_2 (0.49 mmol, theor. 0.50 mmol).

Te with $(CF_3)_3COCl$. To a 50 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar, 0.429 mmol of Te and 3.67 mmol of $(CF_3)_3COCl$ were added. The reaction mixture was maintained at 0°C (100 hr), at room temperature (90 hr), and between 25-30°C (2 hr); an additional 1.08 mmol of $(CF_3)_3COCl$ was added and again maintained at room temperature (24 hr). The materials volatile at -78°C were periodically removed during this time. The materials volatile at room temperature were removed under vacuum, leaving 0.385 mmol of the white solid, $Te[OC(CF_3)_3]_4$, in a 90% yield. Separation and analysis of the volatile materials found: $(CF_3)_2CO$, CF_3Cl, and Cl_2 (0.85 mmol, theor. 0.86 mmol). The new compound sublimes in vacuo at 70°C and melts in a sealed tube from 93-95°C.

Bi with $(CF_3)_3COCl$. To a 50 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar, 0.427 mmol of Bi and 1.941 mmol of $(CF_3)_3COCl$ were added. Additional amounts of $(CF_3)_3COCl$ were added later (2.863, 3.283, and 0.713 mmol). Cumulatively, the reaction mixture was maintained at 0°C (40 hr), room temperature (94 hr), and 25-30°C (6 hr). The materials volatile at -78°C were removed periodically during this time. The materials volatile at 25°C were removed under vacuum, leaving 0.398 mmol of the sublimable white solid, $Bi[OC(CF_3)_3]_3$, in a 93% yield. Separation and analysis of the volatile materials found: $(CF_3)_2CO$, CF_3Cl, $(CF_3)_3COH$, and Cl_2.

Si with $(CF_3)_3COCl$. To a 50 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, 0.602 mmol of silicon and 0.933 mmol of $(CF_3)_3COCl$ were added. The reaction mixture was maintained at 0°C (18 hr) and then at room temperature (24 hr). The volatile material contained only $(CF_3)_2CO$ and CF_3Cl. The weight of the solid left behind increased by only 0.0060 gram. The reaction was not further studied.

S_8 with $(CF_3)_3COCl$. To a 50 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, 2.59 mmol of sulfur and 3.59 mmol of $(CF_3)_3COCl$ were added. The reaction mixture was maintained at 0°C (2 hr). Separation and analysis of the volatile material found: Cl_2 and S_2Cl_2/SCl_2. The white solid left behind was found to be 0.701 mmol of $S[OC(CF_3)_3]_4$, which was formed in a 78%

yield. Melting point and spectral data agree with literature values (28).

$\underline{I_2 \text{ with } (CF_3)_3COCl}$. To a 200 ml Pyrex-glass vessel equipped with a Kontes Teflon valve, 0.403 mmol of I_2 and 4.82 mmol of $(CF_3)_3COCl$ were added. The reaction mixture was maintained at 0°C (44 hr). After removal of the volatile materials under vacuum, 0.780 mmol of the orange solid, $I[OC(CF_3)_3]_3$, was formed in a 97% yield. Separation and analysis of the volatile material found: $(CF_3)_2CO$, CF_3Cl, and Cl_2 (1.20 mmol, theor. 1.21 mmol). The product slowly sublimes at room temperature while under vacuum; m.p. 22.5-23.5°C.

$\underline{CF_3I \text{ with } (CF_3)_3COCl}$. In a 75 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar, 1.019 mmol of CF_3I and 1.837 mmol of $(CF_3)_3COCl$ were added. The reaction mixture was maintained at 0°C (118 hr); an additional 1.079 mmol of $(CF_3)_3COCl$ was added, and again maintained at 0°C (50 hr). Separation and analysis of the volatile material found: $(CF_3)_2CO$, CF_3Cl, CF_3I, and Cl_2 (1.010 mmol, theor. 1.019 mmol). The light yellow solid left behind was found to be 0.953 mmol of $CF_3I[OC(CF_3)_3]_2$, which was formed in a 94% yield. The product slowly sublimes at room temperature while under vacuum.

$\underline{Br_2 \text{ with } (CF_3)_3COCl}$. To a 50 ml Pyrex-glass reaction vessel equipped with a Kontes Teflon valve and Teflon stirring bar, 0.324 mmol of Br_2 and 2.218 mmol of $(CF_3)_3COCl$

were added. After 100 hours at 0°C, there was no unreacted Br_2, and all substances in the reaction vessel were in the gaseous phase. Analysis of the volatile material found: $(CF_3)_2CO$, CF_3Cl, CF_3Br, and Cl_2.

<u>$CoBr_2$ with $(CF_3)_3COCl$</u>. To a 50 ml Pyrex-glass reaction vessel equipped with a Kontes Teflon valve and Teflon stirring bar, 0.128 mmol of $CoBr_2$ and 1.072 mmol of $(CF_3)_3COCl$ were added. After being held at 0°C (18 hr) and at room temperature (48 hr), an additional 0.737 mmol of $(CF_3)_3COCl$ was added. The reaction mixture was maintained at room temperature (48 hr) prior to removing the volatile material from the reaction vessel. A brown solid (0.0641 g) remained, which was found to decompose at 155°C. This material could not be sublimed under vacuum, and was found to give a positive test with $AgNO_3/HNO_3$ indicating either unreacting starting material in the sample, or the presence of a halogen in the new compound formed. Analysis of the volatile material removed from the reaction vessel found: $(CF_3)_2CO$, CF_3Cl, and Cl_2.

<u>CsBr with $(CF_3)_3COCl$</u>. To a 200 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar, 0.957 mmol of CsBr and 2.696 mmol of $(CF_3)_3COCl$ were added. Additional $(CF_3)_3COCl$ (1.414, 1.657, 1.920, and 2.566 mmol) was added over the course of the reaction. The reaction vessel was maintained for a total of 1 day at 0°C and 32 days at room temperature. Volatiles in the reaction vessel

at room temperature were periodically removed during this time. Analysis of this material found: $(CF_3)_2CO$, CF_3Cl, and Cl_2 (0.693 mmol). A light yellow solid (0.4657 g) was formed which decomposes at temperatures above 45°C. Other than taking the IR spectrum of this solid, the reaction was not further studied.

CsI with $(CF_3)_3COCl$. To a 200 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar, CsI (0.923 mmol) and $(CF_3)_3COCl$ (3.793, 4.416 mmol) were added. The reaction was maintained at 0°C (6 d), from 8-14°C (9 hr), and at room temperature (4 d). After the volatiles at room temperature were removed [$(CF_3)_2CO$, CF_3Cl, and no Cl_2], a mixture of brown and white solids remained (1.2979 g) which were found to decompose at temperatures above 72°C (I_2 is given off). Separation of the solids was attempted by extraction with Freon-113, but was unsuccessful due to the decomposition of the solids. Other than attempting to take the IR spectrum of the solid, the reaction was not further studied.

Elemental Analysis

The results of the elemental analysis for the F-(tert-butoxides) are shown in Table X. There is good to fair agreement with the calculated compositions. The deviations are most likely caused by the hydrolytic decomposition of the compounds when handled. The results from the compound

TABLE X

ELEMENTAL ANALYSIS FOR F-(TERT-BUTOXIDES)

Compound	Element	Wt.% Calc.	Wt.% Found
$VO[OC(CF_3)_3]_3$**	Carbon	18.67	17.71
$(CF_3)_3COH \cdot HN(CH_2CH_3)_2$	Carbon	31.07	30.83
	Hydrogen	3.92	3.93
	Nitrogen	4.53	4.65
$Pb[OC(CF_3)_3]_2$	Carbon	14.19	12.81
$Te[OC(CF_3)_3]_4$	Carbon	17.99	17.17
$Bi[OC(CF_3)_3]_3$	Carbon	15.77	15.45
	Fluorine	56.12	54.4
$I[OC(CF_3)_3]_3$	Carbon	17.32	17.39
	Fluorine	61.65	61.3
	Iodine	15.25	15.20
$CF_3I[OC(CF_3)_3]_2$*	Iodine	19.06	18.8
$SbCl_5$ with $(CF_3)_3COCl$	Carbon	-----	7.54
	Fluorine	-----	43.2
	Chlorine	-----	14.46/14.38
$CoBr_2$ with $(CF_3)_3COCl$**	Carbon	-----	5.63

*The weight percent of iodine found in this sample was determined by iodiometric titration of the water soluble species, and by weighing the collected CF_3I gas given off upon decomposition of $CF_3I[OC(CF_3)_3]_2$ in water.

**Elemental analysis was performed at the University of Idaho, Moscow. All other samples were analysed by Beller Microanalytical Laboratories, Gottingen, West Germany.

formed by the reaction of $SbCl_5$ with $(CF_3)_3COCl$ are extremely confusing since ratio of fluorine to carbon is not even close to what it should be, assuming all carbon and fluorine atoms are F-(tert-butyl) groups; e.g. 5.73 found, 3.56 calculated. Likewise, for the compound formed from the reaction to $CoBr_2$ with $(CF_3)_3COCl$, the weight percent of carbon found for the compound can not be explained.

Infrared Spectra

The infrared absorptions are tabluated in Table XI and the actual spectra are shown in the Appendix. The common feature of all the new compounds is the $(CF_3)_3CO$- group, which gives strong absorptions bands in the 1145-1305 cm^{-1} region attributable to the C-F stretching frequency (55, 63); absorption bands in the 720-760 cm^{-1} region for the C-F deformation modes (54); and the C-O stretching frequency around 1000 cm^{-1} (64). Metal oxygen (M=0) stretching vibrations are also found around 1000 cm^{-1} (65) as is seen with $VO[OC(CF_3)_3]_3$ with the V=0 stretching frequency at 1044 cm^{-1}. Metal oxygen (M-0) stretching vibrations are generally seen below 650 cm^{-1} (64) and therefore are not seen in the spectra due to the absorption by the sodium chloride plates used. For the compound $(CF_3)_3COH \cdot HN(CH_2CH_3)_2$, the broad absorption at 2600 cm^{-1} is due to the N-H stretching frequency (66), and absorptions around 2996 cm^{-1} are from the C-H stretching modes (67).

TABLE XI

INFRARED ABSORPTION BANDS FOR F-(TERT-BUTOXIDES)

$I[OC(CF_3)_3]_3$

1256 (s,b)*
1194 (ms)
1172 (ms)
1144 (s)
1104 (s)
1068 (s)
972 (s)
796 (w)
766 (s)
726 (s)
686 (ms)

$VO[OC(CF_3)_3]_3$

1300 (s)
1265 (s,b)
1192 (m)
1140 (s,b)
1044 (w)
977 (s)
847 (ms)
810 (sh)
760 (vw)
753 (w)
727 (s)

$Pb[OC(CF_3)_3]_2$

1304 (ms)
1248 (s,b)
1214 (sh)
1184 (m)
1140 (s)
970 (s)
766 (m)
724 (ms)
674 (w)

$CF_3I[OC(CF_3)_3]_2$

1305 (sh)
1262 (sh)
1244 (s,b)
1215 (sh)
1194 (mw)
1165 (m)
1115 (s)
1071 (w)
1026 (s)
1007 (ms)
980 (s)
969 (s)
768 (m)
744 (ms)
731 (s)
726 (s)
691 (m)

$Te[OC(CF_3)_3]_4$

1308 (sh)
1260 (s)
1172 (m)
968 (ms)
760 (sh)
724 (s)
626 (vs,b)

$Bi[OC(CF_3)_3]_3$

1303 (ms)
1245 (s)
1207 (sh)
1153 (s)
965 (s)
765 (w)
723 (s)

*Refers to the intensity of the absorption where vs = very strong, s = strong, ms = medium-strong, m = medium, mw = medium weak, w = weak, vw = very weak, b = broad, vb = very broad, and sh = shoulder. Absorptions bands are in units of cm^{-1}.

TABLE XI (con't)

$(CF_3)_3COH \cdot HN(CH_2CH_3)_2$

3038 (w)
2996 (m)
2952 (m)
2918 (mw)
2868 (mw)
2600 (m,vb)
1656 (sh)
1648 (m)
1502 (m)
1480 (m)
1458 (m)
1394 (m)
1367 (m)
1290 (sh)
1256 (s)
1220 (s,b)
1172 (s)
1150 (sh)
1064 (m)
1050 (m)
1014 (w)
956 (s)
866 (w)
822 (s)
758 (w)
720 (s)
668 (w)

$CoBr_2$ with $(CF_3)_3COCl$

1304 (sh)
1258 (s)
1180 (s)
1144 (s)
1116 (sh)
996 (sh)
972 (s)
816 (m)
798 (sh)
772 (m)
756 (vw)
746 (sh)
734 (sh)
726 (s)
686 (w)

PPh_3 with $(CF_3)_3COCl$

3614 (w)
3060 (m,b)
1582 (m)
1562 (sh)
1552 (sh)
1542 (sh)
1522 (sh)
1478 (w)
1444 (m)
1422 (sh)
1408 (ms)
1386 (ms)
1274 (s,b)
1186 (sh)
1174 (sh)
1132 (s,b)
1074 (sh)
1054 (mw)
1002 (s)
968 (s)
898 (w)
842 (sh)
826 (w)
768 (mw)
736 (ms)
726 (s)
674 (m)
646 (m)

$SbCl_5$ with $(CF_3)_3COCl$

1300 (sh)
1252 (s)
1140 (s)
970 (s)
800 (sh)
782 (m)
742 (sh)
724 (s)
700 (s)

TABLE XI (con't)

C_6H_6 with $(CF_3)_3COCl$

1376	(sh)
1350	(sh)
1278	(s,b)
1182	(m)
1134	(s)
1016	(ms)
988	(sh)
970	(s)
940	(sh)
912	(sh)
844	(w)
808	(w)
794	(sh)
768	(w)
754	(w)
746	(ms)
736	(s)

CsBr with $(CF_3)_3COCl$

1306	(sh)
1252	(vs,b)
1200	(sh)
1154	(sh)
1104	(sh)
964	(s)
790	(w)
724	(s)

xs C_6H_6 with $(CF_3)_3COCl$

2960	(sh)
2930	(w)
2860	(w)
1658	(w)
1460	(vw)
1410	(w)
1384	(sh)
1360	(sh)
1278	(vs,b)
1226	(sh)
1180	(m)
1144	(s)
1014	(s)
972	(s)
934	(sh)
910	(sh)
880	(vw)
836	(w)
780	(vw)
768	(sh)
756	(w)
744	(s)
736	(s)

The absorptions at 1502, 1480, and 1458 cm^{-1}, and at 1394 and 1367 cm^{-1} are most likely due to the CH_2 and CH_3 deformation modes, respectively (67). The absorption at 1648 cm^{-1} is due to the C-O stretching frequency in the salt (37, 68). For the compounds formed from PPh_3 and F-(tert-butyl) hypochlorite, the broad absorption at 3060 cm^{-1} and the absorption at 1582 cm^{-1} with shoulders, are probably due to the =C-H and C=C stretching frequencies respectively, from both the aromatic and alkene products (69). The compounds formed from the 1 to 7 molar ratio of benzene to hypochlorite show no C-H or C=C stretches. Those formed from the 3.2 to 1 molar ratio of benzene to hypochlorite show a weak absorption centered at 2920 cm^{-1} [aliphatic region (70)], and a very weak absorption at 1658 cm^{-1}, which is characteristic of a C=C stretch.

Nuclear Magnetic Resonance Spectra

The ^{19}F and ^{1}H NMR data for the F-(tert-butoxides) is presented in Table XII. Typical chemical shift values for the $(C\underline{F}_3)_3CO-$ group are between -68.0 to -78.0 ppm relative to an internal $CFCl_3$ standard (28, 31, 37). With exception to the complexes formed from the reaction of F-(tert-butyl) hypochlorite with benzene, all F-(tert-butoxides) prepared fall into this range. The $(C\underline{F}_3)_3CO-$ group is seen as a singlet in all compounds formed except for $CF_3I[OC(CF_3)_3]_2$, where the two fluorine resonances are seen as unresolved

TABLE XII

NMR DATA FOR F-(TERT-BUTOXIDES)

Compound*	Chemical Shifts (ppm)**	Rel. Int.
$VO[OC(C\underline{F}_3)_3]_3$	-73.3	---
$(C\underline{F}_3)_3COH.HN(CH_2CH_3)_2$	-76.3	---
$(CF_3)_3CO\underline{H}.\underline{H}N(CH_2CH_3)_2$	10.10	1.0
$(CF_3)_3COH.HN(C\underline{H}_2CH_3)_2$	2.74 (quartet)	2.0
$(CF_3)_3COH.HN(CH_2C\underline{H}_3)_2$	1.34 (triplet)	3.0
$Pb[OC(C\underline{F}_3)_3]_2$	-74.0	---
$Te[OC(C\underline{F}_3)_3]_4$	-72.1	---
$Bi[OC(C\underline{F}_3)_3]_3$	-74.2	---
$I[OC(C\underline{F}_3)_3]_3$	-72.0	---
$CF_3I[OC(C\underline{F}_3)_3]_2$	-72.6 (multiplet)	6.1
$C\underline{F}_3I[OC(CF_3)_3]_2$	-25.5 (multiplet)	1.0

Reaction	^{19}F Chemical Shifts (ppm)**
$SbCl_5$ with $(CF_3)_3COCl$	-71.3 (major); -72.3 (minor)
PPh_3 with $(CF_3)_3COCl$	-70.0 (broad singlet); ^1H NMR gave bands at 6.60 (singlet) and 7.68 (multiplet)
C_6H_6 with $(CF_3)_3COCl$	7+ bands centered at -68.6; largest at -68.7; ^1H NMR gave 8+ bands from 4.5-5.6 and multiplets at 1.28, 0.90
xs C_6H_6 with $(CF_3)_3COCl$	5+ bands centered at -70.5; largest at -70.9; ^1H NMR gave 6+ bands from 4.5-6.2 and bands at 1.26 and 0.86

*Corresponding chemical shift refers to the element underlined.

**Fluorine and proton chemical shifts are reported relative to internal $CFCl_3$ and TMS standards, respectively. All resonance bands are singlets unless otherwise stated.

multiplets. Surprisingly, the spectra for $(CF_3)_3COH \cdot HN(CH_2CH_3)_2$ shows no observable coupling between the fluorines and hydrogens, or between the ethyl hydrogens and the amino hydrogens. This implies that the rate of intermolecular exchange of the amino hydrogens is fast enough to decouple spin-spin interactions to the ethyl hydrogens. Direct coupling between the nitrogen and hydrogen is also not observed which is not all that uncommon. Coupling between the ethyl hydrogens ($J_{CH_2-CH_3}$) was measured at 7.4 Hz.

For the reactions involving aromatic compounds with F-(tert-butyl) hypochlorite, the ^{19}F NMR spectra showed one broad resonance band for the compound(s) formed from PPh_3, and several resonance bands from the reactions with benzene, all of which were in, or near the specified chemical shift range. The proton spectra for the reactions with benzene were complicated, giving several peaks upfield from the aromatic region suggesting non-aromatic products. For the complex formed from triphenyl phosphine and F-(tert-butyl) hypochlorite, a multiplet in the aromatic region and a singlet upfield to it were seen.

Mass Spectra

The mass spectra are tabulated in Table XIII. All mass spectra taken show fragments resulting from the parent alcohol, $(CF_3)_3COH$, indicating that the samples were at

TABLE XIII

MASS SPECTRA FOR F-(TERT-BUTOXIDES)

M/e	Rel. Int.	Type	M/e	Rel. Int.	Type
$Te[OC(CF_3)_3]_4$			148	8.3	$C_3F_5OH^+$
18	14.7	H_2O^+	166	44.9	$C_3F_6O^+$
28	24.0	CO^+/N_2^+	167	53.5	$C_3F_6OH^+$
29	3.4	COH^+	180	2.6	?
31	9.9	CF^+	197	36.2	$C_4F_7O^+$
32	6.1	O_2^+	198	1.8	$C_4F_7OH^+$
44	5.3	CO_2^+	217	5.8	$C_4F_8OH^+$
50	9.3	CF_2^+	$I[OC(CF_3)_3]_3$		
51	12.8	?	18	0.6	H_2O^+
69	100.0	CF_3^+	28	54.2	CO^+/N_2^+
78	13.0	$C_2F_2O^+$	29	7.0	COH^+
81	2.6	$C_2F_3^+$	32	83.3	O_2^+
89	2.4	?	40	72.9	C_2O^+
93	3.2	?	44	9.6	CO_2^+
97	100.0	$C_2F_3O^+$	50	2.0	CF_2^+
98	3.5	$C_2F_3OH^+$	51	8.7	?
100	8.3	$C_2F_4^+$	69	95.1	CF_3^+
117	4.8	$C_2F_4OH^+$	78	8.1	$C_2F_2O^+$
119	16.5	$C_2F_5^+$	89	2.2	?
128	15.7	$C_3F_4O^+$	97	92.4	$C_2F_3O^+$
129	4.5	$C_3F_4OH^+$	98	2.9	$C_2F_3OH^+$
131	2.2	?	100	5.8	$C_2F_4^+$
147	44.6	$C_3F_5O^+$	117	3.8	$C_2F_4OH^+$

TABLE XIII (con't)

M/e	Rel. Int.	Type
119	14.9	$C_2F_5^+$
128	16.7	$C_3F_4O^+$
129	3.9	$C_3F_4OH^+$
147	53.8	$C_3F_5O^+$
148	10.8	$C_3F_5OH^+$
166	1.0	$C_3F_6O^+$
167	62.5	$C_3F_6OH^+$
168	2.6	?
197	100.0	$C_4F_7O^+$
198	1.4	$C_4F_7OH^+$
217	2.3	$C_4F_8OH^+$
$SbCl_5$ with $(CF_3)_3COCl$		
18	23.9	H_2O^+
28	100.0	CO^+/N_2^+
32	16.7	O_2^+
40	2.5	C_2O^+
44	2.0	CO_2^+
51	5.9	?
69	63.4	CF_3^+
78	5.7	$C_2F_2O^+$
97	65.4	$C_2F_3O^+$
98	2.0	$C_2F_3OH^+$
100	4.6	$C_2F_4^+$
117	2.9	$C_2F_4OH^+$
119	10.5	$C_2F_5^+$
128	11.6	$C_3F_4O^+$
129	2.9	$C_3F_4OH^+$
147	36.6	$C_3F_5O^+$
148	7.5	$C_3F_5OH^+$
167	37.9	$C_3F_6OH^+$
197	18.3	$C_4F_7O^+$
217	3.3	$C_4F_8OH^+$
$VO[OC(CF_3)_3]_3$		
18	82.9	H_2O^+
28	53.7	CO^+/N_2^+
31	11.7	CF^+
36	28.5	?
38	11.0	?
43	11.0	C_2F^+
44	13.9	CO_2^+
50	8.5	CF_2^+
69	100.0	CF_3^+
78	9.3	$C_2F_2O^+$
85	77.6	$VO_2H_2^+$
87	25.6	$VO_2H_4^+$
93	7.8	?
97	63.9	$C_2F_3O^+$
100	7.8	$C_2F_4^+$

TABLE XIII (con't)

M/e	Rel. Int.	Type	M/e	Rel. Int.	Type
101	41.5	$VO_3H_2^+$	$Pb[OC(CF_3)_3]_2$		
103	24.9	$VO_3H_4^+$	18	5.0	H_2O^+
116	15.9	$C_2F_4O^+$	28	11.6	CO^+/N_2^+
119	16.1	$C_2F_5^+$	39	2.4	?
128	10.5	$C_3F_4O^+$	43	1.8	C_2F^+
131	30.5	?	44	3.3	CO_2^+
135	32.7	$VO_5H_4^+$	51	2.7	?
		$V_2O_2H^+$	69	37.7	CF_3^+
137	12.0	$VO_5H_6^+$	78	2.9	$C_2F_2O^+$
		$V_2O_2H_3^+$	97	49.5	$C_2F_3O^+$
147	43.2	$C_3F_5O^+$	98	1.7	$C_2F_3OH^+$
148	7.8	$C_3F_5OH^+$	100	3.7	$C_2F_4^+$
		VOC_2F_3+	117	1.6	$C_2F_4OH^+$
149	11.7	?	119	5.1	$C_2F_5^+$
151	28.8	$V_2O_3H^+$	128	17.1	$C_3F_4O^+$
153	16.3	$V_2O_3H_3^+$	129	1.7	$C_3F_4OH^+$
163	9.8	?	133	3.2	?
167	28.0	$C_3F_6OH^+$	147	58.3	$C_3F_5O^+$
197	24.4	$C_4F_7O^+$	148	19.2	$C_3F_5OH^+$
201	18.3	$V_2O_6H_3^+$	167	100.0	$C_3F_6OH^+$
203	12.2	$V_2O_6H_5^+$	168	3.6	$^{13}CC_2F_6OH^+$
217	7.3	$C_4F_8OH^+$	181	1.5	$C_4F_7^+$
		$VOC_3F_6^+$	197	14.2	$C_4F_7O^+$
267	7.3	$VOC_4F_8^+$	200	2.9	$C_4F_8^+$

TABLE XIII (con't)

M/e	Rel. Int.	Type	M/e	Rel. Int.	Type
207	1.6	?			C_2FO^+
217	2.3	$C_4F_8OH^+$	69	12.7	CF_3^+
441	0.9	$Pb^{206}OC(CF_3)_3^+$			$C_4H_7N^+$
442	1.0	$Pb^{207}OC(CF_3)_3^+$			$C_3H_3NO^+$
443	1.8	$Pb^{208}OC(CF_3)_3^+$	71	1.3	$C_4H_9N^+$
$(CF_3)_3COH \cdot HN(CH_2CH_3)_2$					$C_3H_5NO^+$
18	7.3	H_2O^+	72	17.2	$C_4H_{10}N^+$
28	18.1	CO^+/N_2^+			$C_3H_6NO^+$
29	2.5	COH^+	73	49.0	$C_4H_{11}N^+$
		$C_2H_5^+$			$C_3H_7NO^+$
30	30.5	CH_2O^+	74	2.6	$C_4H_{12}N^+$
32	2.9	O_2^+			$C_3H_8NO^+$
		H_2NO^+	78	1.2	$C_2F_2O^+$
42	1.7	$C_2H_4N^+$	97	18.8	$C_2F_3O^+$
44	11.7	CO_2^+	100	1.5	$C_2F_4^+$
		$C_2H_6N^+$	117	0.7	$C_2F_4OH^+$
		CH_2NO^+	119	2.2	$C_2F_5^+$
51	1.3	?	128	6.6	$C_3F_4O^+$
56	3.1	$C_3H_6N^+$	147	22.5	$C_3F_5O^+$
		$C_2H_2NO^+$	148	6.7	$C_3F_5OH^+$
58	100.0	$C_3H_8N^+$	166	38.6	$C_3F_6O^+$
		$C_2H_4NO^+$	167	1.4	$C_3F_6OH^+$
59	4.0	$C_3H_9N^+$	181	1.2	$C_4F_7^+$
		$C_2H_5NO^+$	197	5.9	$C_4F_7O^+$

TABLE XIII (con't)

M/e	Rel. Int.	Type
200	1.8	$C_4F_8^+$
217	0.9	$C_4F_8OH^+$

least partially decomposed prior to taking the mass spectra, or were hydrolytically decomposed to the alcohol in the sample inlet system or the ionization chamber. In all of the spectra, H_2O^+ was present at a relative abundance ranging from 1% to 83% of the base peak. $Te[OC(CF_3)_3]_4$, $I[OC(CF_3)_3]_3$, and the antimony compound, gave appropriate fragments resulting from the F-(tert-butoxy) group, however, no molecular ion or fragments containing Te, I, or Sb were seen in the spectra. For $VO[OC(CF_3)_3]_3$, in addition to fragments resulting from the F-(tert-butoxy) group, a fragment corresponding to $[V^{51}OC(CF_3)_3-F]^+$ was seen.

Although no molecular ion was observed in the mass spectrum for $Pb[OC(CF_3)_3]_2$, appropriate fragments resulting from the F-(tert-butoxy) group were present, in addition to $Pb[OC(CF_3)_3]^+$ fragments for the three most abundant isotopes of lead. Again, no molecular ion was observed in the mass spectrum of $(CF_3)_3COH\cdot HN(CH_2CH_3)_2$, however, appropriate fragments resulting from F-(tert-butoxy) groups and diethylamine were present.

Ultraviolet Spectrum

The ultraviolet spectrum of F-(tert-butyl) hypochlorite was obtained in perfluoro-2-butyltetrahydrofuran. The λ_{max} was observed at 256 nm which is in the region of organic hypochlorites (71).

REFERENCES CITED

1. J. R. Case, N. H. Ray and H. L. Roberts, J. Chem Soc., 2070 (1961).

2. J. Steward, L. Kegley, H. F. White and G. L. Gard, J. Org. Chem., 34, 760 (1969).

3. R. E. Banks, M. G. Barlow, R. N. Haszeldine and W. D. Morton, J. Chem. Soc., Perkin 1, 1266 (1974).

4. G. L. Gard and C. Woolf, J. Fluorine Chem., 1, 487 (1971).

5. L. H. Cross, G. Cushing and H. L. Roberts, Spectrochim. Acta, 17, 344 (1961).

6. N. Boden, J. Feeney and L. H. Sutcliffe, Spectrochim. Acta, 21, 627 (1965).

7. R. A. DeMarco and W. B. Fox, J. Fluorine Chem., 12, 137 (1978).

8. R. E. Noftle and W. B. Fox, J. Fluorine Chem., 9, 219 (1977).

9. H. F. Efner, R. Kirk, R. E. Noftle and M. Uhrig, Polyhedron, 1, 723 (1982).

10. A. W. Macellis and R. E. Eibeck, J. Fluorine Chem., 5, 71 (1975).

11. C. Woolf and G. L. Gard, U.S. Patent 3,448,121 (1969): Chem. Abstr., 72, 12547h (1970).

12. E. F. Witucke, J. Fluorine Chem., 20, 807 (1982).

13. British Patent 929,990 (1963); Chem. Abstr., 59, 6536g (1963).

14. R. DeBuhr, J. Howbert, J. M. Canich, H. F. White and G. L. Gard, J. Fluorine Chem., 20, 515 (1982).

15. G. H. Cady, "Fluorine Containing Compounds of Sulfur" Advances in Inorganic Chemistry and Radiochemistry, Vol. 2, H. J. Emeleus and A. G. Sharpe, eds., Academic Press Inc., New York, 105 (1960).

16. G. L. Gard and C. Woolf and R. M. Shaw, British Patent 1,167,228 (1969); Chem. Abstr., 72, 16735r (1970).

17. G. L. Gard and C. Woolf, U.S. Patent 3,519,725 (1970); Chem. Abstr., 73, 114434 g (1970).

18. E. E. Gilbert and G. L. Gard, U.S. Patent 3,475,453 (1969); Chem. Abstr., 72, 20877f (1970).

19. J. L. Bach, C. Woolf and G. L. Gard, British Patent 1,167,112 (1969); Chem. Abstr., 72, 21366a (1970).

20. M. Yonekura, Japan. Kokai, 74 123,986 (1974); Chem. Abstr., 82, 175255g (1975).

21. D. E. Young, L. R. Anderson, D. E. Gould and W. B. Fox, J. Am. Chem. Soc., 92, 2313 (1970).

22. C. J. Schack and W. Maya, J. Am. Chem. Soc., 91, 2902 (1969).

23. D. E. Gould, L. R. Anderson, D. E. Young and W. B. Fox, J. Am. Chem. Soc., 91, 1310 (1969).

24. D. E. Young, L. R. Anderson and W. B. Fox, Inorg. Chem., 9, 2602 (1970).

25. D. E. Young, L. R. Anderson and W. B. Fox, Inorg. Nucl. Chem. Lett., 6, 341 (1970).

26. L. R. Anderson, D. E. Young, D. E. Gould, R. Juurik-Hogan, D. Nuechterlein and W. B. Fox, J. Org. Chem., 35, 3730 (1970).

27. Q. C. Mir, D. P. Babb and J. M. Shreeve, J. Am. Chem. Soc., 101, 3961 (1979).

28. Q. C. Mir, K. A. Laurence, R. W. Shreeve, D. P. Babb and J. M. Shreeve, J. Am. Chem. Soc., 101, 5949 (1979).

29. G. L. Gard and J. M. Shreeve, J. Am. Chem Soc., 104, 5566 (1982).

30. D. E. Young and W. B. Fox, Inorg. Nucl. Chem. Lett., 7, 1033 (1971).

31. Q. C. Mir, R. W. Shreeve and J. M. Shreeve, *Phosphorus Sulfur*, 8, 331 (1980).

32. J. M. Canich, G. L. Gard and J. M. Shreeve, *Inorg. Chem.*, 23, 441 (1984).

33. S. Andreades, *J. Org. Chem.*, 27, 4163 (1962).

34. D. E. Young, L. R. Anderson and W. B. Fox, *Inorg. Chem.*, 10, 2810 (1971).

35. D. E. Young, L. R. Anderson and W. B. Fox, *J. Am. Chem. Soc., Chem. Commun.*, 736 (1971).

36. S. D. Morse, K. A. Laurence, G. H. Sprenger and J. M. Shreeve, *J. Fluorine Chem.*, 11, 327 (1978).

37. R. E. A. Dear, W. B. Fox. R. J. Fredericks, E. E. Gilbert and D. K. Huggins, *Inorg. Chem.*, 9, 2590 (1970).

38. F. J. Pavlik, U.S. Patent 3,385,904 (1968); *Chem. Abstr.*, 69, 26753x (1968).

39. R. A. Andersen and G. E. Coates, *J. Chem. Soc., Dalton Trans.*, 12, 1244 (1975).

40. L. J. Turbini, G. M. Golenwsky and F. F. Porter, *Inorg. Chem.*, 14, 691 (1975).

41. F. J. Pavlik, U.S. Patent 3,668,233 (1972); *Chem. Abstr.*, 77 100830d (1972).

42. R. A. De Marco, T. A. Kovacina and W. B. Fox, *J. Fluorine Chem.*, 5, 221 (1975).

43. A. Majid and J. M. Shreeve, *Inorg. Chem.*, 13, 2710 (1974).

44. D. K. Huggins, K. Dale and W. B. Fox, U.S. Patent 3,631,081 (1971); *Chem. Abstr.*, 76, 58956b (1972).

45. D. C. Bradley, M. H. Chisholm, M. W. Extine and M. E. Stager, *Inorg. Chem.*, 16, 1794 (1977).

46. M. H. Chisholm, F. A. Cotton, C. A. Murrillo and W. W. Reichert, *Inorg. Chem.*, 16, 1801 (1977).

47. D. A. Johnson and A. B. Waugh, *J. Fluorine Chem.*, 22, 51 (1983).

48. D. A. Johnson, J. C. Taylor and A. B. Waugh, Inorg. Nucl. Chem. Lett., 15, 205 (1979).

49. K. Baum and C. D. Beard, J. Am. Chem. Soc., 96, 3233 (1974).

50. C. Woolf, R. E. A. Dear and D. E. Young, U.S. Patent 3,761,501 (1973); Chem. Abstr., 79, 136560w (1973).

51. N. S. Walker and D. D. Desmarteau, J. Fluorine Chem., 5, 127 (1975).

52. R. E. Sievers and J. E. Sadlowski, Science, 201, 217 (1978).

53. B. Cohen and A. G. MacDiarmid, Inorg. Chem., 4, 1782 (1965).

54. G. Socrates, Infrared Characteristic Group Frequencies, John Wiley and Sons, Inc., New York, 107 (1980).

55. Socrates, 108.

56. J. K. Brown and K. J. Morgan, "The Vibrational Spectra of Organic Fluorine Compounds," Advances in Fluorine Chemistry, Vol. 4, M. Stacey, J. C. Tatlow and A. G. Sharpe, eds., Butterworth Inc., Washington, 290 (1965).

57. Socrates, 65.

58. Brown and Morgan, 299.

59. Brown and Morgan, 289.

60. C. I. Merril, S. M. Williamson, G. H. Cady and D. F. Eggers Jr., Inorg. Chem., 1, 215 (1962).

61. D. L. Pavia, G. M. Lampman and G. S. Kriz Jr., Introduction to Spectroscopy: A Guide for Students of Organic Chemistry, W. B. Saunders Co., Philadelphia, 96 (1979).

62. R. D. Chambers, J. A. Jackson, W. K. R. Musgrave and R. A. Storey, J. Chem. Soc. (C), 2221 (1968).

63. D. G. Weiblen, "The Infrared Spectra of Fluorocarbons and Related Compounds," Fluorine Chemistry, Vol. 2, J. H. Simons, ed., Academic Press Inc., New York, 456, (1954).

64. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 2nd ed., Wiley-Interscience, New York, 220 (1970).

65. Nakamoto, 114.

66. Pavia, Lampman and Kriz, 68.

67. Pavia, Lampman and Kriz, 29.

68. M. E. Redwood and C. J. Willis, Can. J. Chem., 45, 389 (1967).

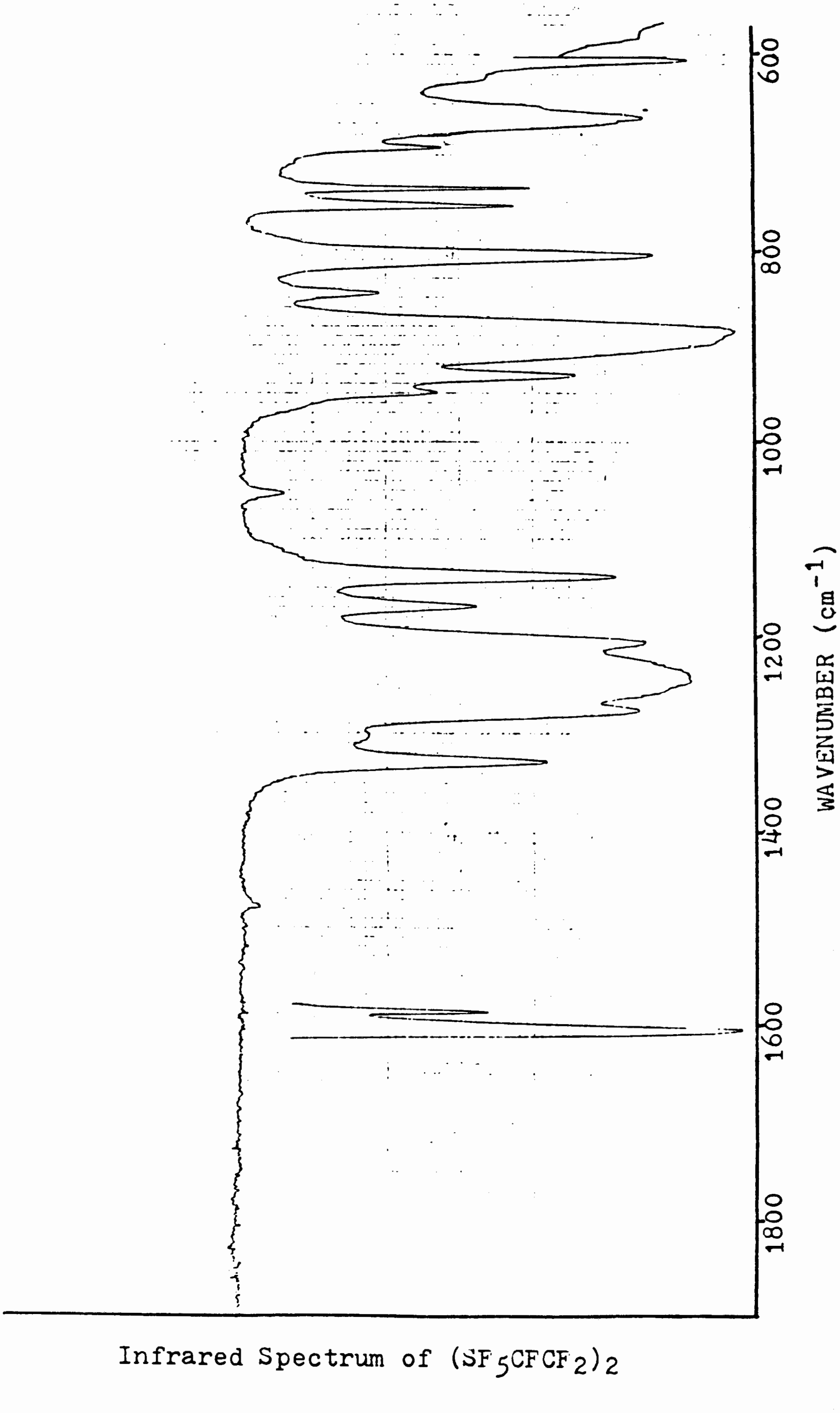
69. Pavia, Lampman and Kriz, 30, 38.

70. Pavia, Lampman and Kriz, 32.

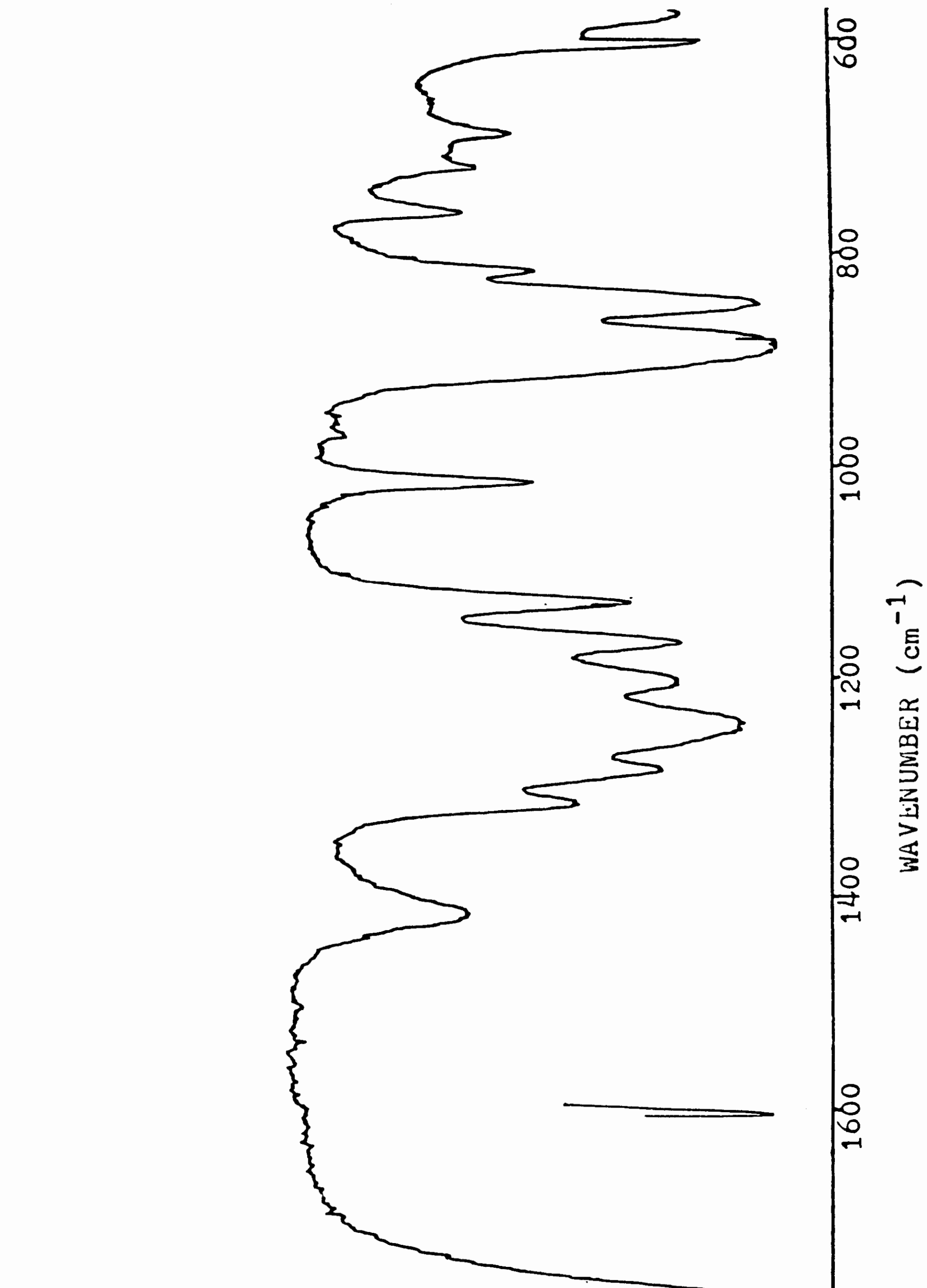
71. J. G. Grasselli and W. M. Ritchey, eds., CRC Atlas of Spectral Data and Physical Constants for Organic Compounds, Vol. 3, CRC Press Inc., West Palm Beach, Florida, 481 (1975).

APPENDIX

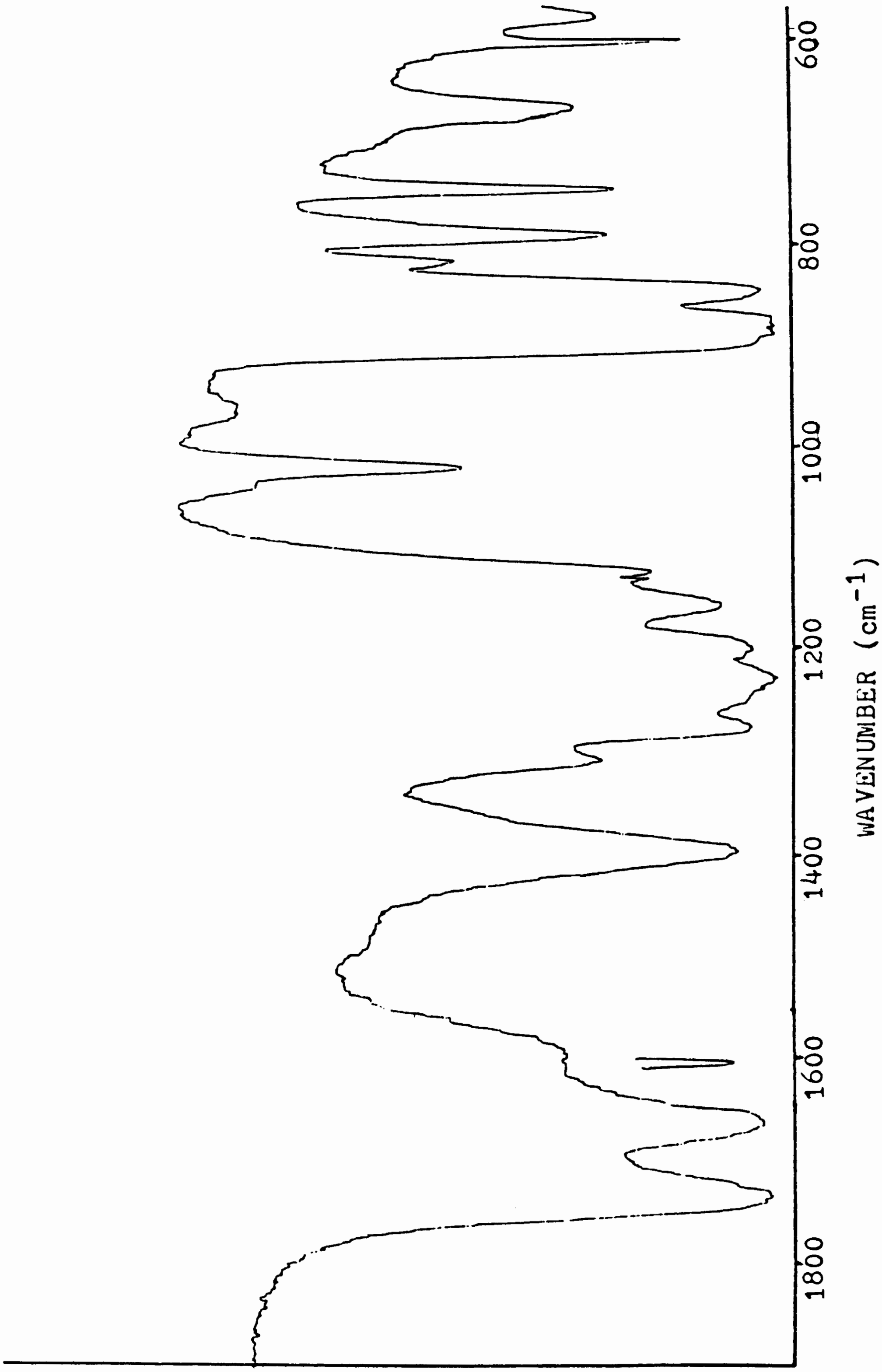
INFRARED SPECTRUM PAGE



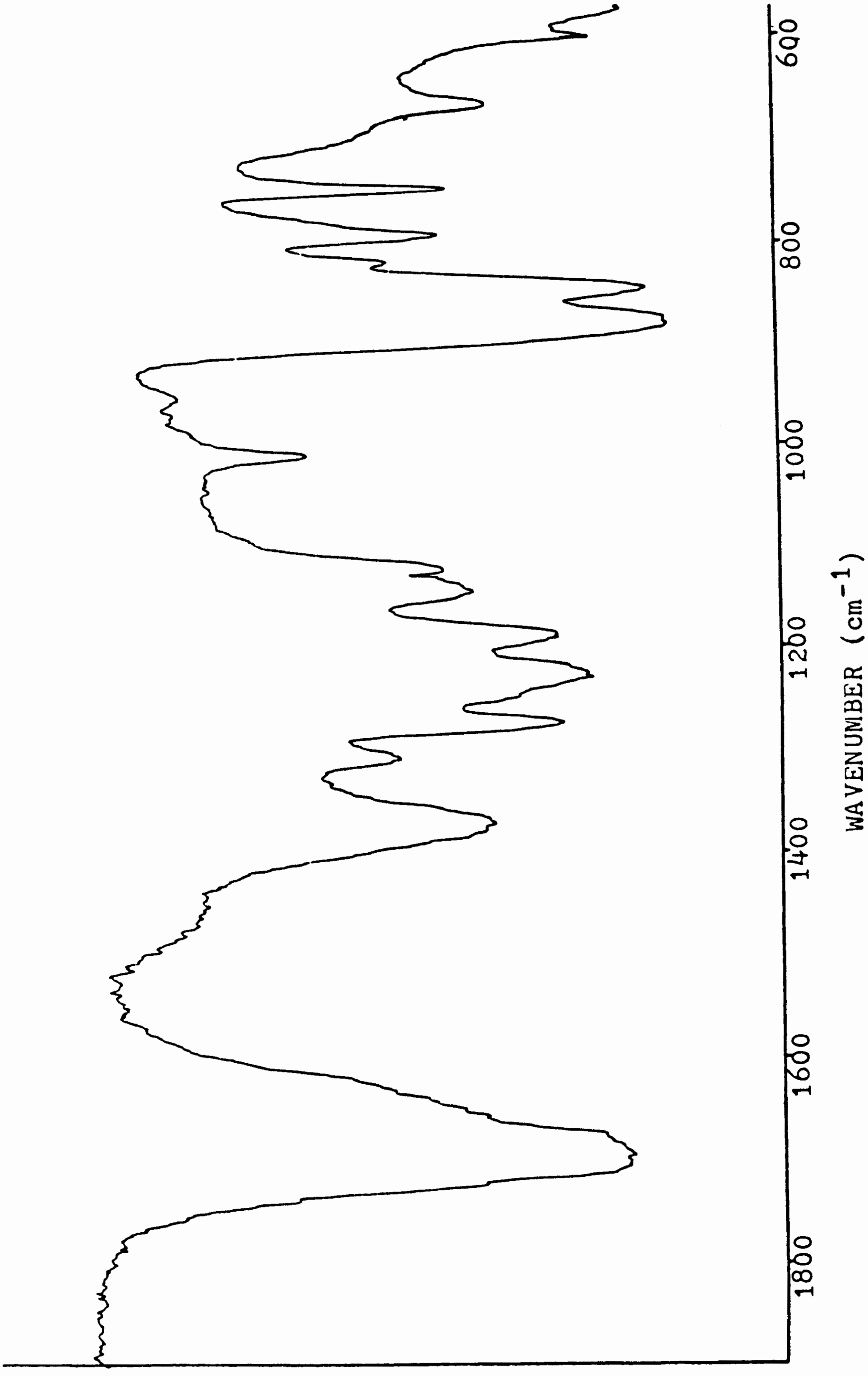
Infrared Spectrum of $(SF_5CFCF_2)_2$



Infrared Spectrum of $SF_5CF(CF_3)CO_2H$



Infrared Spectrum of the Solid from $SF_5CF(CF_3)C(O)F + H_2O$



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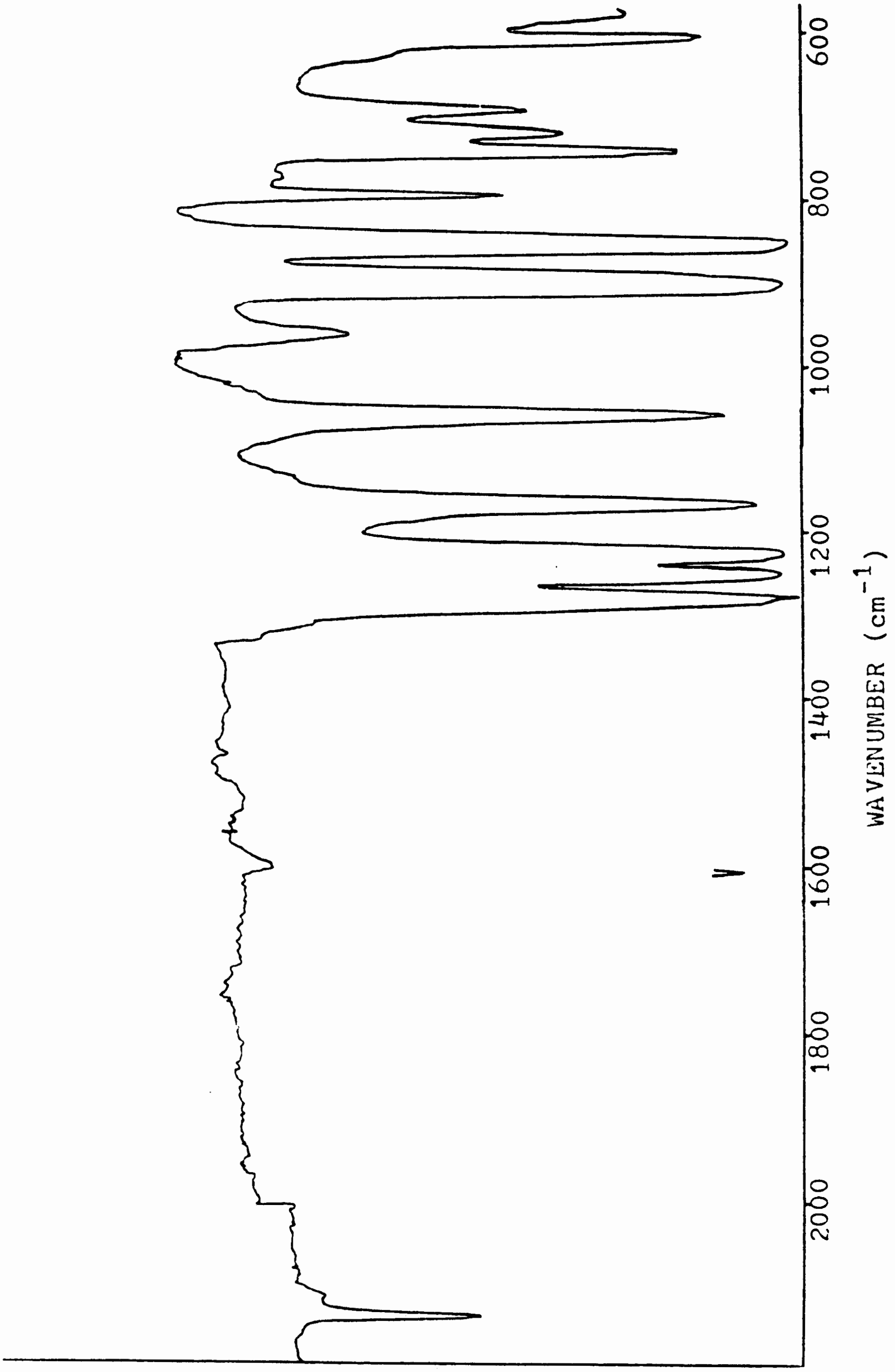

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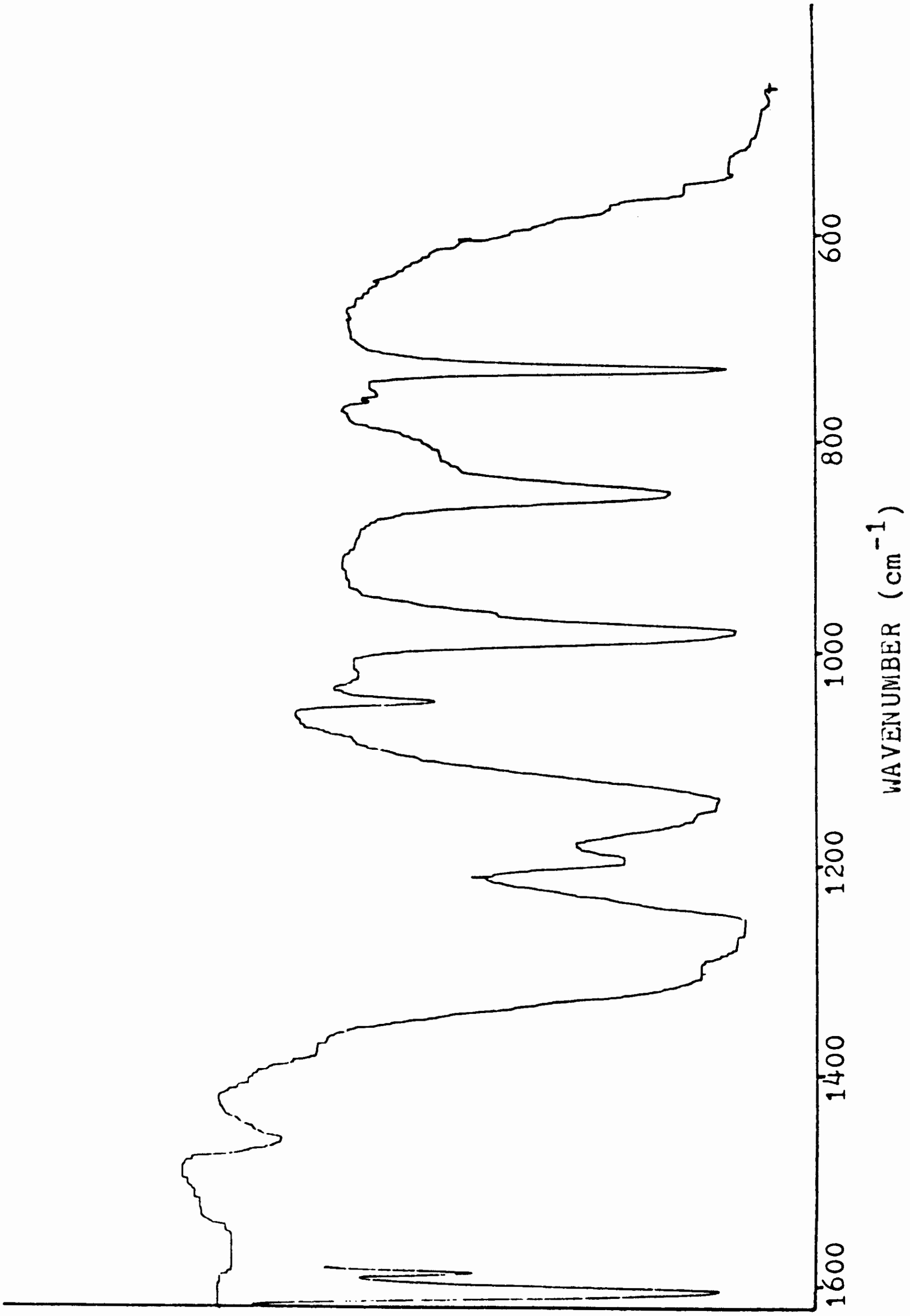
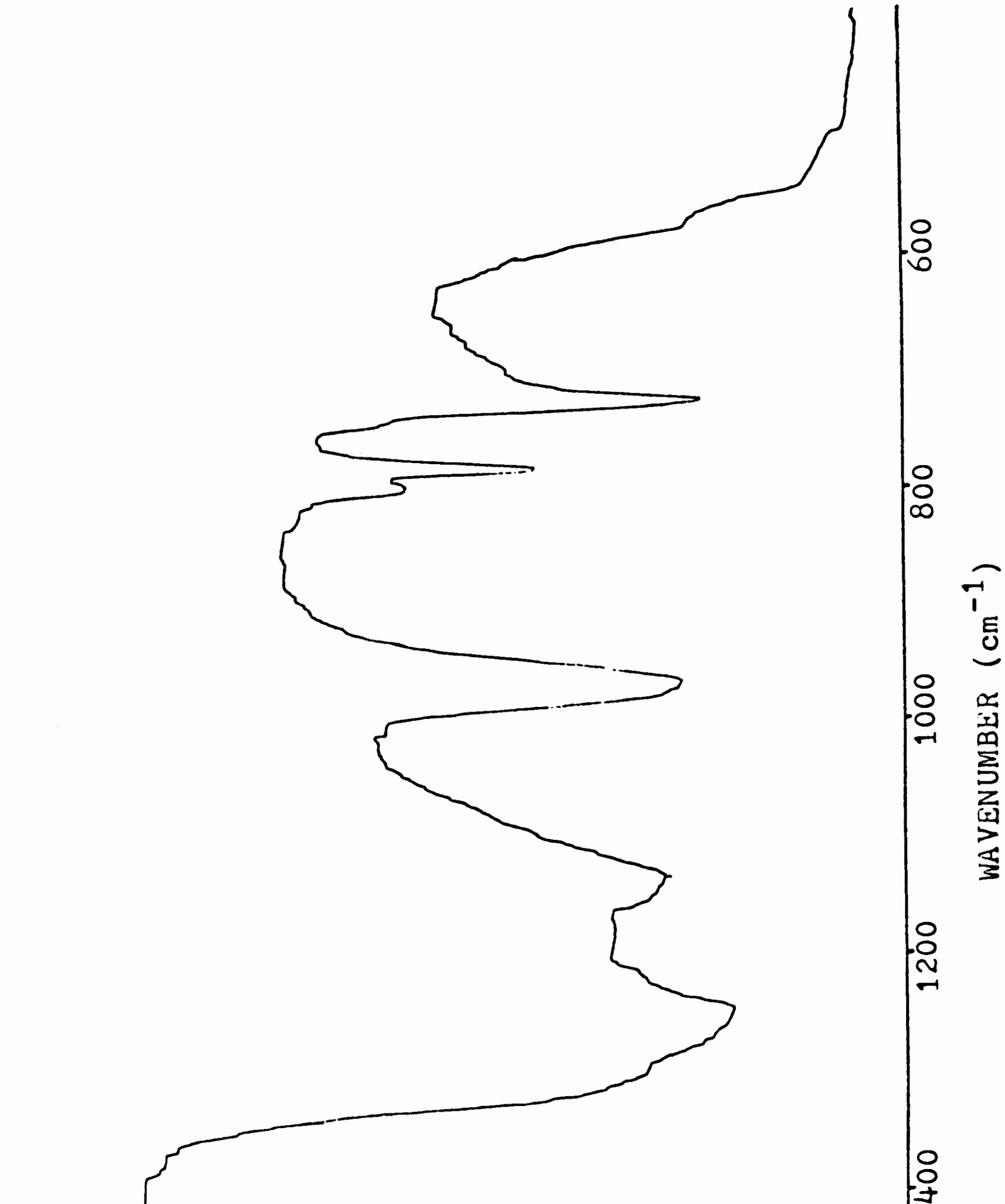
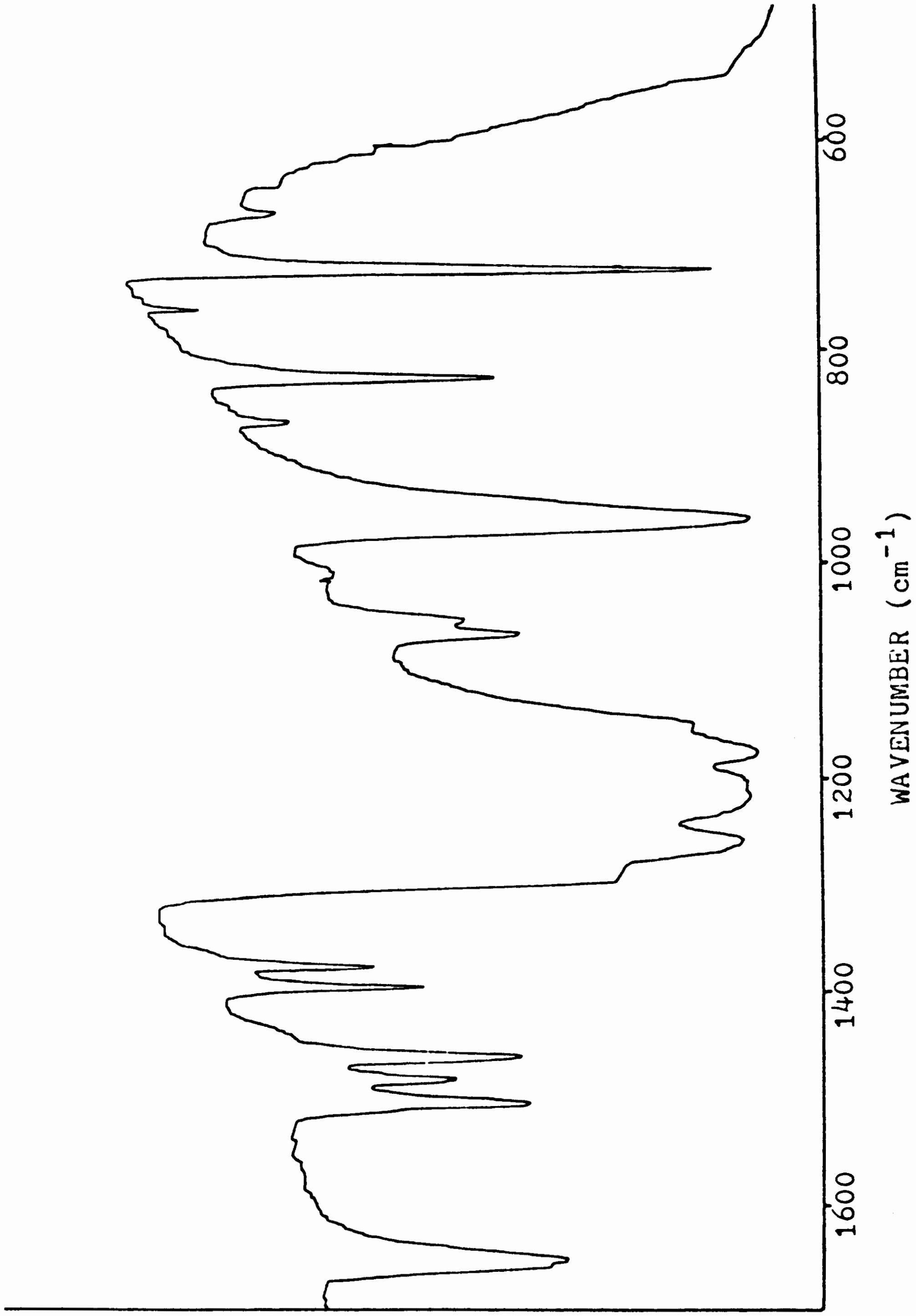


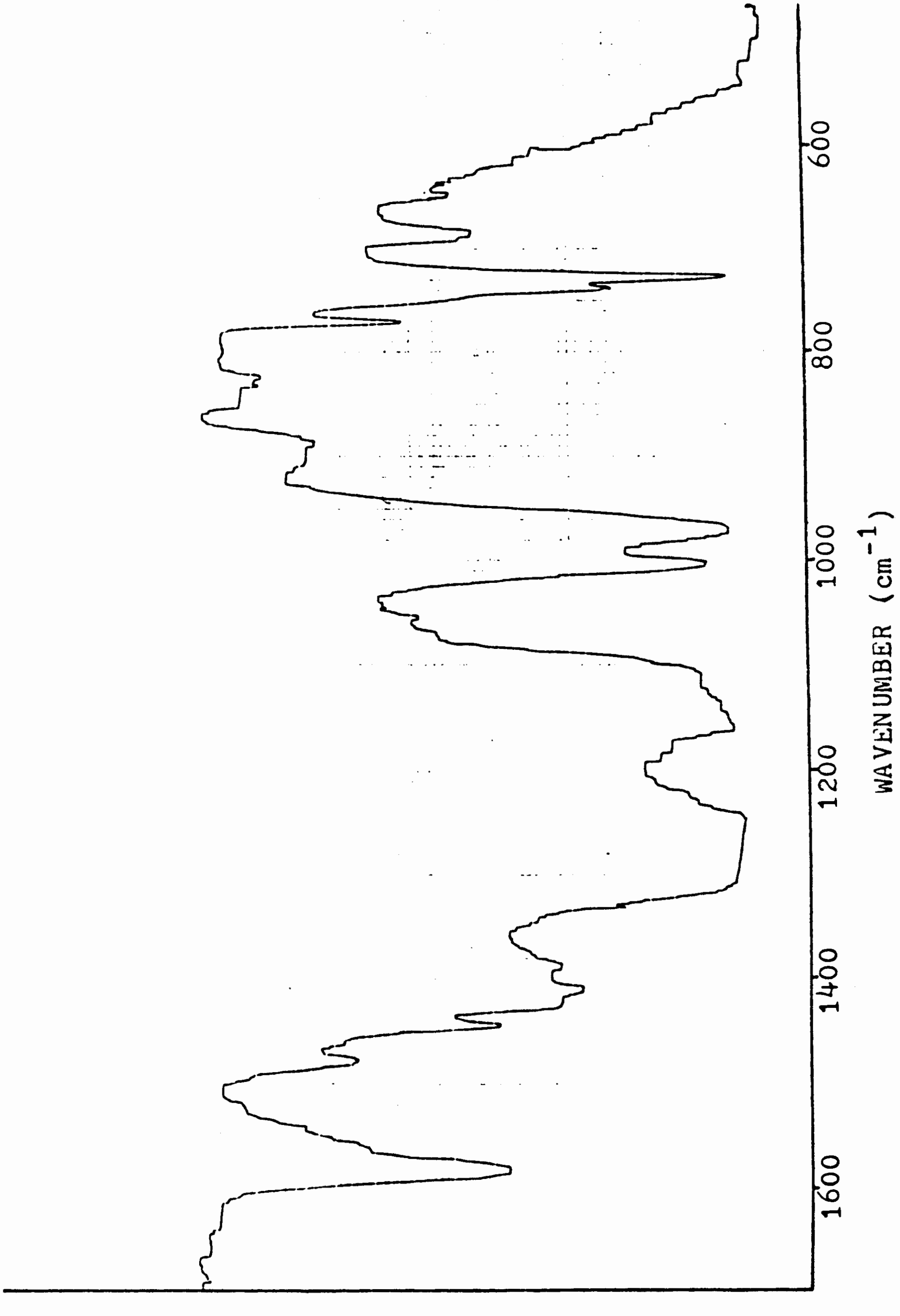
Infrared Spectrum of VO[OC(CF$_3$)$_3$]$_3$



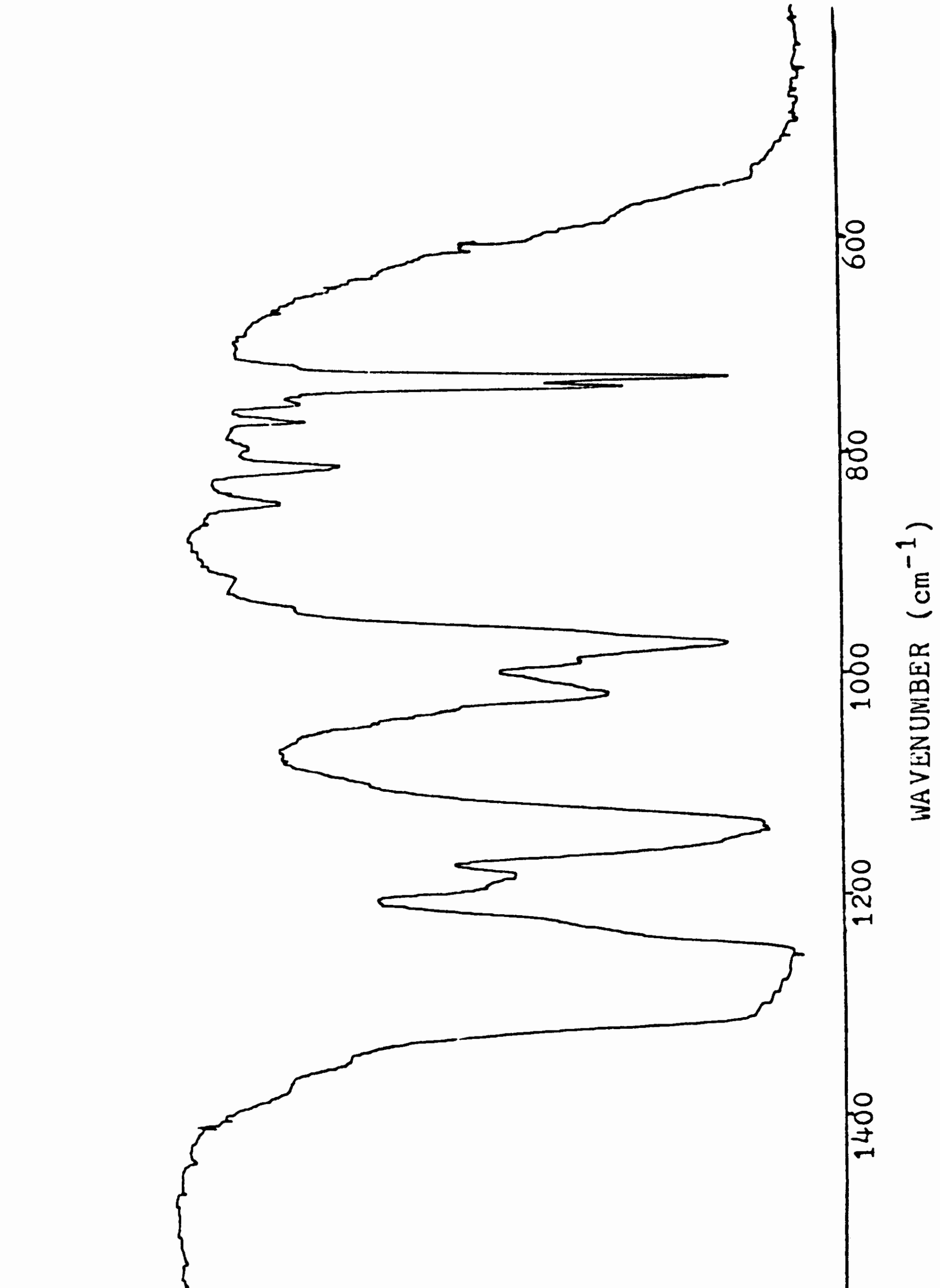
Infrared Spectrum of $SbCl_5$ with $(CF_3)_3COCl$



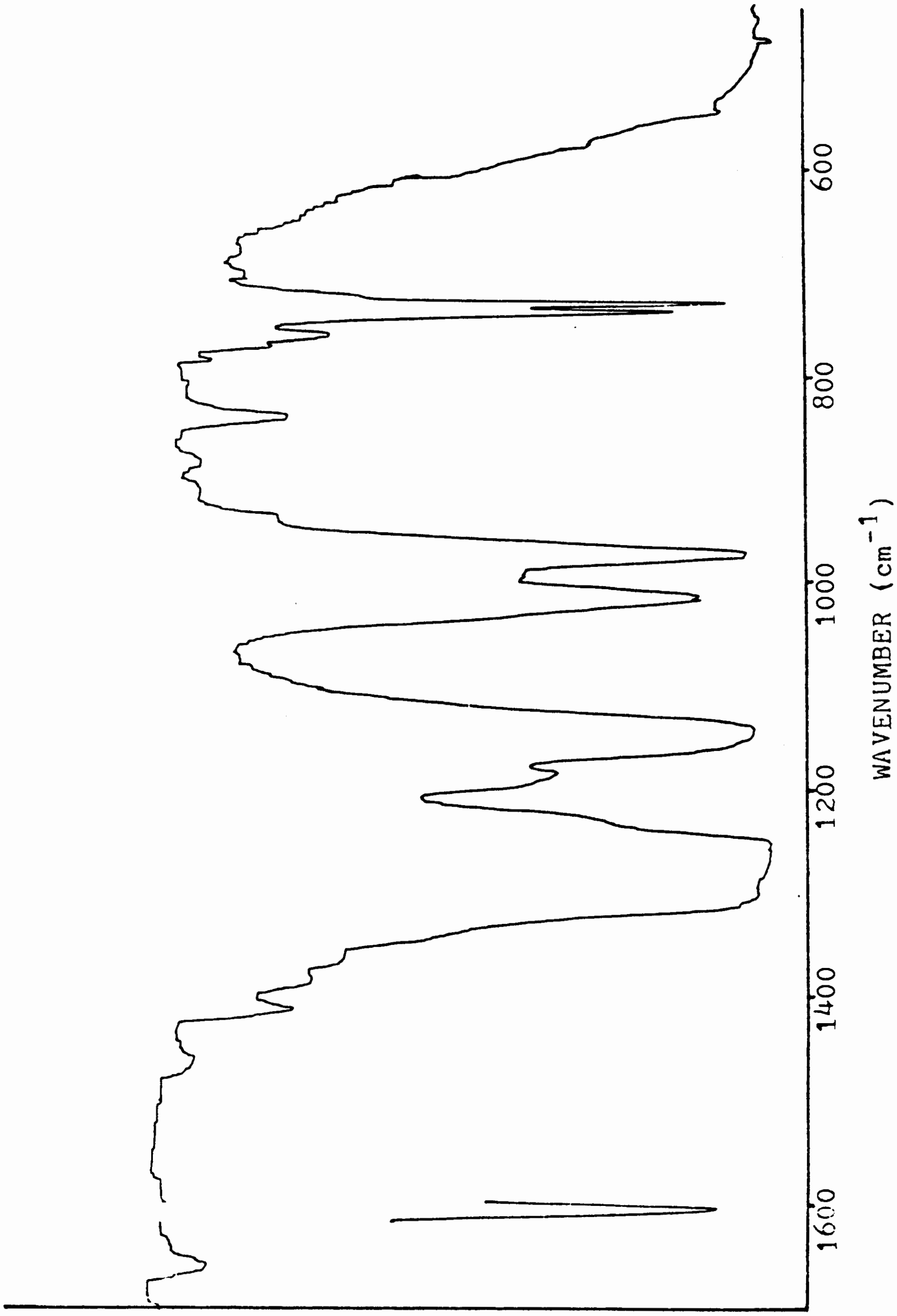
Infrared Spectrum of $(CF_3)_3COH\cdot HN(CH_2CH_3)_2$



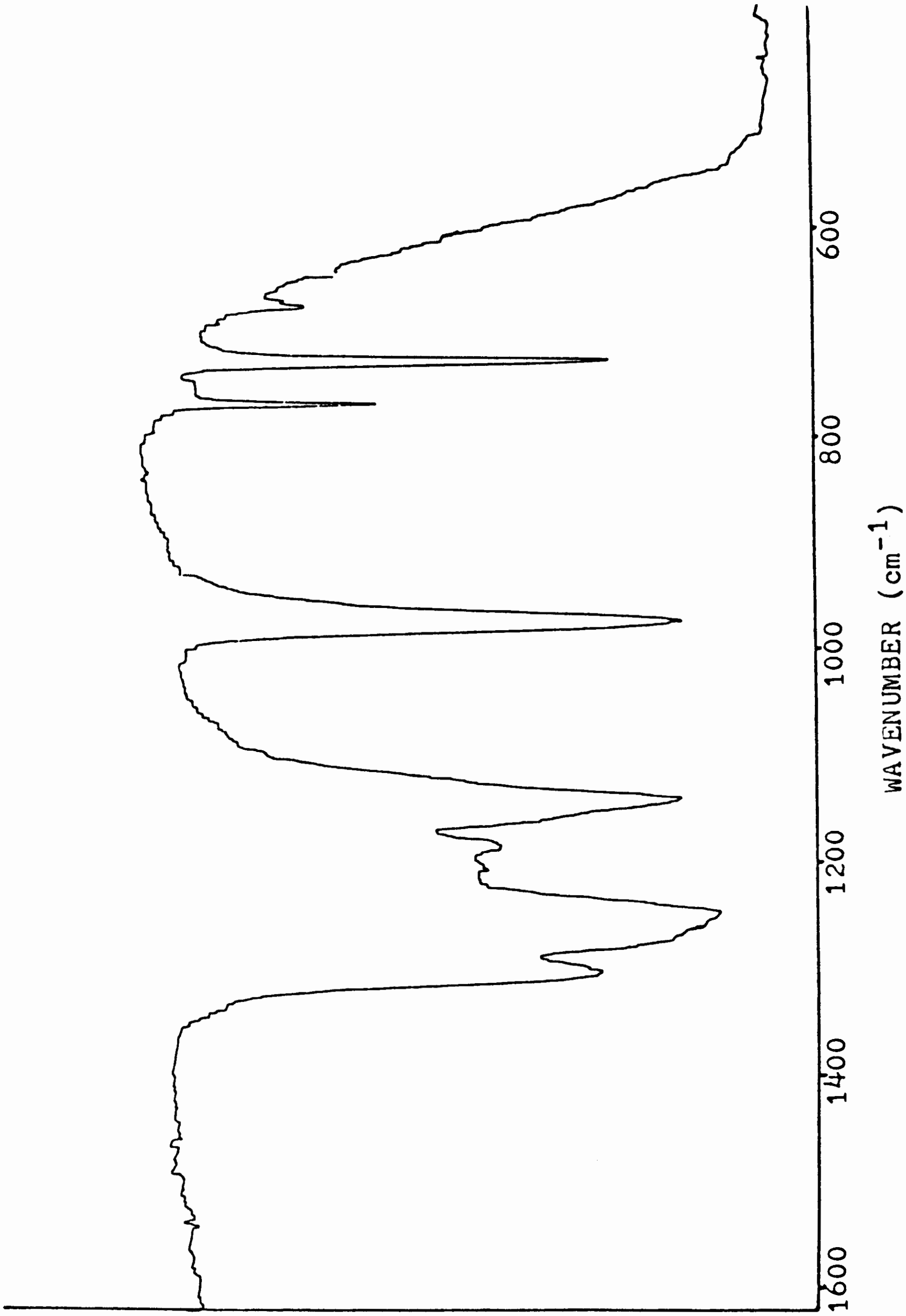
Infrared Spectrum of PPh_3 with $(CF_3)_3COCl$



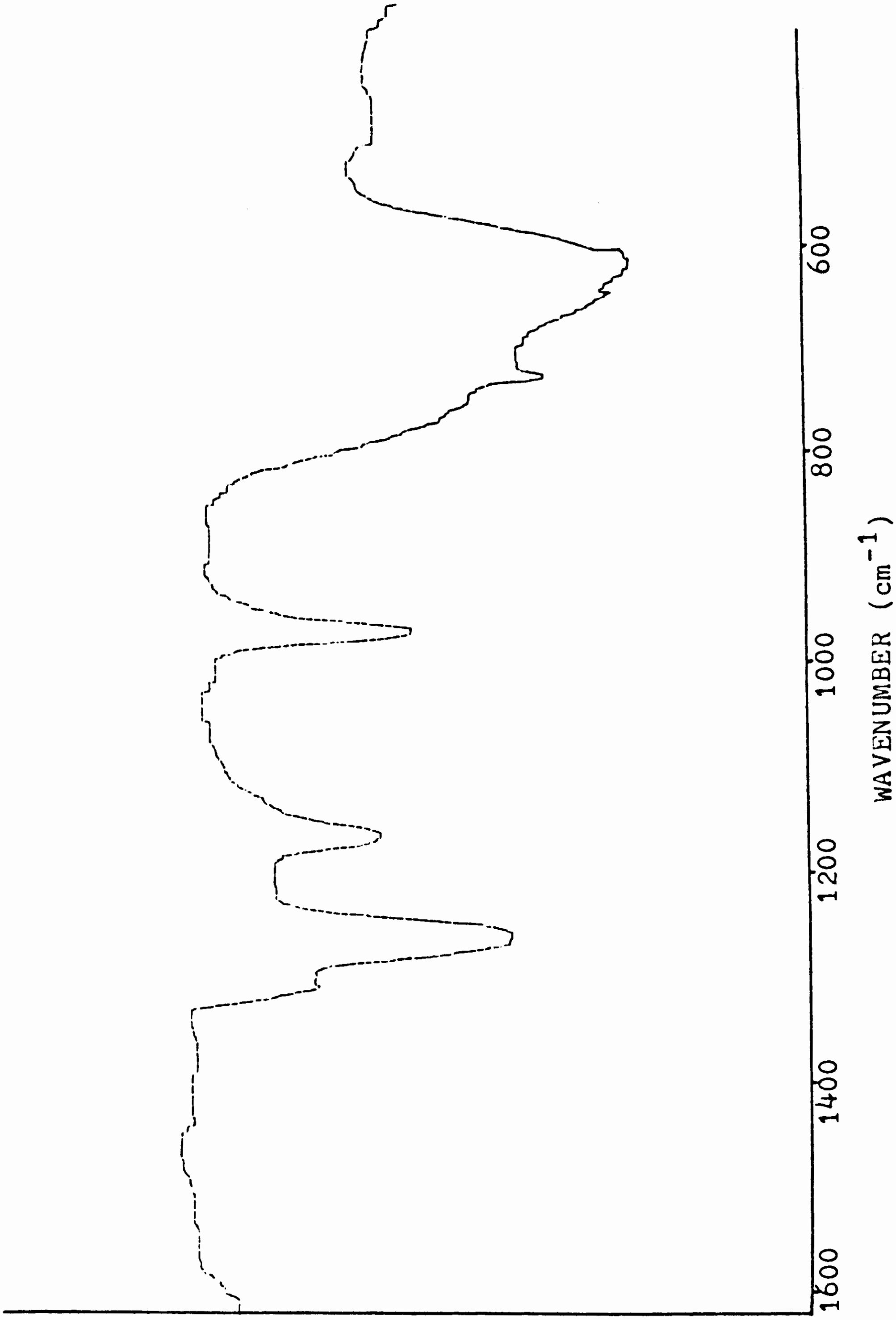
Infrared Spectrum of C_6H_6 with $(CF_3)_3COCl$



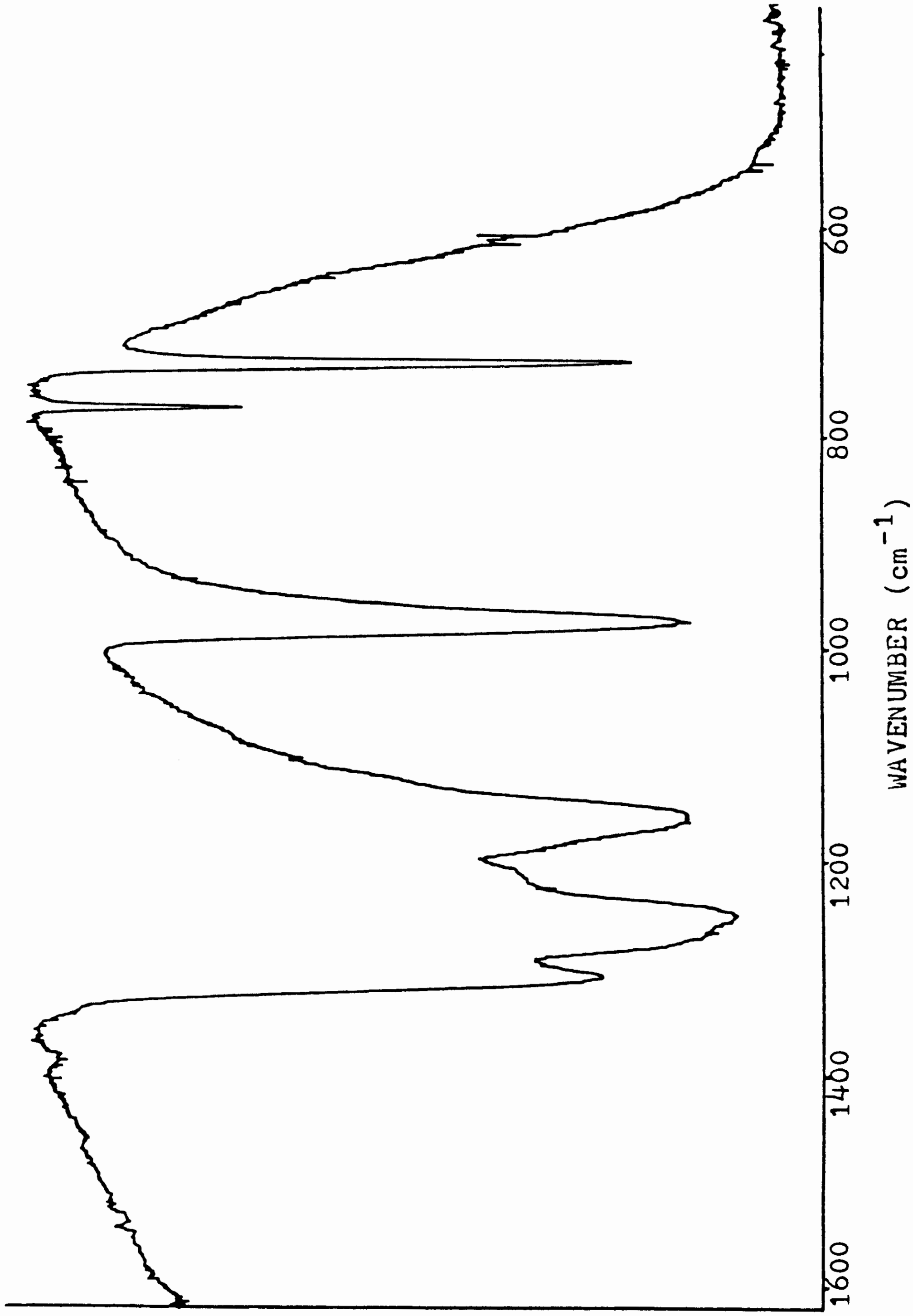
Infrared Spectrum of xs C_6H_6 with $(CF_3)_3COCl$



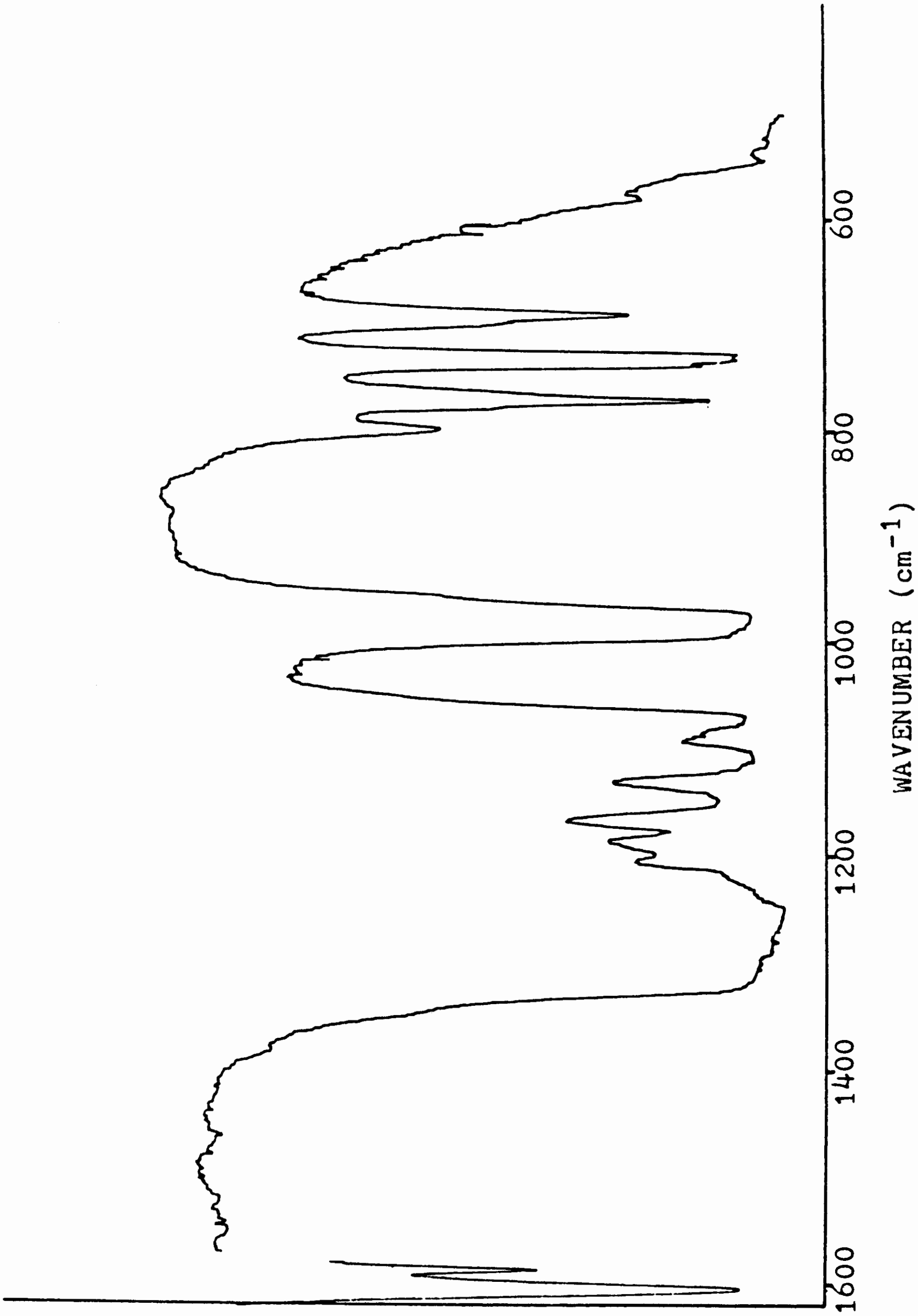
Infrared Spectrum of $Pb[OC(CF_3)_3]_2$



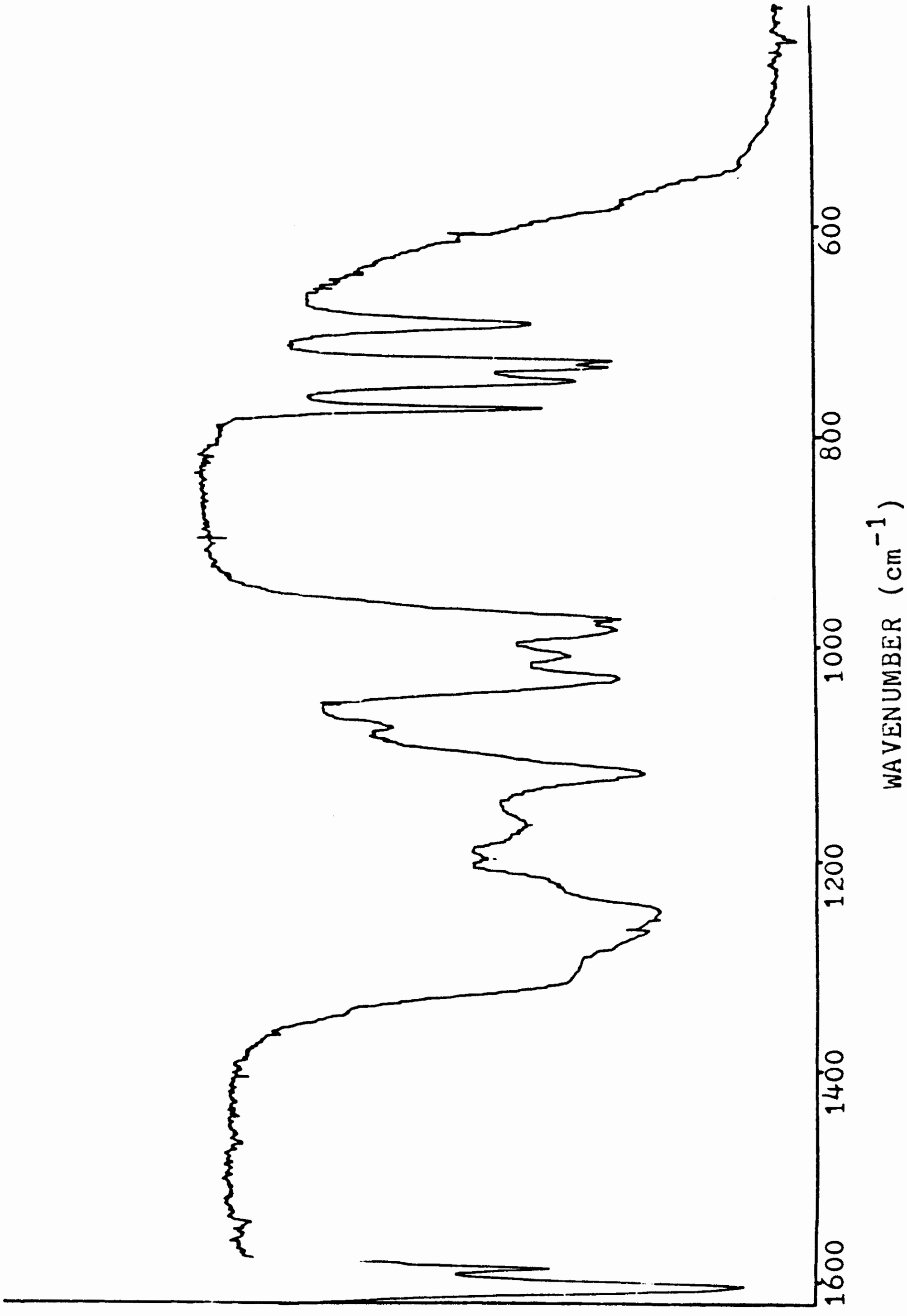
Infrared Spectrum of $Te[OC(CF_3)_3]_4$



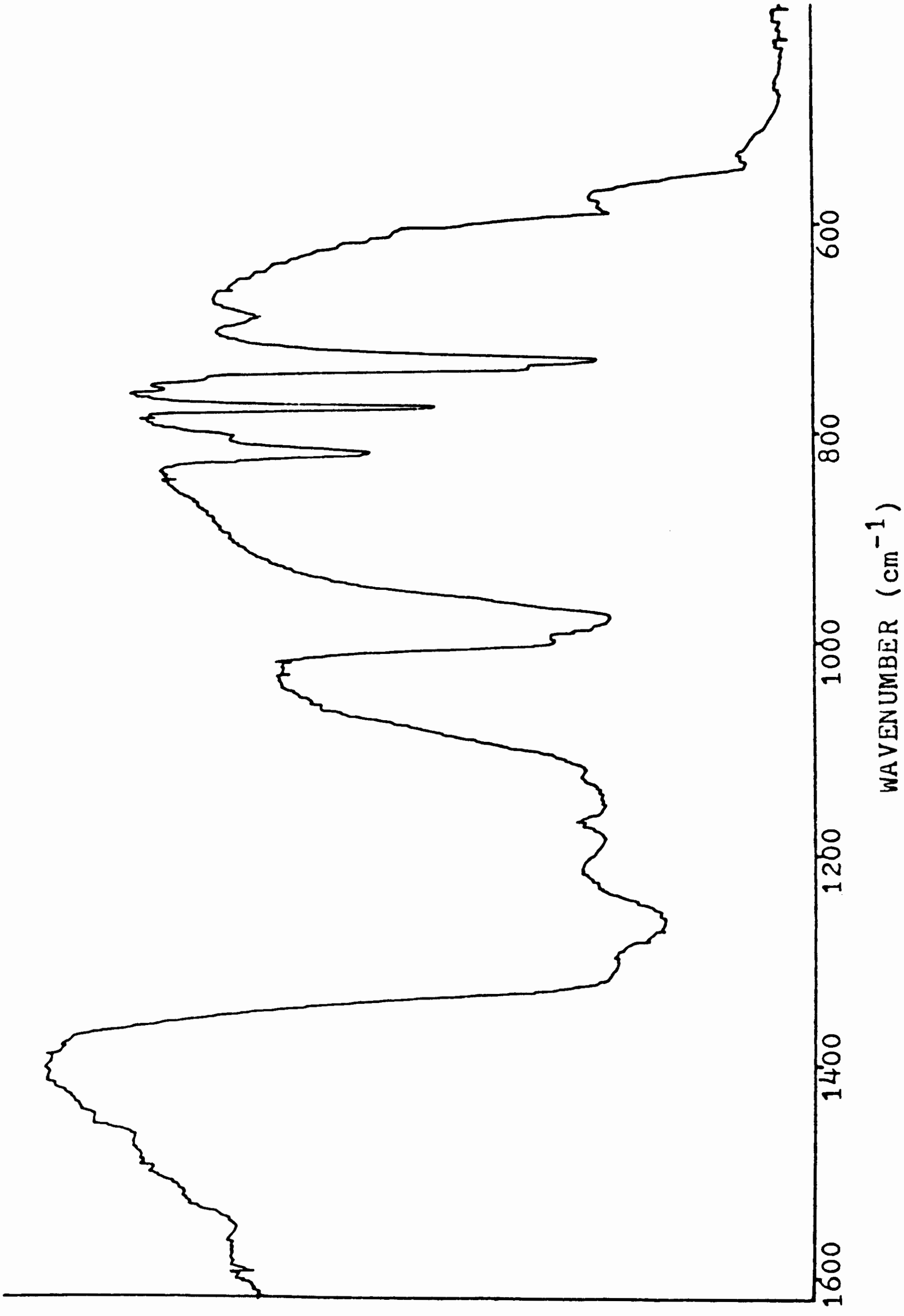
Infrared Spectrum of $Bi[OC(CF_3)_3]_3$



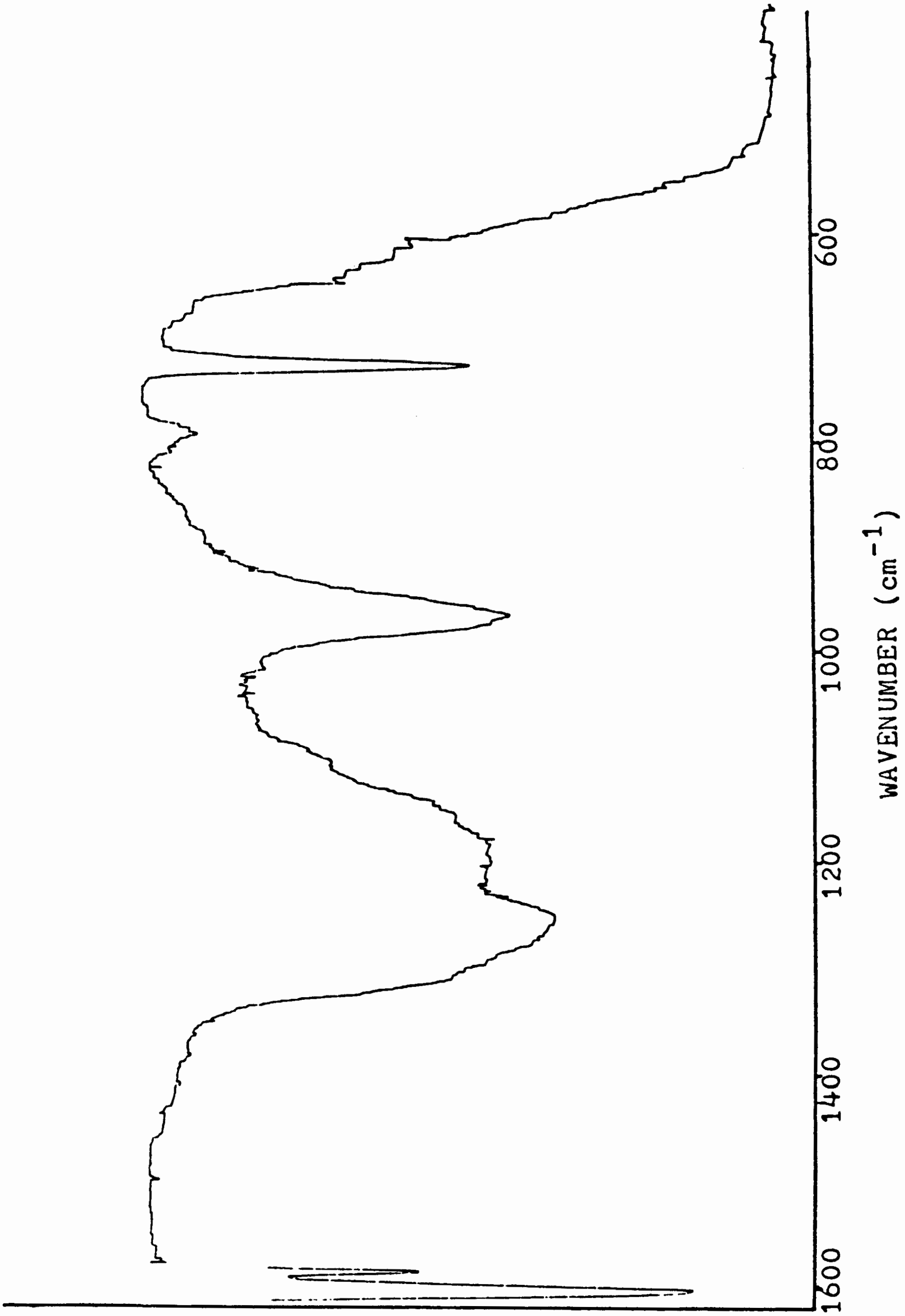
Infrared Spectrum of $I[OC(CF_3)_3]_3$



Infrared Spectrum of $CF_3I[OC(CF_3)_3]_2$



Infrared Spectrum of $CoBr_2$ with $(CF_3)_3COCl$



Infrared Spectrum of CsBr with $(CF_3)_3COCl$