ORGANOMETALLIC DERIVATIVES OF 1,1,1,3,3,3-HEXAFLUOROISOPROPYLIDENIMINE AND REACTIONS WITH XENON DIFLUORIDE

by

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"To all of these lauded wise men of the academic chairs, wisdom meant sleep without dreams:they knew no better meaning of life."

Nietzsche: Also Sprach Zarathustra

and for those still biased:

"Disciplining himself in the cause,he has attained the result and abides in the Samadhi of Emptiness for ever so many aeons"

Huxley: The Devils of Loudun

ABSTRACT

The reactions of 1,1,1,3,3,3-hexafluoroisopropylidenimine with organometallic hydrides of group V and 1,1,1,3,3,3-hexafluoroisopropylideniminolithium with organometallic halides of groups IV and VI are described.

The reactions of the products from these syntheses with xenon difluoride with the aim of obtaining a compound which contains a xenon-nitrogen bond are also described.

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks to Dr.A.F.Janzen for his advice,suggestions and patience during the course of this work. Thanks are also due to Mr.Marv Arneson,who ran the mass spectra,and messrs.J.A.Gibson and D.G.Ibbott,whose helpful hints will never be forgotten. Similar sentiments are due to Dr.O.C.Vaidya,whose croquet tactics are also a source of wonder.

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GENERAL INTRODUCTION

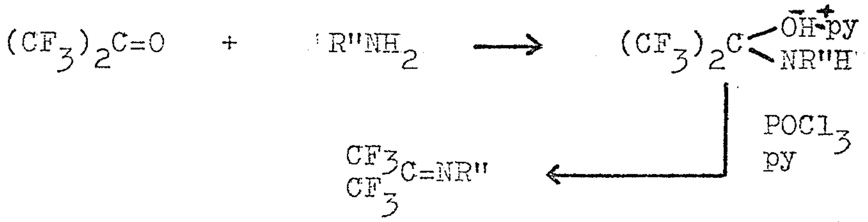
Perfluoroalkyl compounds,that is,compounds in which all the hydrogen atoms have been replaced by fluorine atoms, were first 'synthesized' in 1886 when Moissan burnt carbon in fluorine to produce a mixture of carbon fluorides.[1]

However,it was not until after 1940 that the systematic study of perfluoroalkyl compounds was begun,utilising the synthetic methods by which it is possible to achieve smooth fluorination of the starting materials to yield the desired products. These methods have been the subject of several review articles.[2-6]

During the last fifteen years a large amount of research has been carried out in the area of perfluoroalkyl derivatives of the metals and metalloids. These again have been reviewed in several comprehensive articles; derivatives of transition metals[7-10],main group metals and metalloids[7-9],and also non-metals[8,9] have been covered.

One of the earliest perfluoroalkyl compounds to be synthesized was hexafluoroacetone,by Fukuhara and Bigelow in 1941.[11] This molecule has been the subject of a great deal of research, due to its reactivity,and an excellent review of its properties has been presented.[12] Due to the presence of the highly electronegative trifluoromethyl groups the carbonyl group is electron deficient and hence very resistant to electrophilic attack. Such normally electrophilic reagents as hydrogen fluoride are forced to act as nucleophiles in reacting with hexafluoroacetone.[13]

Compounds containing active hydrogen atoms tend to add exothermically to hexafluoroacetone yielding adducts which are moderately stable at room temperature. Reactions with alcohols,[14,15] thiols,[15] hydrogen fluoride,[13] hydrogen cyanide,[16] silanols,[17] silanes,[18] olefins [19] and acetylenes [19] have been described. Of particular interest to the present work is the reaction of ammonia and amines with hexafluoroacetone to produce 2-aminohexafluoropropan-2-ols.[20] If this reaction is carried out in cold pyridine solution the alcohol salt is formed which reacts with dehydrating agents to produce imines in high yield.[21]



$$(CF_3)_2C=O \;+\; R''NH_2 \longrightarrow (CF_3)_2C\begin{cases}\overset{-}{O}H\overset{+}{-}py \\ NR''H\end{cases} \xrightarrow[py]{POCl_3} \begin{matrix}CF_3\\CF_3\end{matrix}C=NR''$$

The parent imine, $(CF_3)_2C=NH$, 1,1,1,3,3,3-Hexafluoroisopropylidenimine[22], has recently become commercially available[23] and studies of its reactions and derivatives are increasing.

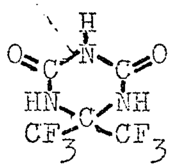
In an analogous fashion to hexafluoroacetone, due to the proximate trifluoromethyl groups the C=N bond is electron deficient, thus nucleophilic attack at the carbon atom of this group is favoured. Concomitant with this the hydrogen atom is acidic, again as a result of the inductive effect of the highly fluorinated group. Both of these facts indicate the reactivity and synthetic potential of the molecule. The organic reactions were investigated earliest[21].

Hexafluoroisopropylidenimine reacts with active-hydrogen-containing compounds to form adducts:

$$(CF_3)_2C{=}NH \quad + \quad RH \longrightarrow (CF_3)_2C{<}^{R}_{NH_2}$$

Middleton and Krespan[21] prepared the adducts with ammonia, isocyanic acid, piperazine, ethylene glycol, hydrazine, methanol, hydrazoic acid, hydrogen cyanide and hydrogen fluoride. These adducts show an unusual stability, the gem-diamine $(CF_3)_2C(NH_2)_2$ boiling at 91° without decomposition.

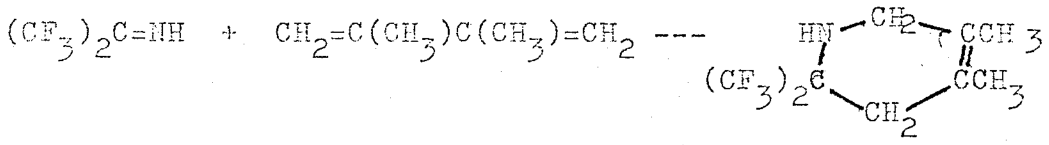
Due to the almost neutral character, hence low nucleophilicity, of the amine radical in these compounds, even the isocyanate derivative can be isolated with a free NCO group. This compound reacts exothermically with water to yield the substituted urea, and also over a long period of time forms the triazine.



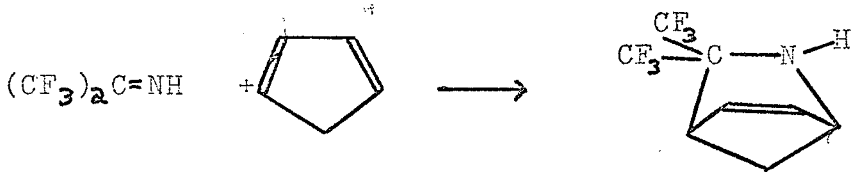
triazine

This reaction occurs due to the small equilibrium concentration of isocyanic acid present. This fact indicates that as with the N-phenyl analogues,[20] the formation of adducts with active hydrogen compounds by the imine is an equilibrium process with the position of equilibrium lying far over towards the adduct.

Hexafluoroisopropylidenimine undergoes Diels-Alder addition with dienes as illustrated by the reaction with 2,3-dimethylbutadiene to produce 2,2-bis(trifluoromethyl)-4,5-dimethyl-1,3,6-trihydropyridine:



Similarly, cyclopentadiene reacts to give 3,3-bis(trifluoromethyl)-2-azabicyclo(2.2.1)hept-5-ene:[21]



As would be expected, due to the electrophilic character of the imine, electrophiles react with difficulty. Reaction of ketene can be achieved by employing boron trifluoride as catalyst however, producing N-acetylhexafluoroisopropylidenimine, $(CF_3)_2C=NC(O)CH_3$.

The acidic proton of the imine can be substituted by lithium to form the iminelithium salt which is useful in introducing the intact $(CF_3)_2C=N-$ moiety into organometallic compounds. This salt is easily reacted with bromine to form the N-bromo derivative, which photolytically couples producing hexafluoroacetone azine, $(CF_3)_2C=NN=C(CF_3)_2$.*[21]

The N-fluoro derivative of the imine has been prepared and studied, together with its analogues, by Knunyants et al.[24] in similar reactions to those described above.

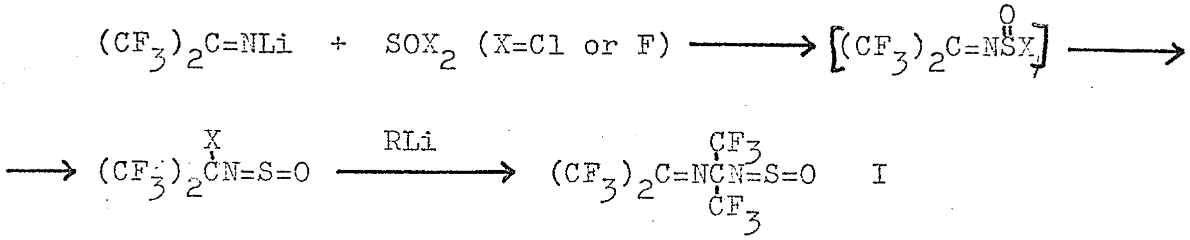
The reaction of sulphur tetrafluoride with hexafluoroisopropylidenimine has been studied by Glemser and Halasz.[25] The reaction is catalysed by caesium fluoride, which acts as a hydrogen fluoride acceptor, at 20° and gives a good yield (83%) of N-heptafluoroisopropyldifluorosulphurimide.

$$(CF_3)_2C=NH \quad + \quad SF_4 \xrightarrow[20^o]{CsF} (CF_3)_2C(F)N=SF_2 \quad + \quad HF$$

Similarly, at 100°, thionyl fluoride reacts to form N-heptafluoroisopropylthionylimine.[26]

$$\mathrm{(CF_3)_2C{=}NH} \quad + \quad \mathrm{SOF_2} \xrightarrow[100^{\circ}]{\mathrm{CsF}} \mathrm{(CF_3)_2C(F)N{=}S{=}O} \quad + \quad \mathrm{HF}$$

Shreeve et al.[27] found that with hexafluoroisopropylidenyllithium in reaction with thionyl halides a halide ion migration apparently occurs and the simple disubstituted thionyl compound is not obtained, instead the product is N-(N-thionyl-2-aminohexafluoroisopropyl)hexafluoroisopropylidenimine:(I)



$$\mathrm{(CF_3)_2C{=}NLi} \quad + \quad \mathrm{SOX_2}\ \mathrm{(X{=}Cl\ or\ F)} \longrightarrow \left[\mathrm{(CF_3)_2C{=}N\overset{O}{\overset{\|}{S}}X}\right] \longrightarrow$$

$$\longrightarrow \mathrm{(CF_3)_2\overset{X}{C}N{=}S{=}O} \xrightarrow{\mathrm{RLi}} \mathrm{(CF_3)_2C{=}N\underset{CF_3}{\overset{CF_3}{C}}N{=}S{=}O} \quad \mathrm{I}$$

This mechanism is supported in the same work by the reaction with $\mathrm{COF_2}$,where,as well as the carbon analogue of I,the proposed intermediate $\mathrm{(CF_3)_2C(F)N{=}C{=}O}$ is also observed.

The interaction of the imine with boron trihalides has also been investigated.Boron trifluoride is such a strong Lewis acid that even the very weakly basic imine forms the adduct $\mathrm{(CF_3)_2C{=}NH.BF_3}$,[21,28] as shown by spectral properties. However,boron trichloride and tribromide add across the C=N bond forming aminoboranes,[28] which are thermally stable.

$$\mathrm{(CF_3)_2C{=}NH} \quad + \quad \mathrm{BX_3} \longrightarrow \mathrm{(CF_3)_2CXNHBX_2}$$

These compounds have been suggested as useful precursors for heterocyclic or polyatomic boron-nitrogen-carbon systems as a result of the reactive boron and carbon sites. Niedenzu et al.[29]

have reported borane derivatives of the imine with the C=N bond intact. This is achieved by reacting a monohalogenoborane with the imine at 0° and then dehydrohalogenation of the resulting adduct with a second molecule of imine.

$$(C_6H_5)_2BBr \quad + \quad (CF_3)_2C{=}NH \longrightarrow (CF_3)_2CBrNHB(C_6H_5)_2 \quad (II)$$

$$II \quad + \quad (CF_3)_2C{=}NH \longrightarrow \underset{III}{(CF_3)_2C{=}NB(C_6H_5)_2} \quad + \quad (CF_3)_2CBrNH_2$$

Cryoscopic measurements show III to be a monomer in benzene,and the material can be distilled under vacuum. The product reacts explosively on hydrolysis.

The N-chloro derivative of the imine is the product of the reaction of the imine with chlorine monofluoride.[30] Reaction is facilitated by the presence of caesium fluoride acting as hydrogen fluoride acceptor.

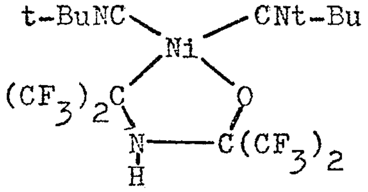
$$(CF_3)_2C{=}NH \quad + \quad ClF \xrightarrow{CsF} (CF_3)_2C{=}NCl$$

Hexafluoroacetone forms interesting coordination compounds with nickel and platinum in which the carbonyl group is coordinated sideways to the metal,these compounds being the first of this type to be prepared.[31]

$$(Ph_3P)_2MC_2H_4 \xrightarrow[Et_2O]{(CF_3)_2CO} (Ph_3P)_2M(CF_3)_2CO$$

This method of coordination has been proved by the crystal structure determination carried out on the nickel compound.[32] Similar complexes with hexafluoroisopropylidenimine have not as yet been reported,but the imine does undergo an interesting insertion reaction with $(t\text{-}BuNC)_2Ni(CF_3)_2CO$ to produce the compound

$(t\text{-}BuNC)_2Ni(CF_3)_2CNH(CF_3)_2CO$.[33] This molecule has been showm to contain a five-membered ring, viz:[32]



proving that the imine molecule has inserted at the Ni-C bond of $(t\text{-}BuNC)_2Ni(CF_3)_2CO$. To explain this Stone[34] has suggested a mechanism involving a six-coordinate intermediate in which both fluorocarbon molecules are bonded to the nickel, both in the side-on configuration.

Preliminary photochemical experiments[35,36] with the imine indicated that unlike hexafluoroacetone, which decomposes via $CF_3^{\cdot}$ radicals to CO and C_2F_6 [37], the imine is photochemically stable. In fact, it has been suggested [35] for use as a UV filter to isolate the 185nm. line from the 254nm. line in mercury arc lamps. Later experiments investigating the reaction of $CF_3^{\cdot}$ radicals with the imine [38] have shown, by comparison with the results obtained earlier,[36] that on photolysis, the imine does produce a low quantum yield of $CF_3^{\cdot}$ radicals, which undergo fast additon to the C=N bond to produce $(CF_3)_3CN(CF_3)_2H$ rather than combine forming C_2F_6.

Detailed spectral studies have been carried out on the imine; the infra-red and Raman spectra [39], and an electron-diffraction study[40] have been published. The results, combined with the fluorine and proton NMR spectra[21,41], indicate that the C=NH group is angular (110°) with strong inter- and possibly intra-molecular hydrogen bonding, even in the vapour state.

Hexafluoroisopropylideniminolithium has been used to introduce the $(CF_3)_2C{=}N\text{-}$ ligand into several organometallic compounds of transition[42] (Ti and Pt group) and also main group elements[27,43], by the straightforward reaction with halides.

$$R_yMX_z + zLiN{=}C(CF_3)_2 \longrightarrow R_yM[N{=}C(CF_3)_2]_z + zLiX$$

Compounds with BCl_3, $(CH_3)_3SiCl$, PCl_3, $AsCl_3$, SCl_2, CF_3SCl, PF_2Cl, PF_3 and CF_3SOF have been prepared.[27]

Shreeve and Swindell [44] have studied the reaction of the lithium salt with sulphur tetrafluoride, and a number of products were isolated due to extensive rearrangements, viz: $(CF_3)_2CFN{=}SF_2$, $(CF_3)_2CFN{=}S{=}NCF(CF_3)_2$, $(CF_3)_2CFN{=}S{=}NC(CF_3)_2N{=}C(CF_3)_2$, $(CF_3)_2C{=}NC(CF_3)_2N{=}S{=}NC(CF_3)_2N{=}C(CF_3)_2$, and $(CF_3)_2C{=}NC(CF_3)_2N{=}C(CF_3)_2$.

The purpose of this thesis is to describe further investigations of the chemistry of 1,1,1,3,3,3-hexafluoroisopropylidenimine in reactions with compounds of elements in groups IV, V, VI and VIII.

Organometallic compounds of group IV containing metal-nitrogen bonds are well known, and in the past ten years a large number of papers dealing with alkylamides of silicon and tin, and to a lesser extent, germanium and lead, have appeared. Several reviews of this type of compound [45-53,61], and a number of comprehensive books of the organometallic chemistry of germanium,[54,55,59] tin[54,56,57,58] and lead[54,60,61] have been published.

However, no perfluoroalkylamine derivatives of these elements have been reported to date, and the present work in part describes the preparation of such derivatives $R_3MN{=}C(CF_3)_2$ with a view to observing any marked difference in reactive properties of the M-N bond as compared to the non-fluorinated derivatives. These compounds were also prepared for use as substrates in reactions with xenon difluoride as also described herein.

Perfluoroalkyl derivatives of tellurium have,with the sole exception of bis(trifluoromethyl)ditelluride[62],been synthesized only since 1968. The most recent reviews [63,64] and book[65] covering organotellurium chemistry only cursorily mention,if at all, such derivatives. The derivatives prepared to date are $(C_6F_5)_4Te$[66], $(C_6F_5)_3TeCl$[67],$(C_6F_5)TeCl_3$[66]$(C_6F_5)_2Te_2$[67],and $[(CF_3)_2NO]_4Te$[68], the latter being bonded through the oxygen atom of the ligand. Thus,attempts to prepare perfluoroimino- derivatives of tellurium(IV) were made during the course of this work.

Although noble-gas chemistry had been speculated on during the early part of the twentieth century[69,-72] and attempts at compound formation made [73,74],including Yost and Kaye's near miss[75],the earnest practical study of this branch only starts with Bartlett's famous preparation of $Xe(PtF_6)_n$ in 1962.[76] Over the succeeding ten years a large amount of research has been directed to the chemistry of xenon in the main,as this is the most easily accessible element and forms the most stable compounds.

Until recently all the compounds of xenon which had been synthesized and characterised contained xenon bonded either to fluorine or oxygen,and it appeared that only these two most electronegative elements would form covalent bonds with this obstinate element. A number of reviews of xenon chemistry have appeared at regular intervals.[77-86]

Xenon difluoride forms a number of adducts with Lewis acids.Compounds have been reported with the pentafluorides of vanadium[87],Ta[88,89](Nb,Ir,Ru,Os,Pt)[89,90],Mn[91,92],P[93],As[94],Sb[95,88]and iodine[96-99]. Bartlett et al.,following up their postulation that the XeF^+ ion is the oxidative species in reactions of xenon difluoride as an oxidative fluorinator[100], showed that the adducts $2XeF_2.MF_5$, $XeF_2.MF_5$, and $XeF_2.2MF_5$, could be formulated as the salts $(Xe_2F_3)^+(MF_6)^-$, $(XeF)^+(MF_5)^-$, $(XeF)^+(M_2F_{11})^-$,[90] respectively, on the basis of X-ray, Raman and infra-red results.

An interesting series of xenon esters of strong oxy-acids has been prepared, with the ligands: CF_3COO-[101], FO_2SO-[102], O_3ClO-[102], and F_5TeO-[103-106]. Crystal structures of $FXeOSO_2F$ [107] and the other fluorosulphate and the perchlorates [108] have been determined.

Attempts to isolate compounds of xenon with the element bonded to atoms other than fluorine or oxygen have been made. Perlow et al.[109-111] have provided evidence for the transient formation of $XeCl_4$, $XeCl_2$ and $XeBr_2$ in Mössbauer studies by the β-decay of ^{129}I to ^{129}Xe in the ions ICl_4^-, ICl_2^- and IBr_2^-, respectively. Meinert[112] presented mass spectral data and Nelson and Pimentel[113] obtained an IR spectrum at 20°K to establish the formation of $XeCl_2$ from Xe/Cl_2 mixtures excited by a microwave discharge.

A novel compound containing a xenon-boron bond has been prepared by Goetschel and Loos[114] and appears simultaneously with a theoretical paper on noble-gas-boron compounds.[115] The reaction of xenon with dioxygenyl tetrafluoroborate at about 173°K yields a compound which the authors, on the basis of vibrational spectral data, assign the structure $FXeBF_2$.

The possibility of the formation of xenon-nitrogen bonds has been considered also; Herman and Herman [116] have measured the visible spectrum of the metastable XeN moiety, produced in a continuous electic dischage in a mixture of Xe and N_2, but no stable (i.e. characterisible by standard spectral techniques) compounds containing a Xe-N bond have been reported. Kaul and Fuchs[117] and Liebman and Allen[118,119] have carried out theoretical investigations on the stability of noble gas compounds, in particular of the lighter members of the group, and suggest that XeN^+ salts should be stable enough to be isolated, if synthesized.

The remaining part of the work of this thesis is hence concerned with attempts to synthesize compounds containing a Xe-N (or FXe^+NR^-) linkage.

Thus, in adumbration, the thesis can be divided into two convenient sections:

1. Reactions of 1,1,1,3,3,3-hexafluoroisopropylidenimine with active hydrogen compounds of group IV and V elements.

2. Reactions of xenon difluoride with 1,1,1,3,3,3-hexafluoroisopropylidenimine and its organic and organometallic derivatives.

GENERAL TECHNIQUE, APPARATUS AND REAGENTS.

GENERAL.

As most of the compounds prepared, or used as starting materials were air and moisture sensitive, they were handled in either a nitrogen atmosphere dry-box or a conventional glass vacuum rack. If at all necessary to expose any of the compounds to the atmosphere, such exposure was kept to a minimum and the container was immediately evacuated again or flushed with dry nitrogen.

Reaction tubes were evacuated and flamed out under dynamic vacuum on the vacuum rack.

Conventional ground-glass-jointed apparatus was dried at 110° for 24 hours before use and allowed to cool in the dry-box.

Liquids were handled with a syringe in the dry-box.

Experiments involving solid xenon difluoride or hexafluoroisopropylideniminolithium were carried out observing the correct safety precautions, due to the fact that both these reagents have been reported to cause explosions.[86,21,120-124]

Microanalyses were carried out by the Alfred Bernhardt microanalysis laboratory of the Max Planck Institute, Germany.

INSTRUMENTAL MEASUREMENTS

Proton and fluorine NMR spectra were recorded on a Varian Associates A56/60 Analytical Spectrometer. Wherever possible, internal tetramethylsilane and trichlorofluoromethane were used as standards for proton and fluorine spectra respectively.

Mass spectra were recorded on a Finnigan Model 1015 quadrupole mass spectrometer. The conditions used are noted for the individual spectra in the experimental section.

Solid samples were introduced directly,and liquid samples were vapourised into the gas inlet system.

Infra-red spectra were recorded on a Perkin-Elmer 337 grating spectrophotometer,linearly covering the range 4000-400 wavenumbers. Liquids were run as films between potassium bromide discs. Solid samples were mulled with nujol and run between potassium bromide discs. Gaseous samples were run at 15mm. pressure in a 9cm. cell fitted with potassium bromide windows.

The infra-red spectrum of xenon difluoride vapour was run using a 10cm. nickel monel gas cell fitted with silver chloride windows. Spectra were calibrated against polystyrene.

REAGENTS

Except for those described below,most of the reagents used were employed without further purification than as supplied. The materials were obtained from the following companies:

Peninsular Chemresearch Inc.
Alfa Inorganics Inc.
Matheson,Coleman and Bell
Eastman Organic Chemicals,Co.
Fisher Scientific Co.
Allied Chemical Co.

Acetonitrile and deuteroacetonitrile were dried over phosphorus pentoxide and distilled.

Tetrahydrofuran (THF) was dried by refluxing over lithium aluminium hydride for six hours and then distilling.

Pyridine was dried over sodium hydroxide then distilled.

Liquid ammonia was dried with sodium metal shavings for a few minutes and then distilled.

Phosphorus oxychloride was redistilled, the fraction boiling at 105-106° being used.

Dimethyl phosphite was purified by shaking with molecular sieve then distilling in vacuo.

Xenon difluoride was prepared by photochemical reaction of the elements. The gases were handled in a nickel monel vacuum line which had been flamed out at 10^{-5} torr. (Fig.1 below; Fig.2 overleaf)

The reaction bulb was prefluorinated by treating with 1 atmosphere of fluorine for 24 hours.

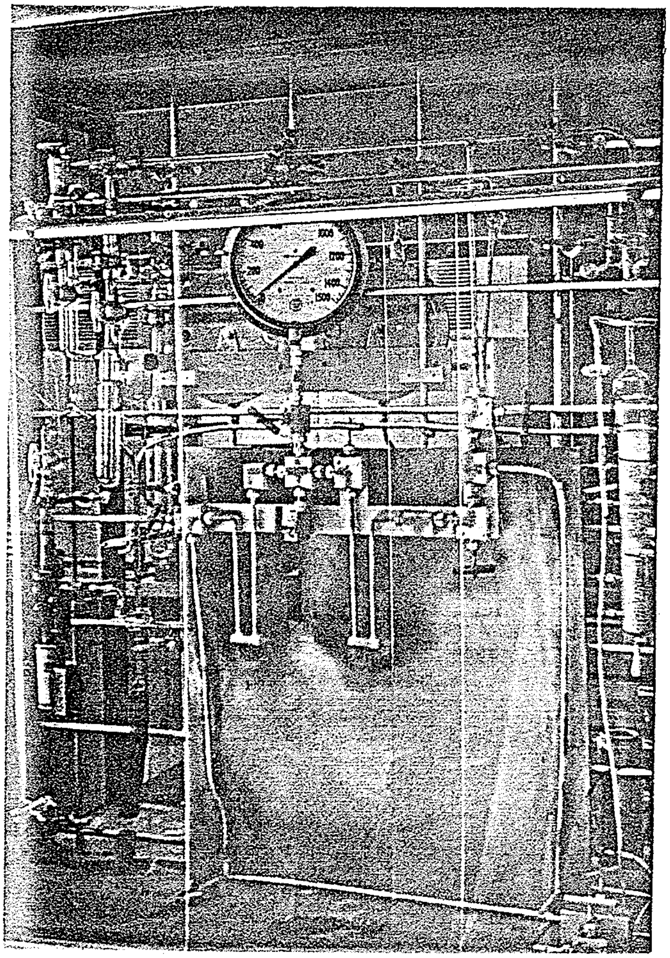


Fig.1

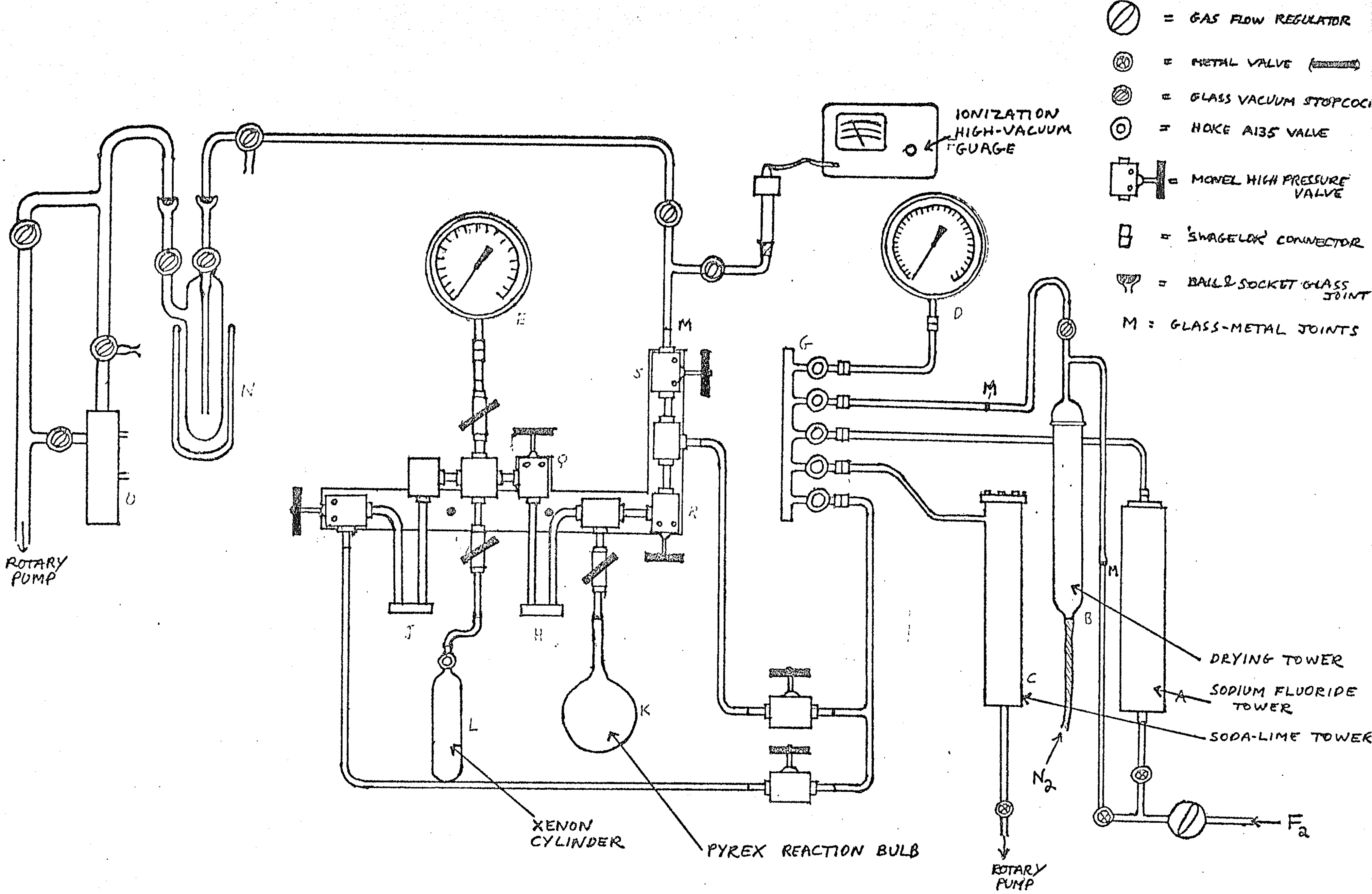

= GAS FLOW REGULATOR
= METAL VALVE
= GLASS VACUUM STOPCOC
= HOKE A135 VALVE
= MONEL HIGH PRESSURE VALVE
= 'SWAGELOK' CONNECTOR
= BALL & SOCKET GLASS JOINT
M = GLASS-METAL JOINTS
IONIZATION HIGH-VACUUM GUAGE
E
D
G
M
S
Q
R
N
O
J
H
L
K
A
B
C
DRYING TOWER
SODIUM FLUORIDE TOWER
SODA-LIME TOWER
N_2
F_2
ROTARY PUMP
ROTARY PUMP
XENON CYLINDER
PYREX REACTION BULB

FIGURE 2

A typical preparation of xenon difluoride involved admitting 380mm.(9mmole) of xenon and 380mm.(9mmole) of fluorine (hydrogen fluoride free) into a 1 litre pyrex bulb fitted with a monel autoclave valve.The bulb was removed from the rack and irradiated with ultraviolet light from a Hanovia Type 30620 mercury arc lamp for ten days. The crystals thus formed were transferred by pumping under vacuum to a smaller bulb cooled to -196°. Dry,redistilled acetonitrile was then distilled onto the crystals,which were then dissolved at room temperature. The resulting solution was then stored frozen at -78°.

The concentration of such a solution was determined by allowing an accurately measured aliquot of solution to react with an excess of mercury in a vacuum rack,and the xenon gas thus liberated was weighed in a standard bulb.

The syntheses of reagents for specific reactions are described in the experimental section.

EXPERIMENTAL SECTION

PART 1 : Reactions of 1,1,1,3,3,3-Hexafluoroisopropylidenimine with active hydrogen compounds of group IV and V elements.

Note; The naming of compounds has been carried out in accord with the rules laid out in references 22 and 125.

Preparation of 1,1,1,3,3,3-Hexafluoroisopropylidenimine[21*]

$(CF_3)_2C{=}NH$

In a 590ml. round-bottomed flask equipped with a gas inlet tube, a condenser cooled by solid carbon dioxide and a mechanical stirrer, were placed 250ml. of pyridine. The flask was cooled to -25° by means of a dry-ice/acetone bath and the stirrer started. Hexafluoroacetone(Matheson Co.), 100gm.(0.6 moles) was distilled into the flask, keeping the temperature between -25° and -30°. Ammonia, 12.5ml. (approximately 10.2gm;0.6 moles) was then distilled into the solution, which was rapidly stirred and kept at -25° to -30°. The cooling bath was removed and replaced by a heating mantle, and the reaction mixture was allowed to warm up to room temperature (25°). The dry-ice condenser was substituted by a water-cooled condenser connected with a trap cooled by a solid carbon dioxide/acetone bath, and the gas inlet tube by a dropping funnel. Phosphorus oxychloride, 50ml.(92gm.;o.6 moles) was added dropwise at such a rate as to maintain gentle reflux and prevent charring. The gaseous product was collected in the cold trap. After completion of the addition, the reaction mixture was heated to 100° and kept at that temperature for a half-hour.

The condensate in the trap was purified by trap to trap distillation in a vacuum line, and 82.5gm (67% yield) of 1,1,1,3,3,3-hexafluoroisopropylidenimine were obtained.

The physical properties of this compound are collected in Table 1, and its spectra in Table 2.

*Note: In later work, commercial material (PCR Inc.) was also obtained.

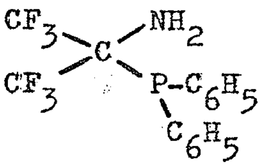
Reaction of Diphenylphosphine with 1,1,1,3,3,3-Hexafluoroisopropylidenimine.

Diphenylphosphine, 0.93gm. (5mmoles), contained in a 20ml. reaction tube connected to a vacuum line, was cooled to -196° by means of a liquid nitrogen bath. The tube was evacuated (10^{-3} torr). Hexafluoroisopropylidenimine, 1.65gm. (10mmoles), was distilled into the reaction tube from a standard weighing Bulb, and the reaction tube was then sealed under vacuum. The tube was transferred to an oil bath at 80° and heated for four days.

During this time the initially colourless mixture took on an orange colouration and increased in viscosity. A small sample was investigated by electron spin resonance, using a Varian Associates E-3 EPR Spectrometer, but no free radicals were observed.

The tube was allowed to cool to room temperature and was opened under nitrogen, fitted with a stopcock and transferred to a vacuum line. The volatile materials, mainly excess imine, were distilled off and collected in a cold trap at -78°. The viscous material remaining in the tube slowly crystallised while under dynamic vacuum,to produce white crystals,M.Pt.38-39°.These were involatile at 100° under dynamic vacuum.

The fluorine nuclear magnetic resonance spectrum, using trichlorofluoromethane as solvent,shows a doublet at +68.8ppm relative to the solvent peak,with J_{FP}= 17Hz. The proton NMR spectrum shows two multiplets in the phenyl region,J_{PH}= ca.40Hz.,centred at -6.92ppm.,and a broad singlet at -1.30ppm. with relative areas 10.3:2. These spectra are indicative of the structure IV.



IV.

(2-Amino-2-diphenylphosphino-1,1,1,3,3,3-hexafluoropropane)

Analysis assuming $C_{15}H_{12}NF_6P$:

Calc. C 51.30%; H 3.45%; F 32.45%

Found.C 51.31%; H 3.09%; F 32.32%

Yield: 1.60gm. (92% based on weight of diphenylphosphine used).

The NMR spectra are shown in Table 3;Nos.1 and 2.

The infra-red spectrum of the compound (nujol mull) is shown in Table 4a. Medium peaks at 3410cm^{-1} and 3340cm^{-1} are assigned to NH_2 assymmetric and symmetric stretching respectively. The N-H scissorring mode appears as a medium peak at 1618cm^{-1}. Aromatic combination and overtone bands characteristic of mononuclear substitution appear at 1970,1900,and 1820cm^{-1}(all weak). The CF_3 stretching modes appear as strong,broad bands in the region 1300-

1060cm^{-1}, and the P-C stretching vibration of the P-C_6H_5 group shows at 997cm^{-1} as a medium peak.

The most abundant ions of the mass spectrum are:

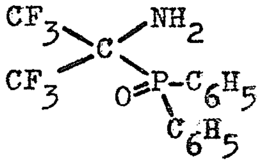
m/e	% abundance	
351	3	(M^+)
223	6	
221	6	
181	100*	
179	100*	
166	20	
147	7	
146	14	
108	34	
96	42	
78	34	
77	91	
69	39	
51	87	

*off scale

Oxidation of 2-amino-2-diphenylphosphino-1,1,1,3,3,3-hexafluoropropane.

A few crystals of 2-amino-2-diphenylphosphino-1,1,1,3,3,3-hexafluoropropane were dissolved in 0.3ml. of trichlorofluoromethane contained in an NMR tube, and a slow stream of dry oxygen was bubbled through overnight. A white precipitate was produced. The tube was transferred to the vacuum line and the solvent was pumped off. The resulting white solid melted at 122-123^{o} and was found to be insoluble in the common organic solvents. The material dissolved in hexamethylphosphotriamide, $((CH_3)_2N)_3PO$, producing a solution which rapidly darkened. No fluorine resonances were observed in the NMR spectrum. While attempting to dissolve the product in chloroform-d an exothermic reaction occurred,but solution did not take place. The fluorine NMR spectrum of the supernate showed a singlet at +67.3ppm. This side-reaction was not investigated further.

The mass spectrum of the solid shows a parent ion corresponding with the phosphorus(V) analogue of IV,namely V.



V

(2-amine-2-diphenylphosphonato-1,1,1,3,3,3-hexafluoropropane)

The major peaks of the mass spectrum are:

m/e	% abundance	
367	2	(M^+)
221	4	
220	4	
219	7	
215	5	
201	100*	
166	2	
146	2	
124	17	
96	7	
78	19	
77	44	
69	8	
51	32	

*off scale

The infra-red spectrum of V,although poorly resolved, is greatly similar to that of the phosphorus(III) compound and is shown in Table 4b.

Here the absorption due to the P=O bond, which in aromatic phosphine oxides usually occurs near $1190cm^{-1}$, is masked by the strong, broad band due to CF_3 stretching modes.

Reaction of 2-amino-2-diphenylphosphino-1,1,1,3,3,3-hexafluoropropane with xenon difluoride.

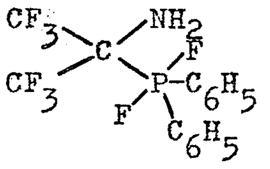
A few small crystals of 2-amimo2-diphenylphosphino-1,1,1,3,3,3-hexafluoropropane were introduced to a carefully dried NMR tube in the dry-box. Approximately 0.3ml. of a 0.5 molar solution of xenon difluoride in deuteroacetonitrile was added and the tube quickly sealed with a pressure cap. A vigorous reaction ensued, with copious gas evolution and precipitation of a small amount of a white solid.

A search of the fluorine NMR spectrum revealed only the following peaks:

shifts: +68.8 doublet due to excess of IV.
+67.4 singlet
+69.0 doublet(a) of triplets(b) J_a=4.5Hz; J_b=12Hz.
+71.1 broad singlet
+72.6 doublet J=7Hz
+74.3 doublet J=7Hz
+75.9 doublet J=6.5Hz

The shifts are quoted with respect to internal trichlorofluoromethane, which was added to the reaction mixture immediately before running the spectrum.

The doublet of triplets at +69.0ppm. is assigned to compound VI. (over). The fluorine of the trifluoromethyl groups are equivalent and are split into a doublet by the phosphorus atom, with J_{CF_3P}=4.5Hz, and further split into triplets by the fluorine atoms on the phosphorus atom, with $J_{C\underline{F}_3P\underline{F}}$=12Hz.



VI

(2-Amino-1,1,1,3,3,3-hexafluoroisopropyl)difluorodiphenylphosphorus(V)

The resonances of the fluorine atoms of the PF_2 group were not observed as the concentration of the product was too low. The theoretical spectrum (first-order) would be a doublet of septets of quintets, with J_{FP}=approximately 500-700Hz. (see, for example, ref.126) and J_{FCF_3}=12Hz, with probable long range interaction between the fluorine atoms and the ortho protons of the phenyl groups with J_{FH}=approximately 1-2Hz.

The proton spectrum shows complex multiplets with resonances due to compound IV and products overlapping in the phenyl region. At -4.1ppm. a septet with J=7.0Hz. appears and a very broad peak centred at -2.85ppm. The latter is assigned to the amino groups of both excess starting material and products. The septet, together with the doublet at +74.3ppm. in the fluorine spectrum are assigned to 1,1,1,3,3,3-hexafluoroisopropylamine, $(CF_3)_2CHNH_2$ [21]

The formation of heptafluoroisopropylamine, $(CF_3)_2CFNH_2$, is uncertain, as the reported preparation[21] identifies the compound as showing a doublet in the CF_3 region of the fluorine spectrum, with a septet "at higher field". Thus, one of the doublets in the spectrum of products is probably due to the presence of this amine.

Again the concentration of this amine was sufficiently small to preclude observation of the septet. The spectra are illustrated in Table 3;Nos.3 and 4.

Reaction of Diphenylarsine with 1,1,1,3,3,3-Hexafluoroisopropylidenimine.

Diphenylarsine,0.56gm.(2.5mmoles) was placed in a reaction tube,which was evacuated and cooled to -196° on a vacuum rack. Hexafluoroisopropylidenimine,0.83gm. (5mmoles) was condensed into the tube,which was then sealed,and shaken at room temperature for six hours. During this time a pale-green tinted crystalline solid separated out of the reaction mixture,leaving a colourless supernate. Electron paramagnetic resonance investigation failed to detect any free-radicals.

The tube was opened under nitrogen,fitted with a stopcock,and connected to the vacuum line. The supernate was distilled into an NMR tube,and the solid was dissolved in deuteroacetonitrile.

The proton NMR spectrum of the solution revealed only phenyl resonances (Table 3;No.5) and the search of the fluorine spectral region indicated that no fluorine was present. The mass spectrum was characteristic of tetraphenyldiarsine,$(C_6H_5)_2AsAs(C_6H_5)_2$ The peak at m/e 474 was due to the formation of $(C_6H_5)_2AsOAs(C_6H_5)_2$, during transfer of the sample tube to the inlet port of the mass spectrometer,aryl compounds of arsenic(III) being particularly air sensitive. The melting point of the solid was determined as $134-5^{\circ}$,confirming the assignment.

The NMR spectra of the supernate showed two doublets in the CF_3region of the fluorine spectrum,at +74.4ppm. and +75.7ppm. with J=7Hz. and J=6Hz. respectively.(Table 3;No.6)

The proton spectrum (Table 3;No.7) is characterised by the following peaks:

shift (external TMS)

-1.42ppm broad
-3.22ppm septet J=7Hz.
-3.81ppm.septet J=6Hz.
-4.54ppm broad
-6.76ppm singlet

The mass spectrum of this mixture of volatiles has a peak at m/e 167,assigned to $(CF_3)_2CHNH_2$,together with its breakdown fragments.(Note.The mass spectral analysis was carried out on the volatile products remaining after removal of the excess of 1,1,1,-3,3,3-hexafluoroisopropylidenimine).

An abundant peak at m/e 78 was assigned to benzene. No peaks due to As,C_6H_5As,or$(C_6H_5)_2As$ were observed. Thus the singlet at -6.76ppm in the proton spectrum can be assigned to benzene, and the septet at -3.22ppm,together with the doublet at +74.4ppm in the fluorine spectrum can be assigned to 1,1,1,3,3,3-hexafluoroisopropylamine. The other septet,coupled with the doublet in the fluorine spectrum,suggests the presence of another $(CF_3)_2CH$ group, however the mass spectrum of the volatiles does not correspond with either $(CF_3)_2CHNHAs(C_6H_5)_2$or the dimer $(CF_3)_2CHNHNHCH(CF_3)_2$.

Repeating the reaction with an excess of diphenylarsine produced identical products. Finally,repeating the reaction in an NMR tube and following its progress spectroscopically again showed the same products,with no indication of the intermediate formation of either$(CF_3)_2CHNHAs(C_6H_5)_2$ or $(CF_3)_2C(NH_2)As(C_6H_5)_2$.

Reaction of Dimethyl Phosphite with 1,1,1,3,3,3-Hexafluoroisopropylidenimine.

This reaction was carried out using three slightly different procedures:

A.[127] Dimethyl phosphite, 1.10gm.(10mmoles) was placed in a reaction tube and dissolved in 10ml. of dichloromethane. The tube was then cooled to -196° and evacuated. Hexafluoroisopropylidenimine, 1.65gm.(10mmoles) was distilled into the tube, which was then sealed under vacuum and transferred to a solid carbon dioxide-acetone bath at -78°. The reaction mixture was allowed to warm up to room temperature over a period of 30 hours. The dichloromethane and unreacted hexafluoroisopropylidenimine were distilled off, and the residue investigated by NMR spectroscopy.

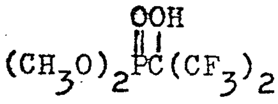
B. The above procedure was repeated except that no solvent was employed.

C. Reaction B. was repeated except that the mixture was heated at 80° for five days.

In Part A the fluorine spectrum of the products (Table 3;8) shows the following peaks:

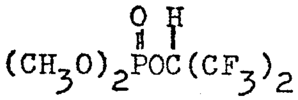
shift		coupling constant
+71.8ppm.	doublet	3 Hz.
+74.6ppm.	doublet	6 Hz.
+79.1ppm.	singlet	
+79.9ppm.	singlet	

The proton spectrum revealed mainly unreacted dimethyl phosphite, with weak resonances masked by the doublet. The doublet at +71.8ppm. is assigned to 2-hydroxy-1,1,1,3,3,3-hexafluoroisopropyldimethyl phosphite, and that at +74.6ppm. to 1,1,1,3,3,3-hexafluoroisopropyldimethyl phosphate (structures VII and VIII respectively).[128]



$(CH_3O)_2\overset{O}{\overset{\|}{P}}\overset{OH}{\overset{|}{C}}(CF_3)_2$

VII



$(CH_3O)_2\overset{O}{\overset{\|}{P}}O\overset{H}{\overset{|}{C}}(CF_3)_2$

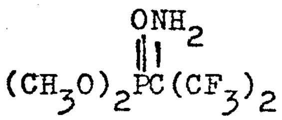
VIII

The peaks at +79.1ppm and +79.9ppm are due to hexafluoroacetone and hexafluoroacetone hydrate respectively.

Addition of a catalytic amount of compound VII to compound VIII,as shown by a decrease in peak height for the former and corresponding increase in peak height for the latter, as reported by Janzen and Smyrl.[127]

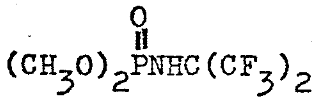
In the cases of reactions B and C above,the main products obtained are complex polymeric materials of uncertain structure,as shown by the spectra illustrated in Table 3.

The expected products,analogous to those above, with structures IX and X were not formed in more than insignificant yield.



$(CH_3O)_2\overset{O}{\overset{\|}{P}}\overset{NH_2}{\overset{|}{C}}(CF_3)_2$

IX



$(CH_3O)_2\overset{O}{\overset{\|}{P}}NHC(CF_3)_2$

X

A small amount of material crystallised out in experiment C and the mass spectrum of this material showed the parent ion of m/e 275 ,but,as attempts to obtain significant amounts of pure material proved fruitless,the study was not pursued further.

Reaction of Trimethylsilanol with 1,1,1,3,3,3-Hexafluoroisopropylidenimine.

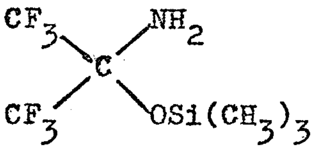
Trimethylsilanol*#,0.23gm(2.5mmoles)contained in an NMR tube was cooled to -196° and the tube was evacuated. Hexafluoroisopropylidenimine,0.85gm.(5mmoles) was condensed into the tube,which was sealed under vacuum and heated at 80° for three days. The tube was then opened under nitrogen in the dry-box,and fitted with a pressure-cap. The fluorine NMR spectrum of the reaction mixture showed three singlets at +80.2ppm.,+82.5ppm.& +83.3ppm. The former is attributed to hexafluoroacetone hydrate,$(CF_3)_2C(OH)_2$.

The proton NMR spectrum showed singlets at -0.14ppm,-0.26ppm.,and -0.07ppm,all attributed to trimethylsilyl groups. The latter was shown to be due to hexamethyldisiloxane, $(CH_3)_3SiOSi(CH_3)_3$,by adding a small amount to the mixture and observing the increase in intensity of the peak at 0.07ppm.# The peak at 0.14ppm is assigned to the methyl groups in 2-trimethylsiloxyhexafluoro-2-propanol,the reported value being 0.18ppm.[129] After crude separation by trap to trap distillation the'singlet' at +82.5ppm.could be assigned to this compound. Janzen[129] reports a splitting of less than 3Hz. in this peak,but in the present case such splitting could not be observed due to poor resolution.

The singlets at 0.26ppm and +83.3ppm are assigned to compound XI,2-amino-1,1,1,3,3,3-hexafluoro-2-trimethylsiloxypropane.

*Kindly donated by Mr.J.A.Gibson

#An approximately equimolar amount of hexamethyldisiloxane was present ,due to the unavoidable difficulty to separate the compounds.



XI

Gas chromatography was employed to separate the products, in order to obtain mass spectra of the pure materials. A Carbowax20M column was used at a temperature of 70°.

The following spectra were obtained:

m/e	abundance(%)	ion
166	2.5	$(CF_3)_2O^+(M^+)$
147	17	$(M-F)^+$
119	3.5	
97	51	$(M-CF_3)^+$
78	4	$(CF_2CO)^+$
69	100	CF_3^+
50	17	CF_2^+ or $(C_2F_4)^{++}$

This spectrum is characteristic of hexafluoroacetone.

m/e	abundance	ion
221	ca.1	$(C_5H_6F_5O_2Si)^+(M-CH_4F)^+$
186	ca.1	$(M-CF_3H)^+$
147	ca.1.5	$(C_2F_5CO)^+$
97	1.5	$(CF_3CO)^+$
90	1.5	$((CH_3)_3SiOH)^+$
75	100	$((CH_3)_2SiOH)^+$
59	2.5	$(CH_3SiO)^+$
44	16	$(SiO)^+$

This spectrum is attributed to 2-trimethylsiloxyhexafluoro-2-propanol. The silicon containing fragments show the correct isotopic ratio, (^{28}Si:92.2%; ^{29}Si:4.7%; ^{30}Si:3.1%)[130] where intensity permits.

m/e	abundance	ion
240	5	$(C_5H_8F_6NOSi)^+$

m/e	abundance	ion
220	16	$(M-CH_4F)^+$
190	40	$(C_4F_7H_4NOSi)^+$
186	16	$(M-CF_3)^+$
144	56	$(C_2H_5F_3ONSi)^+$
124	66	$(C_2H_4F_2ONSi)^+$
116	8	$(M-2CF_3)^+$
96	50	$(CF_3CNH)^+$
77	100	$(C_2H_8NOSi)^+$
73	100	$(C_2H_7NSi)^+$
69	10	CF_3^+
44	40	$(SiO)^+$

Peaks due to silicon containing fragments are in the correct isotopic ratio.

This spectrum is attributed to 2-amino-1,1,1,3,3,3-hexafluoro-2-trimethylsiloxypropane. The parent ion, m/e 255, is not observed, as loss of a methyl group from the $(CH_3)_3SiO-$ moiety is a highly favoured process.

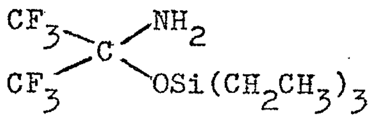
Reaction of Triethylsilanol with 1,1,1,3,3,3-Hexafluoroisopropylidenimine.

Preparation of triethylsilanol:[131]

Triethylchlorosilane, 15.1gm, (0.1mole) was dissolved in 50ml. of diethyl ether in a flask fitted with a magnetic stirrer and a dropping funnel. Using phenolphthalein as indicator the solution was titrated slowly with 1M sodium hydroxide solution until complete conversion of the chlorosilane to silanol was achieved. The ether solution was separated off and the aqueous layer extracted with three 10ml. portions of ether. The combined ether extracts were dried over anhydrous potassium carbonate and the ether was then removed under vacuum. The oily residue was purified by trap-to-trap distillation, purity of the triethylsilanol being checked by NMR spectroscopy.

Triethylsilanol, 1.32gm. (10mmoles), contained in a reaction tube connected to the vacuum line, was cooled to -196°, and evacuated. Hexafluoroisopropylidenimine, 3.30gm. (20mmoles), was distilled into the tube, which was then sealed and allowed to warm up to room temperature. The mixture was shaken for 24 hours, after which time the excess of hexafluoroisopropylidenimine was distilled off. The residue was purified by trap-to-trap distillation.

The proton NMR spectrum (Table 3;12) shows a complex second-order multiplet (A_3B_2) characteristic of ethyl groups bonded to silicon.[132] The fluorine spectrum shows a singlet at +82.8ppm., assigned to equivalent trifluoromethyl groups. This would be expected in the case of XII, 2-amino-1,1,1,3,3,3-hexafluoro-2-triethylsiloxypropane:



XII

The mass spectrum of the compound shows the following peaks:

m/e	abundance(%)	ion
268	0.5	M^+
217	2.5	$(M-CH_2CH_3)^+$
147	4	$(C_3H_2F_5N)^+$
132	10	$((CH_3CH_2)_3SiOH)^+$
115	2.5	$((CH_3CH_2)_3Si)^+$
102	100(off-scale)	$((CH_3CH_2)_2SiO)^+$
97	11	$(CF_3CNH_2)^+$
69	20	CF_3^+

However, analysis of the material was not consistent with compound XII, indicating that either the compound had decomposed in transit, or a more complex reaction had occurred. The results remain inscrutable;

Calc.C=36.36%;H=5.77%;F=38.34%;N=5.38%
Found.C=43.72;H=8.36%;F=------ ;N=0.83%

A strong possibility is that disproportionation of the product back to the starting materials occurs,which would account for the low nitrogen reading.

Reaction of Silanes with 1,1,1,3,3,3-Hexafluoroisopropylidenimine.

Mixtures of 1,1,1,3,3,3-hexafluoroisopropylidenimine with trimethylsilane,dimethylsilane,triphenylsilane and phenyldimethylsilane were prepared in sealed reaction tubes and mechanically shaken for five days. After this time NMR investigation showed that no detectable reaction had occurred. Heating the mixtures at 80° for prolonged periods produced the same result.

Irradiation with UV light[129] was not attempted,as facilities were temporarily out of action.

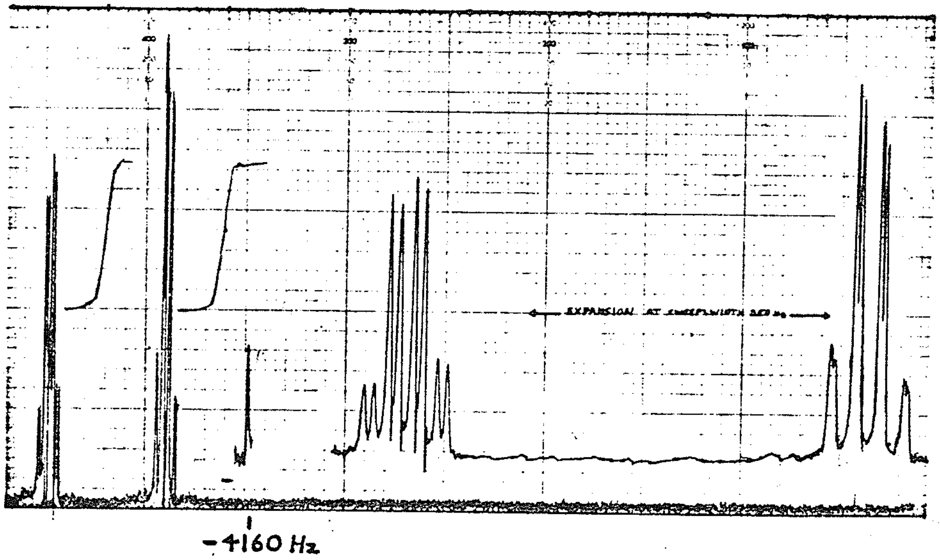
TABLE 1

Chemical Shifts and Coupling Constants of Reagents

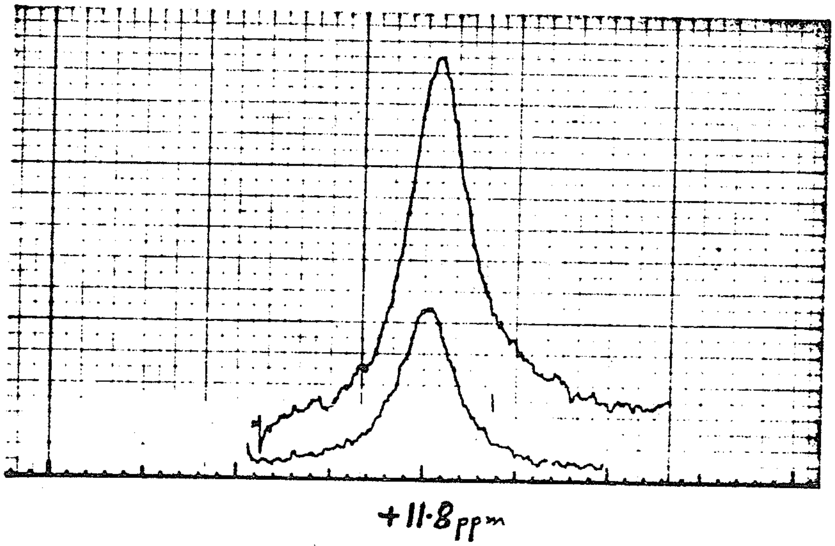
Compound	Shift (ppm)	Appearance	Coupling Constant
$(CF_3)_2C=NH$	(F)+72.8	d.of q.	J_{FF}=6Hz. J_{FH}=2.5Hz.
	(F)+74.8	d.of q.	J_{FH}=1Hz.
$(C_6H_5)_2PH$	- 0.67	multiplet	
	-2.88	singlet	J_{PH}=ca.200Hz
$(C_6H_5)_2AsH$	-6.57	multiplet	
	-4.30	singlet	
$(CH_3O)_2POH$	-3.40	doublet	J_{CH_3-H}=12.5Hz.
	-5.58	doublet	J_{PH}=595.5Hz.
$(CH_3)_3SiOH$	-0.12	singlet	
$(CH_3CH_2)_3SiOH$	ca0.80	multiplet	
	-5.00	singlet	
$C_6H_5(CH_3)_2SiH$	-6.70	multiplet	
	-3.94	septet	J_{CH_3-H} =3.75Hz.
	+0.33	doublet	
XeF_2	(F)+185	singlet	$J_{^{129}Xe-F}$=5630Hz.
$(CH_3)_2TeI_2$	-1.62	singlet	
$(CH_3)_3SiCl$	-0.53	singlet	
$(CH_3)_3SnCl$	-0.63	singlet	$J_{H-^{117}Sn}$=56Hz.
$(CH_3)_3GeBr$	-0.88	singlet	$J_{H-^{119}Sn}$=58.5Hz.

TABLE 2

Spectra of the Starting Materials

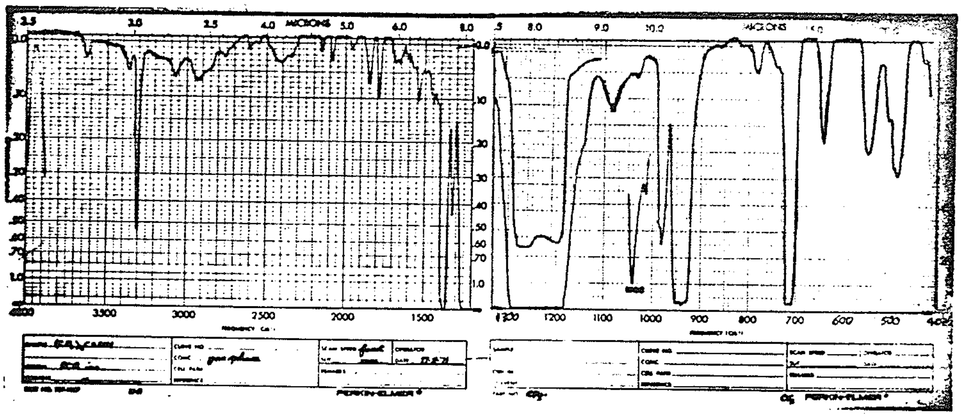


2:1 ^{19}F NMR Spectrum of 1,1,1,3,3,3-Hexafluoroisopropylidenimine.



2:2 ^{1}H NMR Spectrum of 1,1,1,3,3,3-Hexafluoroisopropylidenimine.

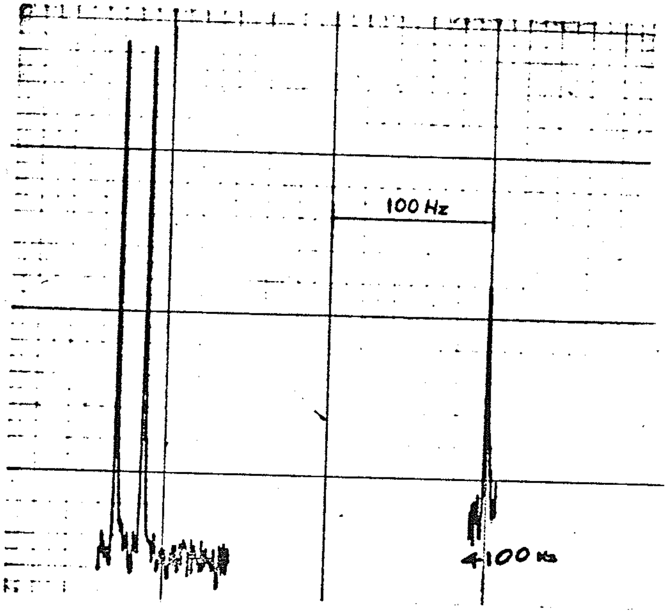
TABLE 2 (cont'd)



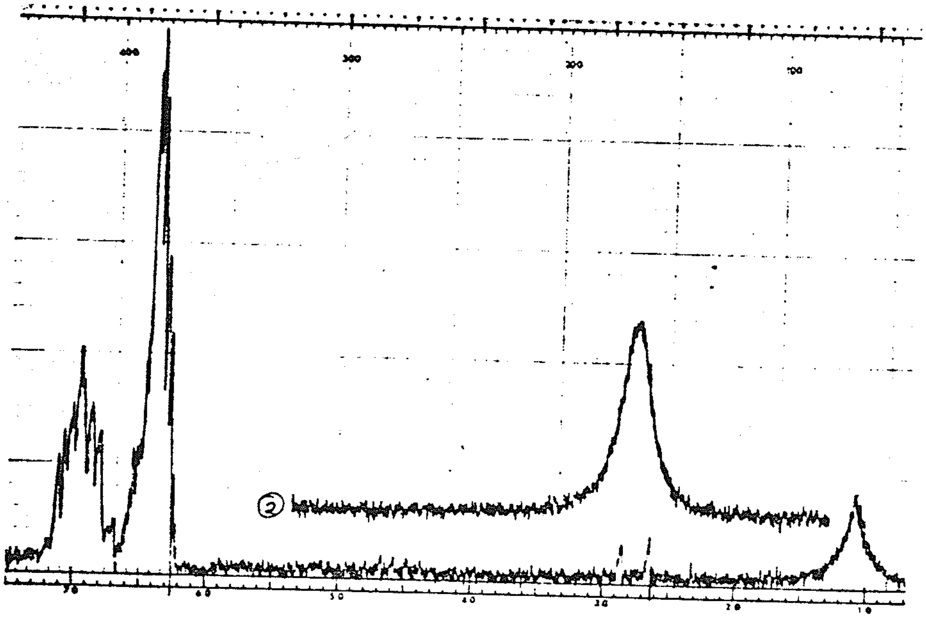
2:3 Infra-red Spectrum of 1,1,1,3,3,3-Hexafluoroisopropylidenimine

TABLE 3

NMR Spectra of Products and By-products.

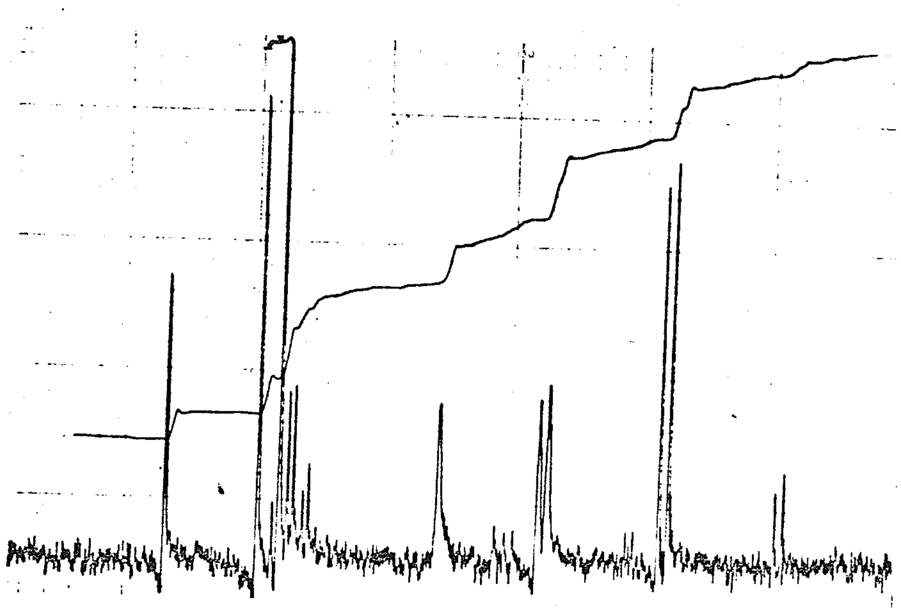


3:1 ^{19}F Spectrum of 2-Amino-2-diphenylphosphino-1,1,1,3,3,3-hexafluoropropane.

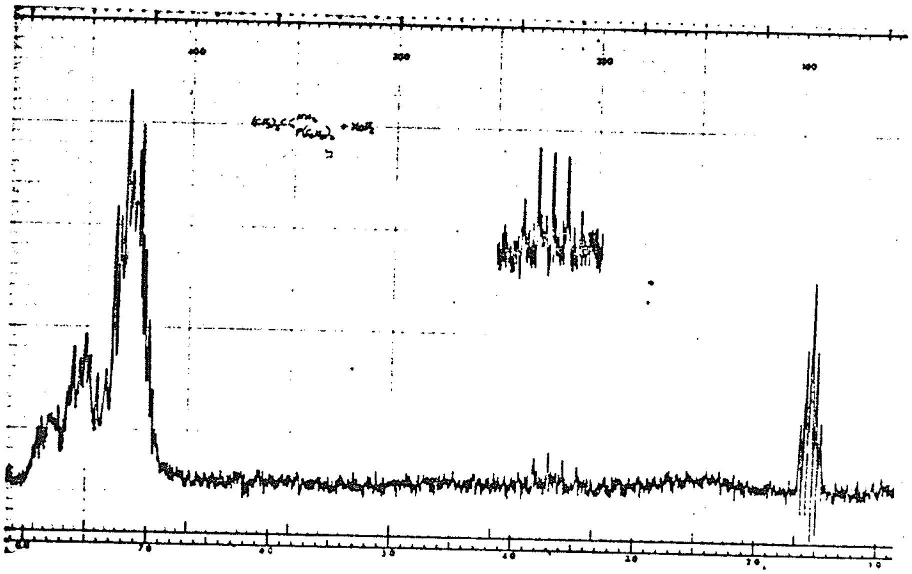


3:2 ^{1}H Spectrum of 2-Amino-2-diphenylphosphino-1,1,1,3,3,3-hexafluoropropane.

TABLE 3 (cont'd)

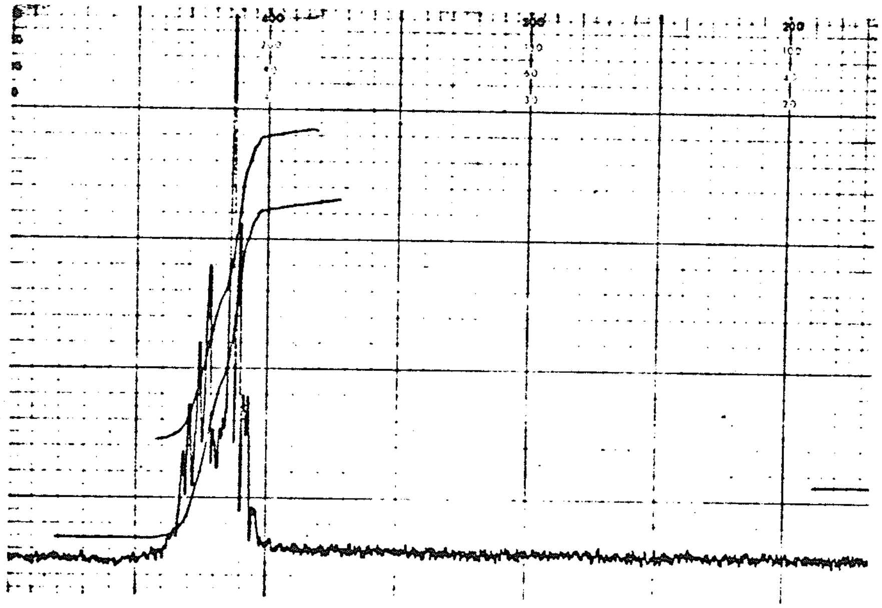


3:3 ^{19}F Spectrum of Products from reaction of XeF_2 with 2-Amino-2-diphenylphosphino-1,1,1,3,3,3-Hexafluoropropan

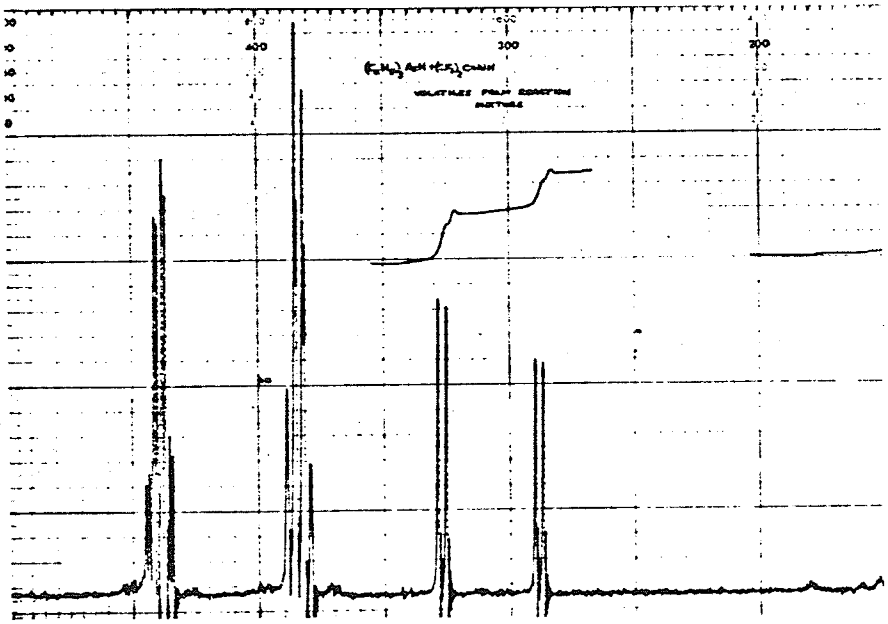


3:4 ^{1}H Spectrum of Products from reaction of XeF_2 with 2-Amino-2-diphenylphosphino-1,1,1,3,3,3-hexafluoropropane.

TABLE 3 (cont'd)

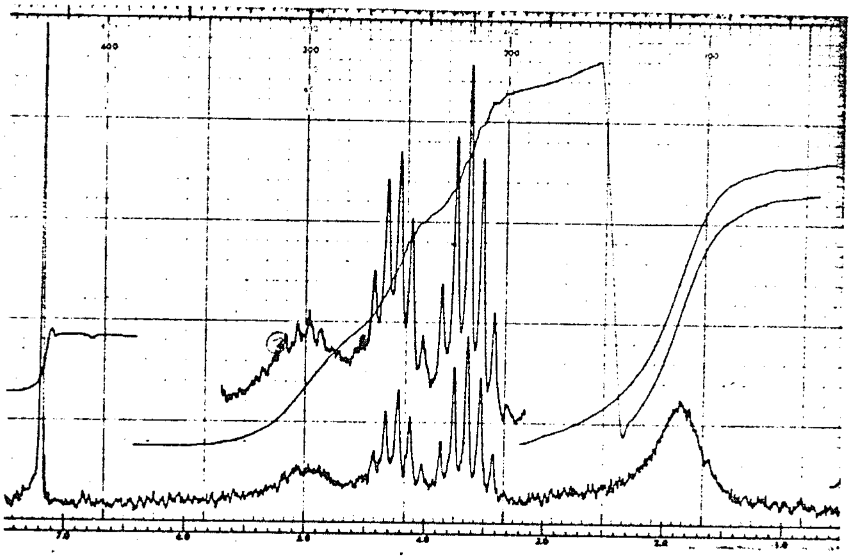


3:5 ^{1}H Spectrum of Tetraphenyldiarsine.

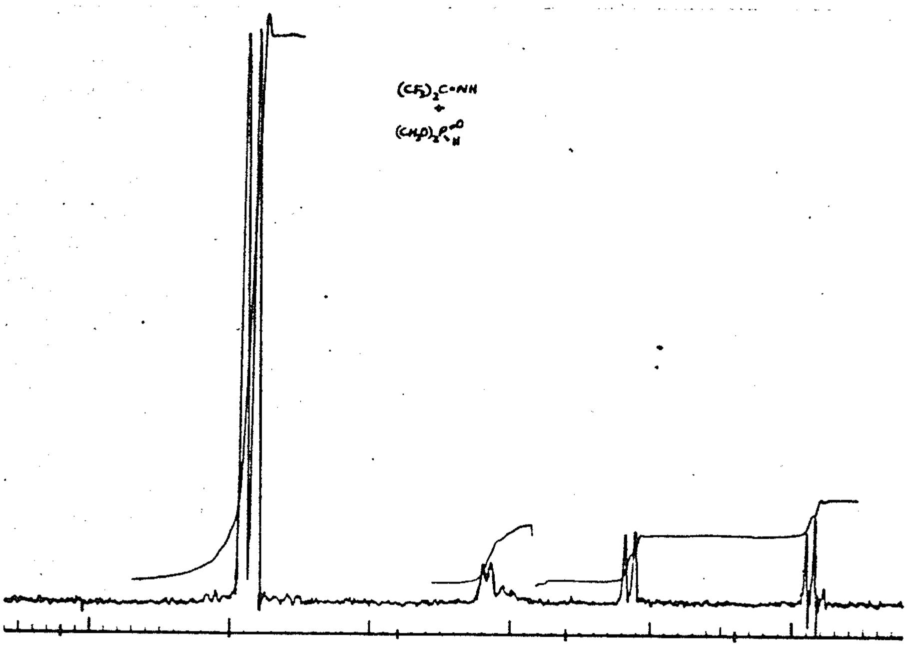


3:6 ^{19}F Spectrum of Products from Reaction of $(C_6H_5)_2$AsHwith $(CF_3)_2C$

TABLE 3 (cont'd)

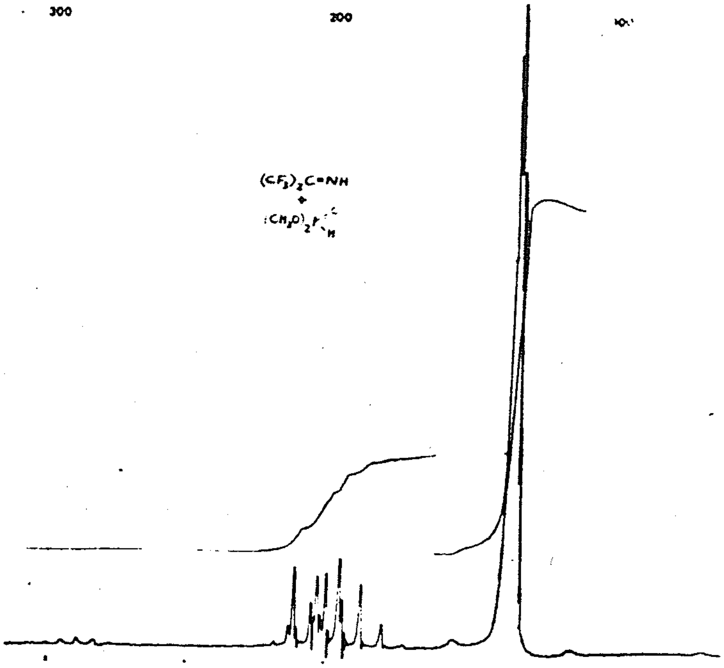


3:7 ^{1}H Spectrum of Products from reaction of $(C_6H_5)_2AsH$ with $(CF_3)_2C$

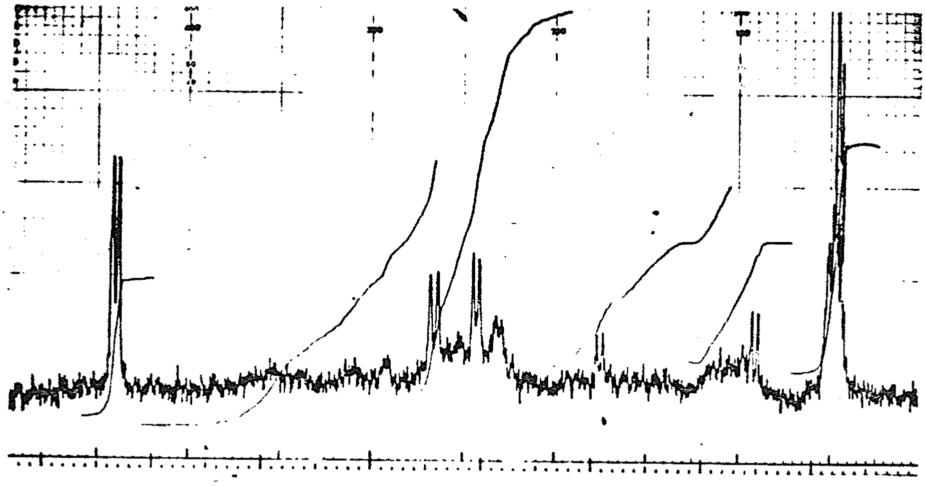


3:8 ^{19}F Spectrum of Products of reaction of $(CH_3O)_2POH$ /$(CF_3)_2C=NH$

TABLE 3 (cont'd)

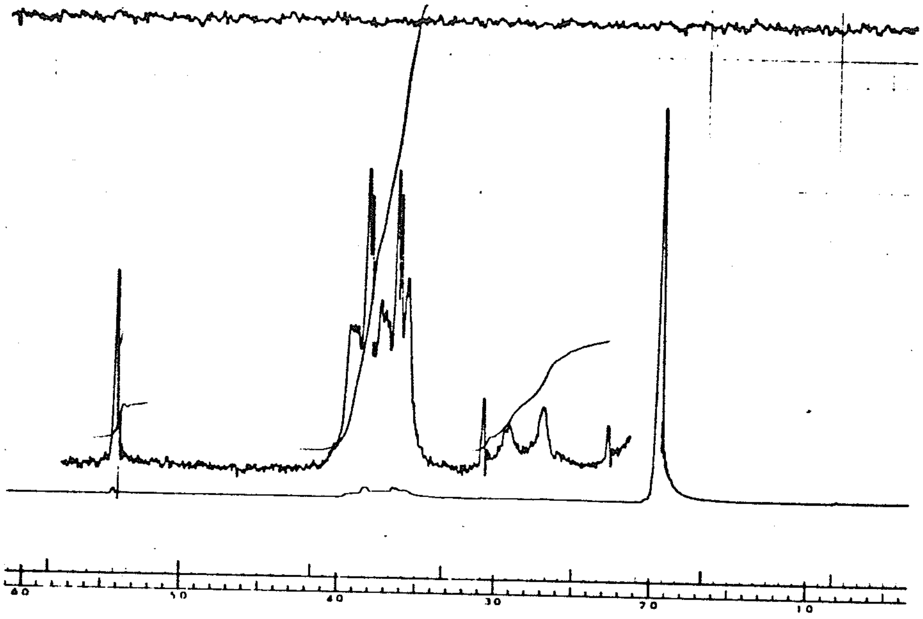


3:9 Volatile products from $(CH_3O)_2POH/(CF_3)_2C=NH$ (C)^{19}F Spectrum.

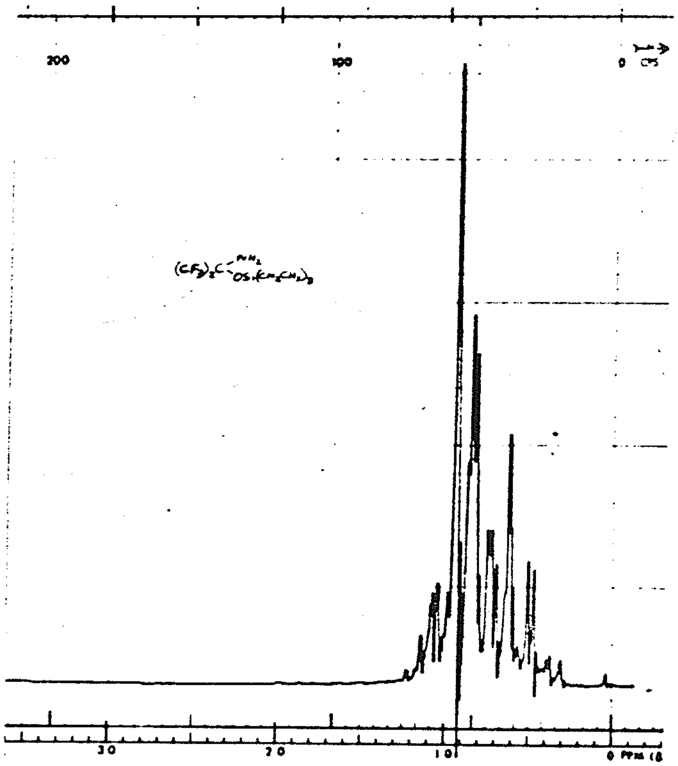


3:10 ^{19}F Spectrum of Polymer from reaction $(CH_3O)_2POH/(CF_3)_2C=NH$.(C

TABLE 3 (cont'd)



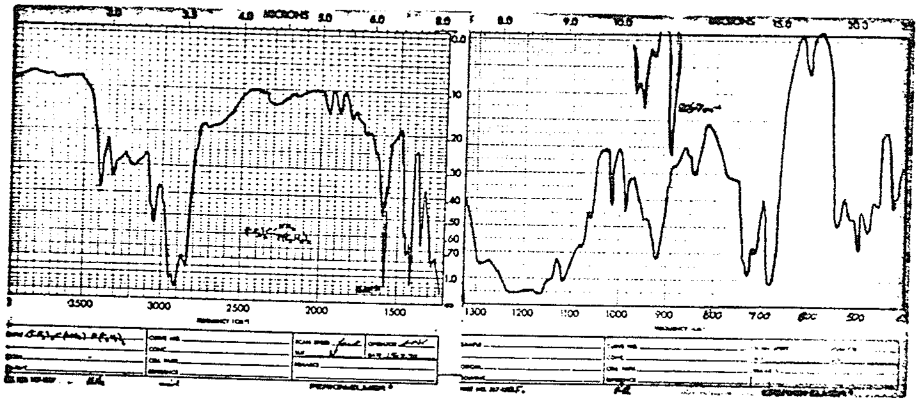
3:11 ^{1}H Spectrum of Polymer from reaction $(CH_3O)_2POH/(CF_3)_2C=NH$.(C)



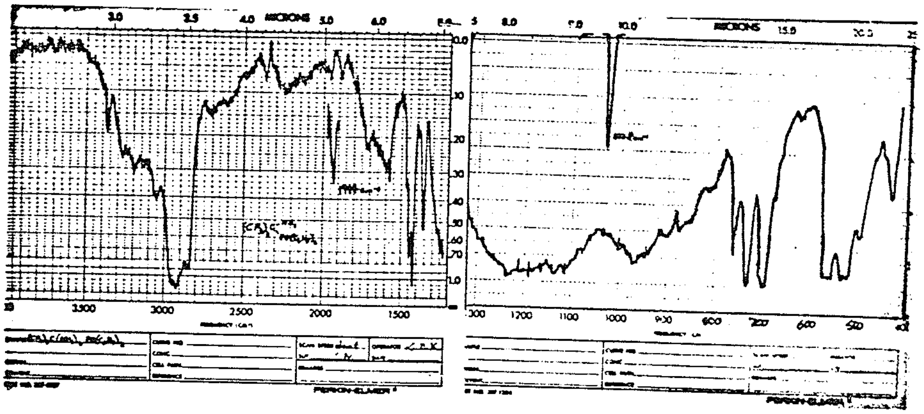
3:12 ^{1}H Spectrum of 2-Amino-1,1,1,3,3,3-hexafluoro-2-triethylsiloxypropane.

TABLE 4

Infra-red Spectra of Products.



4:a 2-Amino-2-diphenylphosphino-1,1,1,3,3,3-hexafluoropropane.



4:b 2-Amino-2-diphenylphosphonato-1,1,1,3,3,3-hexafluoropropane.

PART 2A : Preparation of Organometallic Derivatives of 1,1,1,3,3,3-Hexafluoroisopropylidenimine.

1. Preparation of 1,1,1,3,3,3-Hexafluoroisopropylideniminolithium.[27]

Four-point-five millilitres of a 3.3 molar solution of butyllithium (10mmoles) were placed in a 100ml. boiling flask, equipped with a high-vacuum stopcock, and a dropping-funnel. This was attached to the vacuum line, cooled to -196^{o} and evacuated. 1,1,1,3,3,3-Hexafluoroisopropylidenimine, 2.48gm. (15mmoles) was distilled into the flask, which was then allowed to warm up slowly to room temperature in a Dewar flask. Butane, excess hexafluoroisopropylidenimine and hexane were pumped off to leave approximately 1.7gm. (10mmoles) of 1,1,1,3,3,3-hexafluoroisopropylideniminolithium, a gelatinous brown solid. A solution of this material in trichlorofluoromethane shows a singlet at +71.5ppm. in the fluorine NMR spectrum. (Table 5:1)

This compound was employed as the intermediate to proselytise organometallic compounds to derivatives of the imine, in a well known procedure.

2. Preparation of 1,1,1,3,3,3-Hexafluoroisopropylideniminotrimethylsilane.[27] $(CH_3)_3SiN{=}C(CF_3)_2$

Trimethylchlorosilane, 1.09gm. (10mmoles), was condensed onto 1.7gm. (10mmoles) of 1,1,1,3,3,3-hexafluoroisopropylideniminolithium contained in a 100ml. boiling flask at -78^{o}. The mixture was warmed up to room temperature and shaken for three hours, after which time complete conversion to the product had occurred, leaving a precipitate of lithium chloride. The volatile product was purified by trap-to-trap distillation. Pure material weighing 2.2gm (yield 92.4%) was obtained. The fluorine NMR spectrum shows a singlet at +71.5ppm. and the proton NMR spectrum a singlet at -0.32ppm.

The infra-red spectrum and mass spectrum are reported in reference 27.

3.Preparation of 1,1,1,3,3,3-Hexafluoroisopropylideniminotrimethylgermane. $(CH_3)_3GeN{=}C(CF_3)_2$

Trimethylbromogermane,1.98gm.(10mmoles) was condensed onto 1.7gm.(10mmoles) of 1,1,1,3,3,3-hexafluoroisopropylideniminolithium contained in a 100ml. boiling flask at -78°. The mixture was warmed up to room temperature and shaken for 12 hours to ensure complete reaction. The product was redistilled several times and accurate molecular weight determination by mass spectrometry* gave the following results: Yield: 2.6gm.(91%)

species	mass	
	calc.	found
(^{74}Ge) $(CH_3)_3GeN{=}C(CF_3)_2$	282.98509	282.9842
(^{74}Ge) $(CH_3)_2GeN{=}C(CF_3)_2$	267.96161	267.9609

The fluorine NMR spectrum shows a singlet at +70.7ppm. and the proton spectrum a singlet at -0.54ppm.

The infra-red spectrum (Table 6:1) exhibits the C=N stretching band at 1698cm^{-1}.

The mass spectrum shows the following major peaks:

(see over)

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*The high resolution mass spectrometric measurements were carried out by the mass spectrometry laboratory of the chemistry department of the University of Alberta.

m/e		abundance (%)	ion
283	(^{74}Ge)	3	$((CH_3)_3GeN=C(CF_3)_2)^+$ $(M)^+$
268		6	$(M-CH_3)^+$
218		5	$(C_4H_6F_4NGe)^+$
138		2.5	$((CH_3)_3GeF)^+$
119		100	$((CH_3)_3Ge)^+$
104		14	$((CH_3)_2Ge)^+$
165		33	$((CF_3)_2CNH)^+$
89		50	$(CH_3Ge)^+$
69		42	$(CF_3)^+$
51		13	$(CF_2H)^+$

4.Preparation of 1,1,1,3,3,3-Hexafluoroisopropylideniminotrimethylstannane. $(CH_3)_3SnN=C(CF_3)_2$

A solution of trimethylchlorostannane,2.00gm. (10mmoles) in 10ml. of trichlorofluoromethane was added to 1.7gm. (10mmoles) of 1,1,1,3,3,3-hexafluoroisopropylideniminolithium contained in a 100ml. boiling flask at -78°. The solution was warmed up to room temperature and shaken for 12 hours to ensure completeness of reaction. The trichlorofluoromethane was distilled off and the oily product was purified by trap-to-trap distillation. Yield: 1.83gm.(80%).

The fluorine NMR spectrum shows a singlet at +71.2ppm. and the proton NMR spectrum a singlet at -0.34ppm.

The infra-red spectrum exhibits the C=N stretching band at 1662cm^{-1}.

The mass spectrum shows the following major peaks:

m/e		abundance (%)	ion
329	(^{120}Sn)	23	$((CH_3)_3SnN{=}C(CF_3)_2)^+$ (M^+)
314		2	$(M-CH_3)^+$
299		10	$(M-2CH_3)^+$
214		85	$((CH_3)_3SnF)^+$
195		100	$((CH_3)_3Sn)^+$
165		31	$((CF_3)_2CNH)^+$ & $((CH_3)_2Sn)$
135		42	$(CH_3Sn)^+$
120		30	Sn^+
96		7	$(CF_3CNH)^+$
69		14	$(CF_3)^+$
51		5	$(CF_2H)^+$

The tin isotopes are in the correct isotopic ratio.

Analysis,see over

5. Preparation of 1,1,1,3,3,-Hexafluoroisopropylideniminotrimethylplumbane. $(C_6H_5)_3PbN{=}C(CF_3)_2$

A diethyl ether solution of 4.72gm.(10mmoles) of trophenylchloroplumbane was added to 1.7gm.(10mmoles) of 1,1,1,3,3,3-hexafluoroisopropylideniminolithium contained in a 100ml. boiling flask at -78°. The reaction mixture was warmed up to room temperature and shaken mechanically for 24 hours to ensure completeness of reaction. The ether was removed and the oily residue dissolved in trichlorofluoromethane. This solution was passed through a filter plate under vacuum and the solvent was removed by distillation. The residue was subjected to mass spectral analysis and was found to contain only a small proportion of the desired product,showing a molecular ion peak at m/e 603 for the ^{208}Pb-containing ion,with the other lead isotope peaks in the correct abundance ratio.

Due to the low yields obtained and the relatively high sensitivity to hydrolysis,hence difficulty to purify,the investigation of this compound was not pursued further.

Analyses:

$(CH_3)_3SnN{=}C(CF_3)_2$

calc; C:21.99%; H:2.77%; F:34.77%

found; C:22.08%; H:2.86%; F:34.43%

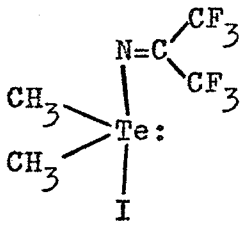
$(C_6H_5)_3PbN{=}C(CF_3)_2$

precluded.

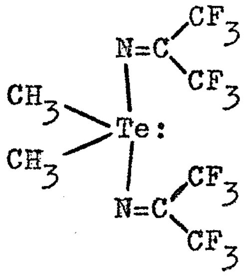
6.Reaction of 1,1,1,3,3,3-Hexafluoroisopropylideniminolithium with diiododimethyltellurium(IV).

A solution of diiododimethyltellurium(IV),2.06gm.,(5mmoles) in 10 ml. of diethyl ether was added to 0.85gm.(5mmoles) of 1,1,1,3,3,3-hexafluoroisopropylideniminolithium contained in a 100ml. boiling flask,cooled to -78°. The mixture was warmed to room temperature and shaken in the dark for three hours. The ether solution was filtered in vacuo to remove lithium iodide and solid by-products. The ether was distilled off,leaving a golden-yellow oil,which decomposed rapidly on exposure to heat,light,moisture,the atmosphere,or on pumping. Formation of either dimethyl-1,1,1,3,3,3-

hexafluoroisopropylideniminoiodotellurium(IV),(XIII),or bis(1,1,1,3,3,3-hexafluoroisopropylidenimino)dimethyltellurium(IV),(XIV), would be expected.



XIII



XIV

The NMR spectra would be expected to be singlet peaks in both the fluorine and proton modes. The spectra of the oily product in $CFCl_3$ solution shows a large number of unresolved broad peaks. The mass spectrum of the oil shows peaks due to $(CH_3)_2Te^+$ and fragments of the $(CF_3)_2C{=}N-$ group,but no fragments which can be assigned to either of the above compounds or their simple breakdown products. A number of high molecular weight peaks up to the limit of the spectrometer's resolution also appear, indicating polymeric species. Repeating the experiment several times gave the same results,and isolation of any identifiable pure compounds was found to be impossible,thus this reaction was not pursued further.

PART 2B : Cleavage reactions of 1,1,1,3,3,3-Hexafluoroisopropylidenimine and it's organometallic derivatives.

1.Hydrolysis.

a. 1,1,1,3,3,3-Hexafluoroisopropylidenimine.

Middleton and Krespan[21] report the synthesis of 2-methoxy-1,1,1,3,3,3-hexafluoroisopropylamine,$(CF_3)_2C(NH_2)OCH_3$

by the reaction of methanol with 1,1,1,3,3,3-hexafluoroisopropylidenimine, but did not report the NMR spectra. (Or other). Thus, a 2:1 excess of the imine was added to methanol in an NMR tube and shaken at room temperature for a few minutes. The fluorine NMR spectrum showed a singlet at +78.8ppm. attributed to the methoxy-amine. A smaller singlet (15% of the former) appears at +79.3ppm. and is pesumably due to the formation of a certain amount of 2,2-dimethoxy-1,1,1,3,3,3-hexafluoropropane, $(CF_3)_2C(OCH_3)_2$. Adding approximately 0.03gm. (16mmoles) of water and 0.1gm. (16mmoles) of methanol to 0.6gm (30mmoles) of 1,1,1,3,3,3-hexafluoroisopropylidenimine and shaking for a few minutes, resulted in the formation of the above products and also hexafluoroacetone and it's hydrate. These appear as singlet peaks in the fluorine NMR spectrum at +81.3ppm and +82.2ppm. respectively.

b. 1,1,1,3,3,3-Hexafluoroisopropylideniminotrimethylsilane.

Approximately 0.015gm. (1mmole) of water in 0.05gm, (2mmoles) of methanol were condensed onto a solution of 0.3gm., (1.3mmoles) of 1,1,1,3,3,3-hexafluoroisopropylideniminotrimethylsilane in trichlorofluoromethane. The mixture was warmed to room temperature and studied by NMR.

After 10 minutes the fluorine spectrum showed the characteristic two doublets of quartets of 1,1,1,3,3,3-hexafluoroisopropylidenimine, together with singlets at +78.8ppm. and +82.2ppm. due to 2-methoxy-1,1,1,3,3,3-hexafluoroisopropylamine and hexafluoroacetone hydrate respectively. The proton spectrum shows a singlet at -0.1ppm. corresponding to trimethylsilanol, and also a small singlet at +0.06ppm. assigned to hexamethyldisiloxane. The latter was checked by adding a small amount of pure compound to the mixture and noting a corresponding increase in the peak height.

After 24 hours hydrolysis was complete, the proton spectrum consisting only of silanol and siloxane, and the fluorine spectrum only the singlet peaks assigned to:

+78.8ppm.	$(CF_3)_2C(NH_2)OCH_3$
+79.3ppm.	$(CF_3)_2C(OCH_3)_2$
+81.3ppm.	$(CF_3)_2CO$
+82.2ppm.	$(CF_3)_2C(OH)_2$

c. 1,1,1,3,3,3-Hexafluoroisopropylideniminotrimethylgermane.

Approximately 0.035gm.(2mmoles) of water were condensed onto 0.3gm.(1mmole) of 1,1,1,3,3,3-hexafluoroisopropylideniminotrimethylgermane in solution in trichlorofluoromethane in a reaction tube cooled to -196°. The mixture was warmed to room temperature and mechanically shaken for 24 hours. After one hour hydrolysis was shown to be in progress by the appearance of the typical spectrum of 1,1,1,3,3,3-hexafluoroisopropylidenimine in the fluorine NMR spectrum. After 24 hours the NMR spectra indicated a quantitative yield of the imine had been obtained, as the singlet due to the germane had disappeared and two doublets of quartets identical to the spectrum, Table 1:1 were present.

The proton spectrum consists of two singlets at -0.33ppm. and -0.52ppm attributed to trimethylgermanol and hexamethyldigermoxane respectively. The intensity of the latter increased with time as the intensity of the former decreased due to condensation of the germanol. After several days hydrolysis products of the imine had appeared.

Due to the positive results obtained with the silicon and germanium compounds,it was considered supererogatory to perform analogous reactions with the tin and lead compounds.

2.Cleavage by Hydrogen Chloride.

a.1,1,1,3,3,3-Hexafluoroisopropylidenimine.

Condensation of a small amount of hydrogen chloride into an excess of 1,1,1,3,3,3-hexafluoroisopropylidenimine contained in an NMR tube resulted in an exothermic reaction. The fluorine NMR spectrum showed a singlet at +77.5ppm. This is attributed to 2-chloro-1,1,1,3,3,3-hexafluoroisopropylamine,$(CF_3)_2C(NH_2)Cl$.

b.1,1,1,3,3,3-Hexafluoroisopropylideniminotrimethylsilane.

A small amount of hydrogen chloride was admitted to an NMR tube containing an excess of the silane. The NMR fluorine spectrum was immediately run and showed singlets at +77.8ppm. and +76.9ppm. intensity ratio 5:1,the former due to $(CF_3)_2C(NH_2)Cl$. The latter peak is assigned to(2-chloro-1,1,1,3,3,3-hexafluoroisopropylamino)-trimethylsilane,$(CF_3)_2CClNHSi(CH_3)_3$,produced by straightforward addition of hydrogen chloride to the C=N bond of the silane.

A 2.5:1 excess of hydrogen chloride was condensed onto 1,1,1,3,3,3-hexafluoroisopropylideniminotrimethylsilane at -78° and sealed in an NMR tube. The mixture was allowed to warm up to room temperature and the NMR spectra of the products in $CFCl_3$solution were taken. The fluorine spectrum showed only a singlet in the CF_3 region due to 2-chloro-1,1,1,3,3,3-hexafluoroisopropylamine. The proton spectrum consisted of a singlet at -0.3ppm. due to trimethylchlorosilane,and a broad singlet at -1.88ppm.assigned to the amino group of the $(CF_3)_2C(NH_2)Cl$.

A white solid separated out from the reaction mixture and was isolated by condensing the liquid products into one end of the tube and leaving the dry solid in the other. This was subjected to mass spectral analysis and revealed peaks characteristic of $(CF_3)_2C(NH_2)Cl$, those above m/e 100 being weak as it was found that the compound was highly unstable towards disproportionation at room temperature, rapidly liberating hydrogen chloride and liquefying (1,1,1,3,3,3-hexafluoroisopropylidenimine).

The mass spectrum shows the following peaks:

m/e	assignment
201/203	$((CF_3)_2C(NH_2)Cl)^+$ (M^+)
185/187	$(M-NH_2)^+$
165	$(M-HCl)^+$
69	$(CF_3)^+$
51	$(CF_2H)^+$
38	$(H^{37}Cl)^+$
36	$(H^{35}Cl)^+$
37/35	Cl^+

The unstable nature of this amine has been previously reported.[28]

c.1,1,1,3,3,3-Hexafluoroisopropylideniminotrimethylgermane.

Hydrogen chloride and the germane were reacted together in an analogous manner to the silane above. The NMR spectra indicated formation of $(CF_3)_2C(NH_2)Cl$, and again the pure material was isolated. A singlet at -0.9ppm. in the proton spectrum was due to trimethylchlorogermane.

PART 2C: Reactions of Xenon Difluoride with 1,1,1,3,3,3-Hexafluoroisopropylidenimine and it's Organic and Organometallic Derivatives.

I.1,1,1,3,3,3-Hexafluoroisopropylidenimine in CH_3CN solution.

A solution of xenon difluoride (0.38M) in acetonitrile was shaken with an approximately 2:1 excess of 1,1,1,3,3,3-hexafluoroisopropylidenimine in an NMR tube for 24 hours at room temperature. After this time the fluorine NMR spectrum revealed that 14% reaction had occurred,with a doublet peak appearing at +80.4ppm.(Table 5:2), with J=5Hz. This is characteristic of a $(CF_3)_2CH-$ group or a $(CF_3)_2CF-$ group[133,134]. In the present case the latter is more likely,as the proton spectrum of the reaction mixture shows only the solvent peak,even at very high gain,while a septet in the $\overset{|}{\underset{|}{C}}H-$ region would be expected if a $(CF_3)_2CH-$ group were present. The doublet can therefore be more reasonably assigned to the $(CF_3)_2CF-$ group in heptafluoroisopropylamine,$(CF_3)_2CFNH_2$. In this case,due to the low concentration,the septet arising from the CF group was not observed in the fluorine search,but see II below. The chemical shifts and coupling constant of this compound have not been reported,as it rapidly attacks glass[21](?). No other products were observed in this reaction,even when carried out at -20° for seven days.

II.1,1,1,3,3,3-Hexafluoroisopropylidenimine with solid XeF_2.

1,1,1,3,3,3-Hexafluoroisopropylidenimine,0.3gm.(2mmoles), were distilled carefully onto xenon difluoride,0.34gm.(2mmoles) in an NMR tube ,at -196°. The tube was allowed to warm to room temperature and left to stand for 85 hours,during which time slow liberation of gas was observed. The NMR spectra are shown in Table 5:3 and 5:4.

The fluorine spectrum consists of the following peaks:

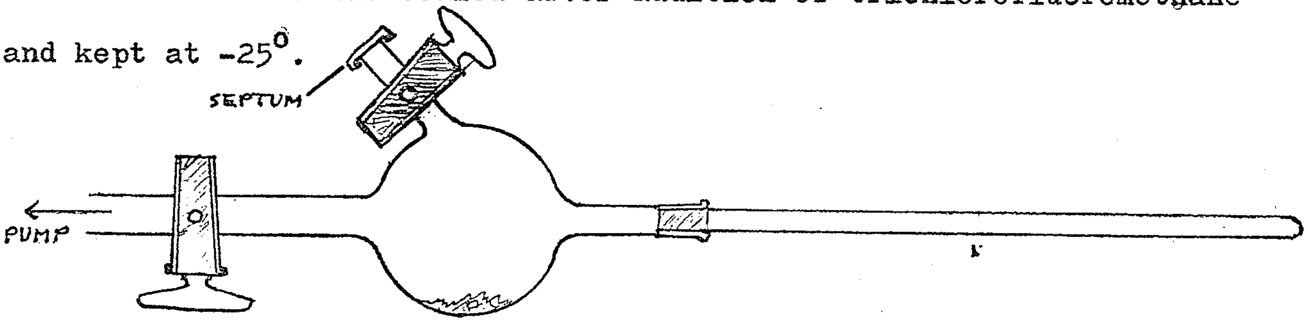
shift		J value	integration
+84.5	doublet	2 Hz	1
+82.9	doublet	4 Hz	13
+78.6	doublet	4 Hz	3
+78.3	doublet	4 Hz	1
+78.1	singlet		2.5
+74.8	quartet	6 Hz	6
+72.8	doublet of quartets	6 Hz & 2 Hz	6
+70.7	broad peak		4.5
+69.7	doublet of quartets	6 Hz & 1.5 Hz	3
+66.7	broad peak		ca.4.5
+66.1	doublet of quartets	6 Hz & 3 Hz	ca. 3
+122.0	septet	4 Hz	125

The quartets at +74.8ppm.and +72.8ppm.are due to unreacted starting material. The broad peaks at +66.7ppm. and +70.7ppm. are assigned to hexafluoroacetone azine,(perfluoro-2,5-dimethyl-3,4-diaza-2,4-hexadiene),$(CF_3)_2C{=}NN{=}C(CF_3)_2$[21]. The doublet at +82.9ppm. and the septet at +122.0ppm. are assigned to heptafluoroisopropylamine,$(CF_3)_2CFNH_2$. The difference in chemical shift for this compound found in this experiment and the above experiment is attributed to a solvent shift due to the acetonitrile,as a similar shift is observed for the 1,1,1,3,3,3-hexafluoroisopropylidenimine;viz.+70.9ppm.and +71.9ppm. The doublets of quartets at +66.1ppm. and +69.7ppm. are characteristic of non-equivalent CF_3-groups in an A_3B_3X system. The spectrum does not correspond to that of N-fluoro-1,1,1,3,3,3-hexafluoroisopropylidenimine,$(CF_3)_2C{=}NF$, however, as the F-F coupling constants are 24Hz. and 12Hz.respectively[135],with $J_{CF_3-CF_3}$=6.5Hz. The possibility of the compound being 1,1,1,3,3,3-hexafluoroisopropylideniminofluoroxenon(II) is not borne out by the fluorine search, as satellite peaks due to coupling of the CF_3 groups with ^{129}Xe would be easily observable, the natural abundance of ^{129}Xe being 26.2%. The spectrum thus remains enigmatic.

The doublet at +78.6ppm. is again characteristic of a $(CF_3)_2CF$- group, and it is reasonable to assign this to the formation of N,N'-bis(heptafluoroisopropyl)hydrazine, $(CF_3)_2CFNHNHCF(CF_3)_2$.

III.1,1,1,3,3,3-Hexafluoroisopropylideniminolithium.

A solution of xenon difluoride (0.38M) in acetonitrile was injected into an NMR tube containing 1,1,1,3,3,3-hexafluoroisopropylideniminolithium prepared in situ by the method described on page 48, using the reaction bulb illustrated below. The reaction tube was sealed after addition of trichlorofluoromethane and kept at -25°.



Reaction bulb for $(CF_3)_2C=NLi + XeF_2$ experiments.

After 1.5 hours the fluorine NMR spectrum appeared as in Table 5:5, with the characteristic spectrum of 1,1,1,3,3,3-hexafluoroisopropylidenimine at +70.8ppm. and +71.6ppm., with two singlets at +76.8ppm and +79.4ppm. and a doublet, J=6.5Hz. at +74.3ppm. After 18 hours the latter had disappeared and the two singlets had increased in intensity. However, the doublet appears weakly in some preparations of the lithium salt and can be ascribed to the formation of a small amount of decomposition product, presumably from "hot-spotting" during the preparation.

It has also been found that butyllithium in THF solution abstracts hydrogen from acetonitrile quite rapidly, even at -80°.[136]

$$C_4H_9Li \quad + \quad CH_3CN \longrightarrow LiCH_2CN \quad + \quad C_4H_{10}$$

Thus to test whether a similar reaction occurred with 1,1,1,3,3,3-hexafluoroisopropylideniminolithium,a 1:1 mixture of this compound with acetonitrile was prepared at -25° and kept at this temperature for 1.5 hours,after which time the fluorine NMR spectrum appeared as in Table 5:6. The singlets at +76.8ppm. and +79.4ppm. are therefore attributed to products arising from the reaction of $(CF_3)_2C{=}NLi$ with acetonitrile rather than with xenon difluoride. The absence of 1,1,1,3,3,3-hexafluoroisopropylidenimine from this reaction does indicate that this is a product of the latter reaction,however. The proton spectrum of this experiment shows two singlets,at -2.0ppm,due to acetonitrile,and at -0.22ppm. assigned to lithioacetonitrile,$LiCH_2CN$.

The reaction was repeated with a solution of xenon difluoride in deuteroacetonitrile and the spectrum of the products is shown as Table 5:7. Again,1,1,1,3,3,3-hexafluoroisopropylidenimine is produced after complete reaction of the lithium salt,i.e.$(CF_3)_2C{=}N\underline{H}$,not $(CF_3)_2C{=}N\underline{D}$. Also,the doublet at +80.4ppm. is assigned to $(CF_3)_2CFN\underline{H}_2$. Vigorous outgassing was observed in these reactions,and the singlet at +185ppm. due to xenon difluoride disappears,showing that a rapid reaction between the salt and XeF_2 takes place. A white precipitate forms,and in one run this was isolated and dried,then investigated by x-ray diffraction using a Picker Type 6147 diffraction unit fitted with a Unicam S-70 powder camera. A second run was made on a pure sample of lithium fluoride and the photographs were compared as shown in the plate on page 63. It can be seen that the solid product from the reaction consists mainly of lithium fluoride;the extra faint lines are due to the presence of a few percent of lithium fluorosilicate.[137]

Finally,repeating the reaction in a Teflon reaction tube again gave rise to 1,1,1,3,3,3-hexafluoroisopropylidenimine as a major product.

IV.1,1,1,3,3,3-Hexafluoroisopropylideniminotrimethylsilane.

1,1,1,3,3,3-Hexafluoroisopropylideniminotrimethylsilane,0.36gm.(1.5mmoles) was condensed onto 0.17gm.(1mmole) of xenon difluoride contained in a flamed-out U-tube at 25°. The mixture was heated at 40° for four hours,during which time gas bubbles were slowly evolved and the crystal dissolved. The products were distilled into a carefully flamed out NMR tube which was then sealed. The fluorine spectrum shows the following peaks:

chemical shift	appearance	coupling constant
+71.1ppm.	doublet of quartets	6Hz & 2.5Hz.
+71.5ppm.	singlet	
+73.3ppm	doublet of quartets	6Hz & 1Hz.
+155ppm.	dectet	7.5Hz
proton spectrum:		
+0.19ppm.	doublet	7.5Hz.
+0.3ppm.	singlet	

Hence the products of the reaction are 1,1,1,3,3,3-hexafluoroisopropylidenimine and trimethylfluorosilane. The same products are obtained when the reaction is carried out using a solution of xenon difluoride in deuteroacetonitrile.

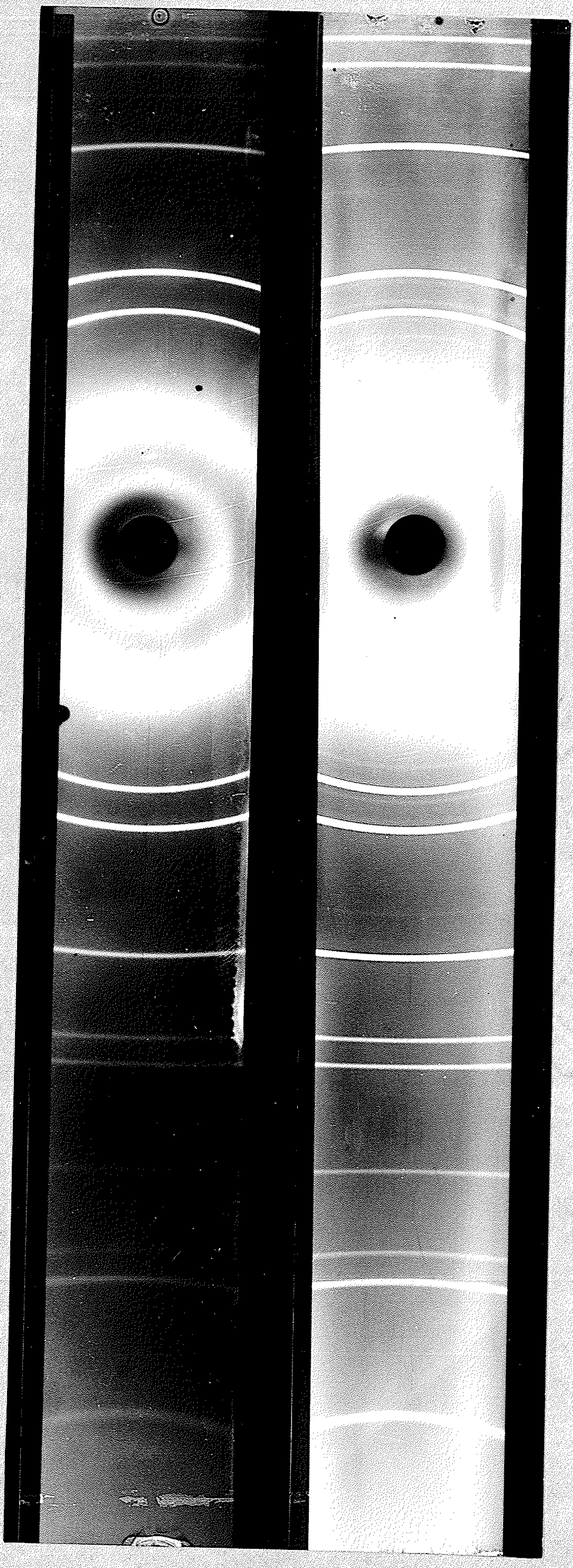
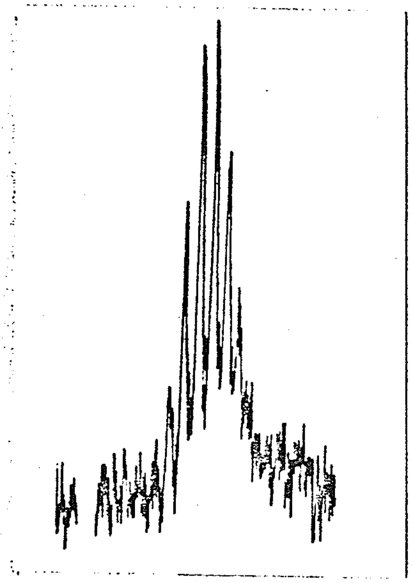


Plate 1.
Left: Diffraction pattern of lithium fluoride.
Right: Diffraction pattern of product of reaction XeF_2 + $(CF_3)_2C{=}NLi$.

V.1,1,1,3,3,3,-Hexafluoroisopropylideniminotrimethylgermane.

The reaction between this derivative and solid xenon difluoride was carried out as for the silicon derivative above. This reaction was more rapid than the latter and outgassing of xenon occurred at a moderate rate at room temperature. The crystal of xenon difluoride had completely disappeared after about three hours. The NMR spectra of the products showed that again the parent imine had been produced, and the characteristic dectet of trimethylfluorogermane appeared at +190.2ppm. with J_{FH}=6.7Hz. In the proton spectrum the doublet of the methyl groups appeared at -0.5ppm.

Repeating the reaction using a CD_3CN solution of XeF_2 in a Teflon reaction tube showed once again only $(CF_3)_2C{=}N\underline{H}$ as product.



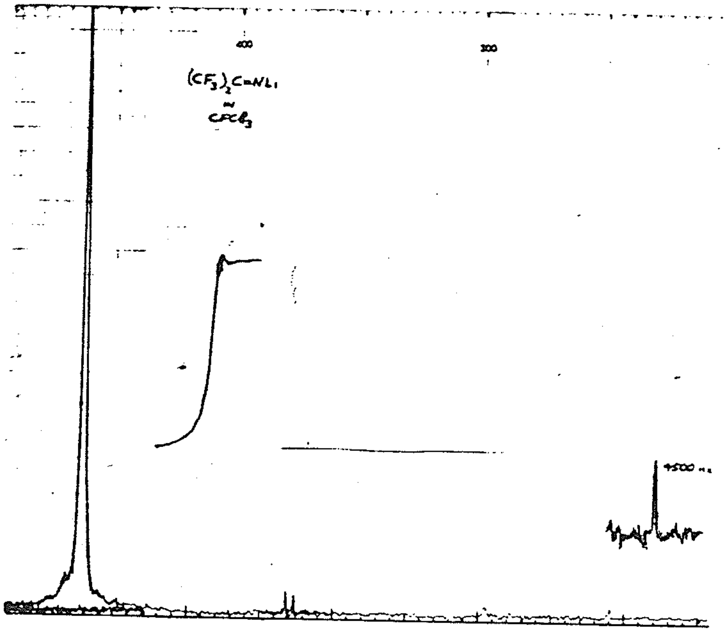
^{19}F resonance of $(CH_3)_3GeF$.

VI.1,1,1,3,3,3-Hexafluoroisopropylideniminotrimethylstannane.

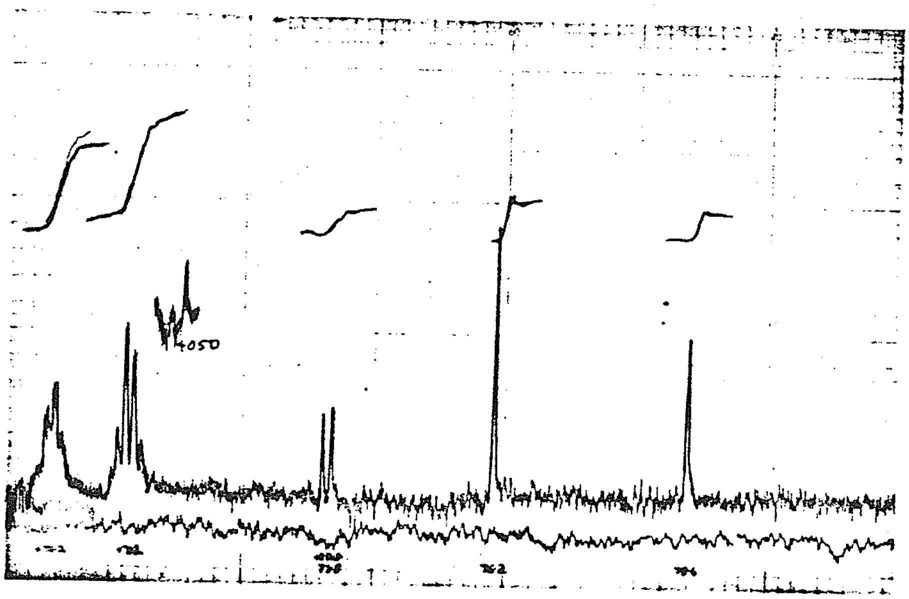
The reaction was carried out identically to those above, but liberation of xenon was much more vigorous. After 1.5 hours at room temperature excess starting material and $(CF_3)_2C{=}NH$ product were distilled off and a white solid remained. This was subjected to mass spectral analysis and found to be trimethylfluorostannane.

TABLE 5

NMR Spectra of Products in Part 2

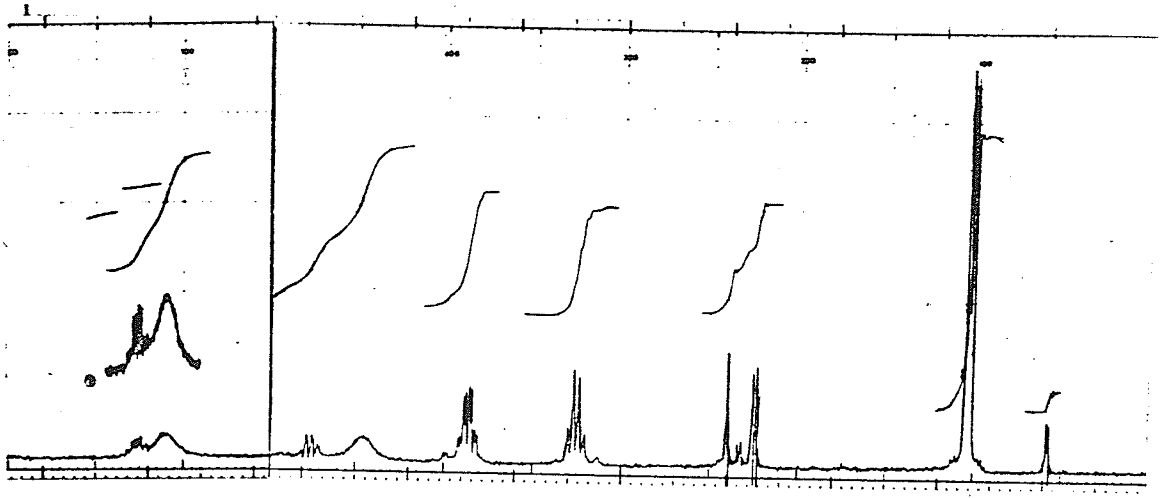


5:1 ^{19}F Spectrum of 1,1,1,3,3,3-Hexafluoroisopropylideniminolithiu

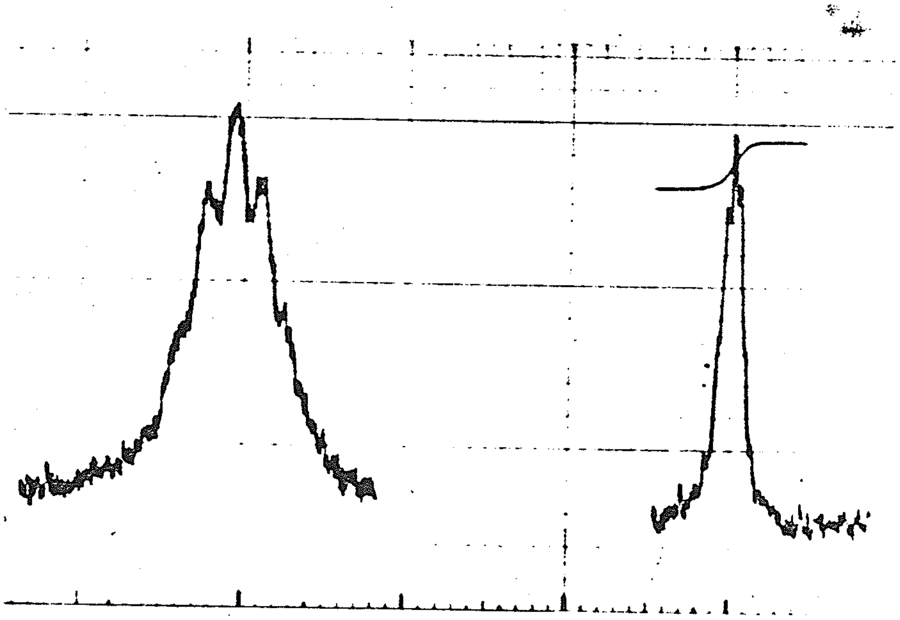


5:2 Products of reaction $(CF_3)_2C=NH + XeF_2$ in CH_3CN. ^{19}F Spectrum.

TABLE 5 (cont'd)

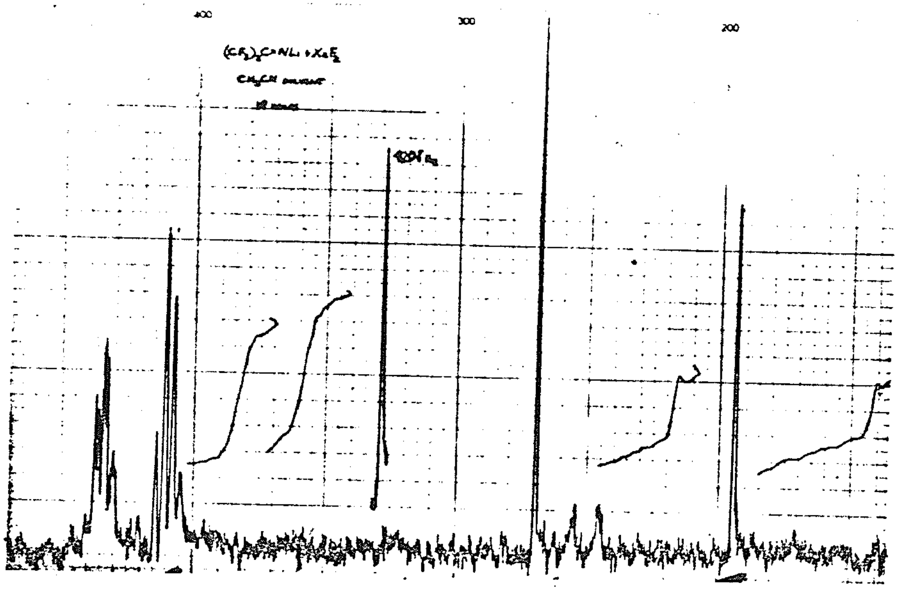


5:3 ^{19}F Spectrum of products from reaction $(CF_3)_2C=NH$ + XeF_2(solid). CF_3 region.

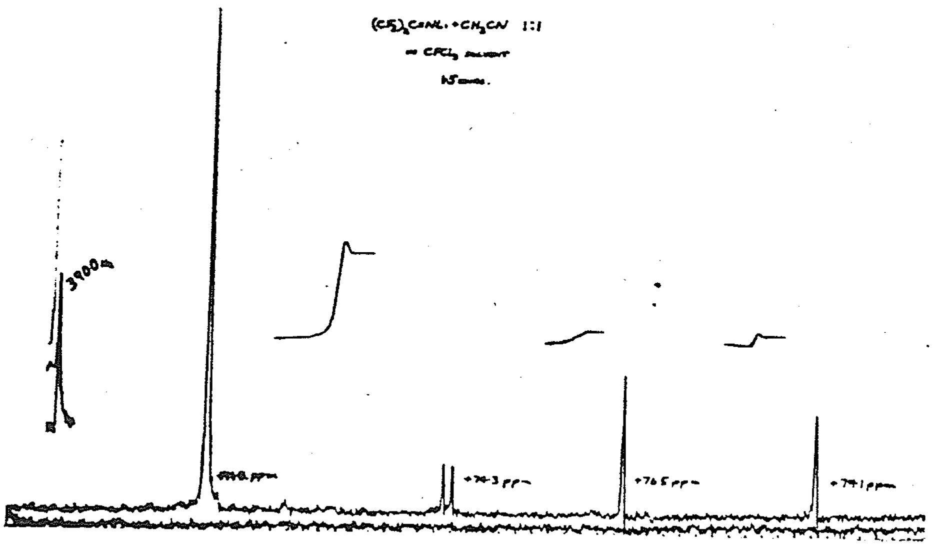


5:4 ^{19}F Spectrum of reaction $(CF_3)_2C=NH$ + XeF_2(solid). Sweep offset +7000Hz.

TABLE 5 (cont'd)

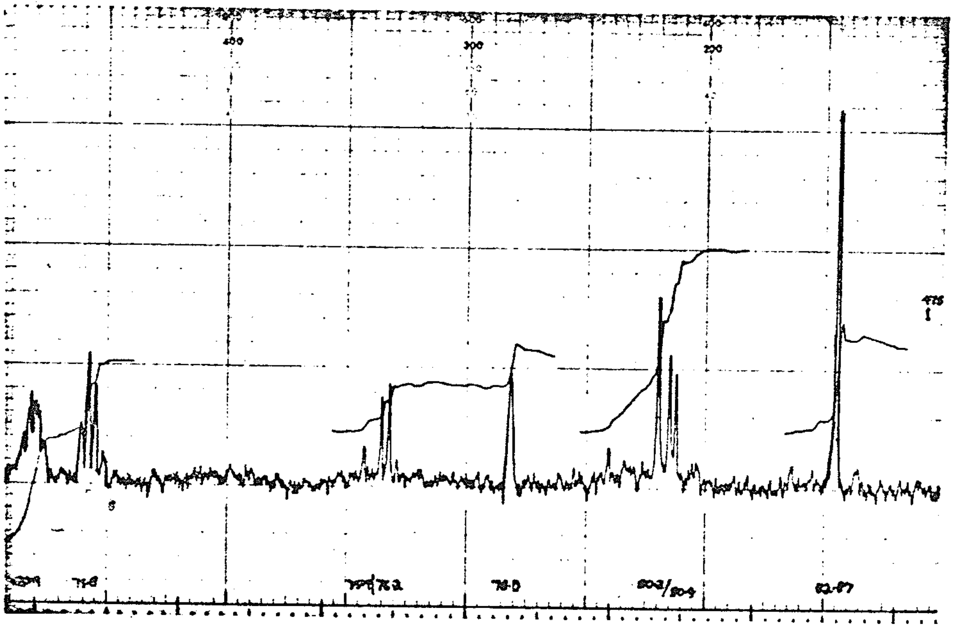


5:5 ^{19}F Spectrum of products of reaction $(CF_3)_2C{=}NLi$ + XeF_2 in CH_3CN.



5:6 ^{19}F Spectrum of products of reaction $(CF_3)_2C{=}NLi$ + CH_3CN.

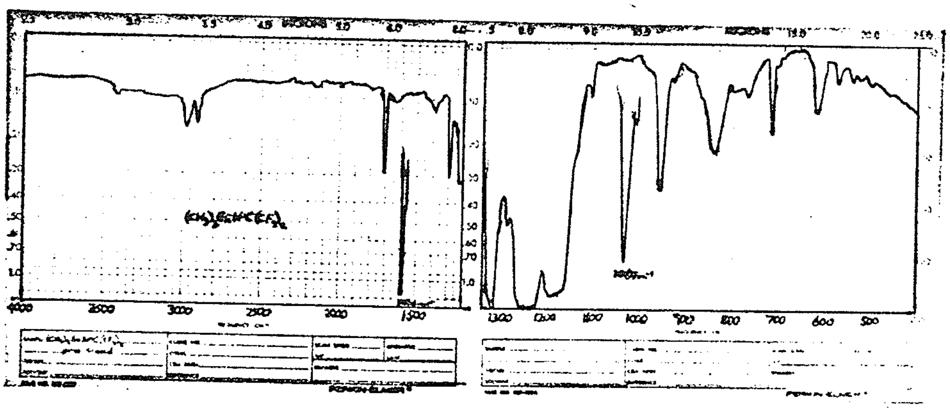
TABLE 5 (cont'd)



5:7 ^{19}F Spectrum of products of reaction $(CF_3)_2C{=}NLi + XeF_2$ in CD_3CN.

TABLE 6

Infra-red Spectra of Products in Part 2



6:1 1,1,1,3,3,3-Hexafluoroisopropylideniminotrimethylgermane (neat).

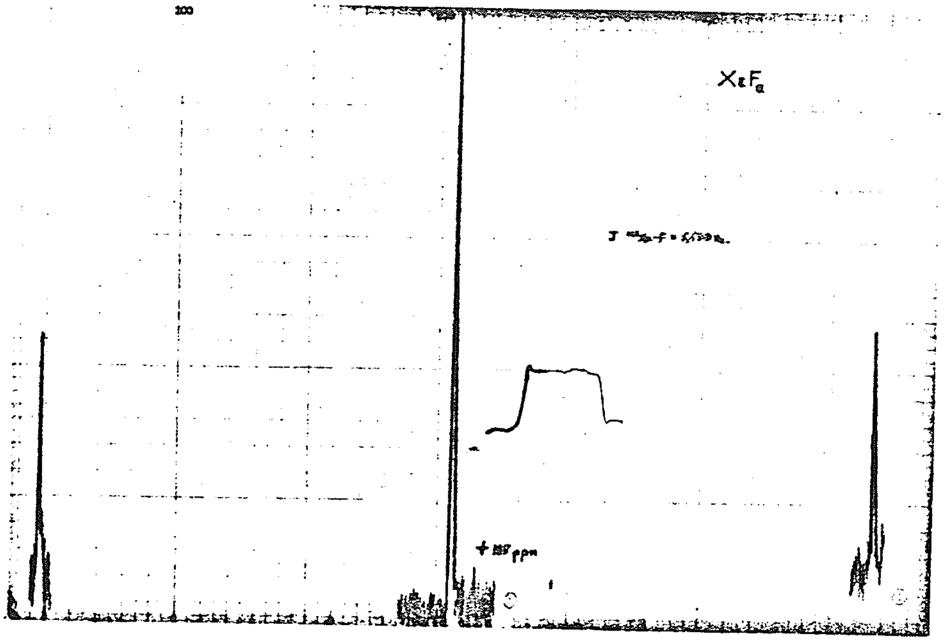


Figure 9. ^{19}F Spectrum of xenon difluoride.

RESULTS AND DISCUSSION

1. Addition of M-H containing compounds to $(CF_3)_2C=NH$

a. Diphenylphosphine.

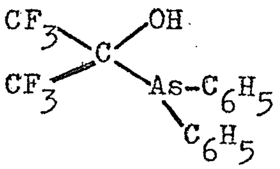
The imino group, C=NH, is isoelectronic with the carbonyl group, and azomethines show many similar reactions to the corresponding carbonyls. The C=N bond is polarised (viz. $-\overset{\delta+}{C}=\overset{\delta-}{N}-$) and the carbon atom is hence susceptible to nucleophilic attack, which in the case of the perfluorinated derivative $(CF_3)_2C=NH$, is enhanced by the highly electronegative nature of the trifluoromethyl groups and resultant large negative inductive effect. One reaction in which the two functional groups differ is hydrogenation; where reduction of azomethines to secondary amines is easily carried out by several methods which are not generally applicable to carbonyls, for example, with reagents such as lithium aluminium hydride[138], sodium borohydride[139], dimethylamine-borane[140] and formic acid[141].

The reaction of diphenylphosphine with 1,1,1,-3,3,3-hexafluoroisopropylidenimine occurs easily by nucleophilic attack of the phosphorus at the carbon to yield 2-amino-2-diphenylphosphino-1,1,1,3,3,3-hexafluoropropane (IV, p.19). No evidence for the formation of $(CF_3)_2CHNHP(C_6H_5)_2$ was obtained. The main indication that IV is the product is the coupling constant of 17.5Hz. of the doublet associated with the CF_3 groups in the ^{19}F NMR spectrum. This value is too large to be associated with F-H coupling in the isopropyl group but is of the expected order of magnitude for F-P coupling across three bonds for phosphorus(III). Although comparable groupings have not been cited in the literature to date, Janzen and Vaidya[142] have recently prepared the hexafluoroacetone adduct, which shows a doublet in the CF_3 region of the spectrum with a coupling constant of 19Hz. This reaction is also complicated by the rearrangement to the phosphine oxide, $(CF_3)_2CHP(O)(C_6H_5)_2$, a previously documented reaction.[143] Support for the assignment of IV would be also provided by the ^{31}P spectrum, which would show a septet. However, although a sample was prepared for this investigation, it decomposed in transit. Further support is given by the mass spectrum of IV which exhibits an abundant peak at m/e 166 due to the $(CF_3)_2\overset{+}{C}NH_2$ ion, produced by cleavage of the P-C bond. Finally the infra-red spectrum shows assymmetric and symmetric stretching modes of an amino group at 3410cm^{-1} and 3340cm^{-1} respectively, and the N-H scissoring mode at 1618cm^{-1}.

Trivalent phosphorus compounds are normally oxidised to the corresponding phosphoryl derivatives by molecular oxygen even in the absence of catalysts.[144] The reaction has been shown to involve free radical processes, as radical initiators accelerate the reaction, whereas hydroquinone inhibits it. Thus compound IV is quite easily oxidised to 2-amino-2-diphenylphosphonato-1,1,1,3,3,3-hexafluoropropane, (V, p.21).

b. Diphenylarsine.

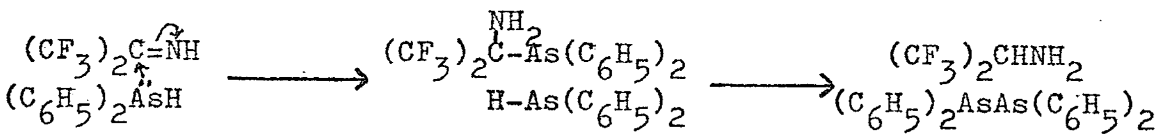
Reaction of diphenylarsine with 1,1,1,3,3,3-hexafluoroisopropylidenimine is fast even at room temperature (see p.24), but a stable adduct does not appear to be produced. This is in contrast to the reaction with hexafluoroacetone, where the only product is the well-characterised compound XV.[142]



XV

The reactions of AsH_3[145] and methyl arsines[146] have also been carried out, with analogous results. Cullen and Styan[146] propose that the products arise by nucleophilic attack by the arsenic lone-pair at the carbonyl carbon. Thus the analogous reaction of diphenylarsine with $(CF_3)_2C{=}NH$ to produce $(CF_3)_2C(NH_2)As(C_6H_5)_2$ would be expected. However, when the reaction is carried out using an excess of either reactant, the products are the same in each case, but the arsinoamine is not isolated or identified. Instead the reduction product 1,1,1,3,3,3-hexafluoroisopropylamine and the dimer tetraphenyldiarsine are the major products, together with an unidentified volatile liquid apparently containing a $(CF_3)_2CH-$ group, but no arsenic or phenyl groups. The most reasonable candidate for the latter is 1,2-(1,1,1-3,3,3-hexafluoroisopropyl)hydrazine, $(CF_3)_2CHNHNHCH(CF_3)_2$, which has not been previously reported. The parent ion for this compound is not observed in the mass spectrum, but this could possibly be due to the ease of cleavage of the N-N bond, which would be expected to be quite weak due to the large electronegative groups bonded to each nitrogen.

To account for the observed products it is necessary to assume the intermediate formation of $(CF_3)_2C(NH_2)As(C_6H_5)_2$ followed by reaction of this with a further molecule of diphenylarsine, at the carbon-arsenic bond:



$$\begin{matrix}(CF_3)_2C{=}NH\\(C_6H_5)_2AsH\end{matrix}\longrightarrow\begin{matrix}(CF_3)_2\overset{NH_2}{C}-As(C_6H_5)_2\\H-As(C_6H_5)_2\end{matrix}\longrightarrow\begin{matrix}(CF_3)_2CHNH_2\\(C_6H_5)_2AsAs(C_6H_5)_2\end{matrix}$$

which infers an exceptionally weak As-C bond in the adduct, as the AsAs bond dissociation energy has been determined as 38kcal/mole in $Me_2AsAsMe_2$.[148]

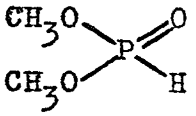
Although the imino group in $(CF_3)_2C{=}NH$ is very weakly basic,its nucleophilicity is probably comparable to the carbonyl group in hexafluoroacetone,and the latter is known to act nucleophilically in some cases.[128,146,147] Thus a possible side reaction would be the formation of the isomer $(CF_3)_2CHNHAs(C_6H_5)_2$,which again may react:

$$2\ (CF_3)_2CHNHAs(C_6H_5)_2 \longrightarrow \begin{array}{c}(CF_3)_2CHNHNHCH(CF_3)_2\\ +\\ (C_6H_5)_2AsAs(C_6H_5)_2\end{array}$$

by nucleophilic attack of nitrogen at arsenic.

c.Dimethyl Phosphite.

Dialkyl phosphites have been reported to add to hexafluoroacetone[128]and azomethines[149]to form adducts.The former has been shown to produce a mixture of isomers,the relative amounts depending on the alkyl groups,whereas the latter appears to give predominantly the amine. Dimethyl phosphite has the structure XVI,and exhibits nucleophilic activity towards strong electrophiles. In the case of hexafluoroacetone addition of the



XVI

P-H bond to the carbonyl group occurs easily at room temperature[128] to produce isomers VII and VIII (p.27)in the ratio 94:6. An analogous reaction might therefore be expected with $(CF_3)_2C{=}NH$ to yield $(CF_3)_2C(NH_2)P(O)(OCH_3)_2$ (IX,p.27) and $(CF_3)_2CHNHP(O)(OCH_3)_2$ (X,p.29). Crystals of material corresponding to such addition products were obtained but only in small yield,due to a number of complex side reactions which took place to produce a large number of unidentified products, including a complex polymer, and also in two cases, compounds VII and VIII. The occurrence of the latter compounds indicates that hexafluoroacetone is produced by hydrolysis of the imino group, and subsequently reacts with dimethyl phosphite. Hydrolysis could occur as a side reaction with water produced in the polymerisation process. The polymer obtained contained CF_3 groups in several different environments as evidenced by the spectrum, Table 3:10, and also methoxy groups, Table 3:11. The mechanisms responsible for the formation of organophosphorus poymers are not fully understood and the structures of most have not been elucidated, so that it is regarded as pedestrian to reproduce here the array of postulated mechanisms for this field, when the experiment is irreproducible; instead a number of exhaustive reviews can be referred to.[144,150,151]

d. Trimethylsilanol and Triethylsilanol.

Trimethylsilanol reacts with hexafluoroisopropylidenimine straightforwardly to produce the siloxy-amino compound XI. (p.29). The reaction produces approximately equal yields of $(CF_3)_2C(NH_2)\text{-}OSi(CH_3)_3$ and $(CF_3)_2C(OH)OSi(CH_3)_3$ as evidenced by their NMR and mass spectra. The reason for this is the unstable nature of the silanol group, which is particularly marked in trimethylsilanol[45], with respect to the reaction:

$$2\ (CH_3)_3SiOH \longrightarrow (CH_3)_3SiOSi(CH_3)_3 \quad + \quad H_2O$$

The water produced in this reaction would hydrolyse the 1,1,1,3,3,3-hexafluoroisopropylidenimine to form hexafluoroacetone, which would compete with the imine in reaction with the trimethylsilanol. The triethylsilanol reaction appears to produce mainly compound XII, in that the NMR spectrum shows only a singlet in the CF_3 region for the crude products. The mass spectrum is indicative of $(CF_3)_2C(NH_2)OSi(CH_2CH_3)_3$ rather than $(CF_3)_2C(OH)OSi(C_2H_5)_3$ (see p.31). However, due to the poor analytical correspondence, the compound cannot be positively identified.

The mechanism of silanol addition to double bonds is again considered to involve nucleophilic attack of the oxygen atom at the imino carbon. The stability of the hydroxy compounds, and therefore by extension, the amino compounds, has been suggested to depend mainly on the strength of the Si-O bond due to p_π-d_π bonding, and on the stabilising effect on the C-O bond exerted by the proximate trifluoromethyl groups.[129,152,153]

e. Silanes.

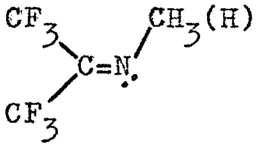
Products with hexafluoroisopropylidenimine would probably arise on irradiation with ultra-violet light. In the case of hexafluoroacetone[129] "abnormal" addition takes place to give alkoxides rather than alcohlos and an ionic mechanism is proposed. In the case of the imine analogous reaction would produce silazanes of the perfluoroisopropyl group, not otherwise easily obtained.

2. Organometallic Derivatives of the $(CF_3)_2C=N-$ Group, Derived From $(CF_3)_2C=NLi$.

The compounds $Me_3MN=C(CF_3)_2$ where M=Group IVB element are straightforwardly prepared by the metathetical reaction $(CF_3)_2C=NLi + XM(CH_3)_3 = LiX + (CH_3)_3MN=C(CF_3)_2$ (M=Si,Sn,Ge,Pb) and in the case of M=C, by the reaction of methylamine with hexafluoroacetone,[21] $(CF_3)_2CO + H_2NCH_3 \xrightarrow{POCl_3,Py} (CF_3)_2C=NCH_3$.

The structures of these compounds are not always certain, as borne out particularly by their NMR spectra, which for the compounds of Si, Ge and Sn consist simply of a singlet for the methyl groups, as expected, and a singlet for the trifluoromethyl groups. A temperature study of the fluorine spectrum of the silicon derivative showed that the singlet persists with no tendency to broaden in the range -90° to $+100^\circ$. This is in contrast to the parent imine itself (p.37) and the N-methyl derivative, which latter shows two quartets of quartets in the fluorine spectrum and a quartet of quartets in the proton spectrum.

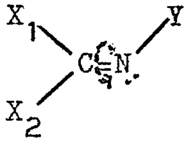
From this it can be seen that the two purely organic compounds exist with an angular structure with sp^2 nitrogen and a large barrier to inversion about the nitrogen. (XVII)



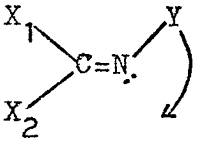
XVII

The corresponding metal derivatives would therefore seem to possess equivalent trifluoromethyl groups. This in turn implies that either exchange, or rapid syn-anti isomerisation is occurring at the N-M bond. Several investigations of isomerisation about the C=N bond have been carried out.[27,154,155]

Two mechanisms for syn-anti isomerisation have been reported, an out -of-plane rotation of the N substituent[156-158], or an in-plane lateral shift[159,160], which are illustrated as:[155]

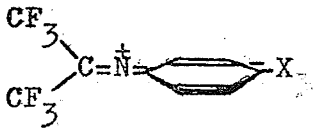


rotation

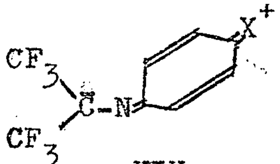


lateral shift

For p-substituted N-phenyl derivatives of the $(CF_3)_2C=N-$ group, the results from kinetic studies by line-shape analysis of NMR spectra at various temperatures[155], have been interpreted as arising from the latter mechanism for the p-NO_2 compound, and the former for the Cl, F, CH_3O, and CH_3 compounds. The respective proposed transition states are shown by XVIII and XIX:



XVIII



XIX

Thus it can be seen that on this interpretation, that when Y is H or CH_3, the inability of these groups to form conjugated intermediates would result in negligible isomerism at normal temperatures and hence the observation of non-equivalent CF_3 groups in the fluorine NMR spectrum, which is the case. This fact also implies a low rate of proton exchange in the parent imine.

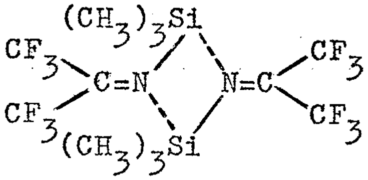
In the case of the Me_3M- derivatives there are several possible reasons for the equivalence of the CF_3 groups;

a. A degree of $p_\pi - d_\pi$ interaction between the nitrogen lone-pair and silicon vacant d orbitals forming a molecular orbital of an allene type. This reduction in bond order for the C=N bond should therefore be reflected in a lowering of the stretching frequency and so consequently a red shift of the absorption band in the infra-red spectrum. The frequencies are adumbrated:

Y substituent	C=N stretching frequency
$-H$	$1675 cm^{-1}$
$-CH_3$	1690
$-Si(CH_3)_3$	1770
$-Ge(CH_3)_3$	1698
$-Sn(CH_3)_3$	1662

Thus, from this tabulation, nothing can be inferred regarding such overlap. The comparatively low frequency for the parent imine is presumably due to effects of hydrogen bonding. The subsequent red shifts obtained in the metal derivatives are probably mainly a reflection of the increase in mass of the substituents.

b. Exchange of the Y substituents via the four-centre intermediate XX.



XX

This process would be expected to be highly temperature dependent, but, as noted above, the fluorine spectrum remains unchanged over a wide temperature range.

c. Formation of the dimer XX as the predominant species in the liquid state of the compounds. This should be weakly bonded and would be expected to be split into the monomer in dilute solution with a donor solvent. However, as a test of this a temperature study of an approximately 0.1M solution of the tin derivative in diethyl ether was carried out. No change from a singlet in the fluorine NMR spectrum of this compound was observed as low as -60°, thus the explanation of these apparently anomalous spectra pends further studies.

3. Reactions of Xenon Difluoride with Organometallic Compounds.

From the results described on pages 57-59 it is shown that xenon difluoride reacts with the metal nitrogen bonds of the compounds $(CF_3)_2C=NM(CH_3)_3$ to produce the trimethylmetal fluoride and $(CF_3)_2C=NH$. Mechanisms have recently been suggested for the reactions of xenon difluoride as a fluorinating agent.[90,100,161] In the case of good fluoride acceptors, the existence of the XeF^+ ion has been established[90,100], and for reactions of XeF_2 with aromatic compounds, an HF catalysed reaction involving XeF^+ and XeF° has been suggested.[161] In the present case the reaction is more likely to resemble the former case, acting as a fluoride ion donor to the good acceptor Me_3M- giving the Me_3MF derivatives with the intermediate formation of some type of Xe-N interaction.

$$(CF_3)_2C=NM(CH_3)_3 + XeF_2 \longrightarrow (CH_3)_3MF + (CF_3)_2C=\overset{-}{N}\cdots\overset{+}{Xe}F$$

This intermediate would then be expected to rapidly decompose to yield the N-fluoro imine and xenon. However, none of the former was observed but only the parent imine, a possible explanation for which might be that the N-M bond is actually cleaved by HF. On the other hand, it has been found that no detectable reaction occurs between xenon difluoride and C-H bonds in organosilicon compounds,[162] thus obviating the methyl groups as a source of hydrogen by direct reaction. Furthermore the reaction of HCl with an excess of the iminosilane (p. 51) showed that cleavage of the M-N bond and addition to the C=N bond were competitive, $(CF_3)_2C(NH_2)Cl$ being formed. Thus in the present reactions it would be expected that some $(CF_3)_2CFNH_2$ would result if HF were involved, but this compound is not observed. It is therefore suggested that the intermediate $(CF_3)_2C=N\cdots XeF$, if formed, reacts with methyl groups to form fluoro-substituted methyl groups, for example, $(CH_3)_2CH_2FMF$, $(CH_2F)_2CH_3MF$ & $(CF_3)_2C{=}NM(CH_3)_2CH_2F$, (the imino derivatives being in excess), liberating xenon and giving the parent imine. The spectra of such products would be complex and in low concentrations, which would preclude ease of observation. The expected weakness of the Xe-N interaction coupled with the decreased acceptor strengths of the metals due to the electron-withdrawing group substituted would explain the observed low rate of reaction, and as the rate increases as M is lower in the group, this is in accord with the increased acceptor properties of the metals going down the group, and the decrease in stability of the M-N bonds.[45,54-59]

The reaction of xenon difluoride with $(CF_3)_2C{=}NH$ appears to be complex. Here the main products are heptafluoroisopropylamine and hexafluoroacetone azine, together with another unidentified material. This suggests that HF is produced in the reaction and adds on to the C=N bond of $(CF_3)_2C{=}NH$ to produce $(CF_3)_2CFNH_2$. The initial formation of HF is probably by direct reaction between the imine and xenon difluoride;

$$(CF_3)_2C{=}NH \; + \; XeF_2 \longrightarrow (CF_3)_2C{=}NXeF \; + \; HF$$
$$\searrow (CF_3)_2C{=}NF \; + \; Xe$$

To account for the formation of the other products, the following reactions are postulated;

$$(CF_3)_2C{=}NH \; + \; HF \longrightarrow (CF_3)_2CFNH_2$$
$$(CF_3)_2C{=}NH \; + \; (CF_3)_2C{=}NF \longrightarrow (CF_3)_2C{=}NN{=}C(CF_3)_2 \; + \; HF$$
$$(CF_3)_2C{=}NN{=}C(CF_3)_2 \; + \; 2HF \longrightarrow (CF_3)_2CFNHNHCF(CF_3)_2$$

Also, a possible free-radical mechanism can be invoked,[161]

$$(CF_3)_2C{=}NH \; + \; XeF_2{-}{-}HF \longrightarrow ((CF_3)_2C{=}NH)^{+\cdot} + \; XeF^{\cdot} \; + \; HF_2^-$$

$$(CF_3)_2C{=}NH \; + \; XeF^{\cdot} \; + \; HF \longrightarrow ((CF_3)_2C{=}NH)^{+\cdot} + \; Xe \; + \; HF_2^-$$

$$((CF_3)_2C{=}NH)^{+\cdot} \; + \; (CF_3)_2C{=}NH \longrightarrow ((CF_3)_2C{=}NHNH{=}C(CF_3)_2)^{+\cdot}$$

$$((CF_3)_2C{=}NHNH{=}C(CF_3)_2)^{+\cdot} \; + \; HF^- \; + \; XeF_2{-}{-}HF \longrightarrow (CF_3)_2C{=}NN{=}C(CF_3)_2 \; + XeF^{\cdot} + 4HF$$

This latter is not borne out experimentally, however, as ESR investigation did not reveal any free-radicals.

The reaction of xenon difluoride with the 1,1,1,3,3,3-hexafluoroisopropylideniminolithium to produce the parent imine is puzzling. It would seem facile for the reaction

$$(CF_3)_2C{=}NLi + XeF_2 \longrightarrow (CF_3)_2C{=}NXeF \; + \; LiF$$

to occur, followed by liberation of xenon and formation of $(CF_3)_2C{=}NF$. Although lithium fluoride is definitely formed, no trace of the N-fluoro imine is found, and as xenon is liberated, the isolation of a stable xenon-nitrogen bonded compound is not indicated.

REFERENCES

1. H.Moissan; Comptes Rend.102,1543 (1886)
2. M.Stacey Progress in Inorganic Chem. 2, 29 (Ed. Cook) (1960)
3. H.J.Emeléus Fluorine Chemistry Vol.2, 321 (Ed. Simons)
4. A.K.Barbour,L.J.Belf,and M.W.Buxton; Adv. Fluor. Chem. 3,181 (1962)
5. J.Burdon and J.C.Tatlow;Adv. in Fluor. Chem. 1,129 (1960)
6. D.H.R.Barton; Pure and Applied Chem. 21,285 (1970)
7. P.M.Treichel;and F.G.A.Stone; Adv. in Organometallic Chem. 1,143
8. R.E.Banks; "Fluorocarbons and their Derivatives" Oldbourne Press London, 1964
9. H.C.Clark; Adv.in Fluor. Chem. 3,19 (1962)
10. R.Nyholm; Quart.Rev. 24,1 (1970)
11. N.Fukuhara and L.A.Bigelow; J.Amer.Chem.Soc. 63,788 (1941)
12. C.G.Krespan and W.J.Middleton; Fluorine Chem. Rev. 1,145 (1967)
13. SS.Andreades,D.C.England and R.U.Lindsey; US Pat.3,030,409 (1962)
14. I.L.Knunyants,T-Y.Chen,and N.B.Gambaryan;Izv.Akad.Nauk CCCP,Otd. Khim.Nauk 1960,686.
15. H.E.Simmons and D.W.Wiley; J.Amer.Chem.Soc. 82,2288 (1960)
16. I.L.Knunyants,E.M.Roxhlin,N.P.Gambaryan,Yu.A.Cherburkov and T-Y.Chen;Khim.Nauka i Promy. 4,802 (1959) ; CA: 54,10851
17. A.F.Janzen and C.J.Willis; Can.J.Chem. 44,745 (1966)
18. R.A.Brown ; Inorg.Chem. 5,1831 (1966)
19. H.R.Davis; Abst.of Papers,140th.Meeting of Amer.Chem.Soc.,Chicago, Ill. Sept.1961 Paper 53,25M
20. Y.V.Zeifman,N.P.Gambaryan and I.L.Knunyants;Dokl.Akad.Nauk SSSR 153,1334 (1963)
21. W.J.Middleton and C.G.Krespan; J.Org.Chem. 30,1398 (1965)
22. IUPAC Nomenclature of Organic Chemistry,Section C,Rule 815.3,p.185
23. W.J.Middleton (E.I.du Pont de Nemours & Co.) US Pat.3,226,439 (1965)
24. B.L.Dyatkin,K.N.Makarov and I.L.Knunyants;Tetrahedron 27,51 (1971)

25.O.Glemser and S.P.von Halasz; Chem.Ber. 102, 3333 (1969)

26.S.P.von Halasz and O.Glemser; ibid 103, 553 (1970)

27.R.F.Swindell,T.J.Ouellette,D.P.Babb and J.M.Shreeve;Inorg.Chem. 11, 242 (1972)

28.K.Niendenzu,K.E.Blick and C.D.Miller;Inorg.Chem. 9, 975 (1970)

29.K.Niendenzu,C.D.Miller and F.C.Nahm;Tetrahedron lett. 1970, 2441

30.R.F.Swindell,L.M.Zaborowski and J.M.Shreeve;Inorg.Chem. 10,1635 (1971)

31.J.Ashley-Smith,M.Green,and F.G.A.Stone;J.Chem.Soc.A 1969,3019

32.R.Countryman and B.R.Penfold;Chem.Comm. 1971,1598

33.M.Green,S.K.Shakshooki &F.G.A.Stone;J.Chem.Soc.A 1971,2828

34.F.G.A.Stone; Pure and Appl.Chem. submitted 1971

35.S.Toby and G.O.Pritchard;J.Phys.Chem. 75,1326 (1971)

36.Idem.& F.S.Toby;Abstracts 162nd.Nat.Meeting of Amer.Chem.Soc., Washington,D.C.,Sept.1971,Phys.034.

37.B.G.Tucker & E.Whittle;Trans.Faraday Soc.61.484 (1965)

38.D.W.Follmer,S.Toby & G.O.Pritchard;J.Phys.Chem. 76, 487 (1972)

39.F.A.Miller & F.E.Kiviat;Spectrochimica Acta 25A,1577 (1969)

40.R.L.Hilderbrandt,A.L.Andreassen & S.H.Bauer;J.Phys.Chem.74,1586 (1970)

41.This work p.37.

42.B.Cetinkaya,M.F.Lappert & J.M.Meeking;Chem.Comm. 1971,215

43.R.F.Swindell,T.J.Ouellette,D.P.Babb & J.M.Shreeve;Inorg.Nuc.Chem. Lett. 7,239 (1971)

44.R.F.Swindell & J.M.Shreeve;Chem.Comm. 1971,1272

45.C.Eaborn "Organosilicon Compounds",p.339 Butterworths 1960

46.E.W.Abel & D.A.Armitage;J.Chem.Soc. 1964,5975

47.W.Fink;Angew.Chem.Int.Ed. 5,760 (1966)

48.K.Jones & M.F.Lappert;Organometallic Chem.Rev.1,67 (1966)

49.K.A.Hooton;Prep.Inorg.Chem. 4,85 (1968)

50.J.Nasielski;Acad.Roy.Belg.Ch.Sci.Mem;Collect 8° 39,504 (1971)

51.MTP(Med.Tech.Publ.Co.)Int.Rev.Sci;Inorg.Chem.Ser.One 4,275 (1972)

52.MTP(Med.Tech.Publ.Co.)Int.Rev.Sci;Inorg.Chem.Ser.One,4,247 (1972)

53.J.E.Bulten; Organometallic Chem.Rev.B 9,248 (1972)

54.M.Dub; "Organometallic Compounds" vol.2 2nd.Ed.Springer-Verlag (1967)

55.F.Glockling;"Chemistry of Germanium" Academic Press,N.Y. (1969)

56.K.Jones & M.F.Lappert;"Organotin Compounds" Vol.2,p509
(Ed.A.K.Sawyer) M.Dekker (1971)

57.W.P.Neumann;"The Organic Chemistry of Tin"(Trans.W.Moser)Wiley (1970)

58.R.C.Poller;"The Chemistry of Organotin Compounds" Academic Press (1970)

59.M.Lesbre,P.Mazerolles & J.Satge;"The Organic Compounds of
Germanium" Wiley Interscience (1971)

60.H.Shapiro & F.W.Frey;"The Organic Compounds of Lead" Wiley Int.(1968)

61.R.Piekos; Przem.Chem. 48,255 (1969)

62.T.N.Bell;B.J.Pullman & B.O.West;Aust.J.Chem.87,722 (1963)

63.N.Petragnani & M.deMoura Campas;Organometallic Chem.Rev.2,61 (1967)

64.K.J.Irgolic &R.A.Zingaro;Organometallic Reactions 2,117 (1971)

65.W.C.Cooper; "Tellurium" Van Nostrand, (1971)

66.S.C.Cohen,M.L.N.Reddy & A.G.Massey;J.Organomet.Chem.11,563 (1968)

67.E.S.Kosrtiner,M.L.N.Reddy,S.Urch & A.G.Massey; ibid. 15,383 (1968)

68.H.L.Ang,J.S.Coombes, & V.Sukhoverov;J.Inorg.Nuc.Chem.31.877 (1969)

69.A.von Anthropoff;Zeit.Angew.Chem. 37,217 (1924)

70. ibid. ; ibid. 37,695 (1924)

71.L.Pauling ; J.Amer.Chem.Soc. 55,1895 (1933)

72.G.Oddo; Gazz.Chim.Ital. 63, 380 (1933)

73.O.Ruff & W.Menzel; Zeit.Anorg.Allgem.Chem. 213,206 (1933)

74.A.von Anthropoff,K.Weil & H.Frauenhof; Naturwiss. 20, 688 (1932)

75.D.M.Yost & A.L.Kaye; J.Amer.Chem.Soc. 55, 3890 (1933)

76.N.Bartlett; Proc.Chem.Soc. 1962, 218

77. "Noble-Gas Chemistry" ed. H.H.Hyman Univ.of Chicago Press;1963

78.J.G.Malm,H.Selig,J.Jortner & S.A.Rice;Chem.Rev. 65,199 (1965)

79.L.J.Moody,& J.D.R.Thomas;Rev.Pure & Applied Chem. 16,1 (1966)

80.H.H.Claassen; "The Noble Gases" Heath,Boston. 1966

81.Gmelins Handbook of Inorganic Chemistry (Main Supplement to 8th. Edition)Vol 1 Noble-Gas Compounds.

82. ibid. System No.14;C,Pt.C Sect.1;Compounds with the noble-gases, hydrogen and oxygen,8th. ed.,Verlag Chemie,Weinheim/Bergstrasse,1970

83.J.H.Holloway;"Noble-Gas Chemistry",Methuen,London,1968

84.L.Stein; Yale Scientific Magazine 44,2 (1970)

85.J.G.Malm & E.H.Appelman;At.En.Rev.7,3 (1969)

86.B.D.Klimov,V.A.Legasov & V.N.Prusakov;Zhur.Priklad.Khim.(Leningrad) 42,2822 (1969).

87.B.Zemva,J.Slivnik;J.Inorg.Nuc.Chem. 33,3952 (1971)

88.A.J.Edwards,J.H.Holloway & R.D.Peacock;Proc.Chem.Soc. 1963,275

89.J.G.Knowles,& J.H.Holloway;J.Chem.Soc.A 1969,756

90.F.O.Sladky,P.A.Bulliner & N.Bartlett;J.Chem.Soc.A 1969,2179

91.B.Zemva,J.Zupan, & J.Slivnik;J.Inorg.Nuc.Chem. 33,3953 (1971)

92. idem. ;Inst.Josef Stefan IJS Rep.1970,R585

93.H.Meinert & S.Reudiger; Z.Chem. 9,71 (1969)

94.J.Binenboym,H.Selig & J.Shamir;J.Inorg.Nuc .Chem.30,2863 (1968)

95.V.M.McRae,R.D.Peacock & D.R.Russell; Chem.Comm. 1969,62

96.N.Bartlett & F.O.Sladky;J.Chem.Soc.A 1969,2188

97.G.R.Jones,R.D.Burbank & N.Bartlett; Inorg.Chem. 9,2264 (1970)

98.V.A.Legasov,U.B.Sokolov & B.B.Chavanov;Zhur.Fiz.Chim.43,2935 (1969)

99.H.Meinert & G.Kauschka; Z.Chem. 9,35 (1969)

100.N.Bartlett & F.O.Sladky; Chem.Comm. 1968,1046

101.M.Eisenberg & D.D.DesMarteau;Inorg.Nuc.Chem.Lett.6,29 (1970)

102.N.Bartlett,M.Wechsberg,F.O.Sladky,P.A.Bulliner,G.R.Jones & R.D.Burbank;Chem.Comm. 1969,703

103.F.O.Sladky;Angew.Chem.Int.Ed. 8,373 (1969)

104. ibid. ; ibid. 8,523 (1969)

105. ibid. ;Monatsh.Chem. 101,1559 (1970)

106. ibid. ; ibid. 101,1571 (1970)

107.N.Bartlett,M.Wechsberg,G.R.Jones & R.D.Burbank;Inorg.Chem.11,1124(1972)

108.M.Wechsberg,P.A.Bulliner,F.O.Sladky,R.Mews & N.Bartlett;Inorg.Chem. in press.

109.G.J.Perlow & M.R.Perlow; J.Chem.Phys. 41,1157 (1964)

110. idem. ; ibid. 48,955 (1968)

111.G.J.Perlow & H.Yoshida; ibid. 49,1474 (1968)

112.H.Meinert ; Zeit.Chem. 6,71 (1966)

113.L.Y.Nelson & G.C.Pimentel; Inorg.Chem. 6, 1758 (1967)

114.C.T.Goetschel & K.R.Loos;J.Amer.Chem.Soc. 94,3018 (1972)

115.J.F.Liebman & L.C.Allen; Inorg.Chem. 11,1143 (1972)

116.L.Herman & R.Herman; Jour.de Phys.et Radium 24,73 (1963)

117.W.Kaul & R.Fuchs; Z.Naturforch.A 15,326 (1964)

118.J.F.Liebman & L.C.Allen;J.Amer.Chem.Soc. 92,3539 (1970)

119. idem. ;Int,J.Mass Spec.Ion Phys. 7,27 (1971)

120.R.B.Smith;ref.77 p.126

121.Fire and Explosion hazards of Noble-Gas Compounds:Health and Safety Inform.USAEC No.181,Feb 10,1964.Div.of Oper.Safety USAEC, Washington D.C.20545

122.Argonne's contribution to Chem.of Xe,Argonne Nat.Lab.1,17 (1964)

123.C.L.Chernick;J.Chem.Ed. 43,619; J.H.Holloway;ibid. 43,614 (1966)

124.J.H.Holloway;Talanta 14,871 (1967)

125.Pure and Applied Chem. 28,1 (1971)

126.E.L.Muetterties,E.L.Mahler,W.Schmutzler and R.Schmutzler; Inorg.Chem. 3,1298 (1964)

127.A.F.Janzen and T.G.Smyrl;Can.J.Chem.50,1205 (1972)

128.A.F.Janzen and R.Pollitt;Can.J.Chem. 48,1987 (1970)

129.A.F.Janzen; Ph.D.Thesis (1966)

130.G.W.C.Kaye and T.H.Laby;Nuclear Species Tables,Longmans,1968

131.L.H.Sommer,E.W.Pietrusza and F.C.Whitmore;J.Amer.Chem.Soc.68,2282(1946)

132.H.Schmidbauer; Chem.Ber. 98,83 (1965)

133.J.W.Emsley,J.Feeney & L.H.Sutcliffe;"High Resolution NMR Spectroscopy"V.2,p875:Pergamon 1968

134.W.S.Brey,Jr. & J.B.Hynes;Fluorine Chem.Rev. 2,111 (1968)

135.J.K.Ruff; J.Org.Chem. 32,1675 (1967)

136.E.M.Kaiser & C.R.Hauser; J.Org.Chem. 33.3402 (1968)

137.

138.A.H.Sommers & S.E.Aaland; J.Org.Chem. 21,484 (1956)

139.Z.Horii,T.Sakai & T.Inoi;J.Pharm.Soc.Japan,75,1161:Chem.Abs,50,7756 (1953)

140.J.H.Billman & J.W.McDowell;J.Org.Chem. 26,1437 (1961)

141.M.L.Moore;"Organic Reactions"V.5,301(1949) Wiley & sons.N.Y.

142.A.F.Janzen & O.C.Vaidya;Submitted to Can.J.Chem.1972

143.S.A.Buckler & M.Epstein;J.Amer.Chem.Soc.82,2076 (1960)

144.A.J.Kirby & S.G.Warren;"The Organic Chemistry of Phosphorus" p.176 (1967) Elsevier.N.Y.

145.A.B.Bruker,E.J.Grinshtein & L.Z.Soborovsky;Zh.Obschei Xhimii 36,1133 (1966)

146.W.R.Cullen & G.E.Styan;J.Organometal.Chem. 4,151 (1965)

147. idem. ;Unpublished results.

148.R.C.Fuson & W.Shive;J.Amer.Chem.Soc. 69,559 (1947)

149.M.I.Kabachnik & T.J.Medved;Dokl.Akad.Nauk SSSR 83,689 (1952) Chem.Abs.47,2724 (1953)

150.Y.L.Gefter (trans.J.Burdon);"Organophosphorus Monomers and Polymers" Pergamon 1962.

151.R.F.Hudson;"Structure and Mechanism in Organophosphorus Chemistry" Academic Press 1965.

151.I.L.Knunyants,B.L.Dyatkin & E.P.Mochalina;Izvest.Akad.Nauk SSSR, Otdel.Xhim.Nauk 1091 (1965)

153.H.E.Simmons & D.W.Wiley;J.Amer.Chem.Soc. 82,2288 (1960)

154.P.H.Ogden;J.Org.Chem. 33,2518 (1968) and Refs. therein.

155.G.E.Hall,W.J.Middleton & J.D.Roberts;J.Amer.Chem.Soc.93,4778 (1971) and refs.therein.

156.N.P.Marullo & E.H.Wagener;Tetrahedron Lett. 1969, 2555

157.R,W.Layer & C.J.Carman; ibid. 1968, 1285

158.N.P.Marullo & E.H.Wagener;J.Amer.Chem.Soc. 88,5034 (1966)

159.H.Kessler & D,Leibfritz;Tetrahedron 26,1805 (1970)

160.D.Leibfritz & H.Kessler;J.Chem.Soc.D 1970,655

161.M.J.Shaw,H,H.Hyman & R.Filler;J.Org.Chem. 36,2917 (1971)

162.J.A.Gibson & A.F.Janzen; Can.J.Chem. 49,2168 (1971)

163.P.L.Corio;Chem.Rev.60,363 (1960)