

THE PREPARATION AND CHARACTERISATION
OF PERFLUOROALKYL DERIVATIVES
OF GROUPS V AND VII.

A Thesis
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Degree in Chemistry

by
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ABSTRACT

The preparation of perfluoroalkyl vicinal hypohalites is described together with a series of perfluoroalkyl derivatives of phosphorus.

The perfluoroalkyl vicinal hypohalites were prepared by the reaction of the disodium alkoxide of perfluoropinacol $(OC(CF_3)_2C(CF_3)_2O)^{2-}2Na^+$ with chlorine, bromine, iodine monochloride, iodine monobromide, diphenyl iodium chloride and phenyl iodium dichloride. The prepared compounds were characterised by ^{19}F N.M.R., infrared spectroscopy and chemical reactions.

A series of phosphorus compounds was prepared by the reaction of hexafluoroacetone with phosphites and dialkyl phosphonates. The reactions occur quite readily to give a variety of fluorinated cyclic oxyphosphoranes and other phosphorus compounds in which the phosphorus atom is either trivalent or pentavalent.

ACKNOWLEDGEMENTS

The author would like to express his gratitude to his research director, Dr. A.F. Janzen, for his continual advice during the course of this work.

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GENERAL INTRODUCTION

Acetyl hypohalites were first obtained in 1861 by Schutzenberger¹ who found that acetyl hypochlorites could be formed by the action of chlorine monoxide on acetic acid. Acetyl hypobromites have been obtained by the action of bromine on the respective acetyl hypochlorite in a solution of acetic acid.

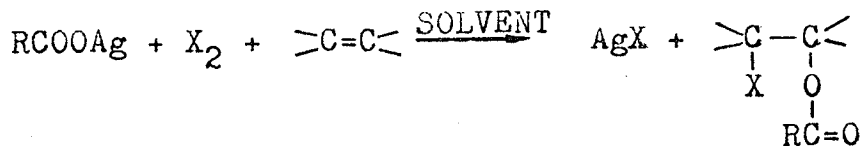
Acetyl hypohalites² have also been formed by the reaction of silver salts of carboxylic acids with the respective halogen, in the cold, in molecular proportions.



The investigators showed that these compounds decomposed quite readily to form the corresponding halo compound.



Research³ has also shown that equimolecular quantities of halogen and silver salt adds to double bonds of olefinic substances to give the corresponding halo esters. The general reaction may be represented as below.



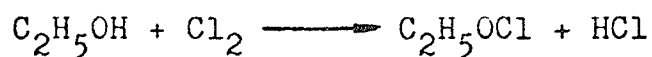
The immediate product of the reaction may be considered to be RCOOX. Treatment of the filtrate from the reaction, -80° , of equimolar quantities of silver acetate and iodine similarly adds to cyclohexene at room temperature to give the acetate of 2-iodo-1 cyclohexane. This is undisputed evidence for the presence in solution of CH_3COOI (methyl hypoiodite).

Treatment of trifluoroacetic acid with fluorine gives an acyl hypofluorite⁴ (trifluoroacetyl hypofluorite).



Various kinetic experiments have also been carried out in which acyl hypohalites have been postulated as intermediates. The existence of acyl hypohalites has also been shown by ultraviolet absorption experiments⁵. Although no acyl hypohalite has been isolated from its corresponding solution, these substances have been shown to be well defined species in solution.

Sandmeyer⁶ in 1885, isolated the first known alkyl hypohalite. He obtained ethyl hypochlorite by the action of chlorine gas on ethyl alcohol.

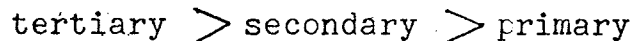


This initial study of Sandmeyer was extended by Chattaway⁷ and Backeberg.⁸ These workers although unable to obtain a pure sample of the hypochlorite due to its instability above

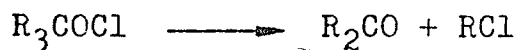
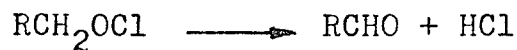
0°C showed it to decompose to give the decomposition products acetaldehyde and hydrogen chloride.



Similarly they were able to postulate the existence of other hypochlorites namely benzyl, propyl, butyl and amyl hypochlorites⁹. It was shown that the order of stability of the newly formed compound was:



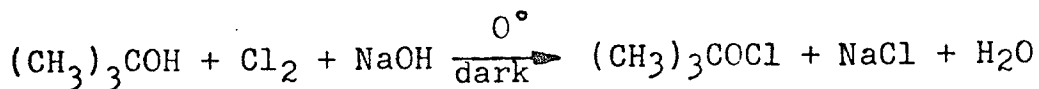
The alkyl hypochlorites were found to be mobile, volatile liquids of strong irritating odour. The primary and secondary hypochlorites were very unstable decomposing explosively on exposure to bright light and even upon the exclusion of light they decomposed rapidly at room temperature with the evolution of heat. The tertiary hypochlorites in comparison, were found to be much more stable and if not exposed to light can be kept for long periods without signs of decomposition. The modes of decomposition were shown to be:



Other workers have also postulated the existence of hypochlorites in oxidation reactions of alcohols^{10,11}.

Tertiary butyl hypochlorite prepared by a variety of

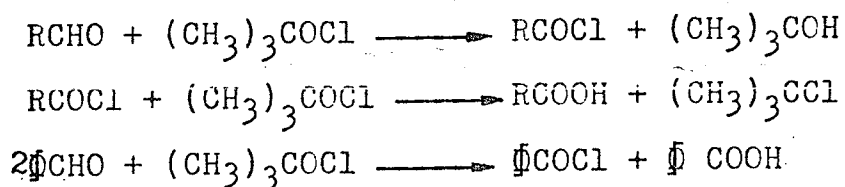
routes e.g. by passing chlorine through a cooled alkaline solution of tertiary butanol, has been quite extensively studied^{5,6,}



due to its reasonable stability and ease of handling.

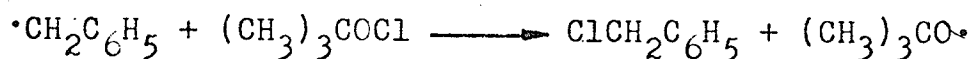
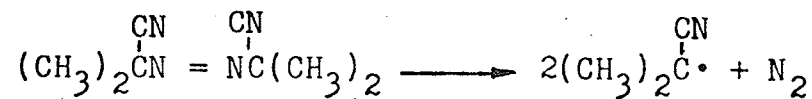
Extensive studies^{14,16} of the reactions of tertiary butyl hypochlorite with organic compounds have been carried out.

Ginsberg^{13,14} investigated the action of tertiary butyl hypochlorite on a number of aromatic aldehydes. The aldehydes are oxidised according to the equations below.



This type of reaction that has been fully exploited provides a useful way of identifying hypochlorites. It is quite conceivable that previously postulated hypochlorites can react in a similar manner thus providing undisputable evidence for their existence.

These oxidation, chlorination reactions have been shown to occur through a free radical mechanism being catalysed by ultraviolet light or such free radical reaction initiators as azobisisobutyronitrile (AIBN)⁴⁵. Consider the AIBN initiation of the chlorination of toluene.

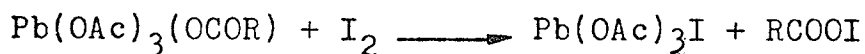


Similarly tertiary butyl hypochlorite has been shown to chlorinate phenols, ketones, hydrocarbons and alcohols. Unfortunately the yields are often only moderate and numerous isomers are produced due to uncontrolled chlorination.

Hypobromites have been formed in solution when bromine is reacted with methanol.



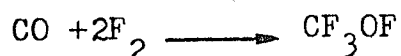
Similarly hypiodites have been prepared in situ by various routes. Welstein¹⁹ and workers have prepared hypohalites in situ by the interaction of lead tetra-acetate, acid and iodine.



Tertiary butyl hypiodite⁷ has also been prepared by the interaction of potassium t-butoxide and iodine in an inert

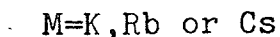
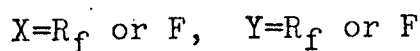
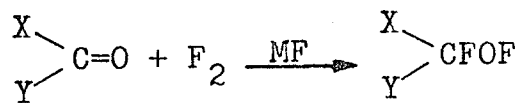
solvent. Similarly these workers showed the in situ existence of t-butyl hypobromite.

A hypofluorite was isolated as early as 1953 by Cady and Kellogg²⁷. The hypofluorite was obtained by fluorination of carbon monoxide, carbonyl fluoride or methanol over a silver catalyst at 160-180°.



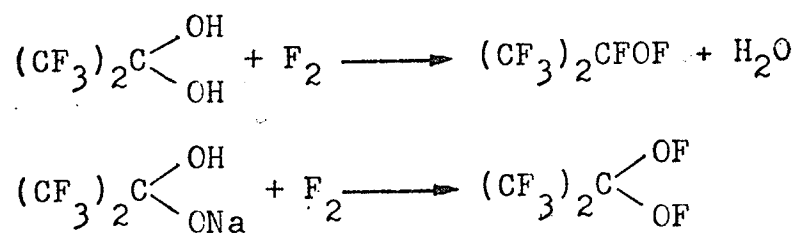
Recently²³ several other monofluoroxy derivatives have been prepared by the direct action of fluorine with the corresponding partially fluorinated alcohol.

Perfluoro organic hypofluorite derivatives²⁴ can be prepared in a pure form by the reaction of fluorine with perfluoro-ketones in the presence of a metal fluoride.



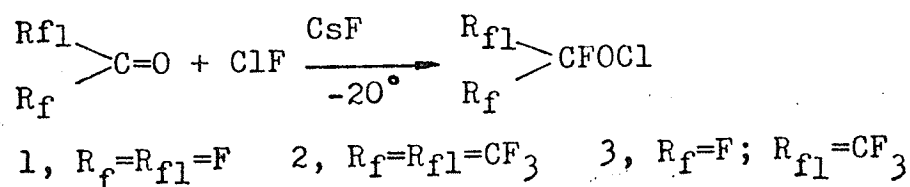
Similarly such compounds as $\text{FOCF}_2\text{CF}_2\text{H}$ and $\text{CF}_3\text{CF}(\text{NF}_2)\text{CF}_2\text{OF}$ have been prepared.

Geminal bisfluoroxy compounds were first reported by Thompson and Pragen²⁵. Hexafluoroacetone hydrate and the monosodium salt of hexafluoroacetone hydrate are readily fluorinated to give hypofluorites.



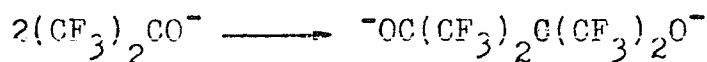
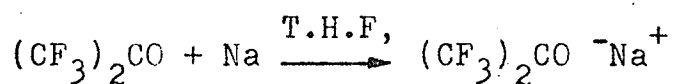
The surprising difference in the products obtained from the two direct fluorinations of these structurally similar materials illustrates the advantage of using salts to prepare fluoroxy compounds particularly when bis-fluoroxy compounds are desired. It was found that better product yields were obtained by use of salts in preference to alcohols. The compounds are reported to have varying degrees of stability. The bis-fluoroxy compound is very prone to explosion while the perfluoro-ethylidene compound is not especially susceptible to explosive decomposition.

During the course of our work a recent publication²⁶ reported the preparation of a new class of compounds, namely perfluoroalkyl hypochlorites. The compounds are prepared superficially similar to the corresponding fluoroxy-perfluoroalkyl compounds by the metal fluoride catalysed reaction of perhaloalkyl carbonyl compounds with chlorine monofluoride.



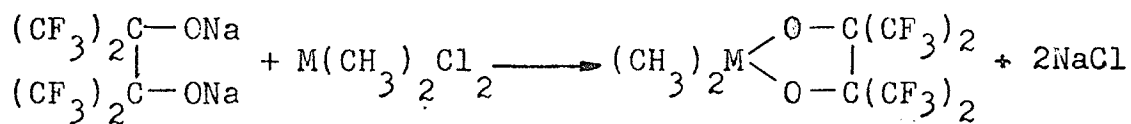
The reported compounds appear much more stable than the corresponding alkyl hypochlorites but decompose when stored at elevated temperatures.

Hexafluoroacetone, first prepared in 1941, has been extensively studied since it is a highly reactive compound. Workers^{27,28} have reported the reaction of hexafluoroacetone with sodium in a donor solvent. The reaction, one of dimerisation, results in the preparation of the stable ionic disodium alkoxide of perfluoropinacol $(CF_3)_2COCO(CF_3)_2^{2-} \cdot 2Na^+$.

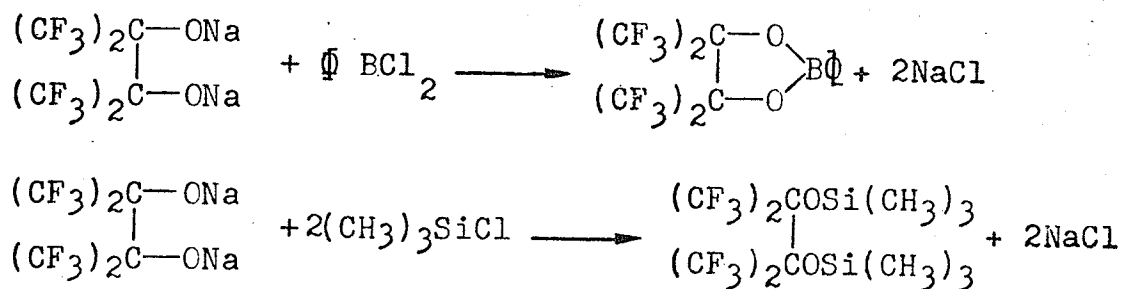


The intermediate in this reaction has been postulated to be a ketyl, dimerisation of which produces the disodium salt.

The disodium salt has been shown to be an excellent reagent for the preparation of linear and cyclic fluorinated alkoxides of various elements. The high reactivity of the ionic alkoxide is illustrated by the reactions below.^{29,30,31.}



M= Si, Ge, Sn.

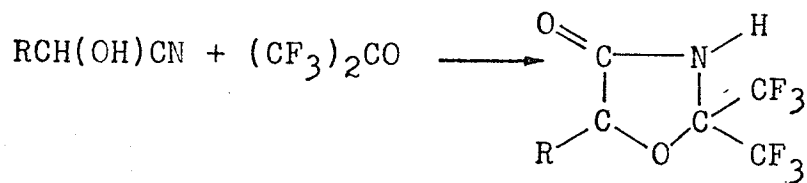


In part of the work described in this thesis the highly stable ionic disodium alkoxide has been reacted with various reagents to produce new vicinal alkyl dihyphalites.

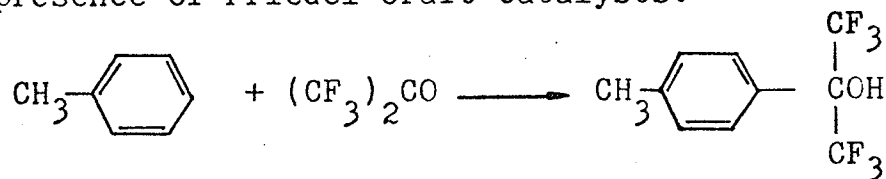
Hexafluoroacetone^{32,34} readily takes part in reactions that involve nucleophilic attack at its carbonyl group. This mode of reaction is favoured by the trifluoromethyl groups which reduce electron density on the adjacent carbonyl function. The general reaction of hexafluoroacetone with nucleophilic reagents is given below.



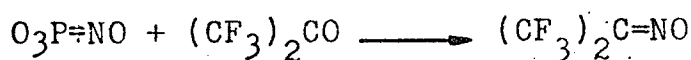
Hexafluoroacetone reacts with cyanohydrins³³ in the presence of catalytic amounts of piperidine.



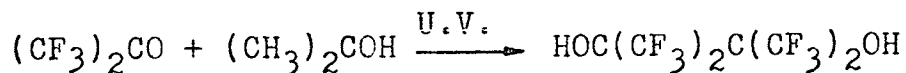
Aromatic compounds³⁶ react with hexafluoroacetone in the presence of Friedel Craft catalysts.



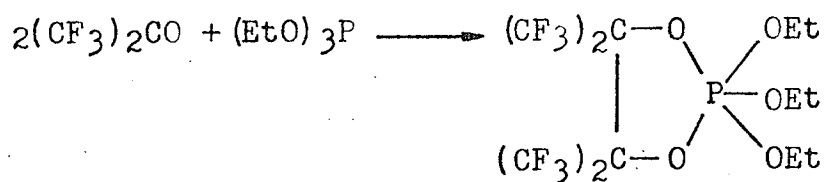
With $\text{O}_3\text{P}=\text{NO}$ ³⁵ hexafluoroacetone readily undergoes the Wittig reaction.



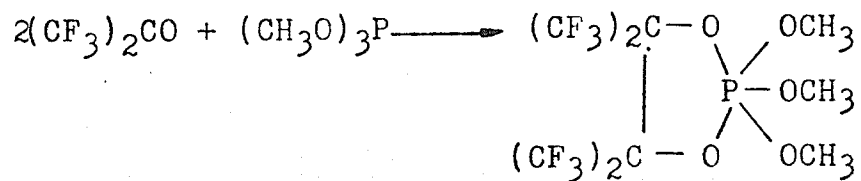
Photochemical irradiation of hexafluoroacetone and isopropyl alcohol yields perfluoropinacol³⁸.



Perfluoropinacol has been prepared via a triethyl phosphite derivative^{35,40}.



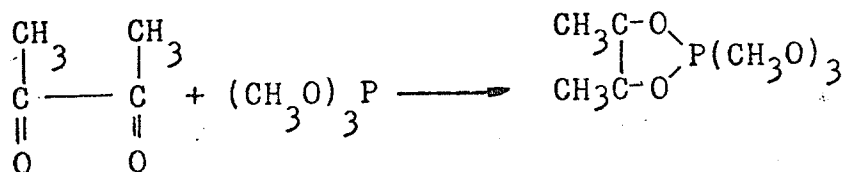
Other such reactions between hexafluoroacetone and phosphites have also been reported⁴¹.



The compounds are reported to be formed via a 1:1 adduct which then condenses with another molecule of hexafluoroacetone under mild conditions to give the 2:1 adduct.

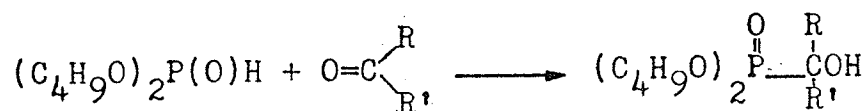
This thesis describes the preparation and characterisation of further compounds which fall into this category.

Phosphites also react with diketones⁴¹ to form compounds with cyclic structures.



Similar compounds are also formed when phosphites react with certain ketones, halo-aldehydes and halo-esters⁴².

Abramov⁴³ has reported the reactions of ketones and aldehydes with dialkylphosphorus acids. Dibutyl phosphite reacts readily with various aldehydes and ketones in the presence of a sample quantity of freshly prepared sodium methyrate.

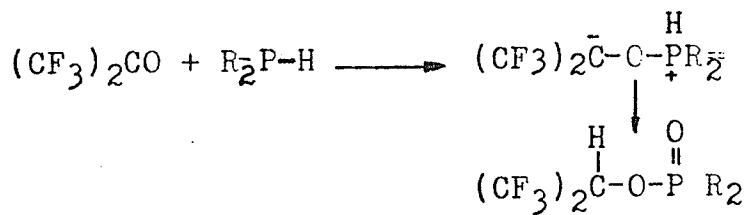


The above reaction usually only takes place in the presence of a base. The exception occurs when a very strong electrophilic carbonyl compound such as chloral is reacted with the neutral species at room temperature.

Dialkyl phosphonates exist in two tautomeric forms, 'phosphite' and 'phosphonate'. The reaction with chloral being accounted for by saying that the tiny portion of the phosphite form is sufficiently concentrated to account for the observed reaction.



Recently,⁴⁴ secondary phosphines have been shown to react with hexafluoroacetone to form phosphinate esters.



This thesis describes some reactions of hexafluoroacetone with dialkyl phosphonates.

GENERAL PROCEDURE, REAGENTS AND APPARATUS

General

Conventional vacuum techniques were used throughout this work to effect preparation of reactants and separation of reaction products. Separation was obtained by use of various cold baths e.g. acetone/dry ice (-78), chloroform/liquid nitrogen (-63), chlorobenzene/liquid nitrogen (-46).

Reactions were carried out in sealed thick walled pyrex glass reaction ampoules. Experiments requiring U.V. irradiation were performed in silica reaction tubes in a closed aluminium foil lined apparatus to reduce accidental spread of U.V. irradiation.

Chemicals.

Hexafluoroacetone was a commercial sample (Matheson Chemical Company), whose purity was checked before use by infrared spectroscopy.

Bromine, iodine, iodine monochloride, iodine monobromide were commercially pure samples (Aldrich Chemicals) and were used without further purification. Chlorine gas was used from a commercial cylinder and dried before use by passing through concentrated sulphuric acid.

Sodium metal was cut free of the outer oxide layer under dried tetrahydrofuran. The oxide free metal was further cut into small pieces before use.

The solvents were all carefully dried before use, e.g.

tetrahydrofuran was dried by refluxing over lithium aluminium hydride for ten hours in a nitrogen atmosphere.

The phosphites were all purified on the vacuum line before use.

Instrumental

All infrared spectra were obtained on a Perkin Elmer 337 instrument using potassium bromide optics. The spectra were calibrated using a polystyrene film. Nuclear magnetic resonance spectra were obtained on a Varian model A-56/60-A instrument, using 60Mc/s and 56.4 Mc/s for proton and fluorine resonance respectively. The spectra were calibrated using internal standards. Freon 11 and tetramethyl silane were used respectively for the fluorine and proton standards. Vapour phase chromatography was carried out on a Varian Aerograph 25/20 instrument using a F.F.A.P. column.

Chemical analyses were carried out by Galbraith Laboratories, Inc. Knoxville, Tenn.37921.

EXPERIMENTALPART 1The Preparation and Characterisation of Perfluoroalkyl
vicinal hypohalites of Perfluoropinacol.Reaction of Hexafluoroacetone with Sodium.

In a typical reaction, hexafluoroacetone (5.66g, 34.0mmole) was transferred to a reaction tube that had been previously partially filled with tetrahydrofuran (10 mls) and sodium metal(0.80 g). The sealed tube was shaken for 3 days at room temperature. The sodium reacted slowly to produce a solution that was free of sodium metal. The final solution was reddish brown in colour.

The solution was placed on a vacuum rack and the excess hexafluoroacetone was carefully removed. The solution was then carefully pumped upon to remove the majority of the solvent (tetrahydrofuran). The tetrahydrofuran that was removed was weighed to enable the amount of tetrahydrofuran remaining to be calculated. The disodium salt of perfluoropinacol that was prepared was stored under vacuum.

The fluorine n.m.r. spectrum in tetrahydrofuran gave a singlet at +71.8 p.p.m. (Int. std.).

Infrared examination of a freshly prepared sample showed

the following absorption bands: 1300 (sh,ms), 1245 (s), 1182 (s), 1130 (s), 1110 (ms), 1050 (s), 985 (w), 955 (sm), 915 (w), 890 (w), 865 (ms), 732 (ms), 712 (ms).

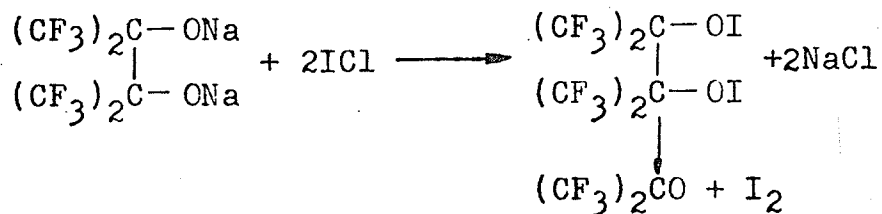
Reaction of $(OC(CF_3)_2C(CF_3)_2)^{2-}2Na$ + with iodine monochloride in freon 11.

To a solution of iodine monochloride (3.00 g, 18.6 mmole) in freon 11 (60 ml) at -196° was added the disodium alkoxide (3.60 g/3 ml T.H.F., 9.54 mmole). The reaction vessel was vacuumed sealed and allowed to warm slowly to room temperature. Reaction was apparent because the solution precipitated a white solid. The solid was separated by careful vacuum filtration. The solid (0.70 g, 12.0 mmole) was undisputedly identified by X ray diffraction analysis as sodium chloride.

The fluorine n.m.r. spectrum taken directly after the reaction showed a sharp singlet at +71.95 p.p.m. (int.std.)

The infrared spectrum showed the lack of C=O or C=C absorption bands and the presence of perfluoroalkyl group absorption bands.

When an attempt was made to remove the last traces of solvent from the prepared sample decomposition occurred to produce hexafluoroacetone and iodine.



The quantity of sodium chloride precipitated showed the reaction to be 64% complete.

Reaction of disodium perfluoropinacol with iodine monochloride in tetrahydrofuran .

To a solution of iodine monochloride (3.0 g, 18.6 mmole) in tetrahydrofuran (20 ml), at -196° , was added the disodium alkoxide (3.51g, 9.3 mmole/3 ml T.H.F.). The reaction vessel was vacuum sealed and allowed to warm to room temperature, before being shaken for 5 days at room temperature.

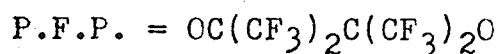
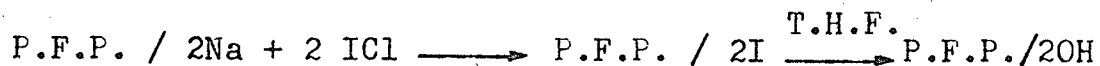
The precipitate formed in the reaction was vacuum filtered and identified as sodium chloride by X ray powder analysis. The resulting solution was vacuum fractionated. This resulted in the collection of a colourless viscous oil.

The fluorine n.m.r. of the compound showed a sharp singlet at +70.71 p.p.m. (int. std.). The proton n.m.r. show the presence of tetrahydrofuran and a sharp singlet at -6.2.

Infrared spectroscopic examination showed the absorption peaks ; 3660 (ms), 3500 (br , s), 1300 (s), 1275 (s),

1220 (s), 1120 (s), 1020 (s), 998 (s), 938 (s), 940 (s),
882(s), 768 (ms), 750 (ms), 720 (ms), 680 (w), 650 (w),
558(ms), 502 (w), 490 (w).

The compound was identified as perfluoropinacol by comparison with an authentic sample.



The Reaction of Disodium Perfluoropinacol with Iodine
Monobromide in Freon 11.

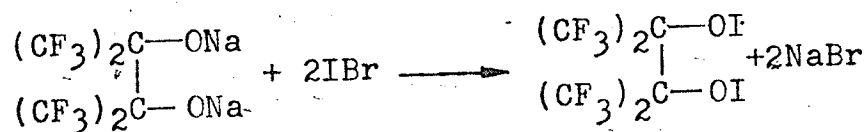
To a solution of iodine monobromide (3.0 g, 14.6 mmole) in freon 11 (60 ml), at -196° , was added the disodium alkoxide (2.76 g, 7.3 mmole / 30ml T.H.F.). The reaction vessel was vacuum sealed and allowed to warm slowly to room temperature before being shaken for 5 days.

The precipitate (0.90 g, 8.82 mmole) formed during the reaction was carefully vacuum filtered. X ray powder diffraction analysis identified the precipitate as sodium bromide.

When an attempt was made to remove the last traces of solvent the compound decomposed to produce hexafluoroacetone and iodine.

The fluorine n.m.r. of the prepared compound showed

a singlet at + 70.82 p.p.m. (int. std.). The infrared spectrum showed the presence of perfluoroalkyl groups and the lack of C=O or C=C groups.



Reaction of Disodium Perfluoropinacol with Iodine Monobromide in Tetrahydrofuran.

To a solution of iodine monobromide (3.0 g, 14.8 mmole) in tetrahydrofuran (20 ml), at -196° , was added the disodium alkoxide (2.76 g, 7.3 mmole/30ml T.H.F.). The reaction vessel was vacuum sealed and slowly warmed to room temperature before being shaken for 5 days.

The resulting precipitate was removed from the solution by vacuum filtration and identified as sodium bromide by X ray powder diffraction analysis. The remaining solution was vacuum fractionated to produce a colourless viscous oil. The oil was characterised by fluorine n.m.r. and infrared spectroscopy and identified as perfluoropinacol.

Reaction of Disodium Perfluoropinacol with Chlorine in Freon 11.

Dry chlorine gas was slowly passed, in the dark, through

a solution of disodium perfluoropinacol (3.21 g, 8.49 mmole/3 ml T.H.F.) in freon 11 (30 ml). The reaction vessel was contained in a cold bath at -22° . Reaction occurred to precipitate a white solid. After 20 minutes the reaction was stopped and the reaction solution quickly filtered. The filtrate was kept at -78° in a stoppered vessel.

The precipitate was identified as sodium chloride (0.96 g, 16.5 mmole) by X ray powder analysis. The filtrate was found to be stable below 0° . Decomposition occurred upon exposure to U.V. light, upon heating or when an attempt was made to remove the solvent. The end product of decomposition was a black tar.

The fluorine n.m.r. spectrum of the solution taken directly after preparation consisted of a singlet at + 70.57 p.p.m.(int. std.). The infrared spectrum showed the lack of C=O or C=C absorption bands and the presence of perfluoroalkyl group absorption bands.

When the reaction was carried out with an excess of chlorine, decomposition occurred. This was indicated in the fluorine n.m.r. spectrum which showed the disappearance of the singlet and the appearance of numerous doublets, triplets and multiplets.

Reaction of Disodium Perfluoropinacol with Chlorine in Tetrahydrofuran.

Dry chlorine gas was passed, in the dark, through a solution of disodium perfluoropinacol (3.20 g, 8.45 mmole/ 3 ml T.H.F.). The solution was carefully maintained at -22° throughout the reaction. Reaction occurred to produce a white precipitate, which after a 20 minute reaction was carefully vacuum filtered. The excess solvent was removed from the filtrate to leave a colourless liquid.

Infrared spectrometric examination showed the following absorption bands: 3660 (ms), 3500 (br,s), 1300 (s), 1275 (s), 1220 (s), 1120 (s), 1020 (s), 998 (s), 938 (s), 940 (s), 887 (s), 768 (ms), 750 (ms), 720 (ms), 680 (w), 558 (ms), 502 (w), 490 (w). The fluorine n.m.r. spectrum showed a singlet at + 70.71 p.p.m. (int. std.). The proton n.m.r. spectrum showed a singlet at 6.2 (δ) and the presence of a small quantity of tetrahydrofuran. The product was identified as perfluoropinacol by comparison with an authentic sample.

Reaction of Disodium Perfluoropinacol with Bromine in Freon 11

Bromine (3.0 g, 19.0 mmole) was added to a frozen solution of disodium perfluoropinacol (3.60 g, 9.55 mmole) in freon 11 (35 ml). The reaction tube was vacuum sealed and placed in an acetone/dry ice bath. The reactants were left in the dark

for 24 hours at this temperature before being transferred to a salt/water/ice bath where they were allowed to react for 4 hours.

The presence of a yellowish-white precipitate indicated that reaction had occurred. The solution was vacuum filtered and the precipitate was identified as sodium bromide (1.84 g, 18.1 mmole) by X ray powder analysis. The filtrate was vacuum fractionated to yield a yellowish oil. The oil was characterised directly after preparation by infrared spectroscopy and nuclear magnetic resonance measurements.

The fluorine n.m.r. spectrum showed the presence of the singlet at + 70.46 p.p.m (int. std.). The infrared spectrum showed the presence of perfluoroalkyl groups and the lack of absorption peaks that could be associated with hydroxyl, carbonyl, or olefinic groups.

The compound decomposed upon warming or exposure to U.V. light to produce a black-brown tar and evolved a gas. The gas was identified as hexafluoroacetone by infrared spectroscopy.

The reaction when carried out in tetrahydrofuran yielded perfluoropinacol that was identified by comparison with an authentic sample.

Reaction of Disodium Perfluoropinacol with Iodine in
Freon 11

To a solution of sodium perfluoropinacol (3.61g, 9.61mmole) in freon 11 (60 ml), at the temperature of liquid nitrogen, was added iodine (2.3 g, 9.06 mmole). The vacuum sealed reaction vessel was shaken for 5 days at room temperature.

Reaction was indicated by the precipitation of a small quantity of a white solid. The reaction solution was carefully vacuum filtered. The precipitate was identified as sodium fluoride by X ray powder analysis.

This shows that the reaction had not proceeded in expected manner to produce a dihypohalite. The reaction was not pursued further.

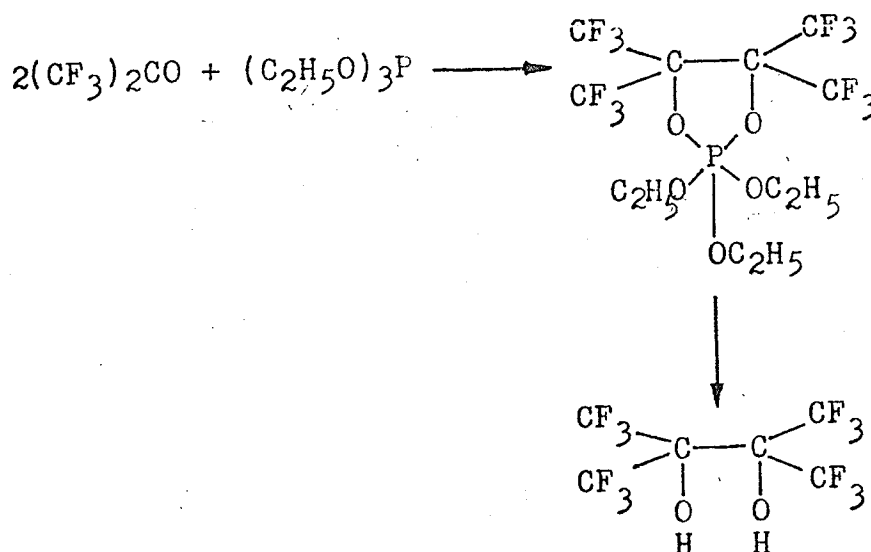
Preparation of Perfluoropinacol.

Hexafluoroacetone (10.0g, 60.15 mmole) was added to a neat sample of triethyl phosphite (5.6 g, 33.8 mmole). The reaction vessel was carefully vacuum sealed and shaken for 5 days at room temperature. The reaction product was identified by fluorine n.m.r. and infrared spectroscopy as a 2:1 adduct of hexafluoroacetone and triethyl phosphite.

The product was shaken with concentrated sulphuric acid (20 ml) to yield colourless crystals. The crystals were dissolved in water (100 ml) and boiled for one hour.

The mixture was cooled and sulphuric acid was carefully added. The mixture was continually extracted with methylene chloride. The collective extracts were distilled to yield a viscous oil (1.2 g, 3.61 mmole).

The oil was identified as perfluoropinacol by infrared spectroscopy and nuclear magnetic resonance measurements. The fluorine n.m.r. showed a singlet at +70.71 p.p.m. (int. std.) Infrared spectroscopy showed the absorption bands; 3660 (ms), 3500 (br ,s), 1275 (s), 1220 (s), 1120 (s), 1020 (s), 998 (s), (58 (s), 940 (s), 882 (s), 768 (ms), 750 (ms), 720 (ms), 680 (w), 650 (w), 558 (ms), 502 (w), 490 (w).



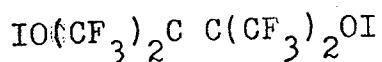
Reaction of 1,2- dihypochlorite perfluoroethane with benzaldehyde in carbontetrachloride.

To a solution of the dihypochlorite (3.6 g, prepared in the usual manner) in a small reaction vessel was added

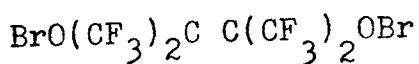
a portion of benzaldehyde (6.0 g, 56.8 mmole) in carbon tetrachloride (15 ml). The reaction vessel was vacuum sealed and placed in a water/ ice/ salt bath. The cold bath was placed in a U.V. irradiation box and the apparatus arranged so that the sample could be easily irradiated. The sample was irradiated for 12 hours, the cold bath being maintained at approximately -22° . The sample was further irradiated over night at room temperature.

Two of the reaction products were identified as benzoyl chloride and benzoic acid. The products were identified by comparison of their vapour phase chromatographs (F.F.A.P column) with those of authentic samples. The benzoic acid was also identified by infrared spectroscopy.

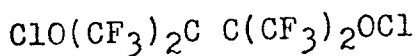
The newly prepared perfluoroalkyl dihypohalites are listed below:



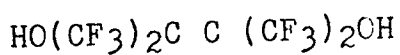
1,2, bis (oxyiodite)tetrakis(trifluoromethyl)ethane



1,2, bis (oxybromite)tetrakis(trifluoromethyl)ethane



1,2, bis (oxychlorite)tetrakis(trifluoromethyl)ethane



1,2, hydroxytetrakis(trifluoromethyl)ethane

Reaction of Disodium Perfluoropinacol with Diphenyl Iodine Chloride in Dimethyl Sulphoxide.

To a solution of disodium perfluoropinacol (1.99 g, 5.28 mmole/2 ml T.H.F.) in dimethyl sulphoxide (20 ml), at -196° , was added diphenyl iodine chloride (1.56 g, 4.95 mmole). The vacuum sealed reaction vessel was shaken for 5 days at room temperature. The white solid, precipitated during the reaction, was identified as sodium chloride (0.36 g, 6.21 mmole) by X ray powder analysis. The resulting solution decomposed on removal of the solvent.

The fluorine n.m.r. spectrum, taken directly after preparation, showed a singlet at + 69.82 p.p.m. (int. std.).

Reaction of Disodium Perfluoropinacol with Phenyl Iodine Dichloride in Tetrahydrofuran.

To a solution of disodium perfluoropinacol (1.50 g, 3.96 mmole/2 ml T.H.F.) in tetrahydrofuran (20 ml), at -196° was added phenyl iodine dichloride (1.08 g, 3.96 mmole). The vacuum sealed reaction vessel was shaken for 5 days at room temperature.

The white solid, precipitated during the reaction was identified as sodium chloride (0.28 g, 4.82 mmole), by X ray powder analysis. The resulting solution decomposed on removal of the solvent to leave a black tar.

The fluorine n.m.r. spectrum, taken directly after preparation, showed a singlet at + 70.35 p.p.m. (int. std.).

PART 11Reactions of Hexafluoroacetone with Phosphite Esters.Preparation of $\overline{\text{P}(\text{OC}(\text{CF}_3)_2\text{C}(\text{CF}_3)_2\text{O})}_3$ ⁴⁶.

To a solution of triphenyl phosphite (2.62 g, 10.0 mmole) in tetrahydrofuran (20 ml) was added a slight excess of hexafluoroacetone (4.12 g, 24.8 mmole). The reaction vessel was vacuum sealed and placed in a dry ice/acetone bath.

After 4 days the sample was shaken for 2 days at room temperature. Vacuum fractionation of the reaction solution produced unreacted hexafluoroacetone and a white solid (5.94 g, 10 mmole). The solid product was recrystallised from benzene.

The fluorine n.m.r. spectrum, in tetrahydrofuran, showed a singlet at +68.17 p.p.m. (int. std.). The infrared spectrum showed the expected C-H and C-F absorption bands and the absorption bands characteristic of the five membered cyclic system $\overline{\text{MOC}(\text{CF}_3)_2\text{C}(\text{CF}_3)_2\text{O}}_3$ ³¹.

The infrared spectrum (nujol) showed the following absorption bands : 1288 (s), 1264 (s), 1234 (s), 1222 (s), 1210 (s), 1184 (ms), 1148 (s), 1108 (s), 1088 (s), 998 (m), 954 (ms), 878 (ms), 806 (ms), 764 (w), 744 (ms), 720 (s), 694 (s), 684 (w), 500 (s), 512 (w), 488 (w).

Reaction of Diphenyl Chlorophosphite with Hexafluoroacetone.

An excess of hexafluoroacetone (5.26 g, 31.6 mmole) was added to a neat solution of diphenyl chlorophosphite (2.53 g, 11.5 mmole). The vacuum sealed reaction vessel was stood in an acetone/dry ice bath. The cold bath was slowly allowed to warm to room temperature. After standing at room temperature for 1 day the reaction vessel was shaken for 3 days. Vacuum fractionation of the reaction mixture yielded excess hexafluoroacetone and an involatile yellow liquid that could not be further distilled without decomposition.

The fluorine n.m.r. spectrum showed a singlet at +67.81 p.p.m. (int.std.).

The infrared spectrum (neat) showed the presence of C-H and C-F absorption bands and the characteristic absorption bands of the 5 membered cyclic system³¹:
3075 (w), 3060 (w), 1950 (w), 1875 (w), 1800 (w), 1775 (w), 1650 (w), 1480 (m), 1440 (ms), 1291 (ms), 1268 (s), 1254 (s), 1242 (s), 1214 (s), 1188 (ms), 1158 (ms), 1132 (ms), 1095 (s), 998 (m), 954 (ms), 878 (m), 812 (m), 762 (w), 743 (s), 720 (s), 688 (s), 588 (w), 558 (m), 530 (ms), 500 (m).

The sample decomposed when moist air came into contact with the surface of the infrared cells. This was indicated by the infrared spectrum which showed the loss of the absorption band at 504 cm^{-1} and the appearance of an absorption band at 3020 cm^{-1} . Contact with moist air for

3 minutes resulted in solidification of the sample.

Anal. Calcd. for $C_{18}H_{10}F_{12}ClPO_2$: C, 39.20; H, 1.81; F, 41.40; Cl, 6.36. Found: C, 49.21; H, 3.00; F, 29.77; Cl, 9.40.

The analysed sample corresponds to a mixture of the starting material (ϕ_2PCl) and the expected product, namely 4,4,5,5-tetrakis (trifluoromethyl)-2 chloro-2, 2-diphenyl-1,3-dioxo-2-phosphocyclopentane, in the ratio 1:2 respectively.

Reaction of Phenyl Dichlorophosphite with Hexafluoroacetone.

An excess of hexafluoroacetone (2.54 g, 15.3 mmole) was added to a neat sample of dichloro phenyl phosphite (0.80g, 4.50mmole). The vacuum sealed reaction vessel was placed in an acetone/dry ice bath. The cold bath was allowed to warm to room temperature. After standing for 1 day at room temperature the reaction vessel was shaken for 3 days.

Vacuum fractionation of the reaction solution yielded the starting materials in unchanged quantities. This unsuccessful reaction was not pursued further.

Reaction of Triphenyl Arsine with Hexafluoroacetone.

To a solution of triphenyl arsine (1.5 g, 4.91 mmole) in tetrahydrofuran (15 ml) was added excess hexafluoroacetone (1.63 g, 9.84 mmole). The vacuum sealed reaction vessel was placed in an acetone/dry ice bath. The cold bath was allowed to warm to room temperature. After standing for 1 day

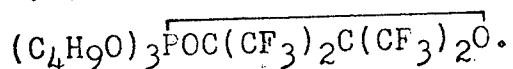
at room temperature the reaction vessel was shaken for 3 days.

Vacuum fractionation of the reaction solution yielded the starting materials in unchanged quantities. This unsuccessful reaction was not pursued further.

Preparation of $(C_4H_9O)_3POC(CF_3)_2C(CF_3)_2O$.

To a neat sample of tributyl phosphite (2.79 g, 11.2mmole) was added an excess of hexafluoroacetone (4.0 g, 24.18 mmole). The sealed reaction vessel was placed in an acetone/dry ice bath which was allowed to warm to room temperature. The reaction vessel, after standing at room temperature for 1 day, was shaken for 3 days.

Vacuum fractionation of the reaction mixture yielded excess hexafluoroacetone and an involatile colourless liquid (5.82 g, 11.2 mmole), namely 4,4,5,5-tetrakis(trifluoromethyl) 2,2,2-tributyl-1,3-dioxa-2-phosphocyclopentane,



Anal. Calcd. for $C_{18}F_{12}H_{27}O_5P$: C, 34.7; H, 4.64:

Found: C, 34.68; H, 4.62:

The fluorine n.m.r. spectrum (neat) showed a singlet at +68.90 p.p.m. (int. std.).

Infrared spectroscopic examination (neat) showed the following absorption bands: 2975 (s), 2950 (ms), 2925 (m), 2890 (ms), 1470 (m), 1380 (m), 1292 (ms), 1275 (s),

1258 (s), 1238 (s), 1210 (s), 1128 (ms), 1162 (ms), 1145 (m),
1124 (m), 1065 (s), 1035 (s), 998 (ms), 965 (s), 910 (m),
880 (ms), 815 (ms), 780 (ms), 745 (ms), 720 (ms), 695 (m),
570 (m), 540 (w), 510 (w).

Reactions of Dialkyl Phosphonates with Hexafluoroacetone.

Reaction of Dimethyl Phosphonate with Hexafluoroacetone.

An excess of hexafluoroacetone (1.71 g, 10.3 mmole) was added to a neat sample of dimethyl phosphonate (1.08 g, 9.83 mmole). The vacuum sealed reaction vessel was placed in an acetone/dry ice bath, which was allowed to warm to room temperature. The reaction vessel, after standing at room temperature for 1 day, was shaken for 3 days.

Vacuum fractionation of the reaction mixture yielded two products in the ratio 94:6. The major product (1) was a volatile oil, $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{OC}(\text{CF}_3)_2\text{H}$ (2.54 g, 7.21 mmole), while the minor product was a colourless involatile oil, $(\text{CF}_3\text{O})_2\text{POC}(\text{CF}_3)_2\text{OH}$ (2).

The fluorine n.m.r. spectrum compound (1) showed a doublet ($J_{\text{F-H}}=7$ c/s) at + 75.18 p.p.m. (int. std.). The proton n.m.r. showed a complicated septet ($J_{\text{H-F}}=7$ c/s) at $\delta=3.3$ p.p.m. and a doublet ($J_{\text{H-P}}=12$ c/s) at $\delta=2.26$ p.p.m. (int.std).

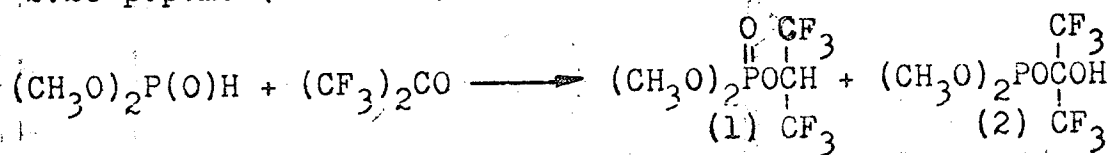
Infrared examination showed the following absorption bands: 3050 (w), 2995 (m), 2875 (w), 1440 (w), 1380 (ms), 1308 (s), 1275 (s), 1235 (s), 1202 (s), 1135 (s), 1069 (s), 900 (s), 890 (ms), 865 (ms), 852 (ms), 770 (m), 725 (m), 680 (s), 582 (w), 520 (w), 501 (m), 470 (m).

Anal. Calcd. for $\text{C}_5\text{F}_6\text{H}_7\text{PO}_3$; C, 21.75; H, 2.54; F, 41.40.

found: C, 21.96; H, 2.50; F, 41.55.

Compound (2) could not be obtained in a pure state since great difficulty was encountered in removing the last traces of compound (1). Both the fluorine and proton n.m.r. and the infrared spectrum of compound (2) show traces of compound (1).

The fluorine spectrum of compound (2) showed a doublet ($J_{F-H}=3c/s$) at +72.38 p.p.m. The proton n.m.r. showed a singlet at $\delta=4.84$ p.p.m. and a doublet ($J_{H-P}=12c/s$) at $\delta=2.26$ p.p.m. (int.std.)



Reaction of Diethyl Phosphonate with Hexafluoroacetone.

An excess of hexafluoroacetone (2.34 g, 14.1 mmole) was added to a neat sample of diethyl phosphonate (1.17g, 8.48 mmole). The sealed reaction vessel was transferred to an acetone/dry ice bath, which was allowed to warm slowly to room temperature. The reaction vessel, after standing at room temperature for 1 day was shaken for 3 days.

Vacuum fractionation of the reaction mixture yielded two products in the ratio 88:12. The major product (1) was a colourless volatile oil, $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{OC}(\text{CF}_3)_2\text{H}$.

(2.20 g, 7.28 mmole), while the minor product was a colourless involatile oil; $(C_2H_5O)_2POC(CF_3)_2OH(2)$.

The fluorine n.m.r. spectrum of compound (1) showed a doublet ($J_{F-H}=7c/s$) at + 74.84 p.p.m. (int. std.) The proton n.m.r. spectrum showed a split quartet ($J_{H-P}=7c/s$) at $\delta=2.56$ p.p.m., a triplet ($J_{H-P}=7c/s$) at $\delta=1.78$ p.p.m. due to the ethyl group and a split septet at ($J_{H-P}=7c/s$) at $\delta=3.38$ p.p.m. (int. std.) due to the single proton.

The infrared spectrum on compound (1) showed the following absorption bands: 3200 (br,vw), 2998 (w), 2950 (w), 2925 (w), 1480 (m), 1290 (ms), 1260 (s), 1240 (s), 1228 (s), 1198 (s), 1105 (s), 1035 (s), 988 (m), 962 (m), 898 (m), 882 (m), 860 (w), 810 (w), 800 (w), 760 (w), 720 (w), 685 (m), 600 (w), 538 (w), 502 (w).

Anal. Calcd. for $C_7F_6H_{11}PO_2$: C, 27.6; H, 3.62; F, 37.5; P, 10.2: found: C, 27.78; H, 3.66; F, 38.78; P, 9.21.

Compound (2) could not be obtained in a pure form, since great difficulty was encountered in removing the last traces of compound (1). Both the fluorine and proton n.m.r. spectrum and the infrared spectrum show the presence of two compounds. The fluorine n.m.r. shows a doublet ($J_{F-H}=3 c/s$) at + 71.89 p.p.m. (int. std.) The proton n.m.r. shows a singlet at $\delta = 6.13$ p.p.m. (int. std.) due to the hydroxyl proton, and the peaks listed above, due to the ethyl groups and due to the single proton of compound (1).

Infrared examination showed the following absorption bands: 3200 (br,s), 3000 (ms), 2975 (m), 2940 (m), 1480 (s), 1298 (s), 1280 (s), 1260 (s), 1234 (s), 1210 (s), 1108 (s), 1035 (s), 945 (s), 898 (ms), 882 (ms), 807 (w), 760 (w), 720 (w), 710 (ms), 685 (w), 662 (m), 601 (m), 582 (m), 564 (m).

Reaction of Dibutyl Phosphonate with Hexafluoroacetone.

An excess of hexafluoroacetone (2.56 g, 15.5 mmole) was added to a neat sample of dibutyl phosphonate (2.11 g, 10.85 mmole). The vacuum sealed reaction vessel was transferred to an acetone/dry ice bath which was allowed to warm to room temperature. The reaction vessel after standing at room temperature for 1 day was shaken for 3 days.

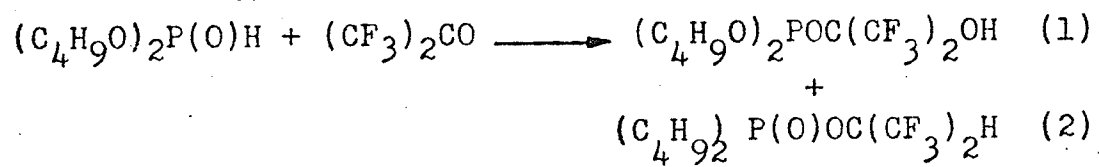
Vacuum fractionation of the reaction products yielded two components in the ratio 95:5. The major product (1) was a viscous involatile colourless liquid, $(C_4H_9O)_2POC(CF_3)_2OH$ (3.80 g, 10.6 mmole), while the minor product (2) was a volatile colourless liquid, $(C_4H_9O)_2P(O)OC(CF_3)_2H$.

The fluorine n.m.r. of compound (1) showed a doublet ($J_{F-H} = 3$ c/s) at + 72.07 p.p.m. (int. std.). The proton n.m.r. spectrum showed a singlet at $\delta = 4.32$ p.p.m. and three complicated multiplets that can be associated with the butyl groups.

Infrared examination on compound (1) showed the following absorption bands: 3180 (br, m), 2980 (ms), 2950 (m), 2890 (m), 1465 (w), 1380 (w), 1290 (w), 1272 (s), 1264 (s),

1242 (s), 1212 (s), 1150 (ms), 1140 (s), 1060 (s), 1038 (s),
962 (m), 942 (m), 748 (w), 718 (w), 584 (m), 534 (w).

Anal. Calcd. for $C_{11}F_{12}H_{19}PO_2$: C, 36.71; H, 5.28 ;
F, 31.72: Found : C, 36.30; H, 5.24; F, 31.86.



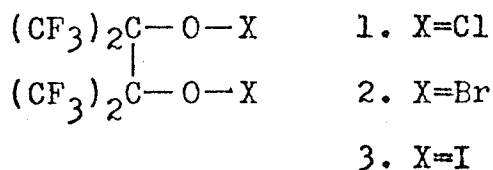
RESULTS AND DISCUSSION

PART 1 PERFLUOROALKYL DIHYPOHALITES

Hypohalites, as is evident from the introduction, have been known for a 100 years. There have however been very limited studies carried out within this field. This is most likely a result of the inability of these compounds to exist out of solution. The numerous reports on the properties and reactions of t-butyl hypochlorite are a consequence of its reasonable stability.

The literature contains only a few reports on the preparation and characterisation of perfluoroalkyl hypohalites, one²⁶ of which appeared during the process of this work. This work is a logical follow through of the work of Dr.A.F. Janzen 27,29,30,31, who prepared the highly versatile reactive compound disodium perfluoropinacol ($(OC(CF_3)_2C(CF_3)_2O^{2-})2Na^+$). The disodium salt being very reactive in reactions that result in the preparation of a stable C-O-M bond.

An investigation of the addition of disodium perfluoropinacol to a variety of halogens and interhalogens showed that reaction occurs quite readily to give a series of highly fluorinated, unstable perfluoroalkyl dihypohalites.



The compounds are best named perfluoro vicinal hypohalites since the two -OX groups are on adjacent carbon atoms.

The compounds were prepared, under a variety of reaction conditions, by two methods, i) reaction with halogen and ii) reaction with interhalogens.

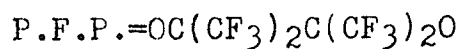


i) X=Cl

ii) X=Br



X=I, X¹=Cl, Br.



Since the products are only stable in solution the percentage yields have to be based on the quantity of sodium halide precipitated during the reaction; no attempt was made to establish optimum reaction conditions.

TABLE 1.

<u>PRODUCT</u>	<u>METHOD OF REACTION</u>	<u>PRECIPITATE</u>	<u>% YIELD</u>
$(CF_3)_2C-OI$	<u>II</u>	NaCl	63
$(CF_3)_2C-OI$	<u>II</u>	NaBr	65
$(CF_3)_2C-OBr$	<u>I</u>	NaBr	94
$(CF_3)_2C-OCl$	<u>I</u>	NaCl	97

The sodium halide that was precipitated in each reaction was positively identified by X ray diffraction analysis. This was considered to be important for the reactions to be consistent with those shown above. This was accomplished because it is conceivable that $X=Cl$, $X^I=I$, or $X=Br$, $X^I=I$. Another possibility that had to be eliminated was that sodium fluoride had been formed via fluoride abstraction from the trifluoromethyl groups or that the precipitate contained a halogen that was in a higher oxidation state, not simply +1 as in sodium chloride. The X ray powder patterns of each precipitate eliminated all these possibilities since the only pattern observed was one of the simple halide.

Great difficulty, however, was encountered in isolating and characterising the compounds. Isolation proved to be absolutely impossible due to the instability of the compounds. The compounds were thus characterised by spectroscopic studies, chemical reactions and modes of decomposition.

The fluorine nuclear magnetic resonance spectra of the dihypohalites taken directly after preparation showed, in each case, a sharp singlet absorption peak in the expected region for perfluoropinacol derivatives^{29,30}. A typical fluorine n.m.r. spectrum is shown over-leaf. This spectrum, of the dihypiodite, shows a sharp singlet, at -3994 c/s ($+70.80$ p.p.m.)(int. std.) which is to be expected for a compound which contains equivalent fluorine atoms. The dihypochlorite and dihypobromite show nearly identical n.m.r. spectrum.

In the baseline noise of this spectrum can be observed a triplet. This is due to an impurity caused by the decomposition of the dihypiodite.

Any decomposition that occurs with these compounds is bound to complicate the fluorine n.m.r. spectrum. This was subsequently found to be the case. Fluorine spectra of decomposed hypohalites show the disappearance of the singlet peak and appearance of numerous triplets, quartets and other multiplets.

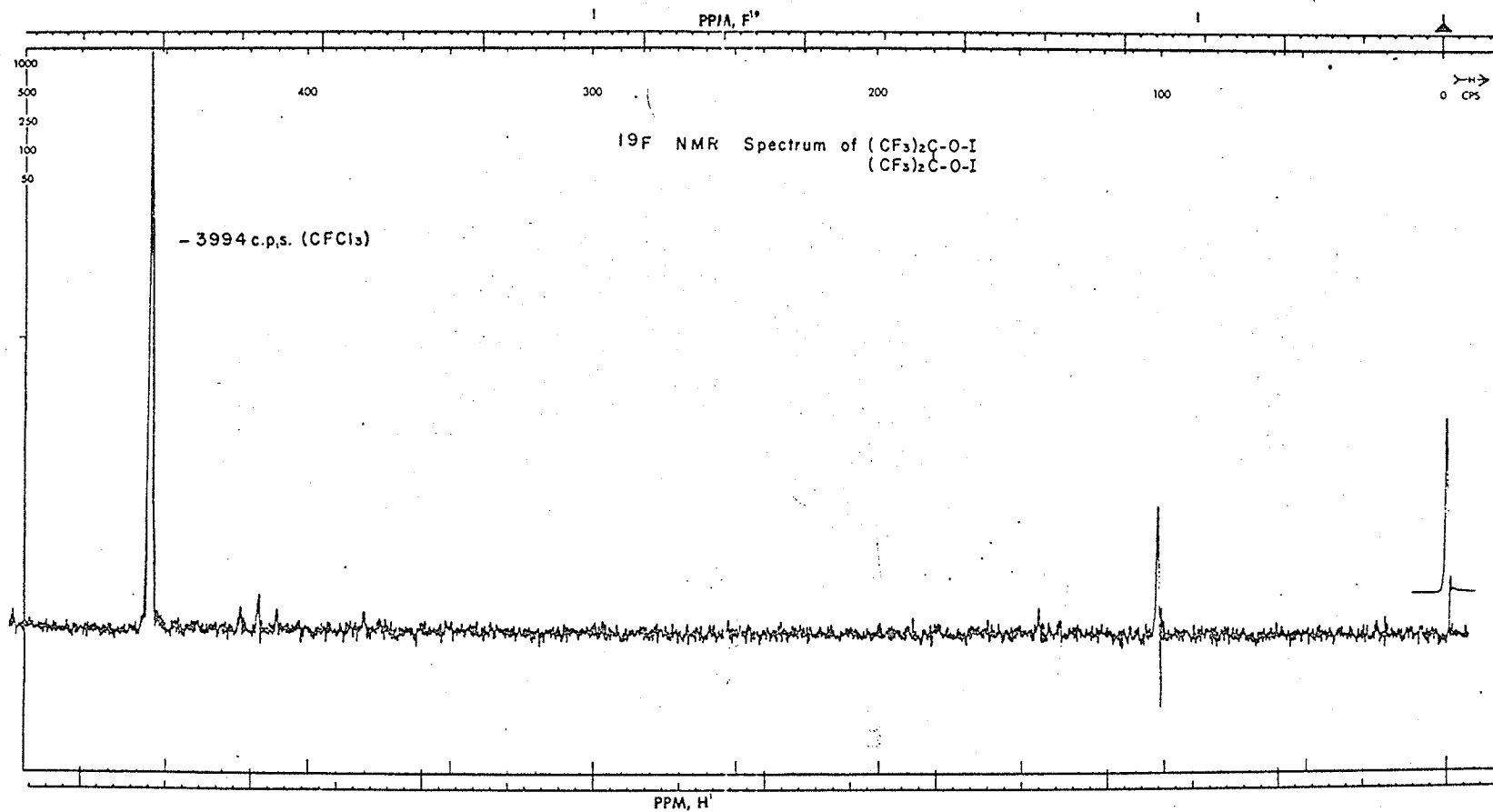


FIGURE 1.

The infrared spectra of the dihypohalites were also consistent with the proposed structure. The spectra showed the strong absorption bands in the regions 1260-1210 cm^{-1} and 725-690 cm^{-1} that can be associated with perfluoroalkyl groups. The infrared spectra also eliminated the possibility of the presence of any carbonyl, olefinic or hydroxyl groups. Great difficulty was encountered in obtaining infrared data due to the compounds decomposing on the potassium bromide infrared cells.

The prepared dihypohalites can be classified as compounds of only moderate stability. This is because although they were found not to be thermally explosive, they could not be obtained in a form that was able to be placed in a bottle, or easily handled. They were found to have varying degrees of stability. The order of stability was found to be dihypiodite > dihypobromite > dihypochlorite.

The dihypiodite was found to be stable at room temperature but decomposed on slight heating or when attempts were made to remove the last traces of solvent.

The dihypobromite was found to be stable only in a solution of trifluorochloromethane at 0°C. At room temperature or above, decomposition occurred to produce hexafluoroacetone and a black tar.

The dihypochlorite was found to be stable only in

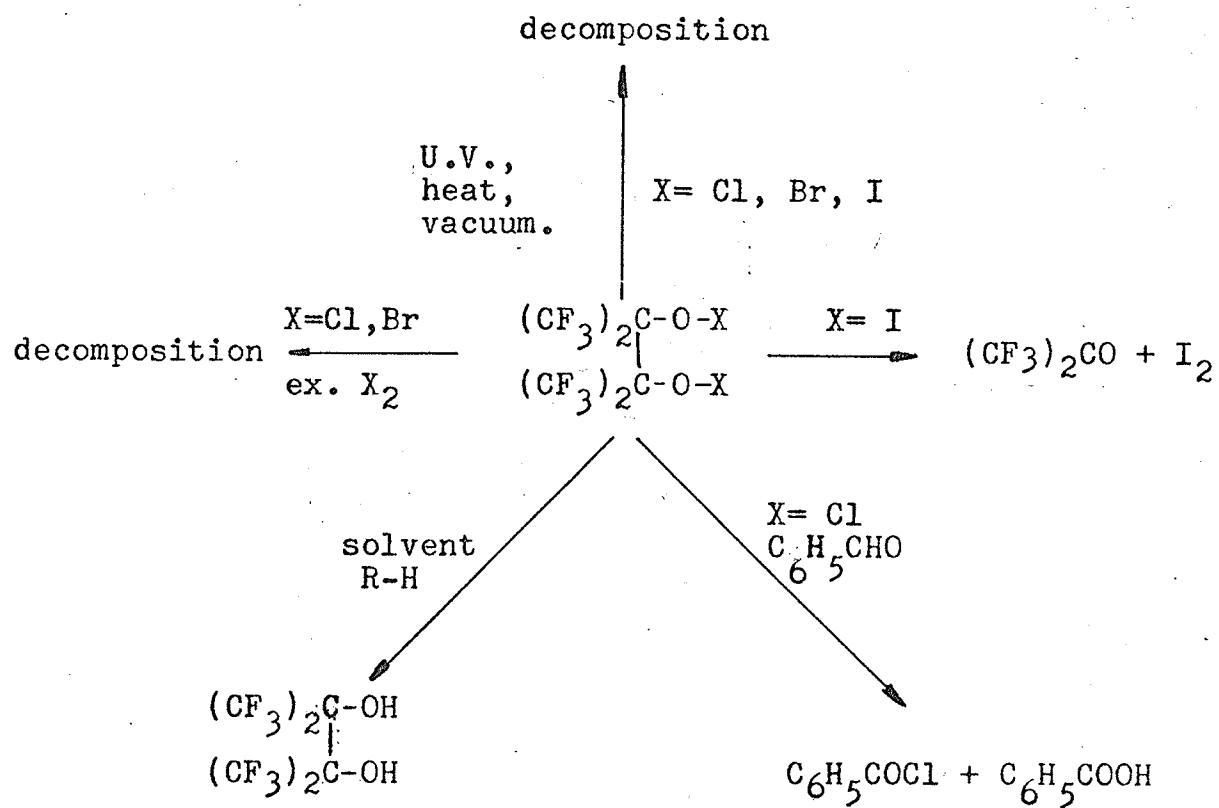
a solution of trifluorochloromethane at below 0°C. Above this temperature decomposition occurred within a few hours.

All three compounds were found to decompose more rapidly when exposed to U.V. light or upon heating. The isolatable compound of decomposition was hexafluoroacetone .

The dihypochlorite and dihypobromite were found to decompose when prepared by a reaction in which excess chlorine or bromine was employed. The reaction was followed by fluorine n.m.r. If approximately stoichiometric quantities of halogen were used in the preparation the fluorine n.m.r. showed a singlet, where as on use of excess halogen the spectrum soon became cluttered with triplets, quartets, and multiplets indicating that decomposition had occurred. The reaction diagram over-leaf clearly shows the decomposition paths of the dihypohalites.

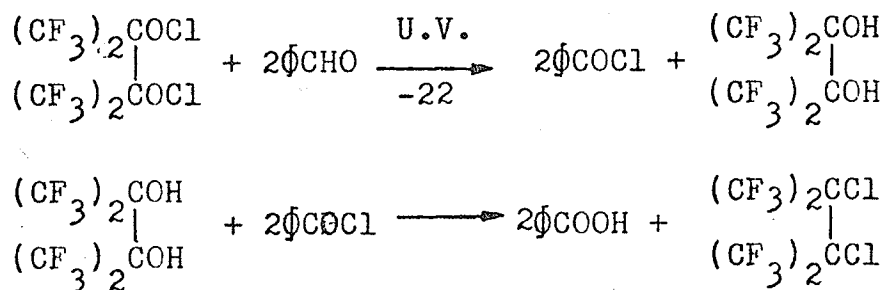
The chemical behaviour of the dihypohalites was also investigated, e.g. if the reactions were carried out in proton containing solvents such as tetrahydrofuran or 1,2-dimethoxyethane, the final product of the reaction was found to be perfluoropinacol. The dihypohalite extracting a proton from the solvent to produce the perfluoropinacol. This reaction with tetrahydrofuran is to be expected from the analogous reaction of t-butyl hypochlorite^{16,18.} in which t-butyl alcohol is formed. These reactions are

FIGURE 2.

Reactivity of Dihypohalites.

extremely well known.

The products of the reaction of the dihypochlorite with benzaldehyde, in carbon tetrachloride, include benzoyl chloride and benzoic acid. Presumably the benzaldehyde reacts with the dihypochlorite to give benzoyl chloride and perfluoropinacol which then reacts to give benzoic acid. The benzoyl chloride and benzoic acid were identified by comparison of their vapour phase chromatographs at various temperatures with those of authentic samples (F.F.A.P. column). The benzoic acid was also identified by the infrared spectroscopy.

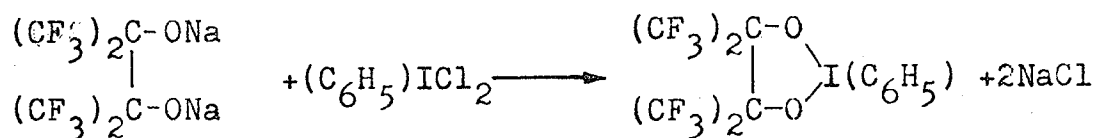
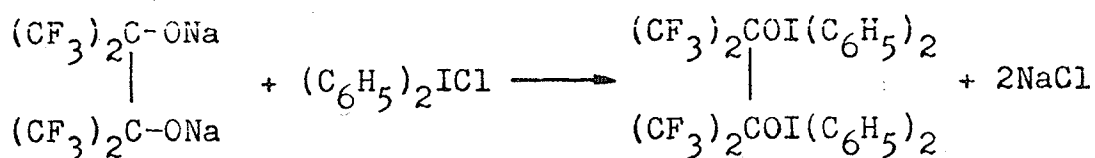


No attempt was made to isolate the other by-products of the reaction.

The reaction is thought to proceed through a free radical mechanism, as with the analogous reaction of *t*-butyl hypochlorite with benzaldehyde.

The reaction of disodium perfluoropinacol with diphenyl sodium chloride and phenyl iodine dichloride was also investigated. The reactions proceeded quite readily

at room temperature, to produce the sodium halide that was positively identified by X ray diffraction analysis. The fluorine n.m.r. spectrum of the product taken directly after the reaction show singlets in the region expected for perfluoropinacol derivatives. The products appear much more reactive than the dihypohalites and decomposed readily on removal of solvent. Decomposition also occurred when an attempt was made to obtain an infrared spectrum. The yields of sodium halide points to the reactions occurring as indicated below. However this is difficult to establish on the data available.



The preparation of these compounds imposes the question, "Why is it possible to prepare perfluoro alkyl dihypohalites where as the analogous hydrocarbon compounds are unknown?" It is quite conceivable that the highly electronegative trifluoromethyl groups play a part in the producing of moderately stable compounds.

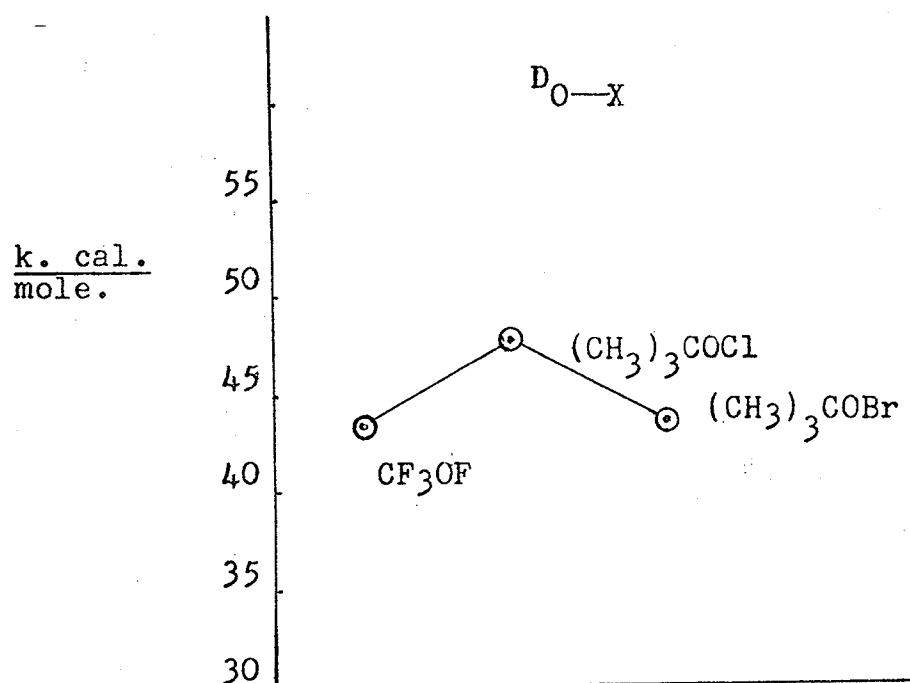
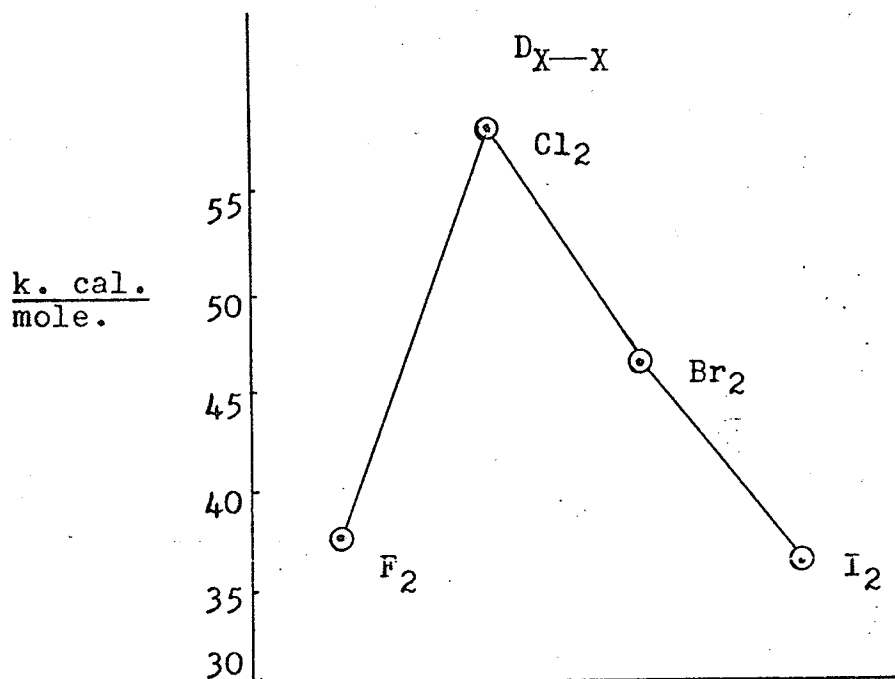
The following explanation, although without experimental evidence, is thought to be reasonable. The

highly electronegative trifluoromethyl groups are capable of reducing repulsion between non-bonded electron pairs on the oxygen and the halogen, thus stabilizing the perfluoro-alkyl hypohalite with respect to unknown hydrocarbon hypohalites. Although there is no direct experimental evidence to support this statement literature reports offer a close analogue: the variation of the bond dissociation energies of the halogens. The low value of fluorine⁴⁷ being attributed to repulsion between non-bonded electron pairs. The repulsion will be greatest in fluorine, where there is a short sigma bond, but will decrease in the remaining halogens where there are longer sigma bonds.

It is possible to compare an oxygen-halogen bond with a halogen-halogen bond. Similarities lie in the fact that oxygen has two non-bonded electron pairs, where as a halogen has three. If this argument is valid for the halogens, it should be valid in the case of hypohalites, if a similar trend was observed. On the page overleaf is a comparison of the bond dissociation energies of the halogens and three hypohalites. It is usually unwise to speculate on the basis of three values, especially since they are for unrelated compounds, however there is a quantitative variation in the same direction as that of the halogens. Thus the repulsion of electrons on oxygen and halogen may help explain the observed variation of

FIGURE 3

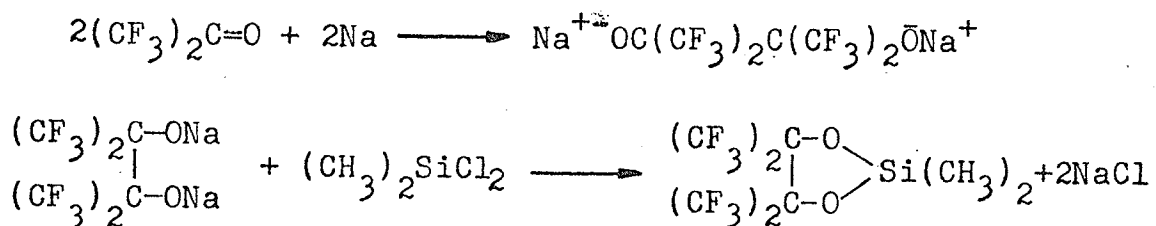
Comparison of Bond Dissociation Energies of Halogens
and Hypohalites



bond dissociation energies of hypohalites. The effect of electronegative substituents would obviously be to reduce the electron repulsion. Thus it may be reasonable to explain the existence of perfluoroalkyl dihypohalites in this manner, especially since the prepared series of perfluoroalkyl vicinal hypohalites appear to have bond dissociation energies that fit this pattern.

PART 2 HEXAFLUOROACETONE AND PHOSPHITE ESTERS.

It is well known³¹ that reductive dimerization of hexafluoroacetone, by reaction with sodium in donor solvent, leads to the ionic disodium perfluoropinacol, a valuable derivative that has already been used in this work to form perfluoropinacol derivatives, namely perfluoropinacol dihypohalites. Cyclic alkoxides of germanium, silicon, tin and boron can be easily prepared by reaction of this reagent with the respective dichloride.



Perfluoropinacol derivatives⁴⁸ have also been prepared by the reaction of perfluoropinacol with a metal sulphate in water/methanol solution.



M=Fe, Al, Mn, Ni.

n=2 or 3



Similar derivatives³² of perfluoropinacol have also

been prepared directly from hexafluoroacetone.



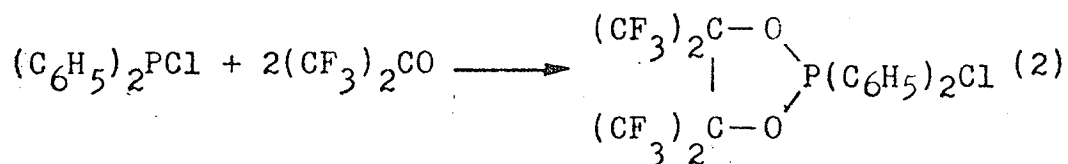
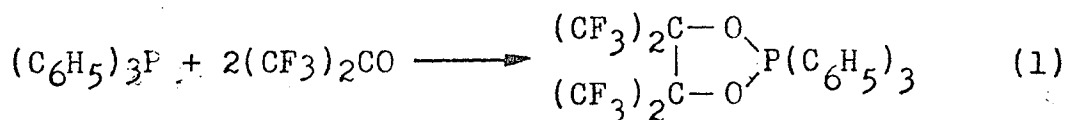
Presented in this thesis are several other such compounds, that were prepared to investigate the possibility of further extending the chemistry of perfluoropinacol.

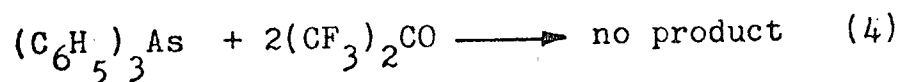
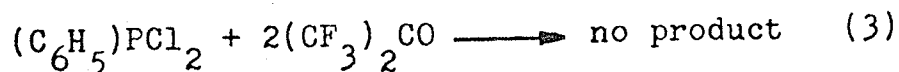
Tributyl phosphite was found to react one hundred percent with a slight stoichiometric excess of hexafluoroacetone.



The product was positively identified by infrared spectroscopy, fluorine n.m.r., proton n.m.r., and chemical analysis.

Triphenyl phosphite has also been reported^{41,46} to react with hexafluoroacetone in a similar manner. It was thought interesting to verify this reaction and to try to extend the reaction to a series of phosphite esters, as well as other compounds of main group V. The reactions below were performed:



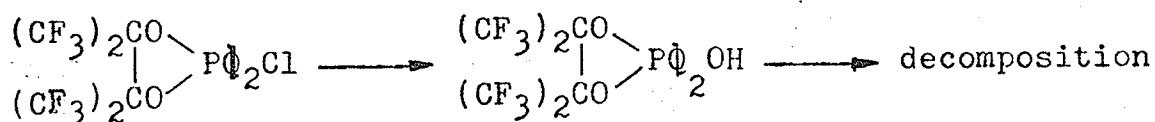


Reaction (1) was found to proceed as reported in the literature to give in this case an 100% yield. The infrared spectrum showed the "cyclic" absorption bands that were first reported by C.J. Willis and A.F. Janzen, to be characteristic of the five membered cyclic perfluoropinacol derivative.

Reaction (2), between hexafluoroacetone and diphenyl chlorophosphite, proceeded to give a product whose infrared spectrum showed the five membered cyclic structure and all the other features expected for this compound. The fluorine n.m.r. spectrum showed a singlet in the region expected for perfluoropinacol derivatives, while the proton n.m.r. showed the presence of the $\phi_2\text{ClP}$ grouping. Chemical analysis of the sample however did not give the expected results. The analysis actually corresponded to a solution of product (66.6%) in starting material ($\phi_2\text{PCl}$ 33.3%). Attempts to vacuum distill the product had proved fruitless since the product was quite involatile and decomposed on application of mild heat. There is no doubt about the existence of the product however, since spectroscopic evidence is undisputable.

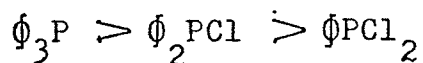
The product was found to be quite sensitive to air or

moisture oxidation. If the infrared optics were left exposed to moist air a gradual solidification of the product would occur. An infrared spectrum taken after a short exposure to moist air showed the loss of the P-Cl absorption peak and the appearance of an hydroxyl absorption peak. The same spectrum after a long exposure to moist air showed a loss of the five membered cyclic structure and decomposition of the product.



It may thus be possible to postulate the above mode of decomposition.

The reaction of hexafluoroacetone with phenyl dichloro phosphite did not yield a product. The order of reactivity along the studied series of compounds is thus as below:



It would thus appear that replacing a phenyl group by a more electronegative group decreases the basicity of the lone pair of electrons on the phosphorus atom which in turn reduces the ability of the phosphorus atom to react in this manner.

The reaction between triphenyl arsine and hexafluoroacetone was unsuccessful under the applied reaction conditions.

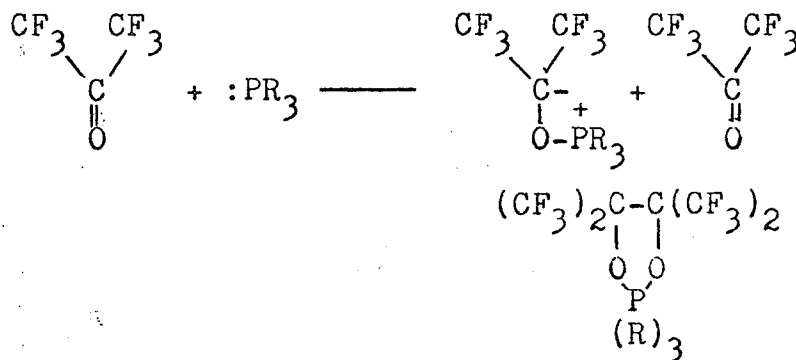
This may possibly be due to an electronegativity effect, arsenic (2.20 A/R) in the trivalent state having a higher electronegativity than phosphorus (2.06 A/R). If this is the case there is no reason to think that similar reactions should not be successful with antimony or bismuth containing compounds.

In order to explain the reactions of hexafluoroacetone with phosphites, the below mechanism have been considered:

1. Nucleophilic attack at a carbonyl oxygen.
2. Nucleophilic attack at a carbonyl carbon.

1. Nucleophilic Attack at a Carbonyl Oxygen.

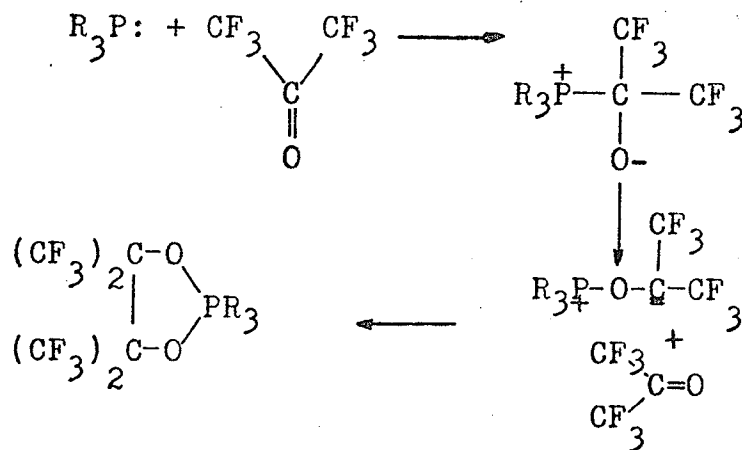
This mode of attack appears possible because the carbonyl function is surrounded by groups (trifluoromethyl) that are capable of stabilizing a negative charge at the carbonyl group.



The initial product of this reaction can attack another molecule of hexafluoroacetone to give the required product. This mode of reaction seems unlikely because it would

involve the polarization of one carbonyl group to be in one direction $\overset{\ominus}{\text{C}}=\overset{\oplus}{\text{O}}$ while in the second molecule the carbonyl would be polarized in the opposite direction $\overset{\oplus}{\text{C}}=\overset{\ominus}{\text{O}}$. However such a mechanism has been postulated by P. Ramirez⁴¹ who prepared similar adducts by the reaction of various phosphites with hexafluoroacetone. Ramirez reports that his data shows conclusively that the "first observable products of the reaction are derived from the intermediates that were formed by an attack by the phosphorous on carbonyl carbon". However he also reports that the 1:1 adducts are too reactive to be detected.

2. Nucleophilic Attack at a Carbonyl Carbon.



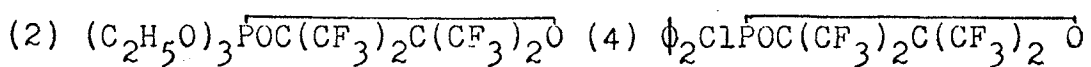
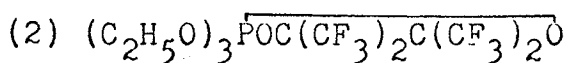
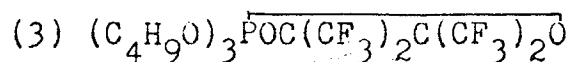
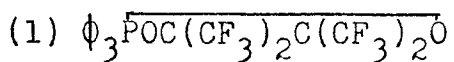
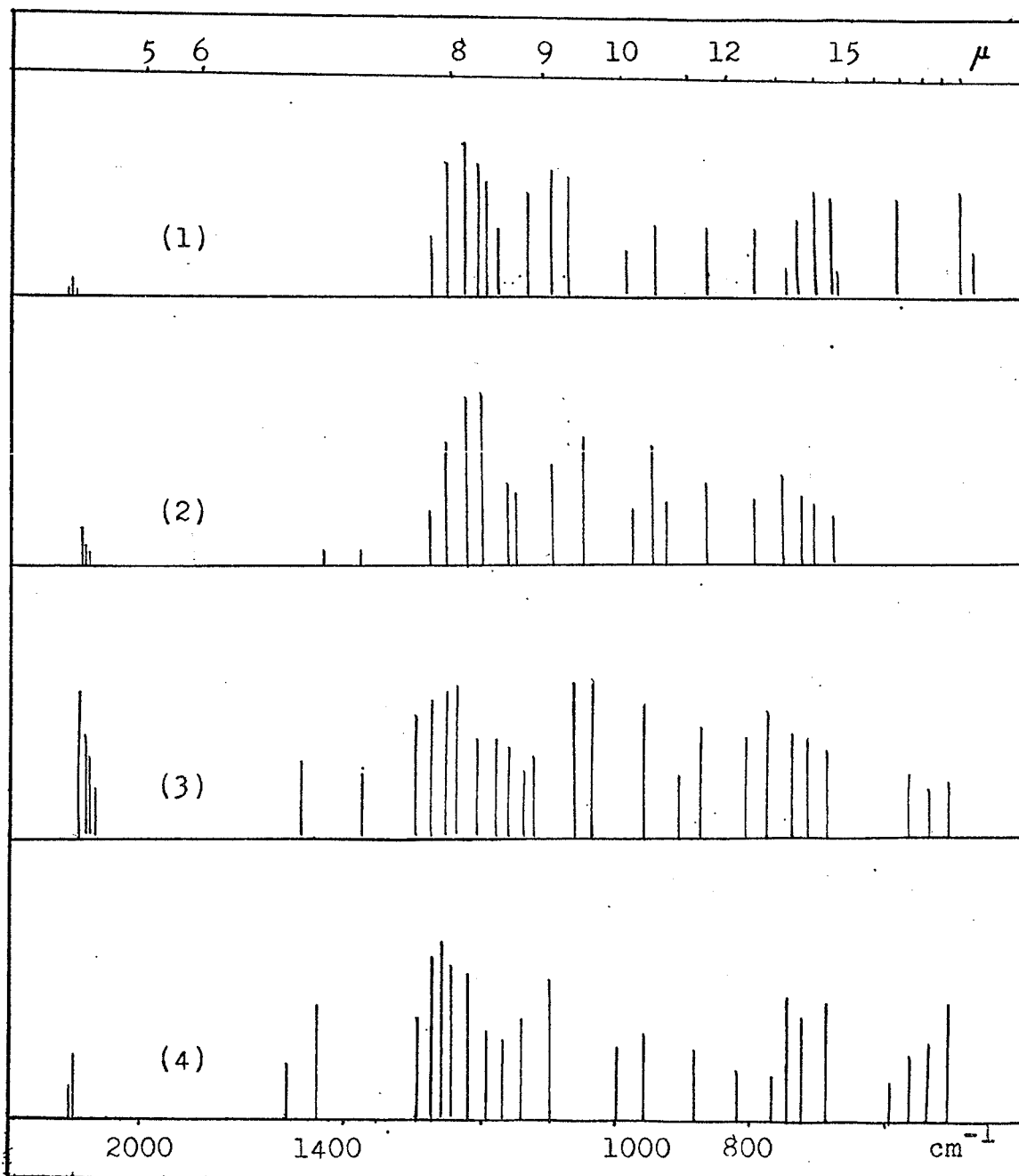
The initial product of the reaction rearranges to give another intermediate that then attacks another carbonyl group to give the required product. This mechanism does not require the carbonyl group to be polarized in two

different directions. However it should be mentioned that in the case of the reaction of aliphatic monoaldehydes with trialkyl phosphites⁴⁹, where the phosphorus did attack the carbonyl carbon, a rearrangement of the 1:1 adduct did not take place.

The infrared spectral data obtained on the prepared compounds is given overleaf.

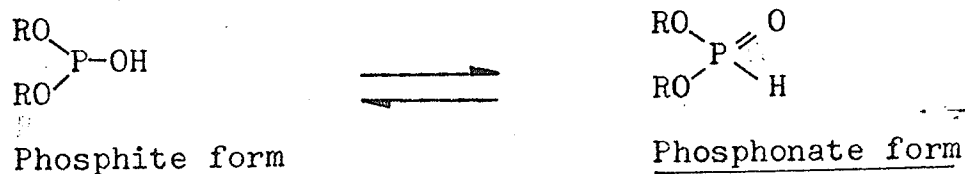
FIGURE 4

Infrared Spectra of the Product of the Reactions of
Hexafluoroacetone with Trialkyl Phosphites



PART 3 HEXAFLUOROACETONE AND DIALKYL PHOSPHONATES

It is well established that in general dialkylphosphonates have little of the nucleophilic reactivity of trialkyl phosphites. This has been established to be a consequence of the two esters having fundamentally different structures. The dialkyl ester can exist in two tautomeric forms.



The dialkyl esters have been shown to exist almost exclusively in the phosphonate form. This preference being attributed to the stability of the phosphoryl bond. Thus in general these compounds, have not been found to act as nucleophiles since they do not have a non bonding electron pair.

Sufficiently strong bases are capable of converting dialkyl phosphonates into anions, which are nucleophiles, usually at the phosphorus atom. The neutral compounds may however show nucleophilic reactivity with strong electrophiles. The reaction in this case obviously occurring exclusively through the trivalent form.

Numerous⁵⁰ spectroscopic investigations failed to produce evidence for the existence of the trivalent form.

Evidence has been produced to show that this is because it is not present in a high enough concentration to be detected spectroscopically. Acceptable evidence for the tautomerism comes from kinetic work.

Dialkyl phosphites, in the presence of catalytic amounts of strong base, add readily to the carbonyl groups of simple aldehydes and ketones to give 1-hydroxyalkyl - 1-phosphonate esters⁵¹.



The active species presumably being the anion produced by the strong base.

Chloral⁵², a strong electrophilic carbonyl compound, reacts with the neutral species even at room room temperature. The reaction presumably being with the phosphite form.

Dialkyl phosphonates⁵³ that contain chlorine in the β - position of the alkyl group, for example $(\text{Cl}_3\text{CC}(\text{CH}_3)_2\text{O})_2\text{P}(\text{O})\text{H}$, reacts in the absence of catalysts even with simple carbonyl compounds. The authors⁵³ suggest that this may be a reaction of the phosphite form which could be present in unusually high proportions in these compounds.

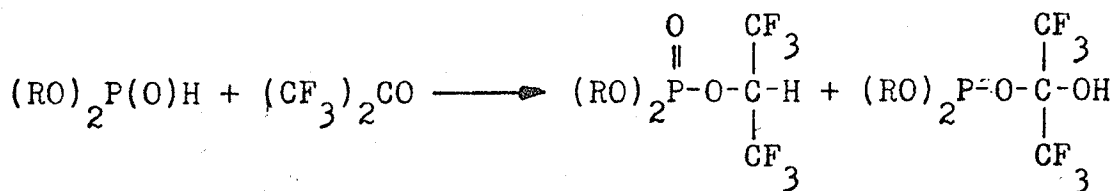
It is thus of an interest to react dialkyl phosphonates with hexafluoroacetone, a very electrophilic carbonyl compound. Investigations showed such reactions to occur

to give two products, both of which are highly fluorinated, stable alkoxy phosphorus compounds. In all cases the reaction was allowed to proceed at -78° and was complete after shaking for 5 days at room temperature. The compounds resulting from the addition reactions of hexafluoroacetone with dimethyl, diethyl and dibutyl phosphonates are summarised overleaf. The quoted yields are based on the relative areas of the fluorine n.m.r. peaks of the respective compounds taken on samples of the initial reaction mixture directly after preparation.

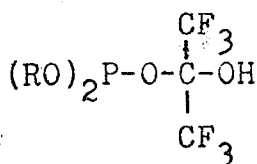
TABLE 2

Products of the Reaction of Hexafluoroacetone with
Dialkyl Phosphonates

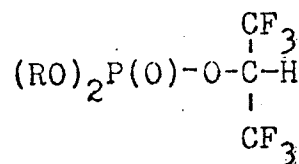
<u>Dialkyl</u> <u>Phosphonate</u>	<u>Reaction Products</u>	<u>Yields</u> %
$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{H}$	$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{O}(\text{CF}_3)_2\text{H}$	95
	$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{O}(\text{CF}_3)_2\text{OH}$	5
$(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{H}$	$(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{O}(\text{CF}_3)_2\text{H}$	88
	$(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{O}(\text{CF}_3)_2\text{OH}$	12
$(\text{C}_4\text{H}_9\text{O})_2\text{P}(\text{O})\text{H}$	$(\text{C}_4\text{H}_9\text{O})_2\text{P}(\text{O})\text{O}(\text{CF}_3)_2\text{H}$	5
	$(\text{C}_4\text{H}_9\text{O})_2\text{P}(\text{O})\text{O}(\text{CF}_3)_2\text{OH}$	95



The prepared compounds were characterised by infrared spectroscopy, fluorine and proton nuclear magnetic resonance spectra and chemical analysis. The infrared data of these compounds are shown in figure 5. Figure 6 shows clearly the difference in the proton n.m.r. spectrum of the two structurally different compounds. Although the given spectra are of two different compounds their characteristics apply to isomers of the same compound. The principal characteristics of the spectra is a singlet assigned to the hydroxyl group of class 1 compound and the complicated multiplet assigned to the proton of class 2 compound.



Class 1.

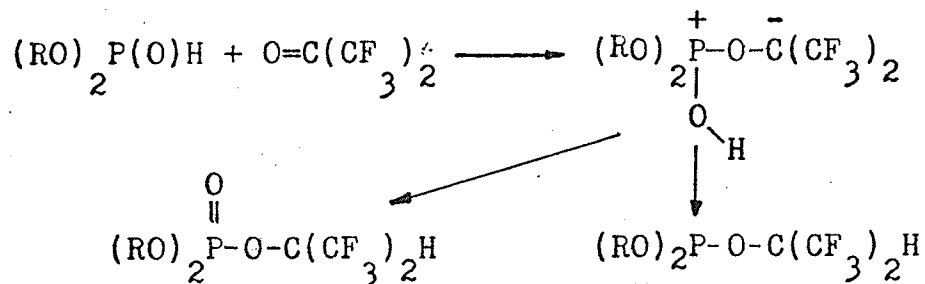


Class 2.

In order to explain the observed reactions the following mechanisms have been considered:

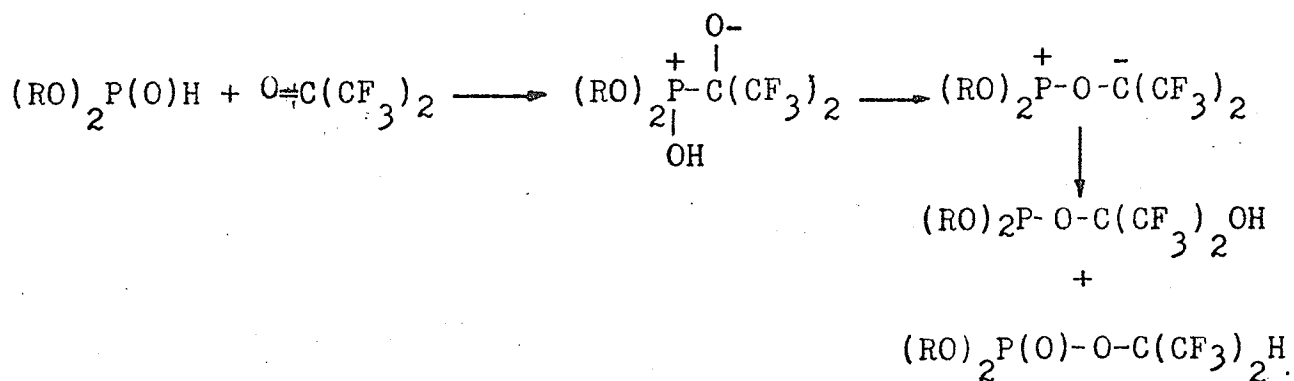
1. Nucleophilic attack at the carbonyl oxygen.
2. Nucleophilic attack at the carbonyl carbon.
3. A concerted addition mechanism.

1. Nucleophilic attack at the carbonyl oxygen.



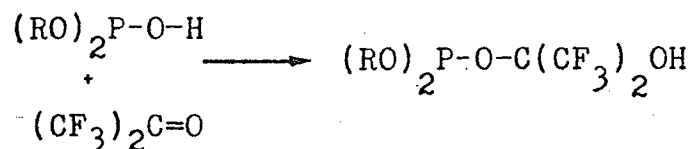
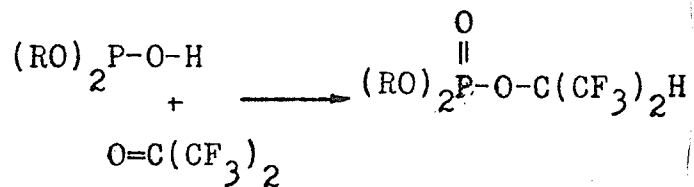
Although the above mechanism is quite feasible it is difficult to explain why the size of the (RO) group should effect the percentage yield of a particular isomer, i.e. as the (RO) group increases in size the trivalent phosphorus compound becomes the major reaction product.

2. Nucleophilic attack at the carbonyl carbon.



The initial nucleophilic attack at the carbonyl carbon is followed by a rearrangement process to yield an intermediate which further rearranges to give the reaction products.

3. A concerted reaction mechanism.

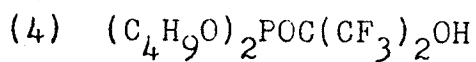
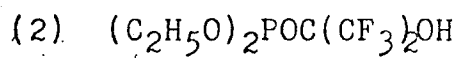
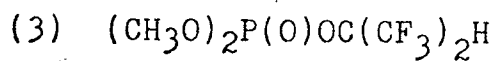
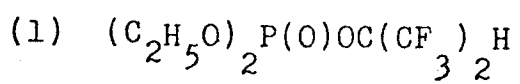
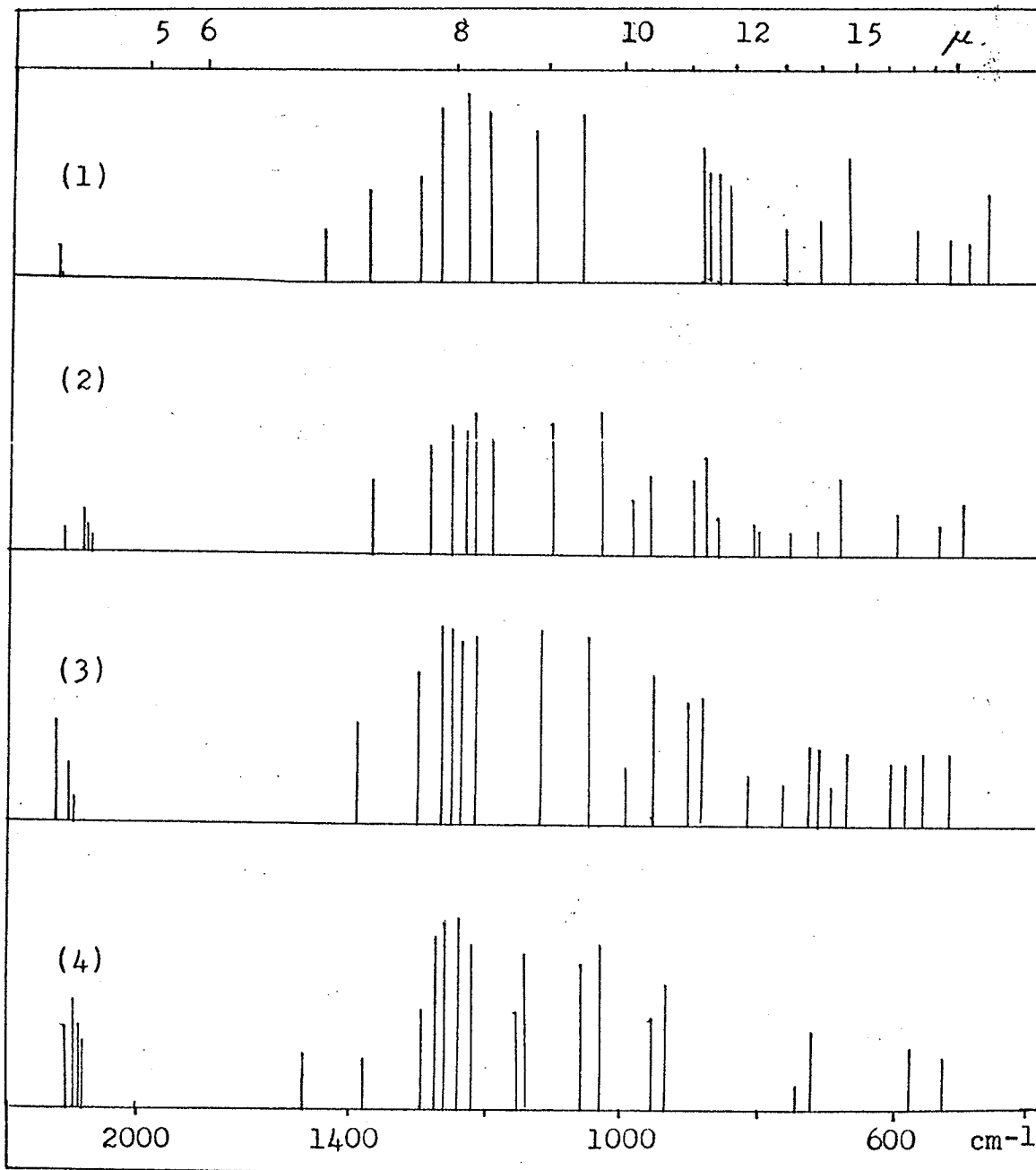


The above concerted addition mechanism, where hexafluoroacetone reacts with the phosphite form, appears quite feasible. In one case addition takes place across the phosphorus-oxygen bond while in the other case, addition occurs across the oxygen-hydrogen bond. Such addition reactions are numerous in organometallic chemistry but unfortunately offer no explanation as to why one isomer should take preference over the other.

Perhaps more insight into these reactions of hexafluoroacetone with dialkyl phosphonates can be obtained by carrying out reactions between the dialkyl phosphonates and chloro-fluoro ketones.

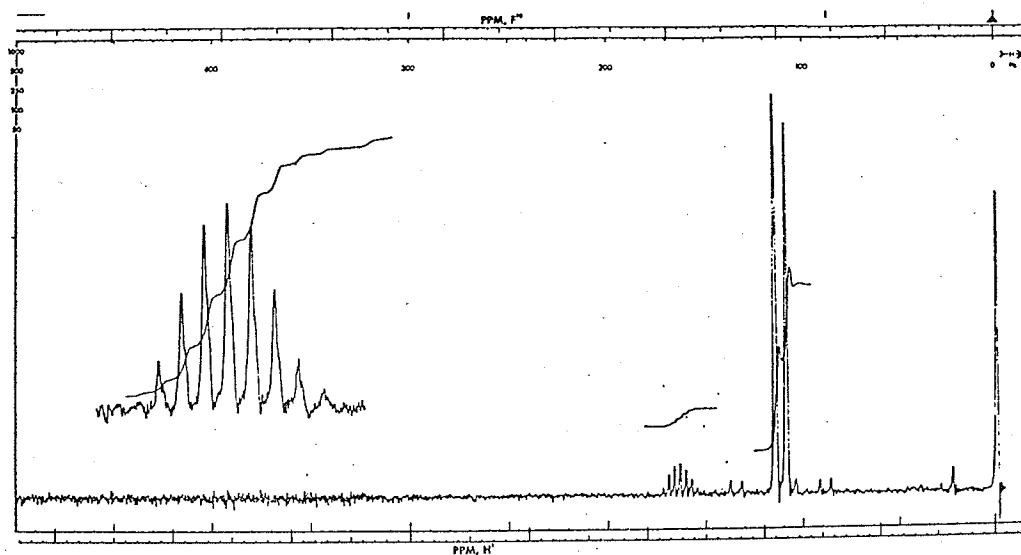
FIGURE 5

Infrared Spectra of the Product of Reaction of
Hexafluoroacetone with Dialkyl Phosphonates

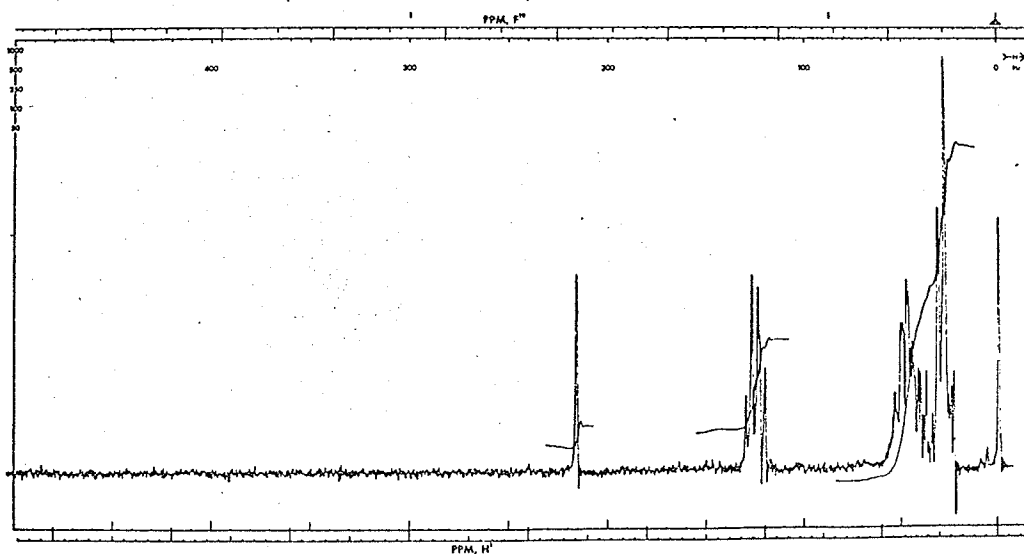


-- FIGURE 6

Proton N.M.R. Spectrum of $(\text{CH}_3)_2\text{P}(\text{O})\text{OC}(\text{CF}_3)_2\text{H}$



Proton N.M.R. Spectrum of $(\text{C}_4\text{H}_9)_2\text{POC}(\text{CF}_3)_2\text{OH}$



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