9631

NATIONAL LIBRARY
OTTAWA

CANADA

BIBLIOTHÈQUE NATIONALE
OTTAWA

NAME OF AUTHOR. ANDREW ALAN PINKERTON

TITLE OF THESIS. THE CHEMISTRY OF SOME TRIFLUOROMETHYL PHOSPHORUS OXIDES AND SULPHIDES

UNIVERSITY ALBERTA

DEGREE FOR WHICH THESIS WAS PRESENTED Ph.D.

YEAR THIS DEGREE GRANTED 1971

Permission is hereby granted to THE NATIONAL LIBRARY OF CANADA to microfilm this thesis and to lend or sell copies of the film.

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

(Signed) A Pinkerton

PERMANENT ADDRESS:

#6 10743 83 Ave
Edmonton
Alta.

DATED 17 June 1971

NL-91 (10-68)

THE UNIVERSITY OF ALBERTA

THE CHEMISTRY OF SOME TRIFLUOROMETHYLPHOSPHORUS OXIDES AND SULPHIDES

by

© ANDREW ALAN PINKERTON

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

of

DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

FALL, 1971

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

"THE CHEMISTRY OF SOME TRIFLUOROMETHYLPHOSPHORUS OXIDES AND SULPHIDES"

submitted by ANDREW ALAN PINKERTON in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

....
Supervisor

....

....

....

....

....
External Examiner

Date June 9, 1971

TO A BIRCH TREE

ABSTRACT

The nature of the polysulphide intermediates in the synthesis of bistrifluoromethyldithiophosphinic acid has been investigated. Two of the possible intermediates, bistrifluoromethylthiophosphoryl-μ-thio-bistrifluoromethylphosphine, $(CF_3)_2P(S)-S-P(CF_3)_2$, and di(bistrifluoromethylthiophosphoryl)disulphide, $(CF_3)_2P(S)-S-S-P(S)(CF_3)_2$, have been isolated and fully characterised by infrared, nmr, and mass spectroscopy and by chemical methods. The disulphide is unusual in that it contains phosphorus in two valencies. Reactions carried out with nucleophiles and electrophiles proceed as expected for diphosphorus compounds containing electronegative substituents. It was also demonstrated that these two compounds are indeed possible intermediates in the synthesis of the dithio acid under the conditions used. All attempts to prepare the trisulphide were unsuccessful.

The previously unknown bistrifluoromethylthiophosphinic acid, $(CF_3)_2P(S)OH$, has been prepared from reaction of amine salts of the acid with sulphuric acid. The acid is thermally unstable, losing water on heating to form the anhydride. It is a strong acid and forms salts with alkali metal and ammonium ions which are quite stable in the air and aqueous solution. The structure of the acid has been shown to be $(CF_3)_2P(S)OH$ by spectroscopic and chemical methods. Reaction with P_4O_{10} easily dehydrates the acid to give good yields of

anhydride, $[(CF_3)_2P(S)]_2O$, which is quite stable and is a true anhydride giving stable aqueous solutions of the acid which may be titrated with standard alkali. The anhydride is remarkably inert towards electrophilic reagents, but reaction with nucleophilic reagents is rapid at room temperature to give thiophosphoryl compounds and salts of the $(CF_3)_2P(S)O^-$ anion.

Hydrolysis reactions have been used as a method of analysis for CF_3 groups attached to phosphorus for many years. The oxyanions produced on hydrolysis had been previously well characterised; these anions and in addition those containing sulphur have been further characterised by nmr. It has also been demonstrated that P-S bonds are often stable to neutral and alkaline hydrolysis in these systems. The hydrolytic method has now been extended such that the structures of trifluoromethylphosphorus compounds may be deduced by carrying out neutral and alkaline hydrolyses as the products from all the representative systems have now been clearly defined.

Some further properties of bistrifluoromethyldithiophosphinic acid, $(CF_3)_2PS_2H$, have been investigated. The possible use of the acid as a chelating agent in transition metal chemistry has been demonstrated.

A C K N O W L E D G E M E N T S

The author wishes to express sincere appreciation to Dr. R. G. Cavell for his direction and assistance during the course of this investigation and to the various members of his group for many helpful discussions.

Thanks are also due to members of the Department of Chemistry technical staff, especially Messrs. D. Gifford and A. Budd whose perseverance produced good nmr and mass spectra from samples that were indeed difficult to handle.

Appreciation is also extended to Mrs. Mary Waters for her able preparation of this manuscript.

Financial assistance from the University of Alberta is gratefully acknowledged.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

I N T R O D U C T I O N

The starting point for the trifluoromethyl chemistry of the elements was the ready availability of trifluoroiodomethane, CF_3I, synthesised [1] according to eq 1.1.

$$AgCO_2CF_3 + I_2 \xrightarrow{100°} CF_3I + CO_2 + AgI \qquad (1.1)$$

The first reported trifluoromethyl compounds of phosphorus were $(CF_3)_3P$, $(CF_3)_2PI$ and CF_3PI_2 which were prepared as a mixture by heating CF_3I, phosphorus and iodine at 200 - 250°.[2] The lability of the phosphorus-iodine bond made possible the preparation of many compounds from the iodophosphines. The initial studies have been extensively reviewed.[3,4,5,6] More recent studies have shown that tristrifluoromethylphosphine can be converted into phosphorus amines [7] according to eq 1.2, which in turn may

$$(CF_3)_3P + (CH_3)_2NH \longrightarrow (CF_3)_2P\text{-}N(CH_3)_2 + CF_3H \qquad (1.2)$$

be cleaved by many electrophilic reagents to form other new compounds according to eq 1.3, where X = halogen,[8]

$$(CF_3)_2P\text{-}N(CH_3)_2 + 2HX \longrightarrow (CF_3)_2PX + (CH_3)_2\overset{+}{N}H_2X^- \qquad (1.3)$$

or other suitable substituent.

Although the trifluoromethyl group is formally related to an alkyl group, the high electronegativity of the group (~3.3) [3] confers a pseudohalogen character on the group which results in a considerable modification of the chemistry of the element to which CF_3 is attached. The consequence, in the present case, is that the chemistry of phosphorus is not easily predictable from a knowledge of organo-phosphorus chemistry and many compounds have been prepared of types which have no formal analogues in classical organo-phosphorus chemistry. For example trivalent organo-phosphorus compounds would generally be expected to be vulnerable to electrophilic attack while pentavalent phosphorus compounds would generally be subject to nucleophilic attack.[9] Alkyl and aryl phosphorus compounds tend to undergo Arbuzov rearrangements to preferentially form the pentavalent state.[9] In the case of trifluoromethylphosphorus compounds the highly electronegative trifluoromethyl group stabilises the trivalent state, and anti-Arbuzov [10] rearrangements are more common. Trifluoromethyl compounds of trivalent phosphorus, in contrast to alkyl compounds, do not form phosphonium salts and there is no adduct formation with Lewis acids unless the possibility exists for back π bonding to the available 3d orbitals or hybrids with d character on phosphorus.[4,5] The 3d orbitals are available for use in

this manner because their energy is probably lowered by the strong electron withdrawing nature of the CF_3 group.[11]

The chemistry of trifluoromethylphosphorus systems is therefore largely concerned with nucleophilic attack at phosphorus (both tri- and pentavalent); typical examples of this behaviour are provided by the hydrolytic attack of OH^-, the cleavage of phosphorus-halogen bonds by amines, etc. Electrophilic attack may take place in some molecules, but the site of attack is not normally phosphorus, but rather the available lone pair electrons on a substituent containing oxygen, sulphur, nitrogen, etc. Even the lone pair electrons on these atoms may be affected by the electronegativity of the CF_3 substituent on phosphorus and become less available for attack.

In order to study phosphorus compounds with highly electronegative substituents, CF_3 has a great advantage over halogen in that the group does not easily migrate, whereas halogenophosphorus compounds undergo redistribution reactions and are inconveniently involatile except for the fluorophosphorus compounds.[6]

Trifluoromethylphosphorus systems are also convenient models to study because, especially in the case of small molecules, they are conveniently handled by conventional high vacuum techniques being much more volatile than alkyl or aryl compounds of comparable molecular weight.[6] Also,

due to this volatility, reactions may be conveniently carried out in the gas phase at moderate temperatures, thus removing any possible side effects due to participation of solvents in the reactions.

Reactions may be followed with ease due to the built-in molecular probes in the form of the 100% abundance of the ^{19}F and ^{31}P nuclei. The development of the nmr technique has greatly assisted the expansion of this field. New compounds may also be simply analysed due to the ease of hydrolytic cleavage of the phosphorus-carbon bond in these systems to give fluoroform which is easily identified by its characteristic infrared spectrum and which may be quantitatively determined by vacuum fractionation and weighing. This is another reaction for which there is no counterpart in alkyl, aryl, or halophosphorus chemistry, and is unusual in that CF_3-Z bonds are usually hydrolytically stable. The nature of the trifluoromethylphosphorus oxyacids and anions produced hydrolytically was one of the first aspects of this field of chemistry to be investigated and is now well understood. More complete details of the chemistry of CF_3-P compounds up to about 1969 are summarised in the several reviews of the field which are available.[3,4,5,6] References to more recent studies will be made specifically throughout the text of this thesis.

Initially the area of major concern was the prepar-

ation and characterisation of possible trifluoromethyl-phosphorus polysulphide intermediates which might be formed in the synthesis of bistrifluoromethyldithiophosphinic acid,[10,11] $(CF_3)_2PS_2H$. Two likely intermediates have been synthesised and characterised. In addition the synthesis and properties of the new monothio acid, $(CF_3)_2P(S)OH$, and its anhydride, $[(CF_3)_2P(S)]_2O$, are described. Also further characterisation of the species produced in solution on hydrolysis of trifluoromethylphosphorus compounds, especially those containing sulphur has been achieved through the application of ^{19}F nmr techniques. Some initial exploration of the possible use of bistrifluoromethyldithiophosphinic acid as a ligand in transition metal chemistry is also reported.

CHAPTER II

MATERIALS AND TECHNIQUES

The materials and techniques described in this Chapter are those which were generally applicable in the preparation and characterisation of the compounds studied in the course of this work. Techniques applicable to specific experiments are described in the appropriate sections.

1. High Vacuum Techniques

Due to the air and moisture sensitivity of many of the reactants and reaction products all manipulations were carried out using standard high vacuum techniques. Separation of volatile compounds was usually achieved by means of a high vacuum trap to trap condensation procedure through a series of traps cooled with slush baths to various temperatures. This procedure is referred to in the text as vacuum fractionation. Final purification of some compounds was carried out using a micro-reflux column with a Dewar jacket containing a cold slush attached to the vacuum line as described by Spielman and Burg.[14] The vacuum system was constructed with Pyrex glass and the stopcocks lubricated with Apiezon grease. Involatile materials and aqueous solutions were handled in the air since it had been found by experience that such products were invariably air stable.

2. Reaction Conditions

All reactions were carried out in sealed Pyrex glass tubes of approximate volumes 10, 25, or 75 cc depending on the scale of the reaction and the maximum calculated pressure expected. Reaction temperatures are quoted in the appropriate sections.

3. Materials

All trifluoromethylphosphorus compounds were prepared by literature methods except those for which new syntheses are described in Chapter IX. Commercially available chemicals of "Reagent" grade were used as supplied without further purification. Reagent gases were usually fractionated before use to remove any moisture or decomposition products.

4. Instrumental Techniques

Infrared spectra of gases were obtained using a 10 cm gas cell with potassium bromide, caesium iodide, or polyethylene windows; spectra of solids were obtained as Nujol mulls. Routine spectra were recorded on a Perkin-Elmer 337 spectrophotometer for identification purposes. Spectra of new compounds were obtained from either a Perkin-Elmer 421 dual interchange machine or a Beckman IR-12 instrument.

Mass spectra were recorded on an AEI MS-9 spectrometer operating at an ionizing voltage of 70 eV. Samples were

introduced as gases using a heated inlet, as low volatile liquids in a heated capillary, or as solids using a direct probe.

All nmr spectra were recorded on either a Varian A56/60A or a Varian HA 100 spectrometer. Proton spectra were recorded at 60.0 MHz and fluorine spectra at 56.4 MHz using the A56/60A instrument. In the case of the HA 100 instrument, proton spectra were recorded at 100 MHz, fluorine spectra at 94.1 MHz, and phosphorus spectra at 40.5 MHz. Proton chemical shifts were measured relative to external tetramethylsilane, fluorine relative to either internal or external $CFCl_3$, and phosphorus relative to a capillary of P_4O_6.[15]

Samples for proton and fluorine nmr experiments were prepared as approximately 15% solutions in $CFCl_3$ for covalent compounds, and as 0.1 - 0.2 molar aqueous solutions for ionic compounds using 5 mm o.d. medium wall sample tubes and a reference capillary. Samples for phosphorus nmr experiments were prepared as neat liquids in similar sample tubes.

CHAPTER III

Bistrifluoromethylthiophosphoryl-μ-thio-bistrifluoromethyl-phosphine

1. Introduction

The synthesis of bistrifluoromethyldithiophosphinic acid and related trifluoromethylphosphine sulphides [12,13] led to an extensive study of the chemistry of this system. In this Chapter and in Chapter IV the preparation and characterisation of two of the possible intermediates in the synthesis of bistrifluoromethyldithiophosphinic acid are described. In Chapter V the unsuccessful attempts to prepare a third possible intermediate are described. The possible existence of bistrifluoromethylthiophosphoryl-μ-thio-bistrifluoromethylphosphine, $(CF_3)_2P(S)\text{-}S\text{-}P(CF_3)_2$, as an unstable intermediate was suggested by Burg and Gosling [13], however, the compound was found to be quite stable and easily handled *in vacuo*.

2. Preparation of $(CF_3)_2P(S)-S-P(CF_3)_2$

(a) From $(CF_3)_2PS_2H$ and $(CF_3)_2P-N(CH_3)_2$

Bistrifluoromethyldithiophosphinic acid [12,13] (0.481 g, 2.06 mmoles) and dimethylaminobistrifluoromethylphosphine [8] (0.220 g, 1.043 mmoles) (prepared from $(CF_3)_3P$ and $(CH_3)_2NH$)[7] were allowed to react at room temperature for 24 hours. Vacuum fractionation gave $(CF_3)_2P(S)-S-P(CF_3)_2$ (0.345 g, 0.86 mmoles) in 83% yield, which was collected at -45°. Purification of the crude product from unreacted $(CF_3)_2PS_2H$ and $(CF_3)_2PN(CH_3)_2$ was best achieved by refluxing the crude fraction at -45° using the micro-reflux column.[14] The salt $(CH_3)_2NH_2^+ S_2P(CF_3)_2^-$ remained as an involatile residue in the reaction tube.

(b) From $(CF_3)_2PS_2H$ and $(CF_3)_2PCl$

Bistrifluoromethyldithiophosphinic acid [12,13] (0.460 g, 1.97 mmoles) and bistrifluoromethylchlorophosphine [16] (1.712 g, 8.37 mmoles) were allowed to react for 4 days at 70°. Vacuum fractionation gave $(CF_3)_2P(S)-S-P(CF_3)_2$ (0.670 g, 1.67 mmoles) in 85% yield, and excess $(CF_3)_2PCl$ collected at -116°. Final purification was achieved by refluxing at -45° using the micro-reflux column.[14]

(c) From $(CF_3)_2P(S)I$ and Hg

Iodobistrifluoromethylphosphine sulphide [12,13] (0.182 g, 0.55 mmoles) and mercury (0.058 g, 0.29 mmoles) were shaken together for 4 days at room temperature. Vacuum fractionation gave a mixture of $(CF_3)_2P(S)-S-P(CF_3)_2$ and $(CF_3)_2P-S-P(CF_3)_2$ trapping at -45°, and excess $(CF_3)_2P(S)I$ passing -45°. A total of 0.083 g of volatile material was obtained from which pure $(CF_3)_2P(S)-S-P(CF_3)_2$ was obtained with difficulty by refluxing in the micro-reflux column.[14]

The reaction tube contained HgI_2 and white crystals of a compound which appeared to be identical to $(CF_3)_4P_2S_4Hg$ described in Chapter IV.

(d) From $(CF_3)_2P-S-P(CF_3)_2$ and sulphur

Di(bistrifluoromethylphosphino)sulphide [15,16] (1.560 g, 4.21 mmoles) was heated at 170° for five days with sulphur (0.192 g, 6.00 mmoles). Vacuum fractionation gave a complex, inseparable mixture of compounds of which $(CF_3)_2P(S)-S-P(CF_3)_2$ was a major constituent according to nmr investigation of the volatile product mixture.

3. Reactions of $(CF_3)_2P(S)-S-P(CF_3)_2$

(a) With Heat

Heating a sample of $(CF_3)_2P(S)-S-P(CF_3)_2$ (0.0354 g, 0.088 mmoles) for 2 days at 165° resulted in almost quantitative recovery (0.0322 g, 0.080 mmoles) of unchanged material.

(b) Alkaline Hydrolysis

Hydrolysis of $(CF_3)_2P(S)-S-P(CF_3)_2$ (0.0533 g, 0.132 mmoles) with 5 ml of 10% NaOH solution for 24 hours at room temperature gave CF_3H (0.0279 g, 0.398 mmoles) as the only volatile material. Nmr spectra of the remaining aqueous solution indicated the presence of the $CF_3PS_2O^=$ ion (see Chapter VIII).

(c) Neutral Hydrolysis

Hydrolysis of $(CF_3)_2P(S)-S-P(CF_3)_2$ (0.0565 g, 0.140 mmoles) with approximately 0.1 ml of H_2O at room temperature for 16 hours gave CF_3H (0.0096 g, 0.137 mmoles) as the only volatile material. Nmr spectra of the remaining aqueous solution indicated the presence of $(CF_3)_2PS_2^-$ and $CF_3P(H)O_2^-$ ions (see Chapter VIII).

(d) With H_2S

Heating hydrogen sulphide (0.0472 g, 1.39 mmoles) with $(CF_3)_2P(S)-S-P(CF_3)_2$ (0.0553 g, 0.137 mmoles) at 150° for 9 days gave 0.057 g of a 1:1 mixture of

$(CF_3)_2PS_2H$ and $(CF_3)_2PSH$ (analysed by nmr) corresponding to a 95% yield.

(e) With HCl

Reaction of excess hydrogen chloride (~1.0 mmole) with $(CF_3)_2P(S)-S-P(CF_3)_2$ (0.0402 g, 0.100 mmoles) for 10 days at room temperature gave 0.0427 g of a 1:1 mixture of $(CF_3)_2PS_2H$ and $(CF_3)_2PCl$ (analysed by nmr). Some difficulty was experienced in separating excess HCl and $(CF_3)_2PS_2H$ in vacuum.

(f) With HBr

A reaction between HBr (~0.4 mmoles) and $(CF_3)_2P(S)-S-P(CF_3)_2$ (0.062 g, 0.155 mmoles) gave 0.0732 g of a 1:1 mixture of $(CF_3)_2PS_2H$ and $(CF_3)_2PBr$ (analysed by nmr). Again some difficulty was experienced in separating excess HBr and $(CF_3)_2PS_2H$ in the vacuum system.

(g) With HI

Room temperature reaction of hydrogen iodide (~0.3 mmoles) and $(CF_3)_2P(S)-S-P(CF_3)_2$ (0.0547 g, 0.136 mmoles) for 30 hours gave $(CF_3)_2PS_2H$ and $(CF_3)_2PI$ as the major products. The volatile materials were returned to the reaction tube along with a further quantity of HI (~0.4 mmoles) and reaction was continued for 3 more days. The volatile products obtained were a mixture of $(CF_3)_2PSH$, $(CF_3)_2PI$ and $(CF_3)_2PH$ in the ratio 4.9:4.5:1.0 (total

weight: 0.560 g) according to nmr spectra. The volatile materials passing -131° were H_2S and excess HI (identified by their reactions with lead acetate) and a trace of SiF_4.

(h) With Cl_2

(i) Reaction of chlorine (0.0328 g, 0.462 mmoles) and $(CF_3)_2P(S)-S-P(CF_3)_2$ (0.0480 g, 0.120 mmoles) while warming slowly from -45° to room temperature over 24 hours gave $(CF_3)_2PCl_3$ (0.0468 g, 0.170 mmoles) trapping at -84° and a little $(CF_3)_2P(S)Cl$ in a more volatile fraction. A yellow low volatile oil having properties expected for S_2Cl_2 was also obtained.

(ii) In a second reaction, chlorine (0.018 g, 0.254 mmoles) and $(CF_3)_2P(S)-S-P(CF_3)_2$ (0.1066 g, 0.265 mmoles) were reacted at -78° for 24 hours. Analysis of the volatile products by nmr and ir spectroscopy showed 11% $(CF_3)_2P(S)-S-P(CF_3)_2$, 25% $(CF_3)_2PCl$, 40% $(CF_3)_2PCl_3$, 8% $(CF_3)_2P(S)Cl$, 16% $(CF_3)_2P(S)-S-S-P(S)(CF_3)_2$.

(i) With Br_2

Reaction of bromine (0.019 g, 0.120 mmoles) with $(CF_3)_2P(S)-S-P(CF_3)_2$ (0.0580 g, 0.144 mmoles) at 0° for 1 hour, followed by room temperature for 24 hours gave a mixture (0.0552 g) of $(CF_3)_2PBr$ (29%) and $(CF_3)_2P(S)Br$ (71%) according to nmr spectroscopy. A small amount of $(CF_3)_2P(S)-S-S-P(S)(CF_3)_2$ was obtained in a less volatile

fraction and in addition a small amount of involatile oil (S_2Br_2) was obtained.

A second reaction with excess bromine and $(CF_3)_2P(S)SP(CF_3)_2$ for 11 days at room temperature gave $(CF_3)_2P(S)Br$ and $(CF_3)_2PBr_3$. A trace of CF_3Br was also detected in the volatile products.

(j) With Hg

Heating mercury (0.025 g, 0.125 mmoles) and $(CF_3)_2P(S)-S-P(CF_3)_2$ (0.129 g, 0.32 mmoles) at 70° for 6 days gave $(CF_3)_2P-S-P(CF_3)_2$ (0.0808 g, 0.218 mmoles). A yellow solid remained which was shown by mass spectrometry to be $(CF_3)_4P_2S_4Hg$ (described in Chapter IV). A similar experiment carried out at 100° gave only $(CF_3)_2P-S-P(CF_3)_2$ and a solid residue of HgS.

(k) With sulphur and oxygen

Heating equimolar portions of freshly sublimed sulphur and $(CF_3)_2P(S)SP(CF_3)_2$ for 2 days at 165° followed by 4 days at 180° led to 90% recovery of unchanged $(CF_3)_2P(S)SP(CF_3)_2$ which was however contaminated with small amounts of unidentified species.

Dry air and $(CF_3)_2P(S)SP(CF_3)_2$ did not react after 9 days at room temperature and the mixed valence compound was quantitatively recovered.

4. Discussion

The reaction of $(CF_3)_2P(S)I$ with a stoichiometric quantity of mercury leads to the coupling of two $(CF_3)_2P(S)$ units to form a dimeric molecule:

$$2(CF_3)_2P(S)I + Hg \longrightarrow (CF_3)_4P_2S_2 + HgI_2 \qquad (3.1)$$

in a manner reminiscent of the synthesis of $(CF_3)_4P_2$.[2] The product however does not possess a P-P bond but rather has the isomeric structure with pentavalent and trivalent phosphorus atoms in the same molecule; that is the structure of the molecule is represented by the formula: $(CF_3)_2P(S)\text{-}S\text{-}P(CF_3)_2$. Reaction of this mixed valence diphosphorus compound with excess mercury gave the known sulphur bridged diphosphine [17,18] $(CF_3)_2P\text{-}S\text{-}P(CF_3)_2$ according to eq 3.2, in agreement

$$(CF_3)_2P(S)SP(CF_3)_2 + Hg \longrightarrow (CF_3)_2PSP(CF_3)_2 + HgS \qquad (3.2)$$

with an earlier report [12] that reaction of $(CF_3)_2P(S)I$ with excess mercury gave only $(CF_3)_2P\text{-}S\text{-}P(CF_3)_2$ in nearly quantitative yield; thus this product arises from a simple reduction of the mixed valence compound and not from the complicated series of exchanges suggested by Burg and Gosling.[13] Reaction (3.1) is not a suitable preparative method for the mixed valence compound

because complete consumption of the iodo compound requires an excess of mercury which results in the formation of only $(CF_3)_2P\text{-}S\text{-}P(CF_3)_2$ since it appears that the second reduction step (eq 3.2) proceeds readily under conditions required for reaction (3.1). The reactants and products are also difficult to separate.

A more suitable synthesis was devised from the knowledge that the structure contained pentavalent and trivalent phosphorus atoms. The reaction

$$2(CF_3)_2P(S)SH + (CF_3)_2P\text{-}N(CH_3)_2 \longrightarrow (CF_3)_2P(S)\text{-}S\text{-}P(CF_3)_2 + (CH_3)_2NH_2^+ \; S_2P(CF_3)_2^- \qquad (3.3)$$

gave a good yield of the mixed valence diphosphorus compound and the product was easily separable from the reactants and other impurities. The desired compound can also be obtained from the reaction

$$(CF_3)_2P(S)SH + (CF_3)_2PCl \rightleftharpoons (CF_3)_2P(S)\text{-}S\text{-}P(CF_3)_2 + HCl \qquad (3.4)$$

which is written as an equilibrium since the reverse reaction was shown to proceed when the mixed valence compound was treated with excess HCl. A good yield of $(CF_3)_2P(S)SP(CF_3)_2$ can be obtained from the reaction if a large excess of $(CF_3)_2PCl$ is used. Since the components

involved in reaction (3.4) can be readily separated from each other, the reaction is also convenient for synthetic purposes.

Other reactions also give this mixed valence compound in reasonable yield. A preliminary experiment conducted in these laboratories in 1967 by Dr. R. C. Dobbie involved heating excess elemental sulphur with tetrakistrifluoromethyldiphosphine for four days at 160°. The mixed valence compound $(CF_3)_2P(S)-S-P(CF_3)_2$ can now be identified as the major constituent of the volatile portion of the products by means of its characteristic nmr spectrum. Two other as yet unidentified volatile products were obtained in the same fraction as the mixed valence compound and an involatile product was also found in the original reaction tube. Similarly, heating sulphur with di(bistrifluoromethylphosphino)sulphide, $(CF_3)_2P-S-P(CF_3)_2$, yields the mixed valence compound plus unidentified volatile products. In neither of these systems can the desired product be easily separated and so these reactions are not particularly useful for synthetic purposes. The presence of these products however suggests that the simple two step synthesis of $(CF_3)_2PS_2H$ from tetrakistrifluoromethyldiphosphine, sulphur and hydrogen sulphide (see Chapter IX) or the synthesis from di(bistrifluoromethylphosphino)sulphide,

sulphur and hydrogen sulphide [13] probably proceeds through the initial formation of $(CF_3)_2P(S)-S-P(CF_3)_2$ which appears to be the most stable member of this phosphorus-sulphur system (see Chapters IV and V). The mixed valence compound is then easily converted to the acid by hydrogen sulphide in the presence of excess sulphur. Higher related polysulphide intermediates may also be involved and cannot be excluded from consideration although their presence is not necessary.

The mixed valence diphosphorus compound was thermally stable to 165° and it was not oxidized by sulphur at this temperature or oxygen at room temperature. Alkaline hydrolysis yielded three moles of CF_3H per mole of compound and $CF_3PS_2O^{=}$ ions as a result of cleavage at the P^{III}-S bond to form $(CF_3)_2POH$ and $(CF_3)_2PS_2H$. The former intermediate, $(CF_3)_2POH$, hydrolyses completely in alkaline solution to yield two moles of fluoroform and a nonfluorinated phosphorus ion. The latter pentavalent compound $(CF_3)_2PS_2H$ hydrolyses to the stable $CF_3PS_2O^{=}$ ion, and one mole of fluoroform. (See Chapter VIII).

The more complex neutral hydrolysis of bistrifluoromethylthiophosphoryl-μ-thio-bistrifluoromethylphosphine gave $(CF_3)_2PS_2^-$ and $CF_3P(H)O_2^-$ ions in solution again suggesting initial attack at the P^{III}-S bond to give $(CF_3)_2PS_2H$ which is not hydrolysed under the con-

ditions of the reaction (see Chapter VIII), and $(CF_3)_2POH$ which is hydrolysed to yield the observed one mole of fluoroform and the $CF_3P(H)O_2^-$ ion.[19] The formation of the latter species provides clear evidence for the presence of tervalent phosphorus.

In general, hydrogen sulphide and the hydrogen halides split the P-S-P bridge, at the P^{III}-S bond according to eq 3.5.

$$(CF_3)_2\overset{S}{\overset{\|}{P}}\text{-S-P}(CF_3)_2 + HX \longrightarrow (CF_3)_2P\overset{S}{\diagdown\!\!\diagup}SH + (CF_3)_2PX \qquad (3.5)$$

(X = SH, Cl, Br)

The observed complex mixture of products obtained from the reaction of hydrogen iodide with the mixed valence compound can be satisfactorily explained if the reaction is considered to proceed initially according to eq 3.5 and the products are then permitted to react further with HI: thus the acid is reduced to $(CF_3)_2PSH$

$$(CF_3)_2P(S)SH + 2HI \longrightarrow (CF_3)_2PSH + H_2S + I_2 \qquad (3.6)$$

(see Chapter IX) and the iodo phosphine is reduced by HI.[20]

$$(CF_3)_2PI + HI \longrightarrow (CF_3)_2PH + I_2 \qquad (3.7)$$

Since reactions (3.6 and (3.7) proceed readily under con-

ditions required for the initial cleavage, the use of a limited quantity of HI leads to a mixture of the above products.

Chlorine and bromine reacted with the mixed valence diphosphorus compound to yield the monophosphorus compounds $(CF_3)_2P(S)X$ and $(CF_3)_2PX$ (X = Cl, Br) expected from cleavage of the P(III)-S bridge bond possibly with the formation of $(CF_3)_2PS_2\cdot$ radicals. Excess halogen oxidizes the trivalent halogenophosphines to the pentavalent compounds $(CF_3)_2PX_3$ and chlorine but not bromine converts $(CF_3)_2P(S)X$ to $(CF_3)_2PX_3$. A small amount of CF_3Br detected in the reaction products may arise from the decomposition of $(CF_3)_2PBr_3$.[21] The sulphur halides which could not be properly characterized, may arise from decomposition of compounds such as $(CF_3)_2P(S)SCl$ which however were not isolated.

Reaction of approximately equimolar ratios of halogen and $(CF_3)_2P(S)\text{-}S\text{-}P(CF_3)_2$ under similar conditions gave essentially the same results except that complete consumption of the original diphosphorus compound was not achieved and only limited oxidation of phosphines to halogenophosphoranes was observed. The new diphosphine tetrasulphide (see Chapter IV) was obtained in small yield from both of these reactions suggesting the presence of $(CF_3)_2PS_2\cdot$ radicals in the system.

The nmr spectra provide the best evidence for the mixed valence structure of $(CF_3)_4P_2S_2$. All parameters are listed in Table 1. The ^{19}F nmr spectrum shows two major doublets; one of which has a chemical shift and coupling constant ($^2J_{FP}V$) which is characteristic of a pentavalent trifluoromethylthiophosphoryl group.[12] Each component of this doublet is clearly split into a doublet of septets (the high field component is illustrated in Fig. 1b) which can be assigned to long range CF_3-P-P^{III} ($^4J_{FP}III$) and long range F-F coupling ($^6J_{FF}$). The second major doublet with equal total intensity to the above has a chemical shift and coupling constant ($^2J_{FP}III$) which is characteristic of a trivalent CF_3P group.[22] Each component of this P^{III} doublet is complex. The high field part of the doublet is shown in Fig. 1a. The P^{III} spectrum is best understood on the basis of a first order analysis with near equality of $^4J_{FP}V$ and $^6J_{FF}$. The ^{31}P spectrum of the mixed valence compound shown in part in Fig. 2 clearly demonstrates the existence of two chemically shifted phosphorus atoms. The P^V region shows a complex pattern of an overlapping doublet of septets due to very similar values of $^2J_{FP}V$ and $^2J_{PP}$. Closer examination of one component shows the "septet" structure due to coupling with the fluorines of the $(CF_3)_2P^{III}$ group ($^4J_{FP}V$). The P^{III} spectrum is fully interpretable on the basis of

TABLE 1

Nuclear Magnetic Resonance Parameters for $(CF_3)_2P(S)-S-P(CF_3)_2$

Chemical Shift (ppm)[a]	P^{III}	P^{V}
ϕ_F (vs CCl_3F)	+ 53.8	+ 68.7
δ_P (vs P_4O_6)	+106.0	+ 65.2

Coupling Constants (Hz)[b]

$^2J_{FP}III$	81.3
$^2J_{FP}V$	111.7
$^2J_{PP}$	103.0
$^4J_{PP}III$	4.9
$^4J_{FP}V$	0.6
$^6J_{FF}$	0.5

(a) Positive values indicate resonances to high field of the reference.

(b) The notation is due to J. I. Musher and E. J. Corey,[23] as modified by R. K. Harris and R. G. Hayter[24] to indicate the particular phosphorus atom involved.

FIGURE 1

Part of the ^{19}F nmr spectrum of $(CF_3)_2P(S)\text{-}S\text{-}P(CF_3)_2$ measured at 94.1 MHz on a 15% solution of the compound in CCl_3F. Temperature of measurement was 40°. Frequencies are measured relative to CCl_3F. (a) The high field component of the doublet arising from CF_3 attached to P(III) which shows the overlapping pattern resulting from near equality of $^4J_{FP}V$ and $^6J_{FF}$. An identical peak is found about 80 Hz to low field. (b) The high field component of the major doublet arising from CF_3 attached to P(V) showing the clearly resolved $^4J_{FP}III$ doubling and the partially resolved "septet" due to $^6J_{FF}$. The vertical scale of arbitrary absorption units has been multiplied by two for this region therefore the total intensity in each of the two regions is identical. Another identical doublet is found about 110 Hz to low field.

Figure 1. ^{19}F nmr spectrum of $(CF_3)_2P(S)-S-P(CF_3)_2$

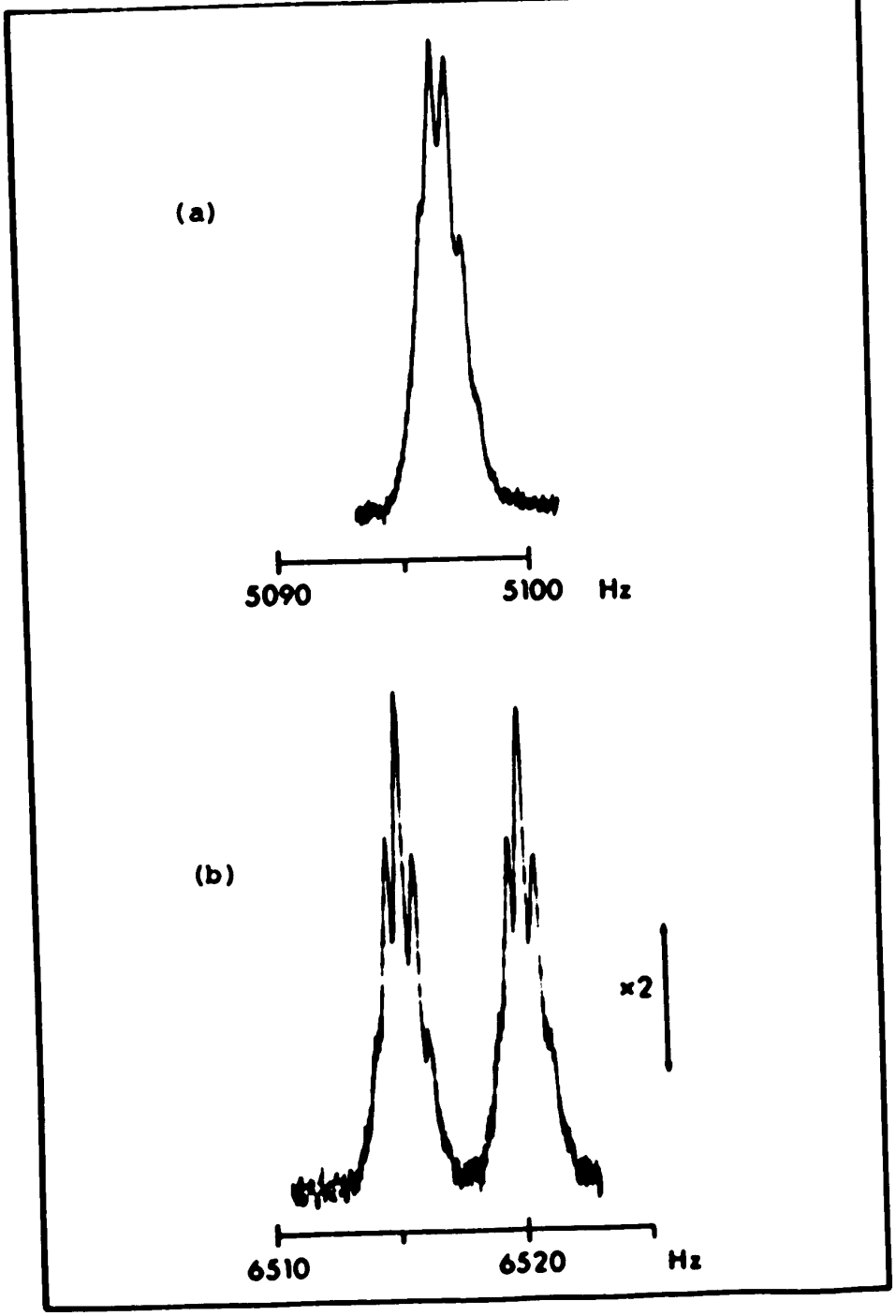
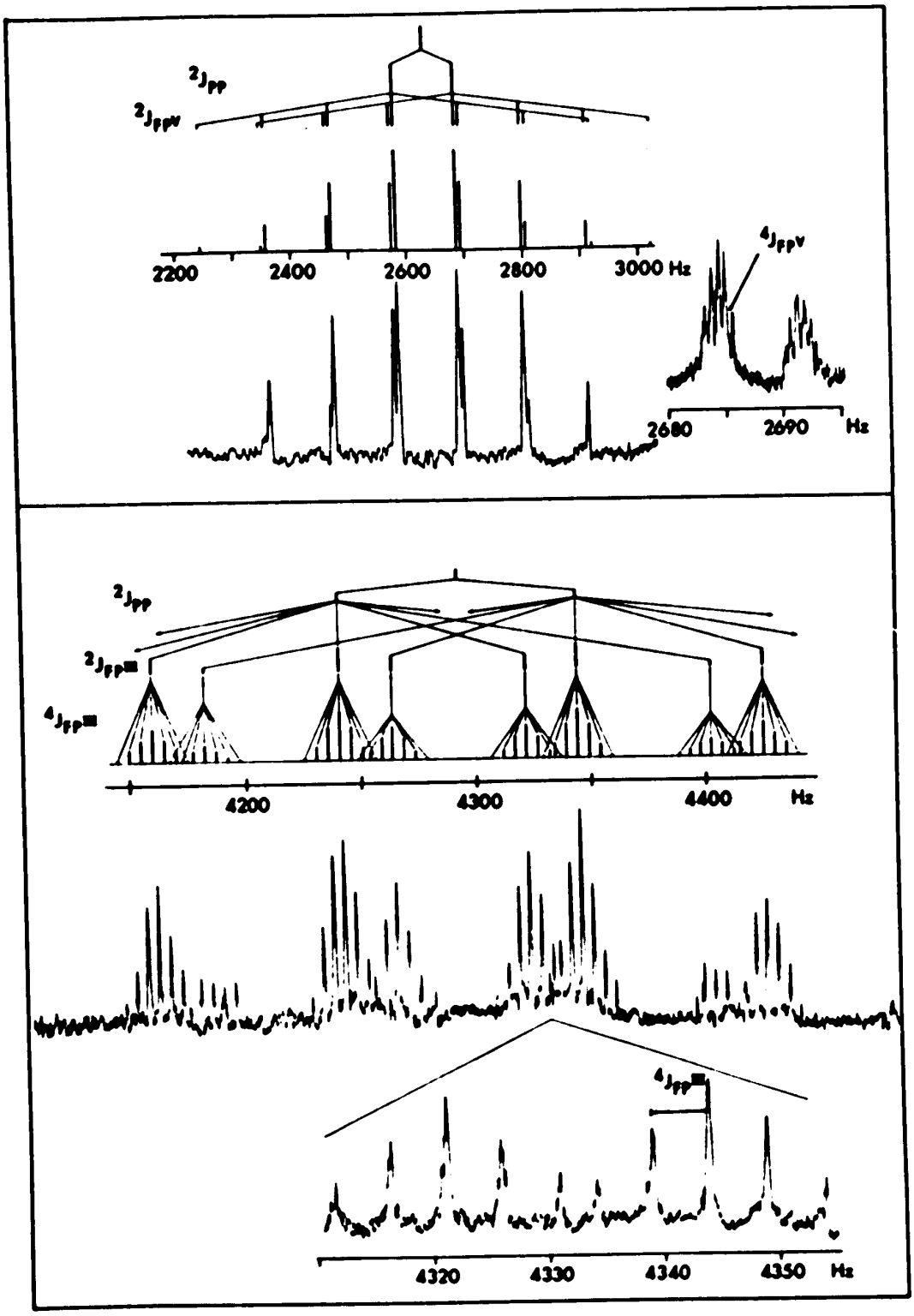


FIGURE 2

Portions of the 40.5 MHz ^{31}P spectrum of $(CF_3)_2P(S)SP(CF_3)_2$. In the upper compartment most of the P^V spectrum is shown illustrating the overlapping pattern due to $^2J_{PP}$ and $^2J_{FP}V$. The higher resolution display of one of the central members in the inset illustrates the pattern which arises from $^4J_{FP}V$ coupling. The lower compartment shows the central portion of the P(III) spectrum arising from $^2J_{PP}$, $^2J_{FP}III$ and $^5J_{FP}III$ coupling interactions on the P(III). The high resolution inset shows clearly the 5 central members of the septets which are in correct intensity ratio for septet components. The frequency scale is measured relative to P_4O_6 with positive sign denoting high field.

Figure 2. ^{31}P nmr spectrum of $(CF_3)_2P(S)-S-P(CF_3)_2$



first order spin coupling interactions. A notable feature of the spectra is the dramatic difference between $^4J_{FP}V$ and $^4J_{FP}III$ coupling constants which contributes to the more clearly resolved P^{III} spectrum. A similar phenomenon is observed [24] in the spectra of $(CH_3)_2P.P(S)(CH_3)_2$ except that in this case the $^3J_{HP}III$ (5.8 Hz) is smaller than $^3J_{HP}V$ (17.6 Hz) whereas the reverse is observed here.

Infrared spectral studies gave less conclusive structural information but did show a complex overlapping series of bands in the CF_3 region and a reasonably strong band at 783 cm^{-1} which could be assigned to a P=S absorption.[25] The complete spectrum is given in Table 2.

The mixed valence compound $(CF_3)_2P(S)-S-P(CF_3)_2$ shows the expected [26] fragmentation and rearrangement patterns in the mass spectrometer but no parent ion. The observed metastable peaks indicate that the molecule decomposes via two pathways: (a) loss of a sulphur atom followed by a fragmentation pattern similar to that of $(CF_3)_4P_2S$ [26b] and (b) loss of CF_3 initially. The smallest unit containing two sulphur atoms is $(CF_3)_2PS_2^+$. The complete spectrum is given in Table 3, those ions mass measured in Table 4, and the metastable transitions in Table 5.

In contrast to the P-P bonded structure observed

TABLE 2

Infrared Spectrum of $(CF_3)_2P(S)-S-P(CF_3)_2$ [a,b]

	Assignment
1202 (vs) 1192 (vs) 1173 (vs) 1160 (vs)	νCF_3
1138 (s) 1125 (s)	
783 (m)	$\nu P{=}S$
749 (w) 734 (m)	δsym CF_3
561 (w) 558 (w) 548 (w)	δasym CF_3
500 (s)	$\nu P{-}S$
480 (w)	$\nu P{-}CF_3$
447 (w)	P=S bend

(a) All values in cm^{-1}

(b) Abbreviations: ν = stretching, δ = deformation, s = strong, m = medium, w = weak, v = very.

TABLE 3

Mass Spectrum of $(CF_3)_2P(S)-S-P(CF_3)_2$

m/e	rel. int.[a]	assignment[b]	m/e	rel.int.[a]	assignment[b]
370	0.7	$C_4F_{12}P_2S$	131	1.1	C_2F_4P, CF_3P_2
351	0.3	$C_4F_{11}P_2S$	119	3.3	CF_4P, C_2F_5
333	3.2	$C_3F_9P_2S_2$	113	3.7	CF_2PS
301	6.1	$C_3F_9P_2S$	101	0.2	SPF_2
283	1.2	$C_2F_7P_2S_2$	100	3.6	CF_3P, C_2F_4
251	2.4	$C_2F_7P_2S$	95	0.3	PS_2
250	0.4	$C_3F_8P_2$	94	0.4	CFPS
233	0.3	$C_2F_6PS_2$	81	1.9	CF_2P
227	0.2	CF_8PS	75	0.5	CPS
201	0.2	C_2F_6PS	69	31.2	CF_3, (PF_2)
169	0.3	C_2F_6P	63	22.7	PS
163	1.4	C_2F_4PS	62	0.7	P_2, C_2F_2, PCF
162	0.4	C_3F_5P	50	2.2	CF_2, PF
151	1.1	CF_4PS	32	0.3	S
150	1.4	C_2F_5P	31	4.5	P, CF

(a) Intensities are expressed relative to the total ionization defined as $\sum_n$(intensity) for all ions with mass greater than 30 whose intensity is greater than 2% of the base peak.

(b) All species are positive ions and masses are calculated for the ^{32}S isotope.

TABLE 4

Mass Measured Ions in the Mass Spectrum of

$(CF_3)_2P(S)-S-P(CF_3)_2$

Ion	m/e calc.[a]	m/e obs.[a]
$C_4F_{11}P_2S^+$	350.9020	350.9024
$C_3F_9P_2S_2^+$	332.8773	332.8779
$C_3F_9P_2S^+$	300.9052	300.9053
$C_2F_6PS_2^+$	232.9084	232.9084

(a) Masses are calculated for the ^{32}S isotope

TABLE 5

Metastable Transitions in the Mass Spectrum of

$(CF_3)_2P(S)-S-P(CF_3)_2$

obs.	calc.[a]	Process
245.0	244.9	$C_4F_{12}P_2S^+ \longrightarrow C_3F_9P_2S^+ + CF_3$
240.5	240.5	$C_3F_9P_2S_2^+ \longrightarrow C_2F_7P_2S_2^+ + CF_2$
209.0	209.3	$C_3F_9P_2S^+ \longrightarrow C_2F_7P_2S^+ + CF_2$
161.0	161.0	$C_2F_7P_2S^+ \longrightarrow CF_5P_2S^+ + CF_2$

(a) Masses are calculated for the ^{32}S isotope

in organodiphosphine disulfides and in diphosphine monoxide and monosulfides [27], both the trifluoromethyldiphosphine disulfide discussed herein and the analogous fluorodiphosphine disulfide and diphosphine dioxide [28,29] possess a P-X-P structure which is confirmed by nmr and infrared structural evidence as well as the chemical synthesis and properties of the compounds.

This marked difference in the structures of diphosphine disulfides may be due to a stabilization of the trivalent state of phosphorus by the CF_3 or F group in keeping with earlier observations on related compounds.[6,10,17,18,30] The observed structure is probably a compromise between full stabilization of the trivalent state of both phosphorus atoms which would lead to the disulfide structure P-S-S-P with probably a readily cleaved S-S bond and the minimal stability provided by the phosphorus-phosphorus bonded pentavalent state.

It is surprising that the mixed valence compound appears to be the most stable compound in the system $(CF_3)_4P_2S_n$ where n = 2-4 (see Chapters IV and V) and this matter will be more fully discussed in subsequent Chapters.

CHAPTER IV

Di(bistrifluoromethylthiophosphoryl)disulphide

1. Preparation of $(CF_3)_2P(S)-S-S-P(S)(CF_3)_2$

The anhydrous sodium salt of bistrifluoromethyldithiophosphinic acid [12,13] was obtained by combining the acid (1.615 g, 6.90 mmoles) with sodium bicarbonate (0.574 g, 6.84 mmoles) in aqueous solution followed by removal of water under vacuum at room temperature. The total yield of salt was combined with bromine (0.55 g, 3.4 mmoles) at room temperature for 3 hours whereupon the bromine colour disappeared. Vacuum fractionation gave $(CF_3)_2P(S)-S-S-P(S)(CF_3)_2$ (1.490 g, 3.20 mmoles) in 94% yield collected at -23°.

Similar results were obtained when the dimethylammonium salt of bistrifluoromethyldithiophosphinic acid was treated with bromine under similar conditions.

2. Reactions of $(CF_3)_2P(S)-S-S-P(S)(CF_3)_2$

(a) Thermal Stability

Heating a sample of $(CF_3)_4P_2S_4$ (0.0370 g, 0.0795 mmoles) for 2 days at 165° gave $(CF_3)_2P(S)-S-P(CF_3)_2$ (0.0270 g, 0.067 mmoles), a little starting material and a trace of unidentified volatile material. Elemental sulphur remained in the reaction tube.

(b) Alkaline Hydrolysis

Alkaline hydrolysis of $(CF_3)_4P_2S_4$ (0.0240 g, 0.051 mmoles) with 5 ml of 10% NaOH solution for four days at room temperature gave CF_3H (0.0070 g, 0.10 mmoles). The aqueous solution contained the $CF_3PS_2O^=$ and $CF_3PSO_2^=$ ions in the ratio 3:1 (see Chapter VIII). A little elemental sulphur was also obtained, but no sulphide ion was present in the solution (sodium nitroprusside test [31]).

(c) Neutral Hydrolysis

Degassed water (0.1 ml) was shaken with $(CF_3)_4P_2S_4$ (0.0473 g, 0.101 mmoles) for 24 hours at room temperature. Elemental sulphur was produced, but no fluorocarbon containing volatiles were obtained. The aqueous solution contained $(CF_3)_2PS_2^-$, $(CF_3)_2P(S)O^-$ and $(CF_3)_2PO_2^-$ ions in the ratio 7.0:3.0:1.0 (see Chapter VIII).

(d) With H_2S

Heating hydrogen sulphide (1.2 mmoles) and $(CF_3)_4P_2S_4$

(0.0566 g, 0.122 mmoles) to 100° for 12 hours gave $(CF_3)_2PS_2H$ (0.0484 g, 0.206 mmoles).

(e) With HCl and HBr

Heating hydrogen chloride (1.2 mmoles) and $(CF_3)_4P_2S_4$ (0.0566 g, 0.121 mmoles) to 100° for 10 days gave a mixture (0.0400 g) of $(CF_3)_2PS_2H$ and $(CF_3)_2P(S)Cl$ in the ratio of 1.0:1.1 (by nmr spectroscopy). A small amount of unchanged $(CF_3)_4P_2S_4$ was recovered and sulphur remained in the reaction tube.

Heating $(CF_3)_4P_2S_4$ (0.0301 g, 0.065 mmoles) with excess HBr (~0.65 mmoles) at 70° for 9 days gave 0.0315 g of a mixture of $(CF_3)_2PS_2H$ and $(CF_3)_2P(S)Br$ in the ratio 1.0:1.3. Sulphur and a small amount of an involatile oil remained in the reaction tube.

In both cases some difficulty was experienced in separating excess HX from $(CF_3)_2PS_2H$.

(f) With HI

(i) Excess hydrogen iodide (0.9 mmoles) was allowed to react with $(CF_3)_4P_2S_4$ (0.0323 g, 0.069 mmoles) at room temperature for 3 days. Formation of I_2 was noted immediately on warming the condensed reactants to room temperature. Vacuum fractionation gave $(CF_3)_2PSH$ (0.0265 g, 0.131 mmoles) and a more volatile fraction which contained a mixture of H_2S and HI identified by their reactions with lead acetate. I_2 crystals remained in the reaction tube.

(ii) In a second reaction a tube containing hydrogen iodide (0.0568 g, 0.445 mmoles) in two fold molar ratio relative to $(CF_3)_4P_2S_4$ (0.0882 g, 0.189 mmoles) was allowed to warm from -78° to room temperature over 10 hours. Vacuum fractionation gave $(CF_3)_2PS_2H$ (0.0781 g, 0.334 mmoles) trapped at -84° and a trace of $(CF_3)_2PSH$ along with H_2S, and HI. I_2 remained in the reaction tube.

(g) With Cl_2 and Br_2

(i) Chlorine (~0.6 mmoles) and $(CF_3)_4P_2S_4$ (0.0253 g, 0.054 mmoles) were slowly warmed from -78° to room temperature and allowed to stand for 3 days. Vacuum fractionation gave 0.0501 g of a mixture of $(CF_3)_2PCl_3$ and a yellow liquid which appeared to be SCl_2, and was difficult to separate. The SCl_2 was identified by its reaction with H_2O to give chloride ion, elemental sulphur, and a reducing solution from which $BaSO_4$ could be precipitated after oxidation.

(ii) The reaction of Br_2 (0.0392 g, 0.245 mmoles) with $(CF_3)_4P_2S_4$ (0.0620 g, 0.133 mmoles) at 100° for 16 hours gave $(CF_3)_2P(S)Br$ (0.0675 g, 0.241 mmoles) on vacuum fractionation. An involatile brown oil was also produced (S_2Br_2 from the stoichiometry and observed physical properties).

(h) With Mercury

A nearly equimolar ratio of mercury (0.0244 g, 0.122 mmoles) was vigorously shaken with $(CF_3)_4P_2S_4$ (0.0550 g, 0.118 mmoles) at room temperature for 4 days. At this point - white crystalline solid plus significant quantities of metallic mercury remained in the reaction tube. Heating the tube to 70° for 3 days led to disappearance of mercury. Further heating to 100° for 24 hours converted the white crystals to yellow plates. Heating to 170° for 24 hours gave a clear liquid which gave white crystals on cooling and a trace of black HgS. A trace of $(CF_3)_2P\text{-}S\text{-}P(CF_3)_2$ was the only volatile product which could be distilled into the vacuum system. The white crystalline solid remaining in the reaction tube was identified as $(CF_3)_4P_2S_4Hg$ by mass spectroscopy including mass measurement of the molecular ion (Found m/e 667.7864, calc for $C_4F_{12}P_2{}^{32}S_4{}^{202}Hg$, m/e 667.7874).

(i) With Sulphur and Oxygen

Heating sulphur (0.0460 g, 1.44 mmoles) with $(CF_3)_4P_2S_4$ (0.0383 g, 0.082 mmoles) for 2 days at 160° gave $(CF_3)_4P_2S_2$ (0.0256 g, 0.064 mmoles) and a trace of unidentified volatile material.

Dry air did not react with $(CF_3)_4P_2S_4$ after 2 days at room temperature; the starting material was recovered unchanged.

3. Reactions of $(CF_3)_2P(S)I$

(a) With Hydrogen Sulphide

$(CF_3)_2P(S)I$ (0.0484 g, 0.147 mmoles) [12,13] was combined with excess H_2S (~1.5 mmoles) at room temperature for 40 hours. Analysis of the mixture trapping at -116° by nmr spectroscopy revealed $(CF_3)_2P(S)I$, $(CF_3)_2PI$, $(CF_3)_2PSH$ and $(CF_3)_2PS_2H$ in the ratio 1:1.2:8.0:11.2.

The reaction of $(CF_3)_2P(S)I$ (0.111 g, 0.337 mmoles) with H_2S (0.006 g, 0.18 mmoles) for 12 hours while warming from -78° to room temperature followed by three days at room temperature gave an unseparated mixture trapped at -116° of $(CF_3)_2PI$, $(CF_3)_2PSH$, $(CF_3)_2PS_2H$, and $(CF_3)_2P(S)I$ in the ratio 1:3.7:5.7:6.8 (by nmr spectroscopy).

(b) With Hydrogen Iodide.

$(CF_3)_2P(S)I$ [12,13] (0.074 g, 0.23 mmoles) and excess HI (~0.9 mmoles) were allowed to react in a sealed tube at room temperature. Visible production of iodine began following mixing of the reagents. Fractionation of the volatile products after 24 hours at room temperature gave $(CF_3)_2PSH$ (0.047 g, 0.23 mmoles), excess HI and a barely detectable trace of $(CF_3)_2PH$ as the only observed products.

4. Discussion

The new tetrasulphide, $(CF_3)_2P(S)-S-S-P(S)(CF_3)_2$, was best obtained from the reaction of salts of the dithiophosphinic acid with bromine.[32]

$$2(CF_3)_2PS_2^-Na^+ + Br_2 \longrightarrow (CF_3)_4P_2S_4 + 2NaBr \qquad (4.1)$$

Heating the tetrasulphide to 165° for two days resulted in thermal decomposition of the compound to $(CF_3)_2P(S)-S-P(CF_3)_2$ and sulphur. No $(CF_3)_2P(S)-S-P(S)(CF_3)_2$ was observed.

Treatment of the tetrasulphide with H_2S gave good yields of $(CF_3)_2PS_2H$, whereas HCl and HBr gave a one-molar equivalent of the same acid plus the halogenophosphine sulphide. Both results can be summarized by the overall equation:

$$(CF_3)_2P(S)-S-S-P(S)(CF_3)_2 + HX \longrightarrow (CF_3)_2P(S)SH + (CF_3)_2P(S)X + S \qquad (4.2)$$

(X = HS, Cl, Br)

Sulphur is also obtained from the reaction.

Hydrogen iodide reactions are much more complicated. Excess hydrogen iodide converts all of the tetrasulphide to $(CF_3)_2PSH$ leaving iodine and hydrogen sulphide as the only other volatile products. A twofold molar ratio of hydrogen iodide gave nearly two moles of the acid

$(CF_3)_2P(S)SH$ from one mole of the tetrasulphide plus small amounts of $(CF_3)_2PSH$, H_2S, HI and a large amount of iodine. Sulphur was not obtained in either reaction. The stoichiometry is best represented by eq 4.2 noting however

$$(CF_3)_4P_2S_4 + 2HI \longrightarrow (CF_3)_2P(S)SH + I_2 \qquad (4.2)$$

that in the presence of excess hydrogen iodide the acid is further reduced to the thiolophosphine $(CF_3)_2PSH$ (see Chapter IX). The reaction probably involves the splitting of the tetrasulphide molecule at the S-S bond with the initial formation of unstable compounds of the type $(CF_3)_2P(S)SX$ rather than $(CF_3)_2P(S)X$ compounds. The unstable sulphenyl compounds either decompose to sulphur and the observed $(CF_3)_2P(S)X$ products:

$$(CF_3)_2P(S)SX \longrightarrow (CF_3)_2P(S)X + S \qquad (4.3)$$

$$(X = Cl, Br, SH)$$

or are reduced to the acid by hydrogen iodide.

$$(CF_3)_2P(S)SI + HI \longrightarrow (CF_3)_2P(S)SH + I_2 \qquad (4.4)$$

Support for this interpretation comes mainly from the formation of only the acid and not $(CF_3)_2P(S)I$ from the

stoichiometric hydrogen iodide reaction since separate experiments have demonstrated that H_2S (which may be present in the system from the reaction of sulphur and HI)[33] only slowly reduced $(CF_3)_2P(S)I$ to a mixture of $(CF_3)_2PS_2H$ and $(CF_3)_2PI$ whereas the process represented by eq 4.2 is fast. Also $(CF_3)_2P(S)I$ is rather quickly reduced to $(CF_3)_2PSH$ by HI.

Chlorine splits the tetrasulphide and removes sulphur to yield $(CF_3)_2PCl_3$ whereas bromine gives only $(CF_3)_2P(S)Br$. Sulphur or air did not react with the tetrasulphide.

Mercury reacted with the tetrasulphide to form the Hg(II) complex $[(CF_3)_2PS_2]_2Hg$ which upon heating gave a small amount of HgS and $(CF_3)_2P\text{-}S\text{-}P(CF_3)_2$. Further studies on this and other dithiophosphinate complexes have been undertaken by other members of the laboratory and will be reported elsewhere.[34]

Alkaline hydrolysis of the tetrasulphide appears to proceed by initial cleavage of the S-S bond with eventual formation of the $CF_3PS_2O^=$ ion as the major product. Some $CF_3PSO_2^=$ ion was also formed however, indicating that the compound may also undergo cleavage at the P-S bond. Only the expected two moles of fluoroform per mole of tetrasulphide were obtained.

Neutral hydrolysis of $[(CF_3)_2P(S)]_2S_2$ gave a mixture

of $(CF_3)_2PS_2^-$, $(CF_3)_2PSO^-$ and $(CF_3)_2PO_2^-$ ions in solution, but no fluorocarbon volatiles. The dominant anionic products $(CF_3)_2PS_2^-$ and $(CF_3)_2PSO^-$ can be explained as the result of the cleavage of the disulphide bridge to form both $(CF_3)_2PS_2H$ (which would form the stable $(CF_3)_2PS_2^-$ ion in aqueous solution) and a sulphenyl intermediate $(CF_3)_2P(S)SOH$ which would probably be very unstable and would either decompose or readily undergo further reaction (c.f. the reaction of HX). This behaviour contrasts with that of the inorganic disulphane diphosphates which appear to hydrolyse through nucleophilic displacement at phosphorus with subsequent loss of sulphur.[35]

The minor but significant quantities of $(CF_3)_2PO_2^-$ may arise from the reaction of the sulphenyl intermediate with water to form OH radicals which then remove sulphur to form the fully oxygenated product. Separate experiments (see Chapter VIII) have demonstrated that sulphur-containing ionic species are desulphurized by peroxide in neutral solution as expected from related studies.[36]

The nmr and infrared spectra of the tetrasulphide are compatible with the disulphide bridge structure. The ^{19}F nmr spectrum is second order showing a sharp doublet due to $|^2J_{PF} + {}^5J_{PF}|$ with smaller peaks on either side of the major doublet (see Fig. 3) characteristic of the

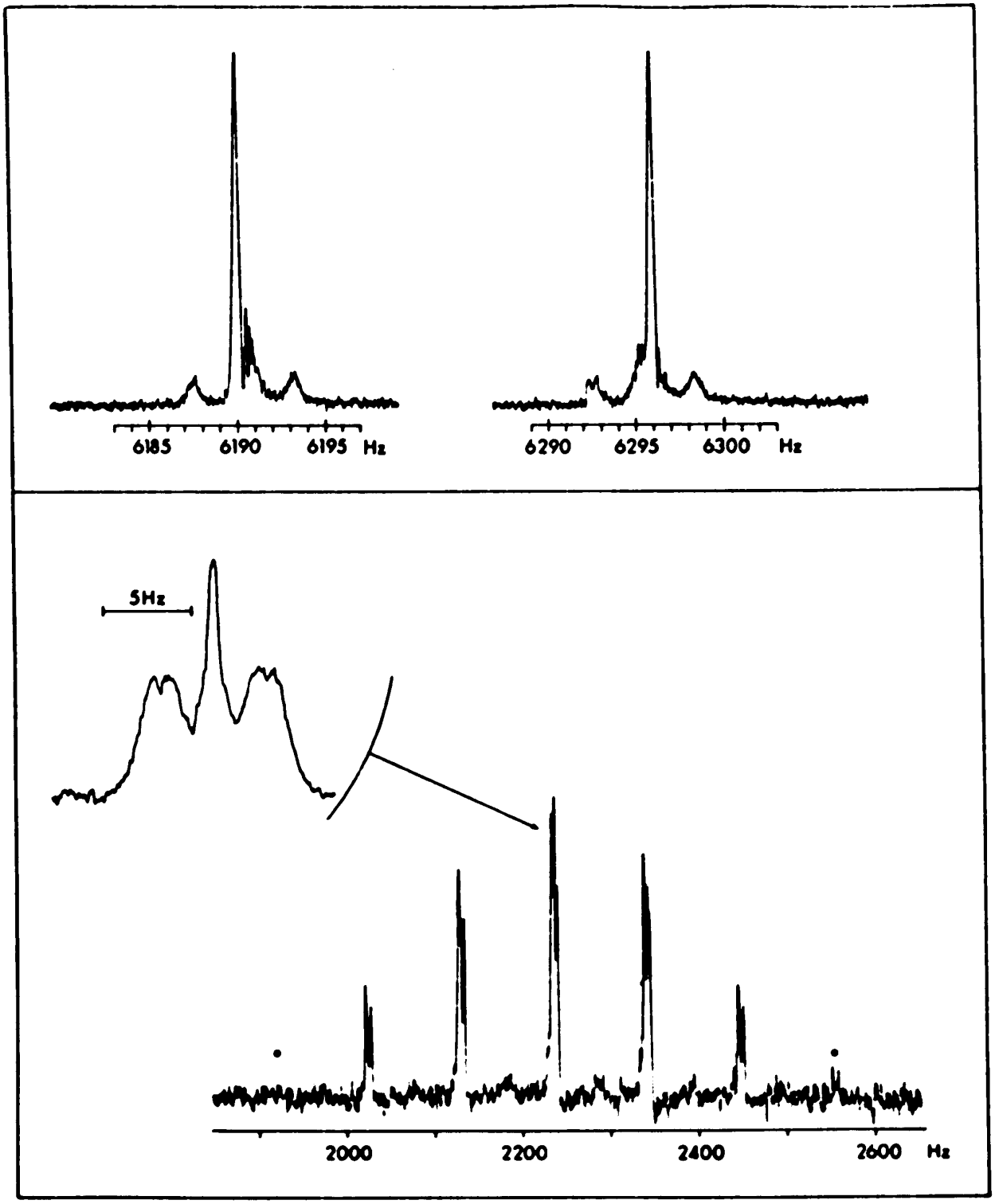
FIGURE 3

The 94.1 MHz ^{19}F and 40.5 MHz ^{31}P nmr spectra of $(CF_3)_2P(S)\text{-}S\text{-}S\text{-}P(S)(CF_3)_2$ at 40°.

The upper compartment shows the two major lines of the ^{19}F spectrum of separation $|^2J_{FP} + {}^5J_{FP}|$ with smaller lines on either side due to the second order effects. The frequency scale is measured relative to CCl_3F with positive sign denoting high field.

The lower compartment shows the ^{31}P nmr spectrum showing the major septet with the same separation as above and the second order effects on the major lines are shown inset. The frequency scale is measured relative to P_4O_6 with positive sign denoting high field. The asterisks denote expected positions of the two outermost components of the septet structure.

Figure 3. ^{19}F and ^{31}P nmr spectra of $(CF_3)_2P(S)-S-S-P(S)(CF_3)_2$



^{19}F spectra of molecules of the type $(CF_3)_2P\text{-}S\text{-}P(CF_3)_2$, $(CF_3)_2P\text{-}O\text{-}P(CF_3)_2$ and $(CF_3)_4P_2$ [37] which may be considered as examples of the $X_6AA'X_6'$ system. The value of $|^2J_{PF} + {}^5J_{PF}|$ is found to be 105.5 Hz and the chemical shifts (vs CCl_3F), ϕ_F = +66.5 ppm; both values are within the expected range for CF_3 groups attached to pentavalent phosphorus. The ^{31}P nmr spectrum (see Fig. 3) shows a septet due to $|^2J_{PF} + {}^5J_{PF}|$ with further fine structure due to second order effects at a chemical shift (vs P_4O_6), δ_P = +55.4 ppm. At this time a full analysis of the spectrum has not proved possible. The infrared spectrum (Table 6) is relatively simple showing strong P(C-F) bands in the 1100 - 1200 cm^{-1} region and a P=S stretching [25] band at 781 cm^{-1}.

The mass spectrum of $(CF_3)_2P(S)\text{-}S\text{-}S\text{-}P(S)(CF_3)_2$ shows a strong parent ion and the expected [26] fragmentation and rearrangement patterns. The initial step in the fragmentation pattern involves loss of CF_3 and then the path splits, the next step involving either loss of S or CF_3. The second pathway is confirmed by the observation of a metastable transition shown with the complete spectrum in Table 7.

TABLE 6

Infrared Spectrum of $(CF_3)_2P(S)-S-S-P(S)(CF_3)_2$ [a,b]

	Assignment
1198(vs) 1183(vs) 1166(vs) 1131(m)	νCF_3
781(m)	$\nu P{=}S$
731(s)	δsym CF_3
554(m) 540(w)	δasym CF_3
477(s)	$\nu P{-}S$
458(w,sh)	$\nu P{-}CF_3$
370(w)	P=S bend

(a) All values in cm^{-1}.

(b) Abbreviations: ν = stretching, δ = deformation, sh = shoulder, s = strong, m = medium, w = weak, v = very.

TABLE 7

Mass Spectrum of $(CF_3)_2P(S)-S-S-P(S)(CF_3)_2$

m/e	rel.int.[a]	Assignment[b]	m/e	rel.int.[a]	Assignment[b]
466[c]	37.5	$C_4F_{12}P_2S_4$	114	0.5	FPS_2
397	5.3	$C_3F_9P_2S_4$[d]	113	0.7	CF_2PS
365	1.7	$C_3F_9P_2S_3$	101	0.7	SPF_2
333	2.3	$C_3F_9P_2S_2$	100	0.5	CF_3P, C_2F_4
297	3.4	$C_2F_6PS_4$	95	1.8	PS_2
283	1.0	$CF_4P_2S_2$	82	0.8	PSF
265	2.3	$C_2F_6PS_3$	69	3.6	CF_3
234	8.8	CF_5PS_3	64	2.1	S_2
233	6.9	$C_2F_6PS_2$	63	5.2	PS
201	2.9	C_2F_6PS	58	1.4	
165	4.2	F_2PS_3	32	1.5	S
133	1.2	F_2PS_2	31	0.5	CF,P
119	3.2	C_2F_4, CF_4P			

(a) Intensities are expressed relative to the total ionization defined as $\sum_n$(Intensity) for all ions with mass greater than 30 whose intensity is greater than 2% of the base peak.

(b) All species are positive ions and masses are calculated for the ^{32}S isotope.

(c) Identified by mass measurement: Found m/e = 465.8167,

TABLE 7 (continued)

required for $C_4F_{12}P_2{}^{32}S_4$ m/e = 465.8168.

(d) The formation of this ion is demonstrated by the metastable transition: observed 338.1, calculated 338.2 for the process

$$C_4F_{12}P_2S_4^+ \longrightarrow C_3F_9P_2S_4^+ + CF_3$$

CHAPTER V

The Attempted Preparation of di(bistrifluoromethylthiophosphoryl) sulphide

1. Introduction.

One of the most likely products of sulphur oxidation of the diphosphine sulphide, $(CF_3)_2P\text{-}S\text{-}P(CF_3)_2$, was considered to be the trisulphide, $[(CF_3)_2P(S)]_2S$.[13] However, this simple sulphur oxidation was shown to lead to a mixture of products (see Chapter III). The fluorine analogue, $[F_2P(S)]_2S$, has been prepared,[38] and the corresponding oxide, $[(CF_3)_2P(S)]_2O$, is known to be stable (see Chapter VII), hence it was considered that completion of the series $(CF_3)_4P_2S_n$ (where n = 0-4) would be fairly simple. However this has not proved to be the case.

The problem may be considered to be the preparation of a sulphur bridge between two bistrifluoromethylthiophosphoryl moieties. Many ways exist for synthesizing P-S-P bridged molecules and a number of reactions are described in this section which, by analogy with other systems, might have been expected to produce the desired product.

2. Attempted Methods of Preparation of $[(CF_3)_2P(S)]_2S$.

(a) From $(CF_3)_2PS_2H$ and $(CF_3)_2P(S)Cl$

A sample of bistrifluoromethyldithiophosphinic acid [12,13] heated at 100° for three days with a twofold excess of bistrifluoromethylthiophosphoryl chloride [12,13] gave a trace of HCl on vacuum fractionation but no other evidence of reaction. Heating for a further six days at 150° produced a trace of elemental sulphur but again the starting materials were recovered.

(b) From $(CF_3)_2PS_2H$ and $(CF_3)_2P(S)-N(CH_3)_2$

Dimethylaminobistrifluoromethylphosphine sulphide[12,13] (0.110 g, 0.45 mmoles) and bistrifluoromethyldithiophosphinic acid [12,13] (0.298 g, 1.27 mmoles) failed to react during 24 hours at 70°. Further heating at 100° for four days produced a mixture of compounds which could not be separated by vacuum fractionation. Analysis of the mixture by nmr spectroscopy showed the main component to be $(CF_3)_2P(S)-S-P(CF_3)_2$. Some unreacted starting materials were also present with traces of unidentified compounds. $(CH_3)_2\overset{+}{N}H_2(CF_3)_2PS_2^-$ was identified in the involatiles.

(c) From $(CF_3)_2P(S)I$ and HgS

Bistrifluoromethylthiophosphoryl iodide [12,13] (0.2118 g, 0.646 mmoles) and mercuric sulphide (0.0747 g, 0.312

mmoles) appeared to react during 24 hours at room temperature with appearance of mercuric iodide. Vacuum fractionation showed only a small amount of reaction had occurred and the product obtained was $(CF_3)_2P(S)-S-P(CF_3)_2$. Much of the initial $(CF_3)_2P(S)I$ was recovered. Further reaction at 100° for five days produced 0.1068 g of $(CF_3)_2P(S)-S-P(CF_3)_2$ containing minor unidentified impurities. The nature of the solid residue was not investigated.

(d) From $(CF_3)_2P(S)I$ and Ag_2S

No reaction took place when bistrifluoromethylthiophosphoryl iodide [12,13] (0.0598 g, 0.182 mmoles) was allowed to react for two days at room temperature with silver sulphide (0.0218 g, 0.088 mmoles). Heating at 70° for a further two days produced 0.0314 g of a mixture identified as $(CF_3)_2P(S)-S-P(CF_3)_2$, $(CF_3)_2P(S)I$, $[(CF_3)_2P]_2S$ and $(CF_3)_2PS_2H$ in the molar ratio 4.8:3.1:1.3:1.0 by nmr spectroscopy as the only volatile products.

(e) From $(CF_3)_2P(S)Cl$ and $(CF_3)_2PS_2^-$

The $(CF_3)_2PS_2^-$ ion was generated by reacting bistrifluoromethyldithiophosphinic acid [12,13] (0.35 mmoles) with trimethylamine (0.35 mmoles). A large excess of bistrifluoromethylthiophosphoryl chloride [12,13] was added to the

solid salt. No reaction occurred after two days at room temperature, but heating for five days at 70° produced a trace of an unidentified compound. As the amine salt was not very soluble in $(CF_3)_2P(S)Cl$, methylene chloride was added as solvent and the reaction continued at 70° for five more days. Again little reaction had taken place although the nmr spectrum of the volatile products did show minor components whose nmr parameters would be consistent with a bridged system containing pentavalent phosphorus atoms. The involatile residue only contained the amine salt.

(f) From $(CF_3)_2P(S)-O-P(S)(CF_3)_2$ and $(CF_3)_2PS_2^-$

The sodium salt, $Na^+(CF_3)_2PS_2^-$, was prepared by reacting bistrifluoromethyldithiophosphinic acid [12,13] (0.6740 g, 2.88 mmoles) and sodium bicarbonate (0.239 g, 2.84 mmoles) in aqueous solution at room temperature followed by removal of solvent and volatiles under vacuum.

The sodium salt (0.0670 g, 0.262 mmoles) dissolved in 0.3 ml. dry acetonitrile (distilled from P_4O_{10}) did not react with bistrifluoromethylthiophosphinic anhydride (0.0930 g, 0.22 mmoles) during two days at room temperature, or on heating at 70° for four more days.

3. Discussion

The diphosphine sulphide, $[(CF_3)_2P]_2S$, is known to exist in equilibrium with HCl, the chlorophosphine, $(CF_3)_2PCl$, and the mercaptophosphine, $(CF_3)_2PSH$, according to eq 5.1.[17] A similar equilibrium has been shown to

$$(CF_3)_2P\text{-}S\text{-}P(CF_3)_2 + HCl \rightleftharpoons (CF_3)_2PSH + (CF_3)_2PCl \qquad (5.1)$$

exist in the case of the mixed valence compound, $(CF_3)_2P(S)\text{-}S\text{-}P(CF_3)_2$ (see Chapter III, eq 3.4). It seemed reasonable to suggest, by analogy with eq 5.1 that the system involving $(CF_3)_2P(S)Cl$ and $(CF_3)_2P(S)SH$ might behave similarly to the phosphino system and that the equilibrium:

$$(CF_3)_2P(S)SP(S)(CF_3)_2 + HCl \rightleftharpoons (CF_3)_2P(S)Cl + (CF_3)_2P(S)SH \qquad (5.2)$$

might be established. Using large concentrations of the right hand side "products" of eq (5.2) might shift the equilibrium sufficiently to the left to allow isolation of the desired trisulfide. Such an example was already provided by one of the synthetic routes to the mixed valence compound (Chapter III eq 3.4). It did not prove possible to identify any $(CF_3)_2P(S)SP(S)(CF_3)_2$ in reaction mixtures of $(CF_3)_2PS_2H$ and $(CF_3)_2P(S)Cl$ even after treatment at elevated temperatures suggesting that the

equilibrium (5.2) lies far to the right.

Phosphorus-nitrogen bonds are known to be readily cleaved by HX according to eq 5.3. These reactions can be generally extended to systems in which HX is a phos-

$$R_2P(S)\text{-}N(CH_3)_2 + 2HX \rightarrow R_2P(S)X + (CH_3)_2\overset{+}{N}H_2\ X^- \quad (5.3)$$

phorus thioacid with resultant formation of compounds containing a P-S-P bridge (Chapter III, eq 3.3). This method was successfully used under mild conditions to prepare $[F_2P(S)]_2S$ where R = F and X = F_2PS_2.[38] When R = CF_3 and X = Cl or Br the reaction can be made to proceed, but only under vigorous conditions.[12,13] When R = CF_3 and X = $(CF_3)_2PS_2$ no reaction occurred at moderate temperatures and heating to higher temperatures led to inseparable mixtures of products, the major component of the mixture being $(CF_3)_2P(S)\text{-}S\text{-}P(CF_3)_2$ presumably arising from the thermal decomposition of the desired product.

Silver and mercuric sulphides have been used to prepare sulphur bridged diphosphorus compounds from iodophosphines, for example the preparation of $(CF_3)_2P\text{-}S\text{-}P(CF_3)_2$ from $(CF_3)_2PI$.[17] A similar reaction utilizes silver carbonate[30] to form P-O-P bridged compounds and this method was successfully employed to prepare the oxy-analogue, $[(CF_3)_2P(S)]_2O$, from $(CF_3)_2P(S)I$ (see Chapter VII). However, $(CF_3)_2P(S)I$ failed to react

with silver sulphide at room temperature and heating at 70° for two days gave the mixed valence compound, $(CF_3)_2P(S)-S-P(CF_3)_2$, as the major product with small amounts of starting material, the diphosphine sulphide, $(CF_3)_2P-S-P(CF_3)_2$, and the dithio acid, $(CF_3)_2PS_2H$; the latter presumably arising from traces of moisture on the metal sulphide. A similar reaction carried out with $(CF_3)_2P(S)I$ and mercuric sulphide also gave $(CF_3)_2P(S)-S-P(CF_3)_2$ as the major volatile product. Again the production of the disulphide on heating suggests that the desired product may be thermally unstable.

The dithiophosphinate ion, $(CF_3)_2PS_2^-$, may be considered to be a nucleophile. Two reactions were carried out to try to displace another group from phosphorus using this potential nucleophile. In the first reaction an attempt was made to displace chloride ion from $(CF_3)_2P(S)Cl$ using, in the first instance, excess chlorophosphorus compound as solvent and in a subsequent experiment methylene chloride as solvent. Very little reaction took place in either case, although some minor unidentified products were obtained from the methylene chloride reaction. Halide ions are known to displace $(CF_3)_2P(S)O^-$ ions from bistrifluoromethylthiophosphinic anhydride, $[(CF_3)_2P(S)]_2O$, in acetonitrile solution to form thiophosphoryl halides (see Chapter VII), but no significant

reaction occurred between $(CF_3)_2PS_2^-$ ions and the anhydride under similar conditions.

The reaction of hexamethyldisilthiane, $[(CH_3)_3Si]_2S$, with halophosphines has been employed to prepare diphosphine sulphides.[35] Reactions involving the disilthiane and bistrifluoromethylthiophosphoryl halides have been shown not to produce any of the desired product, and in fact to only react very slowly at elevated temperatures to form products with P-S-Si bonds in very poor yield.[7]

The tetrasulphide, $[(CF_3)_2P(S)]_2S_2$ (see Chapter IV), may be reduced pyrolytically, however, the major product was shown to be the mixed valence disulphide, $(CF_3)_2P(S)\text{-}S\text{-}P(CF_3)_2$, and no evidence was obtained for the presence of any trisulphide. The disulphide has been shown to be easily reduced with mercury (see Chapter III, eq 3.2), however reaction of a stoichiometric amount of mercury with the tetrasulphide led to compound formation and not reduction to the desired product (see Chapter IV).

In view of the stability of the oxygen bridged analogue, $[(CF_3)_2P(S)]_2O$ (see Chapter VII), and the fluoro analogue $[F_2P(S)]_2S$ [38] and the ease of preparation of the oxygen bridged compound by sulphur oxidation of the diphosphorane, $(CF_3)_2P\text{-}O\text{-}P(CF_3)_2$, there is no apparent reason why the trisulphide, which would be expected to have a monosulphur bridged structure should not be stable.

However, all of our attempts to prepare the compound that gave any products at all invariably involved heating, and the major product was the disulphide which suggests that the desired product is thermally unstable. Thus reactions which occur only at relatively high temperatures do not appear to provide promising avenues for the synthesis of the trisulphide, $(CF_3)_4P_2S_3$.

CHAPTER VI

Bistrifluoromethylthiophosphinic Acid

1. Introduction.

Bistrifluoromethyldithiophosphinic acid has been recently prepared,[12,13] and bistrifluoromethylphosphinic acid has been known for many years,[39] however the mixed monothio acid has not been reported to date. While attempting to prepare the methyl ester, $(CF_3)_2P(S)OCH_3$,[40] from $(CF_3)_2P(S)Cl$ [12,13] and methanol it was noted that a salt rather than a volatile compound was obtained in the presence of trimethylamine. Subsequent studies have shown that the above pure ester also reacts readily with trimethylamine to form a salt. In both cases the reaction stoichiometry indicated that the salt was $(CH_3)_4N^+ (CF_3)_2P(S)O^-$ and this conclusion has now been verified. This Chapter describes the synthesis of the acid, $(CF_3)_2P(S)OH$, from this salt and by other methods, and its characterization by chemical and spectroscopic methods.

2. Preparation of bistrifluoromethylthiophosphinic acid

(a) From $(CF_3)_2P(S)Cl$

Bistrifluoromethylthiophosphoryl chloride [12,13] (0.7317 g, 3.10 mmoles), methanol (~3.8 mmoles) freshly distilled from sodium methoxide, and trimethylamine (~6.3 mmoles) reacted below room temperature to produce a white solid. The volatile products (only excess methanol and trimethylamine) were removed to leave a solid which was then allowed to react with concentrated sulphuric acid while warming slowly from -196° to room temperature. Vacuum fractionation of the volatile products gave $(CF_3)_2P(S)OH$ (0.3495 g, 1.60 mmoles, 51% yield) which was trapped at -63°.

(b) From $(CF_3)_2PSH$ and dry air.

Bistrifluoromethylmercaptophosphine [17] (0.0490 g, 0.242 mmoles) was allowed to react with air (dried by passage through a series of -196° traps) containing ~0.13 mmoles of oxygen for 24 hours at room temperature. Vacuum fractionation gave $(CF_3)_2P(S)OH$ (0.0204 g, 0.094 mmoles) which contained a trace of $(CF_3)_2PS_2H$, trapped at -63°.

(c) Preparation of the deutero-enriched acid

A sample of $(CF_3)_2P(S)OH$ was repeatedly reacted with several fresh samples of DCl until an enrichment of ~60% was achieved.

3. Reactions of bistrifluoromethylthiophosphinic acid

(a) With Heat

A sample of the acid (0.1196 g, 0.550 mmoles) heated at 150° for four days decomposed and rearranged to give 0.0914 g of volatile products which were found to be unreacted $(CF_3)_2P(S)OH$, $(CF_3)_2PS_2H$ and $(CF_3)_4P_2S_2O$ in the molar ratio 3.0:4.9:2.1 by nmr spectroscopy. No involatile material was observed.

(b) With Water

No fluorocarbon-containing volatile products were formed when $(CF_3)_2P(S)OH$ (0.0317 g, 0.145 mmoles) reacted with ~0.5 ml of degassed distilled water for 24 hours. The resultant aqueous solution was quite stable and had the same nmr parameters as aqueous solutions of salts of the acid. The acid was quite volatile in water vapour, and the aqueous solution could be distilled to leave no residue.

(c) With Aqueous Alkali

Room temperature reaction of $(CF_3)_2P(S)OH$ (0.0632 g, 0.290 mmoles) with ~5.0 ml of 10% NaOH solution for 24 hours gave CF_3H (0.0204 g, 0.291 mmoles) as the only volatile product. The aqueous alkaline solution contained $CF_3PSO_2^=$ ions (analysed by nmr spectroscopy, see Chapter VIII). The sodium nitroprusside test [31] indicated the absence of $S^=$ ions.

(d) Preparation of Salts.

(i) $Na^+(CF_3)_2P(S)O^-$

Sodium bicarbonate (0.0206 g, 0.245 mmoles) was dissolved in ~1.0 ml of water and allowed to react with $(CF_3)_2P(S)OH$ (0.0586 g, 0.269 mmoles). When the reaction had ceased, CO_2 and the solvent were removed under vacuum to leave a white solid, the ir spectrum of which suggested a hydrate. Analysis gave 0.79% H (calculated for the monohydrate $Na(CF_3)_2PSO.H_2O$; H, 0.74%). Treatment of the solid with concentrated sulphuric acid gave a small amount of $(CF_3)_2P(S)OH$. The nmr spectrum of an aqueous solution of the salt showed the presence of the same species observed in aqueous solutions of the acid.

(ii) $(CH_3)_2\overset{+}{N}H_2\ (CF_3)_2P(S)O^-$

When $(CF_3)_2P(S)OH$ (0.1146 g, 0.525 mmoles) and dimethylamine (0.0266 g, 0.590 mmoles) were warmed together a rapid reaction occurred below room temperature to produce a white solid. After 18 hours only a trace of $(CH_3)_2NH$ was recovered. The solid dissolved in water to produce a stable solution with the nmr properties of the $(CF_3)_2PSO^-$ ion as recorded.

(e) With $(CF_3)_2P\text{-}N(CH_3)_2$

Dimethylaminobistrifluoromethylphosphine [7,8] (0.0426 g, 0.200 mmoles) and $(CF_3)_2P(S)OH$ (0.0900 g, 0.413 mmoles) were

combined and allowed to warm slowly from -78° to room temperature over a period of three days. Vacuum fractionation gave 0.0662 g of a mixture which contained $[(CF_3)_2P]_2S$ [17,18] and $[(CF_3)_2P(S)]_2O$ in the ratio 1.15:1.0. A white solid remained which was identified as a mixture of amine salts of the $(CF_3)_2P(S)O^-$ ion and the $(CF_3)_2PO_2^-$ ion [39] (see Chapter VIII) in the ratio 1.65:1. A minor amount of an involatile oil which reacted with the air also remained in the reaction tube.

(f) With Hg

No reaction occurred when a sample of $(CF_3)_2P(S)OH$ (0.0727 g, 0.334 mmoles) was maintained in contact with excess mercury for seven days at room temperature. Only unchanged $(CF_3)_2P(S)OH$ (0.0662 g, 0.304 mmoles) was recovered.

(g) With HI

(i) In the absence of Hg

No reaction occurred when $(CF_3)_2P(S)OH$ (0.0747 g, 0.343 mmoles) was treated with hydrogen iodide (~3.5 mmoles) at room temperature for five days. Vacuum fractionation gave $(CF_3)_2P(S)OH$ (0.0608 g, 0.279 mmoles after iodine contamination had been removed by treatment with metallic mercury). Difficulty was experienced in separating all the unreacted acid from the HI in vacuum.

(ii) In the presence of Hg

A similar reaction involving $(CF_3)_2P(S)OH$ (0.0750 g, 0.344 mmoles), hydrogen iodide (~3.4 mmoles) and excess mercury gave unchanged acid (0.0655 g, 0.300 mmoles) and large amounts of hydrogen on vacuum fractionation.

(h) With dry air

Unchanged $(CF_3)_2P(S)OH$ (0.0745 g, 0.342 mmoles) was recovered after four days of room temperature reaction of the acid (0.0817 g, 0.374 mmoles) with air (dried by passage through several -196° traps) containing ~0.4 mmoles of O_2.

4. Reactions of the bistrifluoromethylthiophosphinate anion.

(a) With HCl

No reaction occurred when a sample of $(CH_3)_2\overset{+}{N}H_2$ $(CF_3)_2PSO^-$ was treated with excess HCl at room temperature for 24 hours.

(b) With Cl_2 and Br_2

When $(CH_3)_2\overset{+}{N}H_2$ $(CF_3)_2PSO^-$ (0.0698 g, 0.266 mmoles) was combined with chlorine (0.0110 g, 0.155 mmoles) and warmed slowly from -78° to room temperature the only volatile product obtained was $(CF_3)_2P(S)Cl$ [12,13] (0.244 g, 0.103 mmoles).

A similar reaction between $(CH_3)_2\overset{+}{N}H_2$ $(CF_3)_2PSO^-$ (0.73 mmoles) and bromine (0.42 mmoles) produced only $(CF_3)_2P(S)Br$ [12,13] (0.36 mmoles).

5. Discussion

The reaction of $(CF_3)_2P(S)Cl$ with methanol and trimethylamine forms a white involatile salt formulated as $(CH_3)_4N^+(CF_3)_2P(S)O^-$ according to eq 6.1. Reacting the

$$(CF_3)_2P(S)Cl + CH_3OH + 2(CH_3)_3N \longrightarrow (CF_3)_2P(S)O^- + Cl^- + (CH_3)_4N^+ + (CH_3)_3\overset{+}{N}H \qquad (6.1)$$

solid product with concentrated sulphuric acid under mild conditions (i.e. allowing the mixture to warm slowly from -196° to room temperature) results in a vigorous reaction which produces HCl and the new oxy-thio acid, $(CF_3)_2P(S)OH$, as a mixture of volatile products. These acids may be easily separated by vacuum fractionation.

The acid has also been obtained by the careful oxidation of $(CF_3)_2PSH$ with a small excess of dry air but a pure product was never obtained by this method.

Attempts to prepare the monothio acid by sulphur oxidation of $(CF_3)_2POH$ following the method used [12] to prepare $(CF_3)_2PS_2H$ were unsuccessful due to the combination of high temperatures required to induce reaction and the low thermal stability of the monothio acid.

Salts of the monothio acid give stable aqueous solutions containing the same anions as solutions of the acid itself. The nmr spectra of salt solutions and aqueous acid solutions are identical and show a simple doublet with

a coupling constant,[20] $^2J_{PF}$ = 97.4 Hz at a chemical shift (vs. CCl_3F), ϕ_F = 73.1 ppm in agreement with expected values for pentavalent $(CF_3)_2P$ oxy-thio systems. Solutions of the same anion may be generated by neutral hydrolysis of $(CF_3)_2P(S)Cl$, however neutralization of the solution with silver carbonate led to desulphurization of the anion (see Chapter VIII) leaving the $(CF_3)_2PO_2^-$ ion as the only anionic species in solution. The silver salt of $(CF_3)_2POS^-$ therefore cannot be prepared in aqueous solution in contrast to the preparation[39] of $(CF_3)_2PO_2H$ from the silver salt $AgO_2P(CF_3)_2$ which was obtained from oxidative hydrolysis of $(CF_3)_2PCl$. Alkaline hydrolysis of the monothio acid and its salts liberates one mole of fluoroform per mole of compound to leave the $CF_3PSO_2^=$ ion in solution thus demonstrating the presence of the bistrifluoromethylthiophosphoryl group (see Chapter VIII).

The ^{19}F nmr spectrum of the acid shows a simple doublet ($^2J_{FP}$ = 120 Hz, ϕ_F = +72.2 ppm vs CCl_3F) and the ^{31}P nmr spectrum a septet ($^2J_{FP}$ = 123 Hz, δ_P = +58.4 ppm vs P_4O_6) in agreement with expected values for a pentavalent bistrifluoromethylthiophosphoryl group.[12] The proton nmr spectrum shows a relatively sharp singlet with a chemical shift which varies somewhat from sample to sample which may be due to concentration differences. The signal also moves downfield with decreasing temperature in any one sample. The single line signal could not be resolved into a doublet even at -100° indicating that the proton

is undergoing rapid exchange between environments on the nmr time scale. In contrast the proton spectrum of the dithio acid, $(CF_3)_2PS_2H$, which showed a single peak at ordinary temperatures gave a doublet at -114° which was of the correct order of magnitude for a P-H coupling ($^2J_{PH}$) through sulphur indicating that the exchange rate in this case could be sufficiently reduced by cooling to observe the coupling of the proton, stabilized in one environment, with the phosphorus.[12,37]

The KBr windows of infrared cells were rapidly etched by the acid, but the infrared spectrum could be recorded with windows protected by a film of paraffin wax. The spectrum shows strong bands in the CF_3 region with values typical of those for a pentavalent bistrifluoromethylphosphorus compound. The band at 3615 cm^{-1} (2665 cm^{-1} in the deutero-compound) can be assigned to an OH stretch, and the band at 1000 cm^{-1} to a POH bend. If we assume that the ratio of OH to OD stretching frequencies (1.35) applies also to other motions then the POH bending band should shift from 1000 cm^{-1} to 740 cm^{-1} in the POD compound. This gives the POD bend a frequency very close to that of the P=S stretching absorption in the POH compound. The appearance of bands in the spectrum of the deutero-compound at 810 and 695 cm^{-1}, and the absence of the expected band at 773 cm^{-1} (ν P=S) is therefore attributed

to Fermi resonance between POD bending and P=S stretching vibrations because both vibrations transform as A' under C_s symmetry and are therefore subject to Fermi interaction if they are of similar energy and the above calculation predicts that the energies would indeed be very close. The complete spectrum is shown in Table 8.

The infrared data are consistent with the $(CF_3)_2P(S)OH$ structure in the gas phase rather than the isomeric $(CF_3)_2P(O)SH$ structure. However, the marked variation of proton chemical shift with concentration and temperature suggests that an equilibrium of the type shown in eq 6.2 may be important in non-aqueous solvents.

$$(CF_3)_2P(=S)OH \rightleftharpoons (CF_3)_2P(=O)SH \qquad (6.2)$$

The mass spectrum of the acid has a strong parent ion and shows the expected fragmentation and rearrangement patterns in the mass spectrometer.[26] The complete spectrum is shown in Table 9.

The acid was not oxidized by air at room temperature but it was found to be thermally unstable since heating at 150° for four days led to dehydration, condensation and rearrangements giving the anhydride and the dithio acid as major volatile products. The failure of others[42] to prepare the monothiodifluoro acid is perhaps not surprising in view of the low thermal stability of the CF_3

TABLE 8

Infrared Spectra [a,b]

$(CF_3)_2P(S)OH$	$(CF_3)_2P(S)OD$	Assignments
3615(s)	2665(s)	νOH νOD
1214(vs) 1188(vs) 1145(m)	1214(vs) 1188(vs) 1145(m)	νCF_3
1000(s)		δPOH
925(s)	925(s)	νP-O
	810(s)[c]	see text
773(m)		νP=S
713(m)	713(m)	δsym CF_3
	695(m,sh)[c]	see text
549(m)	549(m)	δasym CF_3
497(m)	497(m)	νP-C
414(w)	414(w)	P=S bend

(a) All frequencies in cm^{-1}

(b) Abbreviations: ν = stretching, δ = deformation, s = strong, m = medium, w = weak, v = very, sh = shoulder.

(c) P=S stretching and POD bending bands shifted from expected positions by Fermi interaction.

TABLE 9

Mass Spectrum of $(CF_3)_2P(S)OH$ [a,b]

m/e	rel.int.	Assignment	m/e	rel.int.	Assignment
218[c]	20.9	C_2F_6PSOH	78	0.5	CFPO
198	0.5	C_2F_5PSO	76	5.8	CPSH
186	1.8	C_2F_6POH	69	13.3	CF_3,PF_2
150	0.4	C_2F_5P	67	13.3	PFOH
149	3.2	CF_3PSOH	66	0.4	FPO
128	2.7		64	0.5	PSH
127	1.2		63	5.7	PS
119	1.1	CF_4P,C_2F_5	51	5.0	CF_2H
117	1.0	CF_3POH	50	1.7	CF_2,PF
101	0.6	SPF_2	48	0.9	SO
100	0.6	CF_3P,C_2F_4	47	3.8	PO
99	4.2	PFSOH	44	1.4	CPH,C_2FH
85	0.5	F_2PO	38	0.8	F_2
83	2.2	FPSH	36	1.0	HOF
82	1.4	FPS	32	0.8	S
80	0.8	PSOH	31	1.8	P,CF

(a) Intensities are expressed relative to the total ionization defined as $\sum_n$(intensity) for all ions with m/e > 30 whose intensity is greater than 2% of the base peak.

TABLE 9 (continued)

(b) All species are positive ions and masses are calculated for the ^{32}S isotope.

(c) Identified by mass measurement: Found m/e = 217.9395, required for C_2F_6PSOH m/e = 217.9390.

analogue.

Solutions of the acid in water are found to be stable. Typical strong acid behavior was demonstrated by formation of 1:1 salts with dimethylamine and sodium bicarbonate. Potentiometric titration of an aqueous solution prepared from the anhydride (see Chapter VII) gave $K_a \sim 3.2 \times 10^{-3}$. Salts of the acid did not react with HCl, again demonstrating the acid strength of $(CF_3)_2P(S)OH$. Attempts to dimerize the anion by halogen oxidation analogous to the preparation of P-S-S-P dimers[32] as described in Chapter IV led only to the formation of thiophosphoryl halides.

The acid reacted smoothly at 70° to cleave the P-N bond in dimethylaminobistrifluoromethylphosphine sulphide and form the anhydride according to eq 6.3.

$$(CF_3)_2P(S)\text{-}N(CH_3)_2 + 2(CF_3)_2P(S)OH \rightarrow (CF_3)_2P(S)\text{-}O\text{-}P(S)(CF_3)_2 + (CH_3)_2NH(CF_3)_2PSO^- \quad (6.3)$$

A reaction of the acid with dimethylaminobistrifluoromethylphosphine did not give the expected mixed valence compound $(CF_3)_2P(S)\text{-}O\text{-}P(CF_3)_2$, in contrast to the ready preparation (see Chapter III) of $(CF_3)_2P(S)\text{-}S\text{-}P(CF_3)_2$ by a similar reaction; instead a mixture of the anhydride $[(CF_3)_2P(S)]_2O$, and the known [17,18] sulphur bridged diphosphine, $[(CF_3)_2P]_2S$, was obtained as the only volatile

product plus a mixture of the amine salts of the $(CF_3)_2PSO^-$ and $(CF_3)_2PO_2^-$ ions. This appears to be a very complex system which involves oxygen-sulphur exchange and mutual oxidation-reduction reactions.

Although the dithio acid is rapidly reduced by hydrogen iodide to $(CF_3)_2PSH$ (see Chapter IX), the monothio acid was found to be resistant to reduction even in the presence of mercury which does not itself react with the monothio acid. That the dithio acid is reduced whereas the monothio acid is not may perhaps be attributed to the reduced availability of the lone pairs on sulphur for bonding a proton in the monothio acid as a result of additional electron withdrawal from phosphorus arising because of the substitution of a very electronegative oxygen atom in place of the sulphur. If the binding of the proton to sulphur is the rate determining step in all of these reactions such a situation would be expected to lead to reduced reactivity. Further support for this interpretation comes from the knowledge that difluorodithiophosphinic acid, F_2PS_2H, with its highly electronegative fluorine substituents, is only slowly reduced [43] by HI even on warming to 65°, whereas the reduction of the $(CF_3)_2PS_2H$ is extremely fast at room temperature.

The variation of vapour pressure with temperature was examined in a Pyrex spiral guage microtensimeter. The

results (given in Table 10) could be expressed by the linear equation 6.4. The calculated heat of vaporization

$$\log P_{mm} = -1954/T + 7.90 \qquad (6.4)$$

(ΔH_{vap}) was 8940 cal mole^{-1}, the extrapolated boiling point 116°, and the Trouton's constant 23.0 e.u.; the latter value indicates limited intermolecular association in the liquid phase. This is somewhat surprising in view of the difficulty encountered in handling and transferring the acid since it seemed to be readily absorbed by the tap grease.

Bistrifluoromethylthiophosphinic acid may be described as a strong mono-basic acid of phosphorus. The chemistry of the acid may be largely explained in terms of the electronegativity of the CF_3 group and also the electronegativity of oxygen. The withdrawal of electrons in this manner leads to the greater acid strength (vs the dithio acid, $(CF_3)_2PS_2H$) and the reduced availability of lone pair electrons on sulphur for reaction with electrophilic reagents. The ready availability of the proton also makes the monothio acid a better electrophilic reagent than the dithio acid, for example, both acids will cleave P^{III}-N bonds, but only the monothio acid reacts with $(CF_3)_2P(S)$-$N(CH_3)_2$ (see Chapters V and VII).

TABLE 10

Vapour Pressure Data for $(CF_3)_2P(S)OH$

Temperature, °C	P(observed)$_{mm}$	P(calculated)$_{mm}$ [a]
4.0	7.5	7.1
10.0	10.2	10.0
14.5	12.7	12.8
20.3	16.4	17.5
24.8	20.8	22.0
31.6	30.2	30.8
35.3	36.6	36.8
40.3	47.1	46.5
44.5	57.4	56.2
50.1	74.8	71.8

(a) Calculated from eq 6.4.

CHAPTER VII

Bistrifluoromethylthiophosphinic Anhydride

1. Introduction

The acid described in the previous Chapter is readily dehydrated to bistrifluoromethylthiophosphinic anhydride, $[(CF_3)_2P(S)]_2O$, by P_4O_{10}. Other synthetic routes to the anhydride are also described and the spectroscopic and chemical properties of the compound are discussed.

2. Preparation of bistrifluoromethylthiophosphinic anhydride.

(a) From $(CF_3)_2P(S)OH$ and P_4O_{10}

Bistrifluoromethylthiophosphinic acid (0.3495 g, 1.60 mmoles) and excess P_4O_{10} (~1 g) were allowed to react for two days at 70°.

Vacuum fractionation gave $(CF_3)_4P_2S_2O$ (0.2681 g, 0.642 mmoles) in 80% yield which was collected at -84°, as the only volatile product.

(b) From $(CF_3)_2P-O-P(CF_3)_2$

Tetrakistrifluoromethyldiphosphoxane [30] (0.0373 g, 0.105 mmoles) was combined with resublimed sulphur (~0.5 g) in the presence of a trace of resublimed Al_2Cl_6 and heated to 100° for three days. Vacuum fractionation of the volatile products gave $(CF_3)_4P_2S_2O$ (0.0153 g, 0.037 mmoles) in 35% yield. A more volatile fraction contained $(CF_3)_2PCl$ and $(CF_3)_2P(S)Cl$. Reaction in the absence of Al_2Cl_6 did not proceed below 180°, and at this temperature led to an inseparable mixture of products.

(c) From $(CF_3)_2P(S)I$ and Ag_2CO_3

Iodobistrifluoromethylphosphine sulphide [12,13] (0.0110 g, 0.335 mmoles) and silver carbonate (0.0484 g, 0.175 mmoles) were allowed to react for 15 hours at room temperature. The reaction actually began well below room temperature.

Vacuum fractionation gave $(CF_3)_4P_2S_2O$ (0.0624 g) which contained about 7% of $(CF_3)_2P\text{-}S\text{-}P(CF_3)_2$ impurity.

(d) From $(CF_3)_2PS_2H$ and $(CF_3)_2P(O)\text{-}N(CH_3)_2$

Bistrifluoromethyldithiophosphinic acid [12,13] (0.0721 g, 0.308 mmoles) and dimethylaminobistrifluoromethylphosphine oxide [44] (0.0378 g, 0.165 mmoles) did not react during four days at room temperature. A further two days at 70° gave $(CF_3)_4P_2S_2O$ (0.0478 g, 0.114 mmoles) contaminated with about 4% of $(CF_3)_2PS_2H$. An involatile oil remained in the reaction tube.

(e) From $(CF_3)_2P(S)OH$ and $(CF_3)_2P(S)\text{-}N(CH_3)_2$

Bistrifluoromethylthiophosphinic acid (0.0864 g, 0.396 mmoles) and dimethylaminobistrifluoromethylphosphine sulphide [12,13] (0.0406 g, 0.166 mmoles) were combined and allowed to warm slowly from -78° to room temperature and the mixture was then allowed to stand for four days at room temperature. Vacuum fractionation gave $(CF_3)_4P_2S_2O$ (0.0430 g, 0.103 mmoles) contaminated with 8.0% of $(CF_3)_2P(S)\text{-}N(CH_3)_2$. The solid which remained in the reaction tube was identified as $(CH_3)_2\overset{+}{N}H_2\ (CF_3)_2PSO^-$.

3. Reactions of bistrifluoromethylthiophosphinic anhydride.

(a) With Heat

A sample of $(CF_3)_4P_2S_2O$ (0.0581 g, 0.139 mmoles) heated to 160° for three days showed no observable change and was almost quantitatively recovered (0.0570 g, 0.136 mmoles).

(b) With Dry Air

Air, dried by passage through several -196° traps, containing ~0.2 mmoles of oxygen, was allowed to react with $(CF_3)_4P_2S_2O$ (0.0454 g, 0.108 mmoles) at room temperature for three days. Almost quantitive recovery of unchanged $(CF_3)_4P_2S_2O$ (0.0446 g) was achieved on vacuum fractionation.

(c) With Water

No volatile fluorocarbon products were obtained when $(CF_3)_4P_2S_2O$ (0.1726 g, 0.413 mmoles) was reacted with 10.0 ml of degassed, distilled water. The aqueous solution contained $(CF_3)_2PSO^-$ ions (demonstrated by nmr). The solution was diluted to ~90 ml and titrated against 0.100 M NaOH under an atmosphere of nitrogen. The endpoint was detected potentiometrically at 8.39 ml corresponding to a molecular weight of 412. The pH at the half neutralization point was 2.49.

(d) With Aqueous Alkali

The reaction of $(CF_3)_4P_2S_2O$ (0.0636 g, 0.152 mmoles) with 5.0 ml of degassed 10% NaOH solution for 24 hours at

room temperature gave CF_3H (0.0207 g, 0.296 mmoles) as the only volatile product. The aqueous alkaline solution contained $CF_3PSO_2^=$ ions (identified by nmr, see Chapter VIII).

(e) With Hydrogen Sulphide

No reaction occurred when $(CF_3)_4P_2S_2O$ (0.0440 g, 0.105 mmoles) was heated for five days at 100° with hydrogen sulphide (~1.1 mmoles). After heating for a further five days at 170°, 0.0386 g of a mixture of $(CF_3)_2PS_2H$,[12,13] $(CF_3)_2P(S)OH$ and $(CF_3)_4P_2S_2O$ in the ratio 6.8:1.6:1.6 (analysed by nmr) was trapped at -132°. A trace of sulphur remained in the reaction tube and a small amount of non-condensible gas (O_2?) was also obtained.

(f) With HCl and HBr

A sample of $(CF_3)_4P_2S_2O$ (0.0386 g, 0.092 mmoles) failed to react with hydrogen chloride (~1.0 mmoles) during four days at 100°. Heating at 160° for a further five days produced 0.0318 g of a mixture of $(CF_3)_2P(S)Cl$,[12,13] $(CF_3)_2PS_2H$,[12,13] and $(CF_3)_4P_2S_2O$ in the ratio 6.9:2.1:1.0 (analysed by nmr) trapped at -132°.

A similar reaction involving $(CF_3)_4P_2S_2O$ (0.0468 g, 0.112 mmoles) and hydrogen bromide (~1.1 mmoles) did not proceed during six days at 100°. A further five days at 150° yielded 0.0486 g of a mixture trapped at -132° of $(CF_3)_2PS_2H$,[12,13] $(CF_3)_2P(S)Br$[12,13] and $(CF_3)_2P(S)OH$ in

the ratio 1.4:7.2:1.4.

(g) With HI

(i) In the absence of Hg.

Very little reaction took place when $(CF_3)_4P_2S_2O$ (0.0893 g, 0.214 mmoles) and hydrogen iodide (~2.1 mmoles) were heated for five days at 100°. A further five days at 150° led to ~50% reaction to give a mixture of products analysed (by nmr) as starting material, $(CF_3)_2P(S)OH$, $(CF_3)_2PS_2H$, $(CF_3)_2PI$, and $(CF_3)_2PSH$ and much iodine trapped at -116°.

(ii) In the presence of Hg

No reaction occurred between $(CF_3)_4P_2S_2O$ (0.0482 g, 0.115 mmoles) and hydrogen iodide (~1.1 mmoles) in the presence of excess mercury during two days at room temperature. Vacuum fractionation recovered unchanged $(CF_3)_4P_2S_2O$ (0.0483 g, 0.115 mmoles). A large quantity of hydrogen gas was also produced.

(h) With $(CH_3)_2NH$

A sample of $(CF_3)_4P_2S_2O$ (0.0340 g, 0.081 mmoles) reacted rapidly below room temperature with excess dimethylamine (~0.8 mmoles). Vacuum fractionation after 17 hours at room temperature gave $(CF_3)_2P(S)\text{-}N(CH_3)_2$ [12,13] (0.0176 g, 0.072 mmoles). The white salt remaining in the reaction tube was identified as $(CH_3)_2\overset{+}{N}H_2$ $(CF_3)_2PSO^-$.

(i) With Sodium Halides

Reactions were carried out by condensing the anhydride onto a frozen solution of the halide in 0.3 ml of acetonitrile. The reaction was allowed to proceed at 70° until there was only one liquid layer (the anhydride is immiscible with acetonitrile), in general about 24 hours. The solvent was removed from the products by vacuum fractionation, but in reaction (iii), total separation proved impossible.

(i) Sodium fluoride (0.0132 g, 0.315 mmoles) reacted with $[(CF_3)_2P(S)]_2O$ (0.1134 g, 0.271 mmoles) to give $(CF_3)_2P(S)F$ [12] (0.0543 g, 0.247 mmoles) and a residue containing $(CF_3)_2PSO^-$ ions (identified by nmr).

(ii) Sodium chloride (0.0214 g, 0.366 mmoles) reacted with $[(CF_3)_2P(S)]_2O$ (0.1364 g, 0.326 mmoles) to give $(CF_3)_2P(S)Cl$ [12,13] (0.0737 g, 0.312 mmoles) and a residue containing $(CF_3)_2PSO^-$ ions (identified by nmr).

(iii) Sodium bromide (0.0323 g, 0.314 mmoles) reacted with $[(CF_3)_2P(S)]_2O$ (0.1110 g, 0.265 mmoles) to give $(CF_3)_2P(S)Br$ [12,13] and a residue containing $(CF_3)_2PSO^-$ ions (identified by nmr).

(j) With Mercury

No reaction occurred when $[(CF_3)_2P(S)]_2O$ was heated for seven days at 100° with excess mercury.

4. Discussion

Dehydration of $(CF_3)_2P(S)OH$ with P_4O_{10} at 70° gave good yields of the anhydride, $(CF_3)_2P(S)-O-P(S)(CF_3)_2$. Low yields of the same compound were also obtained from the Al_2Cl_6 catalyzed addition of sulphur to $(CF_3)_2P-O-P(CF_3)_2$ at 100° according to eq 7.1. Elevated

$$(CF_3)_2P-O-P(CF_3)_2 + 2S \xrightarrow{Al_2Cl_6} (CF_3)_2P(S)-O-P(S)(CF_3)_2 \qquad (7.1)$$

temperatures led to inseparable mixtures of products. Also $(CF_3)_2P(S)I$ reacted rapidly with a stoichiometric amount of silver carbonate to give good yields of the anhydride according to eq 7.2, a reaction which is similar

$$2(CF_3)_2P(S)I + Ag_2CO_3 \longrightarrow (CF_3)_2P(S)-O-P(S)(CF_3)_2 + 2AgI + CO_2 \qquad (7.2)$$

to the preparation [30] of $(CF_3)_2P-O-P(CF_3)_2$, however the product was contaminated with a small amount of $(CF_3)_2P-S-P(CF_3)_2$ which could not readily be removed. Reaction of $(CF_3)_2PS_2H$ with $(CF_3)_2P(O)-N(CH_3)_2$ proceeded smoothly at 70° according to eq 7.3, but instead of giving

$$(CF_3)_2P(O)-N(CH_3)_2 + 2(CF_3)_2PS_2H \longrightarrow (CF_3)_2P(S)-O-P(S)(CF_3)_2 + (CH_3)_2\overset{+}{N}H_2(CF_3)_2PS_2^- \qquad (7.3)$$

the unsymmetrical compound $(CF_3)_2P(O)-S-P(S)(CF_3)_2$ which

might have been expected, the reaction gave only the anhydride, $[(CF_3)_2P(S)]_2O$, contaminated with traces of starting materials which could not be removed by vacuum distillation. Similar results were obtained using $(CF_3)_2P(S)OH$ and $(CF_3)_2P(S)\text{-}N(CH_3)_2$ (eq 7.4)

$$(CF_3)_2P(S)\text{-}N(CH_3)_2 + 2(CF_3)_2P(S)OH \longrightarrow (CF_3)_2P(S)\text{-}O\text{-}P(S)(CF_3)_2 + (CH_3)_2\overset{+}{N}H(CF_3)_2PSO^- \quad (7.4)$$

indicating that the oxygen bridge is more readily formed. Previous studies on the fluorophosphorus system [38] gave similar results; the oxygen bridge was readily formed and the unsymmetrical isomers could only be made with difficulty.

The compound is a true anhydride and may be dissolved in water to give acidic solutions which can be titrated with standard alkali to give a molecular weight of 412 (418 required for $(CF_3)_4P_2S_2O$). The anion obtained by neutral hydrolysis was shown to be $(CF_3)_2P(S)O^-$ by nmr spectroscopy (see Chapter VI). Alkaline hydrolysis yields two moles of fluoroform per mole of compound, and the $CF_3PSO_2^=$ ion may be identified as the only fluorine-containing species present in the hydrolysate; this is consistent with the presence of two bistrifluoromethylthiophosphoryl groups in the molecule (see Chapter VIII).

The ^{19}F nmr spectrum is second order showing a sharp doublet due to $|^2J_{FP} + {}^4J_{FP}|$ with a separation of 129 Hz with less intense lines on either side of the two major lines (as shown in Fig. 4). The pattern is characteristic of the ^{19}F nmr spectra of $X_6AA'X_6'$ systems such as $(CF_3)_2P\text{-}P(CF_3)_2$, $(CF_3)_2P\text{-}O\text{-}P(CF_3)_2$ and $(CF_3)_2P\text{-}S\text{-}P(CF_3)_2$ and supports the symmetric formula. The ^{31}P nmr spectrum shows the same major spacing, 129 Hz, with the major septet having further structure due to the second order effects (as shown in Fig. 4). Complete analysis of the spectrum is not possible at this time, but both the ^{19}F and ^{31}P chemical shift parameters (ϕ_F = +70.7 ppm vs CCl_3F and δ_P = +72.8 ppm vs P_4O_6) are compatible with the existence of equivalent pentavalent phosphorus atoms.

The infrared spectrum shows the expected strong bands in the CF_3 region with values expected for a $(CF_3)_2P$ compound. Three bands centred at 930 cm^{-1} may be assigned to the P-O-P structure [30] and the band at 802 cm^{-1} to a P=S stretching vibration. The complete spectrum is shown in Table 11.

The mass spectrum shows the expected fragmentation and rearrangement patterns [26] and a strong parent ion. The complete spectrum is shown in Table 12.

The anhydride was thermally stable to 160° and was not oxidized by dry air at room temperature. In general

FIGURE 4

The 56.4 MHz ^{19}F and 40.05 MHz ^{31}P nmr spectra of $(CF_3)_2P(S)\text{-}O\text{-}P(S)(CF_3)_2$ at 40°.

The upper compartment shows the two major lines of the ^{19}F spectrum of separation $|^2J_{FP} + {}^4J_{FP}|$ with smaller lines on either side due to second order effects. The frequency scale is measured relative to CCl_3F with positive sign denoting high field.

The lower compartment shows the ^{31}P nmr spectrum showing the major septet with the same separation as above with further structure due to second order effects. The frequency scale is measured relative to P_4O_6 with positive sign denoting high field.

Figure 4. ^{19}F and ^{31}P nmr spectra of $(CF_3)_2P(S)-O-P(S)(CF_3)_2$

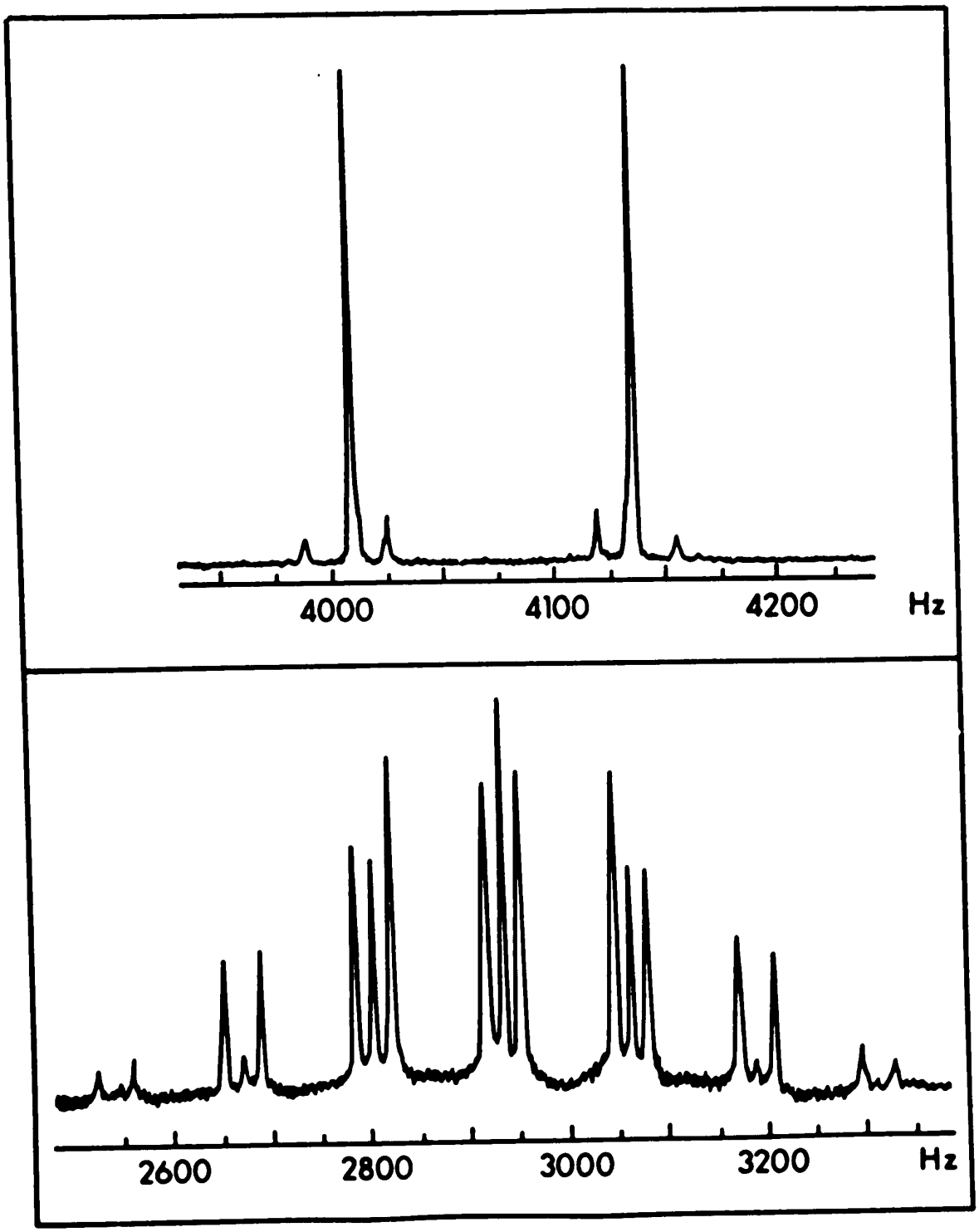


TABLE 11

Infrared Spectrum of $[(CF_3)_2P(S)]_2O$ [a,b]

	Assignment
1206 (vs) 1182 (vs) 1153 (m-sh)	νCF_3
980 (m) 929 (vs) 903 (m)	νasym POP
841 (s)	νPO
803 (m)	νP=S
754 (w)	δsym CF_3
732 (m)	νsym POP
636 (w)	
551 (m)	δasym CF_3
495 (m)	νPC
442 (w-sh)	
413 (m)	P=S bend

(a) All frequencies in cm^{-1}

(b) Abbreviations: ν = stretching, δ = deformation, s = strong, m = medium, w = weak, v = very, sh = shoulder

TABLE 12

Mass Spectrum of $[(CF_3)_2P(S)]_2O$ [a,b]

m/e	rel.int.	Assignment	m/e	rel.int.	Assignment
418[c]	11.1	$C_4F_{12}P_2S_2O$	101	0.7	SPF_2
349	4.1	$C_3F_9P_2S_2O$	100	0.8	CF_3P, C_2F_4
317	1.5	$C_3F_9P_2SO$	81	2.0	CF_2P, C_2F_3
267	3.1	$C_2F_7P_2SO$	80	0.5	S_2O
230	0.5	$C_2F_5PS_2O$	69	14.8	CF_3, PF_2
217	4.5	C_2F_6PSO	64	4.2	S_2
201	0.6	C_2F_6PS	63	19.1	PS
185	1.1	C_2F_6PO	50	1.1	PF, CF_2
167	1.9	CF_4POS	47	4.2	PO
151	1.1	CF_4PS	45	0.6	
135	8.4	CF_4PO	43	0.5	
129	0.9	CF_2PSO	32	4.0	S
119	4.5	C_2F_5, CF_4P	31	3.3	P, CF
113	0.7	CF_2PS			

(a) Intensities are expressed relative to the total ionization defined as $\sum_n$(intensity) for all ions with m/e > 30 whose intensity is greater than 2% of the base peak.

(b) All species are positive ions and masses are calculated for the ^{32}S isotope.

(c) Identified by mass measurement: Found m/e = 417.8672, required for $C_4F_{12}P_2S_2O$ m/e = 417.8675.

the compound was inert towards electrophilic reagents in the gas phase except at elevated temperatures. The products obtained from the high temperature reactions with HX may be explained if initial reaction occurs according to eq 7.5, followed by thermal decomposition of the mono-

$$(CF_3)_2P(S)\text{-}O\text{-}P(S)(CF_3)_2 + HX \longrightarrow (CF_3)_2P(S)OH + (CF_3)_2P(S)X \quad (X = Cl, Br, I, SH) \qquad (7.5)$$

thio acid to give the observed products. In the case of HI, the reaction is further complicated by the reactions (see Chapters IV and IX) of HI with $(CF_3)_2P(S)I$ and with $(CF_3)_2PS_2H$ (formed by the thermal decomposition of $(CF_3)_2P(S)OH$) to give $(CF_3)_2PSH$ in both cases.

Nucleophilic attack by halide ions in acetonitrile solution is rapid as in the case of the fluoro analogue,[42] giving good yields of the expected thiophosphoryl halides and the thiophosphinate anion according to eq 7.6 .

$$(CF_3)_2P(S)\text{-}O\text{-}P(S)(CF_3)_2 + X^- \longrightarrow (CF_3)_2PSO^- + (CF_3)_2P(S)X \quad (X = F, Cl, Br) \qquad (7.6)$$

No reaction occurred when the same system was used to try to prepare $[(CF_3)_2P(S)]_2S$, $(X = (CF_3)_2PS_2)$.

Rapid nucleophilic attack by dimethylamine takes place at low temperature according to eq 7.7 .

$$(CF_3)_2P(S)\text{-}O\text{-}P(S)(CF_3)_2 + 2(CH_3)_2NH \longrightarrow$$

$$(CF_3)_2P(S)\text{-}N(CH_3)_2 + (CH_3)_2\overset{+}{N}H_2(CF_3)_2PSO^- \qquad (7.7)$$

Heating with mercury at 100° for seven days led to no compound formation nor to any desulphurization. The variation of the vapour pressure with temperature was examined with a grease-free, mercury-in-glass microtensimeter. The results (given in Table 13) could be expressed by the linear equation 7.8. The calculated heat of

$$\log P_{mm} = -1941/T + 7.78 \qquad (7.8)$$

vaporization (ΔH_{vap}) was 8880 cal mole^{-1}, the extrapolated boiling point 122.6°, and the calculated Trouton's constant 22.4 e.u.

The symmetrical structure of the anhydride was to have been expected from work on analogous fluoro systems,[38,42] and is clearly demonstrated by the pattern shown by the ^{19}F nmr spectrum,[37] and from the products obtained from the rapid attack of a variety of nucleophiles. The marked resistance to electrophilic attack is noted and may perhaps be explained in terms of the low availability of the lone pairs on sulphur due to the added electronegativity of the bridging atom combined with that of the CF_3 groups. The

TABLE 13

Vapor Pressure Data for $[(CF_3)_2P(S)]_2O$

Temperature, °C	P(observed)$_{mm}$	P(calculated)$_{mm}$ [a]
8.1	8.5	7.7
10.7	9.0	8.9
13.5	10.2	10.3
15.5	11.2	11.5
17.5	12.7	12.8
20.0	14.1	14.6
22.3	15.8	16.4
24.2	17.9	18.1
25.6	19.5	19.4
27.5	21.3	21.4
30.1	23.8	24.3
33.4	28.1	28.4
36.3	31.8	32.6
39.4	37.7	37.6
42.3	42.7	42.9
45.1	49.0	48.6
48.4	56.6	56.1
52.4	67.6	66.6
56.9	82.6	80.3
59.9	91.9	90.7

(a) Calculated from eq 7.8

susceptibility of the anhydride to nucleophilic attack may indicate that the P-O-P bridge is able to act as a moderately good Lewis acid.

CHAPTER VIII

Anionic Chemistry of Trifluoromethylphosphorus Compounds

1. Introduction

The synthesis and characterisation of the diphosphorus compounds $(CF_3)_2P(S)\text{-}S\text{-}P(CF_3)_2$ (see Chapter III), $[(CF_3)_2P(S)]_2S_2$ (see Chapter IV) and $[(CF_3)_2P(S)]_2O$ (see Chapter VII) has required further knowledge of the identity of the trifluoromethylphosphorus anions which remain in the hydrolysates of these and related systems.

The quantitative nature of the alkaline hydrolysis and the relationship of the yield of fluoroform to the valence and structure of the trifluoromethylphosphorus compound has been so well established [19,39,45,46] that the alkaline hydrolysis reaction is generally used as an analytical procedure in this field. The trifluoromethylphosphorus oxy-anions which remain in solution have been characterized [19,25,45,46] chemically but none of the thiophosphorus anions have been characterized to date. It was therefore of interest to determine the identity of the species in solution since the apparent resistance of the P=S bond to hydrolysis has been noted [12,13,25] and it seemed likely that a variety of oxy-thio phosphorus anions would exist. In the course of the study complete ^{19}F nmr data of the new oxy-thio phosphorus anions and the previously characterized [19,25,45,46] oxyphosphorus anions has been obtained.

2. Hydrolysis Reactions of Representative Systems.

A. Neutral Hydrolyses in Aqueous Solution

All reactions were carried out by condensing the compound on to 1.0 ml of degassed, distilled water, and then reacting for two days at room temperature. Fluoroform was weighed after vacuum fractionation and identified by infrared spectroscopy.

(i) Phosphines

(a) $(CF_3)_2PCl$ [16] (0.0738 g, 0.36 mmoles) yielded CF_3H (0.0256 g, 0.37 mmoles) and $CF_3P(H)O_2^-$ which remained in solution.

(b) $(CF_3)_2PSH$ [17] (0.0613 g, 0.30 mmoles) yielded CF_3H (0.0210 g, 0.30 mmoles) and H_2S (0.0107 g, 0.32 mmoles), the two compounds being obtained as a mixture and the amount of H_2S obtained by difference after absorbing with lead acetate solution. $CF_3P(H)O_2^-$ remained in the original solution.

(c) $(CF_3)_2POH$ [30] (0.0619 g, 0.33 mmoles) gave CF_3H (0.0234 g, 0.33 mmoles) and $CF_3P(H)O_2^-$ which remained in solution.

(ii) Phosphoryl- and Thiophosphoryl- Compounds

No fluorocarbon containing volatiles were obtained from any of the following reactions except reaction (f).

(a) $(CF_3)_2P(O)Cl$ [30,40,44] (0.1007 g, 0.46 mmoles)

gave the $(CF_3)_2PO_2^-$ ion in solution.

(b) $CF_3P(S)Cl_2$ [13] (0.0399 g, 0.20 mmoles) gave the $CF_3PSO_2H^-$ ion in solution.

(c) $(CF_3)_2P(S)Cl$ [12,13] (0.0987 g, 0.42 mmoles) gave the $(CF_3)_2PSO^-$ ion in solution. Addition of excess silver carbonate precipitated silver sulphide as well as the chloride ion leaving the $(CF_3)_2PO_2^-$ ion in solution.

(d) A sample [13] of $(CH_3)_3NH(CF_3)_2PS_2^-$ gave a stable aqueous solution.

(e) $(CF_3)_2PS_2H$ [12,13] (0.1079 g, 0.60 mmoles) gave the $(CF_3)_2PS_2^-$ ion in solution. Treatment of the aqueous solution with excess silver carbonate precipitated silver sulphide and gave a filtrate containing the $(CF_3)_2PO_2^-$ ion.

(f) Slightly impure $(CF_3)_3P{=}S$ [25] (0.1157 g, 0.43 mmoles) gave CF_3H (0.0285 g, 0.41 mmoles) and the aqueous solution contained $(CF_3)_2PSO^-$ ions.

B. Alkaline Hydrolyses in Aqueous Solution

All reactions were carried out by condensing the compound onto 4.0 ml of degassed 10% NaOH solution, and reacting for two days at room temperature. The products were treated as above. The presence or absence of sulphide ion was demonstrated with sodium nitroprusside where applicable.[31]

(a) $(CF_3)_2P(O)Cl$ [30,40,44] (0.1081 g, 0.49 mmoles) gave CF_3H (0.0345 g, 0.49 mmoles) and the $CF_3PO_3^=$ ion which remained in solution.

(b) $(CF_3)_2P(S)Cl$ [12,13] (0.0888 g, 0.38 mmoles) yielded CF_3H (0.0264 g, 0.38 mmoles). The resultant solution contained the $CF_3PSO_2^=$ ion, but no sulphide ion.

(c) $CF_3P(S)Cl_2$ [13] (0.0490 g, 0.24 mmoles) gave no fluorocarbon-containing volatiles, but the solution contained the $CF_3PSO_2^=$ ion.

(d) $(CF_3)_2PS_2H$ [12,13] (0.0791 g, 0.34 mmoles) yielded CF_3H (0.0237 g, 0.34 mmoles) and the $CF_3PS_2O^=$ ion in solution. The solution gave a negative test for the sulphide ion.

(e) $(CF_3)_2P(O)SCH_3$ [40] (0.0320 g, 0.14 mmoles) gave CF_3H (0.0113 g, 0.16 mmoles) and both sulphide and $CF_3PO_3^=$ ions remained in the hydrolysate.

(f) $(CF_3)_2P(S)OCH_3$ [40] (0.0870 g, 0.38 mmoles) yielded CF_3H (0.0290 g, 0.41 mmoles) and the aqueous solution contained $CF_3PSO_2^=$ but no sulphide ion.

(g) $(CF_3)_2P(S)SCH_3$ [13] (0.0847 g, 0.34 mmoles) produced CF_3H (0.0278 g, 0.40 mmoles) and the hydrolysate contained $CF_3PSO_2^=$ and sulphide ions.

(h) Slightly impure $(CF_3)_3P{=}S$ [25] (0.1189 g, 0.44 mmoles) gave CF_3H (0.0588 g, 0.84 mmoles) and an aqueous solution which contained the $CF_3PSO_2^=$ ion.

C. Reactions with Hydrogen Peroxide

Reactions were carried out by condensing the reactants onto 1.0 ml of 5% H_2O_2 solution and allowing the reaction to continue at room temperature for four days.

(a) $(CF_3)_2PS_2H$ [12,13] (0.30 mmoles) began to react as soon as the tube reached room temperature with appearance of elemental sulphur. The solution contained the $(CF_3)_2PO_2^-$ ion and another unidentified CF_3-P containing species.

(b) $(CF_3)_2P(S)Cl$ [12,13] (0.30 mmoles) reacted as above to give the same species in solution and elemental sulphur.

D. Preparation of Tetraphenylarsonium Salts

(i) $(C_6H_5)_4As^+ CF_3PSO_2H^-$

Trifluoromethylthiophosphoryldichloride [13] (0.1257 g, 0.62 mmoles) was hydrolysed with 5.0 ml of 10% NaOH solution for six days. The tube was then opened and tetraphenylarsonium chloride (1.0 g, 2.4 mmoles) dissolved in the minimum amount of water was added. The salt was precipitated by acidifying with concentrated hydrochloric acid dropwise using phenolphthalein indicator. The white solid was filtered off and dried under vacuum at room temperature. The yield of salt was 0.281 g (0.512 mmoles). The salt was characterized by analysis: Found: C, 53.88; H, 3.70; S, 5.79%; calculated for $C_{25}H_{21}AsPF_3SO_2$: C, 54.75; H, 3.86; S, 5.68%. Acidification of the initial solution

without addition of the arsonium salt gave a solution whose nmr spectrum was consistent with a protonated anion.

The salt could be redissolved in 10% NaOH solution to regenerate $CF_3PSO_2^=$ ions according to the nmr spectrum.

(ii) $\underline{(C_6H_5)_4As^+\ CF_3PS_2OH^-}$

Bistrifluoromethyldithiophosphinic acid [12,13] (0.2158 g, 0.92 mmoles) was hydrolysed as above and after removal of CF_3H (0.0646 g, 0.92 mmoles), treated with tetraphenylarsonium chloride (1.5 g, 3.6 mmoles) and hydrochloric acid. The pale yellow solid was filtered off and dried under vacuum at room temperature. The yield of salt was 0.455 g (0.81 mmoles). The salt was characterized by analysis: Found: C, 53.00; H, 3.67; S, 11.25%. Calculated for $C_{25}H_{21}AsPF_3S_2O$: C, 53.20; H, 3.75; S, 11.36%.

Acidification of a sample of the initial solution in the absence of the arsonium salt produced a solution whose nmr spectrum was consistent with the anion postulated. The tetraphenylarsonium salt was soluble in 10% NaOH solution to give $CF_3PS_2O^=$ ions according to the nmr spectrum.

E. Titrimetric Determinations

(i) Alkaline hydrolysates obtained by reacting known amounts of trifluoromethylphosphorus compounds with 4.0 ml of 10% NaOH solution (carbonate free) for 2 days were diluted to ~90 ml after removal of volatile fluorocarbon products, and titrated with 1.00 N HCl under a nitrogen

atmosphere, and the curve after the first end-point compared with that of the starting NaOH solution.

(a) The alkaline hydrolysate of $CF_3P(S)Cl_2$ [13] (0.0891 g, 0.44 mmoles) gave an end-point at 8.75 ml corresponding to the neutralization of excess base remaining in the solution. The pH after addition of 8.97 ml was 3.2 (cf. 2.7 for the addition of 0.22 ml of acid to the neutralized parent alkali solution). A further addition of 0.44 ml of acid yielded a pH of 2.5 (cf. 2.3 in the case of the parent alkali), but there was no pronounced break in the curve.

(b) $(CF_3)_2PS_2H$ [12,13] (0.1093 g, 0.47 mmoles) produced a titration curve with the first end-point due to neutralization of unconsumed alkali at 9.56 ml. The pH after the addition of 9.79 ml was 3.1 (cf. 2.7 for a further addition of 0.23 ml of acid to the neutralized starting alkali). After addition of 10.25 ml of acid the pH was 2.5 (cf. 2.3 in the case of the parent solution).

(ii) An acid solution was obtained from the hydrolysis of $CF_3P(S)Cl_2$ [13] (0.0870 g, 0.43 mmoles) with 10 ml of water for 24 hours. After diluting to ~90 ml the solution was titrated with 0.100 N NaOH solution under an atmosphere of nitrogen to give a curve with an end-point at 17.11 ml corresponding to 4 moles of base consumed per mole of starting material. There was however only one

distinct break in the curve. The pH values at the 1/8, 3/8, 5/8 and 7/8 neutralization points (corresponding to the half-neutralization point for each proton) were 2.15, 2.25, 2.50 and 3.25.

3. Discussion

A. Neutral Hydrolysis

Both bistrifluoromethyldithiophosphinic acid,[12,13] $(CF_3)_2PS_2H$, and bistrifluoromethylthiophosphinic acid, $(CF_3)_2P(S)OH$ (see Chapter VII), dissolve in water to provide stable aqueous solutions of their respective anions, $(CF_3)_2PS_2^-$ and $(CF_3)_2PSO^-$. Alkali metal and ammonium salts of these acids behave similarly (see Chapter VII) yielding the same anions which appear to be resistant to CF_3-P as well as P-S bond cleavage in moderately acidic or neutral solution. The $(CF_3)_2PSO^-$ ion is formed by neutral hydrolysis of $(CF_3)_3PS$ [25] which also yields one mole of CF_3H and the same ion is also formed when $(CF_3)_2P(S)Cl$ [12,13] is dissolved in water further demonstrating the stability of $(CF_3)_2PS_{2-x}O_x^-$ (x = 0,1) ions in neutral or moderately acidic solution. Similarly the $(CF_3)_2PO_2^-$ (i.e. x = 2) ion was obtained upon neutral hydrolysis of $(CF_3)_2P(O)Cl$ [30,40,44] as would be expected in view of the previous demonstration of the stability of this ion in neutral and acidic solutions.[19]

The $CF_3P(H)O_2^-$ ion [19,39,45,46] was obtained from the neutral hydrolysis reactions of various bistrifluoromethylphosphines and the reaction occurred with the liberation of one mole of fluoroform. In the case of $(CF_3)_2PSH$ [17] one mole of hydrogen sulphide was also obtained, demonstrat-

ing the facile nucleophilic attack which occurs at trivalent phosphorus in these systems. The frequently proposed hydrolysis intermediate, $(CF_3)_2POH$,[30,45] was also shown separately to react further with water to yield fluoroform and the expected[19,45] anionic product, $CF_3P(H)O_2^-$ which was readily characterized by the large P-H coupling observed in its nmr spectrum.

B. Alkaline Hydrolysis

Pentavalent phosphoryl compounds such as $(CF_3)_2P(O)Cl$ generate the previously reported[19,39,45] $CF_3PO_3^=$ ion on alkaline hydrolysis with the liberation of one mole of fluoroform. In a similar fashion the alkaline hydrolysis of pentavalent monothiophosphoryl compounds such as $(CF_3)_2P(S)Cl$[12,13] and $(CF_3)_2P(S)OH$ (see Chapter VII) liberates one mole of fluoroform and forms the analogous monothio anion, $CF_3PSO_2^=$. Tristrifluoromethylphosphine sulphide[25] yielded the same anion and two moles of fluoroform. The alkaline hydrolysis of $CF_3P(S)Cl_2$[13] also yielded the $CF_3PSO_2^=$ ion as the result of the loss of only the chlorine substituents upon alkaline hydrolysis. All of these reactions indicate clearly the resistance of the monothiophosphoryl function to hydrolysis in these systems and the absence of $S^=$ ions in solution was clearly demonstrated in all cases by means of the sodium nitroprusside test[31] on the hydrolysate.

Bistrifluoromethyldithiophosphinic acid gave one mole of fluoroform and formed the $CF_3PS_2O^=$ ion in the solution. The absence of $S^=$ was demonstrated as above.[31]

Alkaline hydrolyses of a series of methyl esters of bistrifluoromethylphosphinic acids were also considered because the possibility of several competing reactions existed. In all three cases more than one mole of fluoroform was obtained in agreement with previous observations.[40] The monothio ester $(CF_3)_2P(S)OCH_3$ [40] gave only the $CF_3PSO_2^=$ ion and no sulphide. The dithioester $(CF_3)_2P(S)SCH_3$ [13,40] gave sulphide ion and the $CF_3PSO_2^=$ ion as the only detectable trifluoromethylphosphorus species indicating that hydrolysis of the ester involves attack of the P-SCH_3 bond which results in eventual formation of $S^=$ in the solution. Loss of CF_3H from a species such as $(CF_3)_2PSO^-$ in subsequent steps to produce the observed products is to be expected in view of the pattern established above. The phosphoryl thioester $(CF_3)_2P(O)SCH_3$ [40] likewise demonstrated cleavage at the P-S bond rather than the S-C bond giving only the $CF_3PO_3^=$ ion in the hydrolysate. Again the $S^=$ ion was detected and CF_3H was liberated. The liberation of fluoroform in excess of the expected quantity may be due to a difference in the hydrolysis reaction mechanism in cases where the reaction may involve SCH_3 containing intermediates since it has been shown elsewhere[47]

that the alkaline hydrolysis of the methyl ester of bis-trifluoromethylphosphinic acid, $(CF_3)_2P(O)OCH_3$, gave exactly one mole of fluoroform. Any non-fluorinated phosphorus ions formed from further reaction of the monotrifluoromethyl phosphorus anions cannot of course be detected by ^{19}F nmr spectroscopy.

C. Behavior of Thiophosphorus Anions in Solution

The new oxy-thio anions $CF_3PS_2O^=$ and $CF_3PSO_2^=$ did not precipitate from alkaline solution upon the addition of large cations such as the tetraphenylarsonium ion. Neutralization of the solutions with concentrated hydrochloric acid yielded salts of the protonated anions $CF_3PS_2OH^-$ and $CF_3PSO_2H^-$ whose constitution is fully supported by the analytical results. Dissolution of the tetraphenylarsonium salts in 10% NaOH solution reconstituted the parent dianions. The marked but consistent variations of ^{19}F coupling constants and chemical shifts with the pH of the solutions clearly indicates that the species in alkaline solution are not identical to the species which exist in the neutral solution. The monoanionic products precipitated from neutral solution are presumed to reflect the major species present in these solutions. The behavior of the system is entirely consistent with the proposal that the species $CF_3PS_2OH^-$ and $CF_3PSO_2H^-$ are weak acids formed by protonation of the

dianions. The parent dibasic acid is presumably a strong acid. Titration curves of alkaline hydrolysates of $CF_3P(S)Cl_2$ [13] and $(CF_3)_2PS_2H$ [12,13] with HCl, and of the neutral hydrolysate of $CF_3P(S)Cl_2$ [13] with NaOH were plotted and showed typical weak acid behavior. The pH at the half-neutralization point gave the approximate K_a values of 6×10^{-4} for the $CF_3PSO_2H^-$ species and 8×10^{-4} for the $CF_3PS_2OH^-$ species.

The parts of the curves relevant to the parent dibasic acids were in agreement with the hypothesis that both were strong acids, but there were no distinguishable breaks in the curves corresponding to the first end points (cf. $CF_3P(O)(OH)_2$).[19]

Infrared spectra of mulls of the protonated salts did not show OH or SH stretching bands although a weak band in the $CF_3PSO_2H^-$ salt at 2250 cm^{-1} could be due to hydrogen bonded OH stretch similar to that observed [19] for $CF_3PO_3H^-$. Bending modes could be assigned to the bands at 882 and 918 cm^{-1} and both are probably due to OH bending although SH bending motions cannot be ruled out. The complete spectra are shown in Table 14.

The ^{19}F nmr spectra of the ions were obtained in aqueous solution. All of the coupling constant and chemical shift values quoted in Table 15 are the limiting values obtained in either acid or strongly alkaline media since intermediate values, suggesting rapid exchange pro-

TABLE 14

Infrared Spectra of Protonated Oxythiophosphoryl Salts [a,b,c]

$CF_3PS_2OH^-$	$CF_3PSO_2H^-$	Assignment
	2250 (w broad)	OH-hydrogen bonded
1188(s)	1212 (m)	νP-O
1118(s)	1135(s)	νCF
1107(s)	1105(s) 1190(m)	
882(s)	918(s)	δOH
741(s)	743(s)	νP=S
732(m)	732(m)	δ sym CF_3
695(s)	654(s)	P-O bend
574(m)	506(m)	δ asym CF
423(m)	421(m)	νP-CF

(a) All values in cm^{-1}

(b) All values were obtained from Nujol mulls of the tetraphenylarsonium salts by subtracting the spectrum of tetraphenylarsonium chloride from the observed spectra.

(c) Abbreviations: ν = stretching, δ = deformation, s = strong, m = medium, w = weak.

TABLE 15

Nmr Data for Trifluoromethylphosphorus Anions in Aqueous Solution

Ion	ϕ ppm[a]	$^2J_{FP}$ Hz	Original Prep. of anion
$(CF_3)_2PS_2^-$	72.9	92.0	13
$(CF_3)_2PSO^-$	73.1	97.0	this work
$(CF_3)_2PO_2^-$	72.8	103.6	39
$CF_3PS_2O^=$	76.1	86.6	this work
$CF_3PSO_2^=$	74.6	89.9	this work
$CF_3PO_3^=$	72.0	93.0	19,39,45
$CF_3PS_2OH^-$	77.1	99.0	this work
$CF_3PSO_2H^-$	75.8	103.0	this work
$CF_3P(H)O_2^-$	77.8	100.9[b]	19,39,45,46

(a) Relative to CCl_3F

(b) τ = 2.7 (relative to tetramethylsilane, τ = 10.0); $^1J_{HP}$ = 589 Hz; $^3J_{HF}$ = 4.1 Hz.

cesses (on the nmr time scale), are observed for solutions of intermediate pH which appear to contain comparable quantities of the dianions and their singly protonated derivatives. It is interesting to note that the limiting coupling constants ($^2J_{FP}$) within each series of isostructural anions are found to increase with increasing numbers of oxygen atoms replacing sulphur atoms (i.e. with increasing total electronegativity of substituents) in accord with other observations.[37]

The ^{19}F and ^1H nmr spectra of the $CF_3P(H)O_2^-$ ion confirm its previously deduced structure [19] (see Table 15).

The bistrifluoromethylthiophosphorus anions $(CF_3)_2PS_2^-$ and $(CF_3)_2PSO^-$ have been characterized elsewhere [12,13] (see Chapter VI). Silver ion in aqueous solution resulted in a rapid desulphurization of the anions precluding the use of silver salts as a source of the acids. Similarly desulphurization occurred in the presence of hydrogen peroxide as expected from previous results.[36]

The characterization of the anionic trifluoromethyl phosphorus hydrolysis products by ^{19}F nmr permits rapid, positive identification of the species produced in these hydrolysis reactions. Fuller understanding of the hydrolysis pathways can be provided now that all the representative systems, with the exception of the few systems which are known to produce fluoride and carbonate[2,45]

on hydrolysis, have been fully investigated. In addition it is possible to deduce more reliably the structures of the parent compounds from their hydrolysis behaviour. The present results clearly indicate that sulphur attached to trivalent phosphorus is readily and completely removed by both neutral and alkaline hydrolysis, presumably as a result of the susceptibility of these systems to nucleophilic attack at P^{III}. Terminal P=S groups on pentavalent phosphorus appear to be generally resistant to alkaline and neutral hydrolysis and the resultant anions contain the initial number of sulphur atoms even though trifluoromethyl groups are hydrolysed by alkali to yield only the monotrifluoromethyl species in the hydrolysate. The reason for the liberation of fractionally more than one mole of CF_3H from the pentavalent esters containing P-S-CH_3 functions is not clear at this time and this behaviour may be indicative of a very complex hydrolysis mechanism which may yield a variety of products other than those identifiable by ^{19}F nmr spectroscopy. Further study of the hydrolysis of these thioesters is clearly warranted. Under neutral conditions the P=S group is hydrolysed by hydrogen peroxide and is reduced by silver ions.

CHAPTER IX

Some Chemistry of Bistrifluoromethyldithiophosphinic Acid

1. Introduction

New syntheses for bistrifluoromethyldithiophosphinic acid,[12,13] $(CF_3)_2PS_2H$, and bistrifluoromethylmercaptophosphine,[17] $(CF_3)_2PSH$, which may also be used as a source of the dithio acid [12] were devised in the course of this study. It was also necessary to investigate the properties of the dithio acid more fully than had been done in previous work,[12,13] especially the reduction of the acid with HI. An approximate determination of the acid strength of $(CF_3)_2PS_2H$ was also undertaken. In addition some preliminary preparations of bistrifluoromethyldithiophosphinate complexes of transition metals from reactions of metals and metal halides with the acid are reported.

2. A New Synthesis for Bistrifluoromethyldithiophosphinic Acid.

The diphosphine,[2] $(CF_3)_2P\text{-}P(CF_3)_2$, (0.420 g, 1.24 mmoles) and excess sulphur (~1g) were allowed to react for two days at 170°. The unidentified products of the reaction were heated at 100° for a further 24 hours with excess H_2S (~2.4 mmoles). Vacuum fractionation gave $(CF_3)_2PS_2H$ (0.481 g, 2.06 mmoles) in 83% yield (collected at -63°) which was identified by comparison with products prepared by literature methods.[12,13]

3. A New Synthetic Route to Bistrifluoromethylmercapto-phosphine.

(a) Reaction of $(CF_3)_2P\text{-}N(CH_3)_2$ with H_2S

Dimethylaminobistrifluoromethylphosphine [8] (0.29 mmoles) and hydrogen sulphide (0.73 mmoles) were heated to 70° for 12 hours. Fractionation of the volatiles gave only H_2S, and a white solid remained. Hydrogen chloride (~0.6 mmoles) was added to the solid and fractionation of the volatiles after five hours at room temperature gave a good yield of $(CF_3)_2PSH$.[17]

(b) From $(CF_3)_3P$, $(CH_3)_2NH$ and H_2S

Tristrifluoromethylphosphine [2] (2.44 g, 10.3 mmoles), hydrogen sulphide (~10.4 mmoles) and dimethylamine (~10.3 mmoles) began to react below room temperature. After 24 hours fluoroform and excess H_2S and $(CH_3)_2NH$ were pumped away and hydrogen chloride (~10.3 mmoles) added. Rapid reaction took place and, after standing for twelve hours, vacuum fractionation gave $(CF_3)_2PSH$ [17] (1.94 g, 9.6 mmoles) in 93% yield.

4. The Reaction of Bistrifluoromethyldithiophosphinic Acid with Hydrogen Iodide.

$(CF_3)_2PS_2H$ [12,13] (0.117 g, 0.50 mmoles) and HI (0.160 g, 1.23 mmoles) reacted immediately on contact at room temperature. After 24 hours vacuum fractionation gave $(CF_3)_2PSH$ [17] (0.096 g, 0.475 mmoles) in 95% yield collected at -95°. The more volatile fraction contained H_2S and excess HI identified by their reactions with lead acetate solution. Iodine crystals remained in the reaction tube.

5. Determination of Acid Strength of Bistrifluoromethyldithiophosphinic Acid.

$(CF_3)_2PS_2H$ [12,13] (0.0950 g, 0.406 mmoles) was dissolved in ~5.0 ml of distilled water. The solution was diluted to ~90 ml and titrated with 0.100 N NaOH solution under an atmosphere of nitrogen, and a graph of pH vs mls of NaOH plotted to give an end-point at 3.97 ml corresponding to a molecular weight of 239 (234 required for $(CF_3)_2PS_2H$) and a pH at the half-neutralization point of 2.91 corresponding to $K_a \sim 1.2 \times 10^{-3}$.

6. Reactions of Bistrifluoromethyldithiophosphinic Acid With Metals and Metal Halides.

(a) With Hg

A sample of bistrifluorodithiophosphinic acid condensed onto metallic mercury slowly formed white crystals. In the presence of excess mercury reaction was incomplete after four weeks. Heating at 60° for a further seven days did not drive the reaction to completion. Analysis of the volatiles gave unreacted $(CF_3)_2PS_2H$, $(CF_3)_2PSH$, a little H_2S and some noncondensible gas (H_2). The solid product was contaminated with metallic mercury but its infrared spectrum indicated a dithiophosphinate complex.[34]

(b) With Cu

A sample of the dithio acid began to react with small copper turnings almost immediately on contact. After four hours at room temperature the product could be seen to be a white powder. The infrared spectrum indicated a dithiophosphinate complex.[34]

(c) With Fe

A rapid reaction took place when a small amount of iron powder was warmed to room temperature in contact with the dithio acid. After three hours green crystals had formed. Vacuum fractionation yielded large quantities of non-condensible gas (H_2) and excess acid. The crystals

rapidly darkened on opening the product to the air.

(d) With Cr

Room temperature reaction of the dithio acid with chromium powder rapidly produced purple crystals and hydrogen gas.

(e) With Mn

A similar reaction with the dithio acid and manganese powder slowly produced an off-white powder.

(f) With $HgCl_2$

Mercuric chloride (0.07 mmoles) reacted with $(CF_3)_2PS_2H$ (0.1 mmoles) at room temperature to generate HCl. The solid product rapidly darkened on standing in vacuo.

(g) With $NiCl_2$

Anhydrous nickel chloride (0.4 mmoles) failed to react with $(CF_3)_2PS_2H$ (0.9 mmoles) during 24 hours. Heating at 160° for four hours gave a dark green/blue solid and excess acid, some $(CF_3)_2P(S)Cl$ and $(CF_3)_2PSH$ with the expected large amount of HCl. The infrared spectrum indicated the presence of a dithiophosphinate complex.[34]

(h) With $CdCl_2$

A similar reaction carried out with cadmium chloride

(0.3 mmoles) and the dithio acid (0.6 mmoles) gave little evidence of reaction even after 10 days at 150°. Repeating the reaction in aqueous solution led to precipitation of cadmium sulphide almost at once.

(i) With $CuCl_2$

Reaction of the dithio acid with cupric chloride in aqueous solution at low temperature formed a dark green/brown soluble complex. On warming to room temperature a white insoluble solid product was obtained.

7. Discussion

Both the diphosphine,[2] $(CF_3)_2P\text{-}P(CF_3)_2$, and the diphosphine sulphide,[17,18] $(CF_3)_2P\text{-}S\text{-}P(CF_3)_2$, form mixtures of volatile compounds, containing mainly the mixed valence compound, $(CF_3)_2P(S)\text{-}S\text{-}P(CF_3)_2$, on oxidation with limited amounts of sulphur. The mixture of thiophosphorus compounds may be converted to the dithio acid, $(CF_3)_2PS_2H$, by reaction with H_2S and more sulphur (see Chapter III). On reaction with excess sulphur both $(CF_3)_2P\text{-}P(CF_3)_2$ and $(CF_3)_2P\text{-}S\text{-}P(CF_3)_2$ form some involatile products (see Chapter III). The unidentified involatile products from the reaction of the diphosphine sulphide and sulphur were used by Gosling and Burg to prepare the dithio acid by reaction with H_2S,[13] which suggested that a similar synthesis using the diphosphine should be possible, and this has proved to be the case. The new synthesis is more convenient because the diphosphine is more readily prepared in good yield than the diphosphine sulphide, both of which must be initially prepared[2,17,18] from the iodophosphine, $(CF_3)_2PI$.

The case of P^{III}-N bond cleavage with HX suggested that even a weak electrophile such as H_2S might react in like manner. Reaction in fact does occur in the expected fashion however only the dimethylammonium adduct of $(CF_3)_2PSH$[17] is obtained as shown in eq 9.1 because H_2S

$$(CF_3)_2P\text{-}N(CH_3)_2 + H_2S \longrightarrow (CH_3)_2\overset{+}{N}H_2(CF_3)_2PS^- \qquad (9.1)$$

is too weak an acid to displace the mercaptophosphine from the adduct. However the solid adduct reacts rapidly with HCl according to eq 9.2 thus to yield the desired mercapto-

$$Me_2\overset{+}{N}H_2(CF_3)_2PS^- + HCl \longrightarrow (CF_3)_2PSH + Me_2\overset{+}{N}H_2Cl^- \qquad (9.2)$$

phosphine providing a convenient two-step synthesis. Since the dimethylaminophosphine, $(CF_3)_2P\text{-}N(CH_3)_2$, can be prepared from the reaction of $(CF_3)_3P$ and dimethylamine [7] according to eq 9.3, this reaction may be used as an <u>in</u>

$$(CF_3)_3P + (CH_3)_2NH \longrightarrow (CF_3)_2P\text{-}N(CH_3)_2 + CF_3H \qquad (9.3)$$

<u>situ</u> source of $(CF_3)_2P\text{-}N(CH_3)_2$ which can then be reacted with H_2S to form the same salt as above. A rapid synthesis of the mercaptophosphine in two simple steps from $(CF_3)_3P$ is therefore available.

Although it was known that the dithio acid, $(CF_3)_2PS_2H$, could be reduced with HI [13] to form the mercaptophosphine according to eq 9.4, little was known about the rate or

$$(CF_3)_2PS_2H + 2HI \longrightarrow (CF_3)_2PSH + H_2S + I_2 \qquad (9.4)$$

efficiency of the reaction. In order to interpret the reactions of the disulphide, $(CF_3)_2P(S)\text{-}S\text{-}P(CF_3)_2$, and tetrasulphide, $[(CF_3)_2P(S)]_2S_2$ with HI (see Chapters III

and IV) it was necessary to have a better understanding of the above reaction of the dithio acid with HI. Reaction is rapid at room temperature, excess HI leading to almost quantitative yields of the mercaptophosphine. Presumably the driving force for the reaction is the thermodynamic stability of H_2S and $(CF_3)_2PSH$, the stability of the latter being enhanced by the CF_3 substituents on phosphorus as noted by earlier workers.[6,10,17,18,30]

The approximate acid strength of the dithio acid, $(CF_3)_2PS_2H$, was determined from its titration curve with standard alkali ($K_a \sim 1.2 \times 10^{-3}$) for comparison purposes and was found to be slightly less than that of the monothio acid, $(CF_3)_2P(S)OH$, ($K_a \sim 3.2 \times 10^{-3}$; see Chapter VI). Having demonstrated that the acid $(CF_3)_2PS_2H$, is relatively strong it seemed reasonable that reactions with metals and metal halides to form dithiophosphinate complexes would occur readily. A series of dithiophosphinate complexes of transition metals was already under investigation in the laboratory and in view of this interest the reactions of $(CF_3)_2PS_2H$ with metals and metal halides were carried out. It was thought that the complexes would be of interest since, at that time, no dithiophosphinate complexes had been prepared with very electronegative substituents on the phosphorus. Following the commencement of these studies a report appeared on the complexes of the

fluoro analogue,[48] F_2PS_2H. In agreement with the behavior of the fluoro acid, syntheses of complexes from the metals and excess trifluoromethyl acid give good yields in many cases. This method was used to prepare the Hg(II), Cu(I), Fe(II), Cr(III) and Mn(II) complexes. In the case of mercury, some reduction of the ligand was observed to give the mercaptophosphine and this reduction has subsequently been observed with other metals.[49] The iron(II) complex when pure has been shown to be yellow [34,49] but rapidly oxidised in the air to the dark green iron(III) complex. The white product obtained with copper would be expected to be a copper(I) complex. The purple chromium(III) complex, and the white manganese(II) complex, have been more fully characterised elsewhere.[49]

Reactions with halides tend not to be as convenient syntheticlly, but may also be used. The Hg(II) complex is formed readily by this method. The Ni(II) compound is only formed on strong heating with some reduction of the acid also occurring. No complex formation occurred with cadmium chloride. Formation of the Cu(I) species in aqueous solution appeared to go through a transient Cu(II) species as has been shown in other dithiophosphinate systems.[34,50]

The identities of the above complexes have since been

confirmed and their spectral and magnetic properties determined by other workers.[34,49]

BIBLIOGRAPHY

1. A. L. Henne and W. G. Finnegan, J. Amer. Chem. Soc., 72, 3806 (1950).
2. F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, J. Chem. Soc., 1565 (1953).
3. J. J. Lagowski, Quart. Revs., 13, 233 (1959).
4. H. C. Clark, Adv. in Fluorine Chem., 3, 19 (1963).
5. R. E. Banks and R. N. Haszeldine, Adv. in Inorg. and Radiochem., 3, 337 (1961).
6. A. B. Burg, Acc. Chem. Research, 2 , 353 (1969).
7. R. G. Cavell and R. D. Leary, unpublished observations.
8. G. S. Harris, J. Chem. Soc., 512 (1958).
9. R. F. Hudson, Structure and Mechanism in Organo-Phosphorus Chemistry, Academic Press (1965).
10. J. E. Griffiths and A. B. Burg, Proc. Chem. Soc., 12 (1961).
11. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience, 2, 412 (1966).
12. R. C. Dobbie, L. F. Doty and R. G. Cavell, J. Amer. Chem. Soc., 90, 2015 (1968).
13. K. Gosling and A. B. Burg, J. Amer. Chem. Soc., 90, 2011 (1968).
14. J. R. Spielman and A. B. Burg, Inorg. Chem., 2, 1140 (1963).

15. A. C. Chapman, J. Homer, D. J. Mowthorpe and R. T. Jones, Chem. Commun., 121 (1965).

16. A. B. Burg and J. F. Nixon, J. Amer. Chem. Soc., 84, 356 (1964).

17. R. G. Cavell and H. J. Emeléus, J. Chem. Soc., 5825 (1964).

18. A. B. Burg and K. Gosling, J. Amer. Chem. Soc., 87, 2113 (1965).

19. F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, J. Chem. Soc., 3598 (1954).

20. R. G. Cavell and R. C. Dobbie, J. Chem. Soc. (A), 1308 (1967).

21. A. B. Burg and J. E. Griffiths, J. Amer. Chem. Soc., 82, 3514 (1960).

22. K. J. Packer, J. Chem. Soc., 960 (1963).

23. The notation for coupling constants is due to: J. I. Musher and E. J. Corey, Tetrahedron, 18, 791 (1962).

24. R. K. Harris and R. G. Hayter, Can. J. Chem., 42, 2282 (1964).

25. R. G. Cavell and H. J. Emeléus, J. Chem. Soc., 5896 (1964).

26. R. G. Cavell and R. C. Dobbie (a) Inorg. Chem., 7, 101 (1968), (b) ibid, 7, 690 (1968).

27. D. E. C. Corbridge in Topics in Phosphorus Chemistry, ed. by M. Grayson and E. J. Griffiths, Interscience

(New York), 3, 57 (1966).

28. R. G. Cavell and T. L. Charlton, Inorg. Chem., 8, 2436 (1969).

29. D. D. DesMarteau, J. Amer. Chem. Soc., 91, 6211 (1969).

30. J. E. Griffiths and A. B. Burg, J. Amer. Chem. Soc., 82, 3442 (1962).

31. W. J. Criddle and G. P. Ellis, Qualitative Organic Chemical Analysis, p2, Butterworths (1967).

32. L. Maier in Topics in Phosphorus Chemistry, ed. by M. Grayson and E. J. Griffith, Interscience (New York), 2, 43 (1965).

33. T. L. Charlton and R. G. Cavell, Inorg. Chem., 7, 2195 (1969).

34. R. G. Cavell and E. D. Day, unpublished observations.

35. D. E. Rogers and G. Nickless in Inorganic Sulphur Chemistry, ed. by G. Nickless, Elsevier (Amsterdam) p281 (1968).

36. H. Falius, Angew. Chem. Intern. Ed. in Engl., 2, 561 (1963).

37. R. G. Cavell, unpublished observations.

38. T. L. Charlton and R. G. Cavell, Inorg. Chem., 9, 379 (1970).

39. H. J. Emeléus, R. N. Haszeldine and R. C. Paul, J. Chem. Soc., 563 (1955).

40. R. G. Cavell and W. Sim, unpublished observations.

41. F. A. Cotton, Chemical Applications of Group Theory, 2nd ed., Wiley-Interscience, p330 (1971).

42. C. B. Colburn, W. E. Hill and D. W. A. Sharp, J. Chem. Soc. (A), 2221 (1970).

43. T. L. Charlton and R. G. Cavell, Inorg. Chem., 8, 281 (1969).

44. A. B. Burg and A. J. Sarkis, J. Amer. Chem. Soc., 87, 238 (1965).

45. F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, J. Chem. Soc., 3896 (1954).

46. A. B. Burg and J. E. Griffiths, J. Amer. Chem. Soc., 83, 4333 (1961).

47. A. B. Burg and I. B. Mishra, Inorg. Chem., 8, 1199 (1969).

48. F. N. Tebbe and E. L. Muetterties, Inorg. Chem., 9, 629 (1970).

49. R. G. Cavell and P.M. Watkins, unpublished observations.

50. D. Shopov and N. D. Yordanov, Inorg. Chem., 9, 1943 (1970).