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REACTIONS OF SOME UNSATURATED FLUOROCARBON DERIVATIVES
WITH ORGANO COMPOUNDS OF ARSENIC, SILICON, GERMANIUM AND TIN

ABSTRACT

Hexafluoroacetone readily adds to primary and secondary arsines to form arsino-1,1,1,3,3,3-hexafluoropropanols and to tetramethyldiarsine to form a moderately stable 1:1 complex at 20°. Trimethylarsine affords a 1:1 complex with hexafluoroacetone at 0° although the complex is completely dissociated at 20°. Trimethylsilane, trimethylgermane, and trimethyltin hydride react with hexafluoroacetone to form 1,1,1,3,3,3-hexafluoropropoxy derivatives and to dialkyltin dihydrides to form the bis(hexafluoropropoxy) derivatives. Addition of a second mole of hexafluoroacetone to form 1:1 complexes with propoxygermane and propoxysilane occurs at 20° in the presence of excess hexafluoroacetone. The analogous 1:1 tin complex can be isolated and is stable at 25°. Dimethylbis(1,1,1,3,3,3-hexafluoropropoxy)tin gives a stable complex containing two moles of hexafluoroacetone. The structures of the arsine- and Group IV- hexafluoroacetone complexes and some of their reactions are discussed.

The fluorocycloolefins, perfluorocyclobutene and 1,2-dichlorotetrafluorocyclobutene react with secondary arsines to give arsinocyclobutene derivatives. Perfluorocyclobutene affords the 1:1 adduct when heated with trimethylsilane and trimethylgermane. Trimethyltin hydride adds to perfluorocyclobutene at 20° to form the 1:1 adduct which subsequently slowly decomposes to trimethyltin fluoride. The reaction of Group IV hydrides with 1,2-dichlorotetrafluorocyclobutene affords a number of products the nature of which varies with the Group IV metal or metalloid. Thus the reaction of the dichlorocyclobutene with triethyltin hydride gives only triethyltin chloride, with trimethylsilane chlorotrimethylsilane and 1-chlorotetrafluorocyclobutyl-2-trimethylsilane are obtained, and with trimethylgermane reaction gives a variety of cyclobutenyl and cyclobutylgermanes as well as chlorotrimethylgermane. The configuration and conformation of the cyclobutyl derivatives of the Group IV elements are established from an analysis of their ¹H n.m.r. spectra.

Hexafluorobut-2-yne adds quantitatively to tin hydrides at 20° to afford the 1,1,1,4,4,4-hexafluorobutenyl derivatives. Hexamethylditin, tetrakis(trifluoromethyl)diarsine, trimethylsilane and triethylgermane add to hexafluorobut-2-yne on ultraviolet irradiation to give 1:1 adducts. The 1:1 trimethylsilane-hexafluorobut-2-yne adduct also forms at 235°. Trimethyltin hydride and 1,1,1-trifluoropropyne react slowly at 20° to afford the 1:1 adduct. A study of the isomer distribution of the 1:1 acetylene adducts indicates in all cases a predominant formation of the trans isomer. Trimethylsilane catalyzes the conversion of trans-1,1,1,4,4,4-hexafluorobutenyltrimethylsilane to the cis-isomer and trimethyltin hydride catalyzes the conversion of cis-1,1,1-trifluoropropenyl-3-trimethyltin to the trans-isomer. The diadducts, $(\text{CH}_3)_3\text{SiCHCF}_3$, $\text{CH}(\text{CF}_3)\text{Si}(\text{CH}_3)_3$ and $((\text{CH}_3)_3\text{Sn})_2\text{CHCH}_2\text{CF}_3$, are also obtained simultaneously with the formation of the respective 1:1 adducts although they are not formed by addition of the hydrides to the 1:1 adducts.

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PUBLICATIONS

- W. R. CULLEN and G. E. STYAN. Complex Formation by Hexafluoroacetone. Part I. Group IV Hydrides. Inorg. Chem., In press.
- W. R. CULLEN and G. E. STYAN. Reaction of Hexafluoroacetone with Arsines. J. Organometal. Chem., In press.
- W. R. CULLEN, D. S. DAWSON, and G. E. STYAN. Some Reactions of Hexafluorobut-2-yne with Compounds of Arsenic and Tin. J. Organometal. Chem., 3, 406 (1965).
- W. R. CULLEN, D. S. DAWSON, P. S. DHALIWAL and G. E. STYAN. 1-Dimethylarsino-2-chlorotetrafluorocyclobutene and Related Compounds. Ind. (London), p. 502 (1964).
- W. R. CULLEN, D. S. DAWSON, N. K. HOTA and G. E. STYAN. Some New Derivatives of Dimethylarsine. Chem. Ind. (London), p. 983 (1963).

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

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of

Chemistry

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

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ABSTRACT

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The fluorocycloolefins, perfluorocyclobutene and 1,2-dichlorotetrafluorocyclobutene react with secondary arsines to give arsino-cyclobutene derivatives. Perfluorocyclobutene affords the 1:1 adduct when heated with trimethylsilane or trimethylgermane. Trimethyltin hydride adds to perfluorocyclobutene at 20° to form the 1:1 adduct which subsequently slowly decomposes to trimethyltin fluoride. The reaction of Group IV hydrides with 1,2-dichlorotetrafluorocyclobutene affords a number of products the nature of which varies with the Group IV metal or metalloid. Thus the reaction of the dichlorocyclobutene with triethyltin hydride gives only triethyltin chloride, with trimethylsilane chlorotrimethylsilane and 1-chlorotetrafluorocyclobutyl-2-trimethylsilane are obtained

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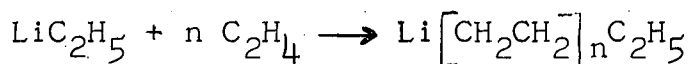
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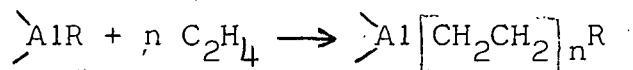
Throughout my graduate work the National Research Council of Canada has awarded me a Bursary (1962-1963) and Studentships (1963-1965) which are gratefully acknowledged.

GENERAL INTRODUCTION

The study of the reactions of unsaturated organic compounds, particularly olefins, with organometallic compounds was greatly stimulated by the large demands made for stable polymeric materials, such as synthetic rubber, during World War II. The addition of organometallic compounds to olefins was discovered more than thirty-five years ago^{1,2} but the greatest commercial impetus was supplied by Ziegler and coworkers in 1950³ who found that ethylene could be polymerized by lithium alkyls,



and in 1952⁴ these same workers discovered an analogous polymerization of ethylene by trialkylaluminum compounds.



The superior high temperature properties of organosilicones⁵ and the unexpected high stability of ferrocene⁶ led to an interest in the incorporation of organometallic compounds into polymeric materials. The high thermal stability and general inertness of fluorocarbons relative to their hydrocarbon analogues led to their application as refrigerants in 1928 and later to their use as propellants in the aerosol industry. The large production of fluorocarbons for these two basic applications necessarily led to the development of by-products⁷. The use of fluoroolefins as intermediates for polymeric materials such as resins, elastomers and plastics has become an important outlet for fluorocarbon chemicals.

The commercial availability of fluoroolefins and fluoroacetylenes has allowed for numerous investigations of the reactions of these fluorocarbons with organometallic compounds. There is a considerable commercial interest in the reaction

products as intermediates for polymer formation, particularly fluoroörganosilicones which might be expected to combine the thermal stability of siloxanes with the resistance to solvents of fluorocarbons. The reactions of fluoroölefins with silanes^{8,9,10}, tin hydrides^{11,12} and transition metals¹³ have been of recent interest.

The initial interest in fluorocarbons was due to their high thermal stability and general inertness. However, the high electronegativity of fluorine does not always result in an overall decrease in activity, and substitution of fluoroalkyl groups for alkyl groups can give rise to an extremely reactive molecule. The first chapter of this thesis is concerned with one such molecule, hexafluoroacetone. A recent review¹⁴ substantially covers the reactions of perfluoroketones with organic compounds, but little information is available regarding the reactions of perfluoroketones with organometallic compounds other than Grignard reagents.

The second chapter of this thesis involves the investigation of the reactions of some cyclic fluoroölefins, perfluorocyclobutene, 1,2-dichlorotetrafluorocyclobutene, and 1,2-dichlorohexafluorocyclopentene. Thermochemical data concerning the chlorination of fluoroölefins--the enthalpy of chlorination of perfluorocyclobutene ($\Delta H = -37.4$ kcal/mole) is 20 kcal/mole greater than that of tetrafluoroethylene ($\Delta H = -57.3$ kcal/mole)¹⁵--demonstrates that perfluorocyclobutene should be a particularly interesting intermediate for the formation of vinyl derivatives. The preparation of such vinyl silanes from cyclic fluoroölefins has been well investigated in a U.S. patent⁸.

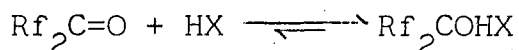
The third chapter of this thesis deals predominantly with some reactions of hexafluorobut-2-yne. Whereas the effect of the trifluoromethyl groups on the carbonyl group in hexafluoroacetone enhances its reactivity, the inductive effect of the trifluoromethyl groups on the triple bond in hexafluorobut-2-yne makes it more susceptible to nucleophilic attack but less susceptible to electrophilic attack than its hydrogen analogue, but-2-yne. There has been considerable interest in the reactions of hexafluorobut-2-yne with transition metal compounds^{13,16}.

CHAPTER I

HEXAFLUOROACETONE

INTRODUCTION

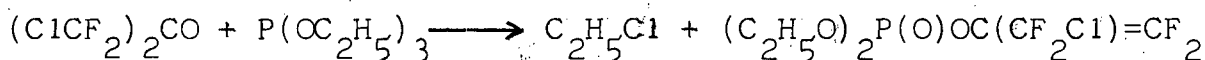
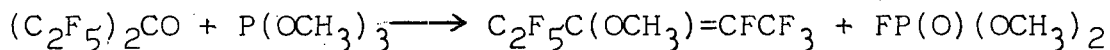
A large number of completely fluorinated ketones have been prepared in recent years^{17,18,19,20}. Hexafluoroacetone was prepared for the first time by Fukuhara and Bigelow¹⁷ in 1941. The strong electron withdrawal exerted by polyfluoroalkyl groups alpha to a carbonyl group is obvious from the ease of addition of HX molecules to the functional group¹⁴. Thus the equilibrium reaction



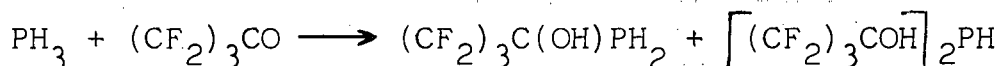
lies far, and often completely, to the right. The reaction conditions necessary for the addition of a weak nucleophile such as water are extremely mild, quantitative addition taking place at room temperature^{18,19,21}. At low temperatures addition of mineral acids (X = F, Cl, Br, I) to perfluorocyclobutanone²² gives high yields of α -haloalcohols. A number of other acids have been added to similar fluorinated ketones to give 1:1 adducts^{23,24}. The formation of hemiketals (X = OR) with fluorinated ketones has been investigated fairly extensively by Simmons and Wiley²⁵.

Previous work on the reactions of fluorinated ketones with Group V compounds has been largely confined to the addition of the ketones to the N-H bonds of ammonia²⁶, amines^{24,25}, amides²⁷ and ureas²⁷. It was found that primary amides and primary ureas will form 1:1 adducts with fluorinated ketones but secondary amides, secondary ureas, thioamides and sulphonamides are unreactive²⁷. Some work has been done on the reactions of fluorinated ketones with trialkyl phosphites^{21,28}, and it was found that the products vary with the ketone as is shown by the following

examples:

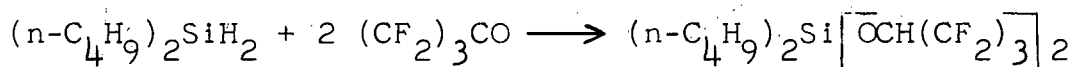


Addition of these ketones to the phosphites occurs under very mild conditions, for example the highly reactive perfluorocyclobutan-1,2-dione adds to trimethyl phosphite at -70° . Addition of perfluorocyclobutanone to phosphine occurs in the same manner as addition to amines²⁹.

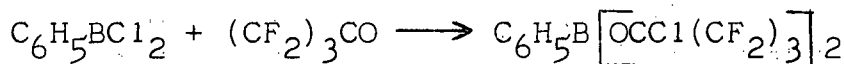


The ratio of the monoadduct to the diadduct varies with the ratio of the reactants.

The only previously reported reaction involving a Group IV compound and a fluorinated ketone is the addition of perfluorocyclobutanone to di-n-butylsilane²⁹.



Note that the direction of addition is different from acid and Group V addition in that no OH group is formed. Parshall²⁹ also found that perfluorocyclobutanone reacts with both boron trichloride and phenyldichloroborane in a similar manner.



Some reactions of hexafluoroacetone with Group IV and Group V organometallic compounds have been studied in the present investigation, and the results are presented in the following discussion and experimental sections.

EXPERIMENTAL

A. Apparatus and Techniques

The following description will cover the apparatus and general techniques used for the experimental work described in this thesis in all three chapters, Hexafluoroacetone, Cyclobutenes, and Fluoroalkynes.

Reactants and products were manipulated using standard vacuum techniques. Except where otherwise indicated, volatile materials were purified by trap-to-trap distillation using suitable low temperature baths to cool the traps. Reactions were carried out in thick-walled Pyrex tubes. For reactions initiated by ultraviolet irradiation the Pyrex Carius tube containing the reactants was placed 30 to 40 cm from the light source. Pyrex effectively absorbs any ultraviolet radiation below 3000 Å. Where necessary non-volatile materials were manipulated in an inert atmosphere chamber. Molecular weights were measured by Regnault's method except where otherwise indicated.

For the preparation of the volatile hydrides (arsines, germanes and tin hydrides) the experimental set-up described by Jolly and Drake³⁰ was used with little or no modification.

An Aerograph, model A-90-P, was used for v.p.c. analysis. The chromatographic columns were of two sizes, 5' x $\frac{1}{4}$ " and 10' x $\frac{1}{4}$ ". The flow rates normally varied from 2 to 15 cc/min. with either helium or nitrogen as the carrier gas. Separations were made with the injector approximately 25° above, and the detector 35° above, the column temperature.

Infrared spectra reported in cm^{-1} were run on a P.E. 21 instrument, those reported in microns were run on a calibrated P.E. 137. The ^{19}F and ^1H n.m.r. spectra were obtained with a

Varian H.R. 60 (at 56.4 Mc/s) and A-60 spectrometers. Unless otherwise indicated ^{19}F spectra are reported in p.p.m. relative to external trifluoroacetic acid and ^1H spectra in p.p.m. relative to external tetramethylsilane references (negative values to low field side). Microanalyses were carried out by Dr. Alfred Bernhardt, Mülheim, Germany (arsenic and silicon compounds) and by the Schwartzkopf Microanalytical Laboratory, Woodside 77, N.Y., U.S.A. (tin and germanium compounds). Microanalyses in which only the carbon and hydrogen are reported were carried out by Mrs. C. Jenkins, Department of Chemistry, University of British Columbia.

B. Reaction of Arsines with Hexafluoroacetone

(1) Synthesis of Starting Materials

The hexafluoroacetone (H.F.A.) was kindly supplied by General Chemical Division, Allied Chemical Corporation, U.S.A. and was purified by trap-to-trap distillation (mol. wt. Found: 166; Calc: 166).

(a) Tetramethyldiarsine--The diarsine (cacodyl) was prepared by the reduction of dimethylarsinic acid with excess hypophosphorous acid in 2.5N hydrochloric acid³¹. The diarsine was distilled under reduced pressure, b.p. 74° (46 mm). Its purity was checked by ^1H n.m.r. which showed only one peak at -1.13 p.p.m. The following vapour pressure data were obtained for the diarsine.

$T^\circ\text{K}$	p cm	log p	$\frac{1}{T} \times 10^3 \text{ }^\circ\text{K}^{-1}$
292	0.25	-0.602	3.42
309.5	1.25	+0.096	3.23
326.6	2.6	0.415	3.06
336.8	3.9	0.591	2.97
350.8	6.8	0.832	2.85
361.5	9.95	0.998	2.77
374	15.1	1.178	2.67
377.1	16.75	1.223	2.65

$T^{\circ}\text{K}$	$p \text{ cm}$	$\log p$	$\frac{1}{T} \times 10^3 \text{ }^{\circ}\text{K}^{-1}$
388.3	23.65	1.373	2.57
394.8	28.7	1.457	2.53
402.4	35.65	1.551	2.49
411.2	45.4	1.657	2.43
418.8	55.45	1.743	2.39

A linear plot of $\log p$ against $\frac{1}{T}$ was obtained for the whole range.

This was used to give:

$$\text{b.p.} = 158.4 \pm 0.2^{\circ} \text{ }^{\text{a}}$$

$$L_v = 9.05 \text{ kcal/mole}$$

$$\text{Trouton's const.} = 22.1 \text{ e.u.}$$

(b) Dimethylarsine--Chlorodimethylarsine was prepared by the reduction of dimethylarsinic acid with hypophosphorous acid^{31,33}. The chlorodimethylarsine was dissolved in hydrochloric acid and was reduced by an alcoholic zinc solution to produce dimethylarsine³⁴. The dimethylarsine was purified by first sealing it off in a Carius tube with sodium hydroxide and then repeating this procedure with phosphorus pentoxide. The identity and purity was established by its infrared spectrum which showed a strong As-H absorption at 4.8μ and by its molecular weight of 107.5 (Calc: 106.0). The ¹H n.m.r. spectrum showed two sets of peaks; one, a doublet, centered at -0.87 p.p.m. ($J = 6.7 \text{ cps}$) and the other, a septet, centered at -2.29 p.p.m. ($J = 6.8 \text{ cps}$) of relative intensities 1:5.9 (Calc. 1:6.0).

(c) Methylarsine--Dichloromethylarsine was prepared by the reduction of methylarsonic acid by sulphur dioxide³⁵. Dichloromethylarsine was reduced to the corresponding hydride by the same procedure used to reduce chlorodimethylarsine to dimethylarsine^{36,37}. Methylarsine was purified in the same manner described for dimethyl-

^a A boiling point of 170° has been reported³².

arsine. Its infrared spectrum showed a strong, broad As-H absorption at 4.75μ . Its ^1H n.m.r. spectrum showed a triplet at -0.78 p.p.m. ($J = 7.2$ cps) and a quartet at -1.83 p.p.m. ($J = 7.1$ cps) of relative intensities 2:3.1 (Calc. 2:3.0).

(d) Trimethylarsine--Trimethylarsine was recovered from the thermal decomposition of cacodyl³⁸. It was purified by trap-to-trap distillation and identified by its infrared spectrum and molecular weight of 123 (Calc: 120). The ^1H n.m.r. spectrum showed only one peak at -0.74 p.p.m.^a

(2) Reaction with H.F.A.

(a) Dimethylarsine--Dimethylarsine (2.9 g) and the ketone (3.9 g) were left at 20° for one day although a vigorous exothermic reaction took place immediately on mixing. Dimethylarsine (0.2 g) which went through a -78° trap was recovered. A fraction (0.1 g) which went through a -23° trap and condensed in a -78° trap was identified as 1,1,1,3,3,3-hexafluoropropan-2-ol (Found: C, 21.4; H, 1.3; F, 67.2 %; mol. wt., 172. Calc. for $\text{C}_3\text{H}_2\text{F}_6\text{O}$: C, 21.4; H, 1.2; F, 67.9 %; mol. wt., 168). Infrared spectrum (vapour): 3664 w, 2990 w, 1426 w, 1380 s, 1273 vs, 1248 s, 1207 vs, 1112 vs, 892 m, 735 w, 685 m cm^{-1} .

The main product (6.5 g) which was recovered from a -23° trap was identified as 2-dimethylarsinohexafluoropropan-2-ol (Found: C, 22.1; H, 2.7; As, 27.8; F, 42.1 %. Calc. for $\text{C}_5\text{H}_7\text{AsF}_6\text{O}$: C, 22.1; H, 2.6; As, 27.6; F, 41.9 %). Infrared spectrum (vapour): 3635 m, 3020 w, 2950 w, 1428 w, 1379 m, 1269 vs, 1228 m (sh), 1205 vs, 1138 m, 1107 s, 943 m, 873 m, 851 m, 750 m, 708 m cm^{-1} . N.m.r. spectra: the ^1H n.m.r. spectrum showed two peaks, one at -1.16 p.p.m. ($-\text{CH}_3$) and the other at -3.52 p.p.m. ($-\text{OH}$). The

^a Chemical shifts relative to benzene and water have been reported³⁹.

addition of a large excess of H.F.A. shifted the peaks to -1.20 p.p.m. and -3.45 p.p.m. The ^{19}F n.m.r. spectrum showed one peak at -6.63 p.p.m. Addition of excess H.F.A. did not produce any further product peaks.

The following vapour pressure data were obtained for the arsine:

$T^{\circ}\text{K}$	p cm	log p	$\frac{1}{T} \times 10^3 \text{ }^{\circ}\text{K}^{-1}$
314	2.28	0.357	3.19
335	6.94	0.841	2.99
346	11.86	1.074	2.89
351	15.41	1.188	2.85
371.2	30.75	1.486	2.70
379.1	42.56	1.628	2.64
388	56.32	1.742	2.58
395.6	71.54	1.855	2.53

A linear plot of log p against $\frac{1}{T}$ was obtained to give an extrapolated boiling point of $124 \pm 0.5^{\circ}$.

(b) Methylarsine--Methylarsine (4.8 g) and H.F.A. (3.3 g) were left at 20° for three hours. Methylarsine (3.3 g) which went through a -78° trap was recovered. The reaction product, hexafluoro-2-methylarsinopropan-2-ol (4.4 g), was recovered from a -78° trap (Found: C, 18.4; H, 1.8; As, 28.9; F, 44.4 %; mol. wt., 251. Calc. for $\text{C}_4\text{H}_5\text{AsF}_6\text{O}$: C, 18.6; H, 1.9; As, 29.1; F, 44.1 %; mol. wt., 258. Infrared spectrum (vapour): 3620 w, 2955 w, 2925 vw, 2145 m, 1424 w, 1377 w, 1277 vs, 1230 m (sh), 1206 vs, 1143 m, 1106 s, 953 m, 882 m, 843 w, 741 m, 700 cm^{-1} . N.m.r. spectra: the ^1H n.m.r. spectrum showed three peaks, a singlet at -1.22 p.p.m. ($-\text{CH}_3$) and -3.62 p.p.m. ($-\text{OH}$) and a multiplet at -3.6 p.p.m. (As-H) ($J_{(\text{As-CH}_3)-(\text{As-H})} = 7.5 \text{ cps}$).

The following vapour pressure data were obtained for the methylarsinopropanol:

$T^{\circ}\text{K}$	p cm	log p	$\frac{1}{T} \times 10^3 \text{ }^{\circ}\text{K}^{-1}$
314	6.5	0.813	3.19

$T^{\circ}\text{K}$	p cm	log p	$\frac{1}{T} \times 10^3 \text{ }^{\circ}\text{K}^{-1}$
321.6	10.3	1.013	3.11
331	16.4	1.215	3.03
344	28.45	1.454	2.91
352	38.3	1.584	2.95
360.8	50.0	1.700	2.77
367	57.25	1.758	2.73

Slight decomposition of the compound occurred, consequently the extrapolated boiling point of $117 \pm 2^{\circ}$ is not very accurate.

In a second experiment methylarsine (3.5 g) and excess ketone (16.9 g) were left at 20° for one day. H.F.A. (6.2 g) which went through a -78° trap was recovered. The methylarsinopropanol (4.7 g) of known infrared spectrum was produced.

(c) Methylarsinohexafluoropropan-2-ol--The arsinopropanol (4.4 g) and H.F.A. (6.5 g) were left at 20° for 20 days. H.F.A. (3.6 g) was recovered. A fraction (0.5 g) which stopped in a -78° trap was identified as 1,1,1,3,3,3-hexafluoropropanol by its infrared spectrum. An involatile colourless solid (6.8 g) which was extremely air sensitive and which was not identified was also produced.

(d) Trimethylarsine--It was found that mixtures of the ketone and trimethylarsine could not be separated by trap-to-trap distillation. The mixture repeatedly stopped in a trap cooled to -64° , thus showing lower volatility than either component separately (H.F.A. goes through a -96° trap and trimethylarsine goes through a -78° trap).

N.m.r. spectra: At 20° the ^1H n.m.r. spectrum of trimethylarsine showed one peak at -0.74 p.p.m. At 20° a solution of trimethylarsine in excess H.F.A. gave only a single unsplit peak at -0.44 p.p.m., and at 20° the ^{19}F n.m.r. spectrum also showed only one peak. At 0° the same solution showed a broad methyl peak ($J \approx 0.5$ cps). The solution solidified between -5 and -10° .

(e) Chlorodimethylarsine--The chloroarsine (3.2 g) and H.F.A. (6.1 g) were immiscible at 20° and temperatures up to 100°. The reactants were then heated to 120° for three hours, 200° for 15 hours and 250° for five hours without result. Recovery of both reactants was nearly quantitative (3.1 g and 6.1 g).

(f) Tetramethyldiarsine--Preliminary studies on a mixture of the diarsine and H.F.A. indicated that they react to produce a nonvolatile liquid which is unstable to air. The infrared spectrum of a solution of diarsine (0.65 g) and H.F.A. (0.2 g) showed the following absorption bands: 3.35 w, 3.45 w, 3.57 w, 5.5 vw, 5.87 vw, 7.1 m, 8.05 vs, 8.5 vs, 9.05 vs, 10.25 m, 10.65 m, 11.15 m, 11.78 m, 12.13 m, 12.63 vw, 13.36 w, 13.57 w, 13.8 w, 14.12 w μ . N.m.r. spectra: the ¹H n.m.r. spectrum of the diarsine consists of one peak at -1.13 p.p.m.^a A mixture of the diarsine and excess H.F.A. (2:7 by volume) results in two peaks of equal area at -0.71 p.p.m. and -0.93 p.p.m. In a 1:1 molar mixture the two peaks are shifted downfield to -1.07 p.p.m. and -1.30 p.p.m., the high field peak being a multiplet ($J \approx 0.8$ cps). The ¹⁹F n.m.r. spectrum of the diarsine in excess H.F.A. shows two peaks, one at -1.36 p.p.m. (excess H.F.A.) and another at -7.94 p.p.m.

(3) Reactions of the Diarsine-H.F.A. Adduct

(a) With Water--The diarsine (3.1 g) and H.F.A. (9.7 g) were left at 20° for a few hours. The excess ketone was removed and water was added to the remaining liquid. Tetramethyldiarsine (3.0 g), of known ¹H n.m.r. spectrum, was recovered from a -23° trap.

(b) With Hexafluorobut-2-yne--Tetramethyldiarsine (2.8 g) and

^a A chemical shift of -1.11 p.p.m., relative to internal tetramethylsilane, for a chloroform solution has been reported⁴⁰.

H.F.A. (5.2 g) were left at 20° for a few hours. The excess ketone (2.9 g) was recovered and hexafluorobut-2-yne (13.7 g) was added to the remaining 1:1 adduct. The volatiles (13.0 g) were recovered and added to water to remove H.F.A. as a hydrate. Hexafluorobut-2-yne (11.5 g) which went through a -78° trap was recovered. The involatile reaction product (5.1 g) which remained in the reaction tube was identified as a mixture of cis- and trans-2,3-bis(dimethylarsino)hexafluorobut-2-ene, b.p. 91° (12 mm) (lit. 99° (17 mm))⁴¹, by means of its known infrared and ¹⁹F n.m.r. spectra⁴¹. The ¹⁹F n.m.r. spectrum consisted of peaks at -24.3 and -26.3 p.p.m. of relative intensities 10:1 (cis:trans).

(c) With Hexafluorobut-2-yne in the Presence of Excess H.F.A.

--Tetramethyldiarsine (3.5 g) and H.F.A. (10 g) were left at 20° for two hours and then hexafluorobut-2-yne (7.5 g) was added. The reaction product isolated two days later was identified as a mixture of cis- and trans-2,3-bis(dimethylarsino)hexafluorobut-2-ene, b.p. 98° (15 mm) (lit. 99° (17 mm))⁴¹, which the ¹⁹F n.m.r. spectrum showed to be 94% cis-isomer.

C. Reaction of Group IV Hydrides with Hexafluoroacetone

(1) Synthesis of Starting Materials

Trimethylsilane was purchased from Peninsular Chemresearch Inc., Gainesville, Florida, and was used without further purification. Its purity was checked by its infrared spectrum and molecular weight of 74.7 (Calc: 74.1).

(a) Trimethylgermane--Tetramethylgermane was prepared by the reaction of methylmagnesium iodide and germanium tetrachloride⁴². Tetramethylgermane was sealed in a Carius tube with 0.05 mole excess bromine and left at 20° for 8 days, to give trimethylgermanium bromide⁴³. The germanium bromide was dissolved in 1M

hydrobromic acid and reduced by sodium borohydride to trimethylgermane⁴⁴. Trimethylgermane which went through a -78° trap was purified by trap-to-trap distillation. Its purity was checked by its infrared spectrum (Ge-H at 4.9μ) and its molecular weight of 118 (Calc: 118.6).

(b) Trimethyltin Hydride and Dimethyltin Dihydride--Trimethyltin chloride was prepared by the direct addition of stannic chloride to tetramethyltin without the use of a solvent. Dimethyltin dichloride (purchased from M & T Chemicals) and trimethyltin chloride were then respectively reduced by lithium aluminum hydride in n-butyl ether⁴⁵. The hydrides were purified by trap-to-trap distillation. The purity of trimethyltin hydride was checked by its infrared spectrum and its molecular weight of 163 (Calc: 164.7). Dibutyltin dihydride was similarly prepared.

(2) Reactions with H.F.A.

(a) Trimethylsilane--Trimethylsilane (2.2 g) and H.F.A. (9.0 g) were heated at 145° for 5 days. H.F.A. (3.2 g) which went through a -96° trap was recovered. The main fraction (5.9 g) which went through a -23° trap and condensed in a -96° trap was identified as 1,1,1,3,3,3-hexafluoropropoxytrimethylsilane, b.p. 86° (757 mm), (Found: C, 29.7; H, 4.3; F, 47.2 %. Calc. for $C_3H_9F_6OSi$: C, 30.0; H, 4.2; F, 47.5 %). Infrared spectrum (vapour): $3004\ m$, $2950\ w$, $1808\ vw$, $1589\ vw$, $1420\ vw$, $1378\ s$, $1307\ vs$, $1270\ s$, $1232\ vs$, $1212\ vs$, $1172\ s$, $1111\ s$, $1071\ s$, $879\ s$, $849\ s$, $758\ m$, $720\ w$, $685\ m\ cm^{-1}$. N.m.r. spectra: the 1H n.m.r. spectrum showed two peaks, one, a singlet at 0.16 p.p.m. ($-CH_3$) and the other, a septet, at -3.90 p.p.m. ($-CH$) ($J = 6.0\ cps$). The ^{19}F n.m.r. spectrum showed one peak, a doublet, at -0.65 p.p.m. ($J = 6\ cps$).

Some less volatile material (2.0 g) was also isolated from a

-23° trap. N.m.r. spectra: the ^1H n.m.r. spectrum of this material showed methyl absorptions at 0.02 and 0.14 p.p.m. and septets at -3.95 and -4.49 p.p.m. ($J = 6.0$ cps). It was found that this spectrum could be duplicated by the addition of H.F.A. to excess 1,1,1,3,3,3-hexafluoropropoxytrimethylsilane. Upon addition of excess H.F.A. the ^1H n.m.r. spectrum showed only one methyl absorption at 0.08 p.p.m. and one downfield septet at -4.45 p.p.m. ($J = 5.8$ cps) and the ^{19}F n.m.r. spectrum showed three peaks, the central one being due to H.F.A. and the other two, of equal area, being situated at 5.09 and -2.51 p.p.m. from internal H.F.A.

Other experiments which were followed by ^1H n.m.r. spectra indicated that trimethylsilane and H.F.A. react slowly but completely (17 hours) at 20°.

(b) Trimethylgermane--The germane (6.35 g) and H.F.A. (2.3 g) were left at 20° for 15 hours. Trimethylgermane (4.80 g) which went through a -78° trap was recovered. The product, 1,1,1,3,3,3-hexafluoropropoxytrimethylgermane (3.81 g), b.p. 117° (758 mm), condensed in a -78° trap (Found: C, 25.3; H, 3.6 %. Calc. for $\text{C}_6\text{H}_{10}\text{F}_6\text{GeO}$: C, 25.4; H, 3.7 %). Infrared spectrum (vapour): 3015 w, 2920 w, 1418 w, 1374 s, 1304 vs, 1275 s, 1217 vs, 1153 s, 1106 s, 894 m, 868 m, 827 s, 760 s, 685 m cm^{-1} . N.m.r. spectra: the ^1H n.m.r. spectrum showed a singlet at -0.25 p.p.m. ($-\text{CH}_3$) and a septet at -3.96 p.p.m. ($-\text{CH}$) ($J = 6.1$ cps), of relative intensity 1:8.9 (Calc: 1:9.0). The ^{19}F n.m.r. spectrum showed a doublet at -1.65 p.p.m. ($J \approx 6$ cps). A 2:1 molar propoxygermane-H.F.A. solution gave a ^1H n.m.r. spectrum with methyl peaks at -0.43 and -0.27 p.p.m. and also septets at -4.74 and -3.98 p.p.m. The ^1H n.m.r. spectrum of the propoxygermane in excess H.F.A. shows only one methyl peak at -0.27 p.p.m. and one septet at -4.56

p.p.m. ($J = 6.1$ cps). The ^{19}F n.m.r. spectrum shows three peaks, the central one being H.F.A. and the other two, of equal intensity, situated at 3.4 p.p.m. and -2.9 p.p.m. from internal H.F.A. The low field peak is a multiplet ($J = 6$ and 2.5 cps).

(c) Trimethyltin Hydride--Trimethyltin hydride (5.0 g) and H.F.A. (3.6 g) reacted immediately on mixing. Trimethyltin hydride (1.2 g) which went through a -46° trap was recovered. The reaction product, 1,1,1,3,3,3-hexafluoropropoxytrimethyltin (7.3 g), b.p. 76° (58 mm), condensed in a -46° trap (Found: C, 21.3; H, 3.1 %; mol. wt. (benzene), 664. Calc. for $\text{C}_6\text{H}_{10}\text{F}_6\text{OSn}$: C, 21.8; H, 3.0 %; mol. wt., 331). Infrared spectrum (vapour): 3020 w, 2910 vw, 1374 s, 1300 vs, 1275 s, 1210 vs, 1164 s, 1101 s, 893 m, 859 m, 766 m, 746 m, 683 m cm^{-1} . N.m.r. spectra: the ^1H n.m.r. spectrum showed a singlet at -0.38 p.p.m. ($-\text{CH}_3$) and a septet at -4.14 p.p.m. ($-\text{CH}$) ($J = 6.1$ cps). The ^{19}F n.m.r. spectrum showed a doublet at -1.7 p.p.m. ($J \approx 6$ cps).

(d) Hexafluoropropoxytrimethyltin--The addition of H.F.A. to the propoxytin compound gave an exothermic reaction. The excess H.F.A. was removed by pumping and the remaining material was identified as a 1:1 propoxytin-H.F.A. complex, m.p. 23° (Found: C, 21.9; H, 2.2; F, 45.5; Sn, 23.8 %. Calc. for $\text{C}_9\text{H}_{10}\text{F}_{12}\text{O}_2\text{Sn}$: C, 21.7; H, 2.0; F, 46.0; Sn, 23.9 %). Infrared spectrum (liquid film): 3005 w, 2935 w, 1373 s, 1353 m, 1308 s, 1289 s, 1220 vs (b), 1110 s, 1101 w (sh), 970 s, 898 m, 882 w, 783 m, 747 w, 725 w, 718 m, 684 m, 667 w cm^{-1} . N.m.r. spectra: the ^1H n.m.r. spectrum of the complex in H.F.A. shows a singlet at -0.27 p.p.m. ($-\text{CH}_3$) and a septet at -4.58 p.p.m. ($-\text{CH}$) ($J = 6.1$ cps), of relative intensity 1:8.5 (Calc. 1:9.0). The ^{19}F n.m.r. spectrum shows broad peaks of equal intensity of 4.4 and -3.1 p.p.m. from internal H.F.A. reference. The ^1H n.m.r. spectrum of a mixture

of the complex and the uncomplexed species (1,1,1,3,3,3-hexafluoropropoxytrimethyltin) shows only one methyl peak at -0.47 p.p.m. but two downfield septets, one at -4.13 p.p.m. and the other at -4.84 p.p.m. The ^{19}F n.m.r. spectrum of the same mixture shows three peaks, a well-defined doublet at -1.45 p.p.m. and broad peaks at 2.9 and -4.75 p.p.m.

(e) Dimethyltin Dihydride--Dimethyltin dihydride (1.64 g) and H.F.A. (4.43 g) reacted immediately on mixing. No volatiles were recovered. The product, bis(1,1,1,3,3,3-hexafluoropropanoxy)dimethyltin, was purified by distillation, b.p. 92° (25 mm), (Found: C, 20.1; H, 1.7 %. Calc. for $\text{C}_8\text{H}_8\text{F}_{14}\text{O}_2\text{Sn}$: C, 19.9; H, 1.7 %). Infrared spectrum (liquid film): 2915 w, 1374 m, 1292 s, 1265 m, 1213 vs (b), 1189 vs, 1145 m, 1098 s, 892 m, 855 m, 790 m, 747 m, 685 m cm^{-1} . N.m.r. spectra: the ^1H n.m.r. spectrum shows a singlet at -0.85 p.p.m. ($-\text{CH}_3$) and a septet at -4.57 p.p.m. ($-\text{CH}$) ($J = 6.2$ cps) of relative intensity 1:3.05 (Calc. 1:3.0). The ^{19}F n.m.r. spectrum of a 60% solution in carbon tetrachloride shows a doublet at -2.07 p.p.m. ($J \approx 6$ cps).

(f) Bis(propanoxy)dimethyltin--The bis(propanoxy)dimethyltin (0.4044 g) and H.F.A. were reacted at 20° . The excess H.F.A. was removed by pumping and a 1:2 complex (0.6759 g) of bis(propanoxy)-dimethyltin-2H.F.A. resulted (Found: C, 20.8; H, 1.5; H.F.A., 40.2 %. Calc. for $\text{C}_{14}\text{H}_8\text{F}_{24}\text{O}_4\text{Sn}$: C, 20.6; H, 1.0; H.F.A., 40.7 %). Infrared spectrum (liquid film): very similar to the uncomplexed species with the addition of three bands: 970 s, 1024 w, 718 w cm^{-1} . Rapid hydrolysis of the compound caused broadening in CF stretching region making it difficult to assign bands.

N.m.r. spectra: the ^1H n.m.r. spectrum shows a singlet at -1.03 p.p.m. ($-\text{CH}_3$) and a septet at -4.88 p.p.m. ($J = 6.0$ cps) of

relative intensity 1:2.9 (Calc. 1:3.0). The ^{19}F n.m.r. showed two broad peaks of equal intensity at 4.36 and -2.94 p.p.m. with respect to internal H.F.A. Various mixtures of the uncomplexed species, bis(1,1,1,3,3,3-hexafluoropropoxy)dimethyltin, and the 1:2 complex showed three methyl peaks in the ^1H n.m.r. spectrum. For example: an approximate 1:1 molar mixture of the above-mentioned species showed peaks at -0.80, -0.92 and -1.05 p.p.m. of relative intensities 2:5:2 respectively.

(g) Dibutyltin Dihydride--Dibutyltin dihydride (3.3 g) and H.F.A. (12.4 g) reacted immediately upon mixing. H.F.A. (4.1 g) was recovered. The involatile fraction (11.5 g) was distilled at 10^{-3} mm and at approximately 50° loss of H.F.A. occurred. The H.F.A. was identified by its infrared spectrum and molecular weight of 165 (Calc: 166). The main fraction which distilled at 76° (10^{-3} mm) was identified as bis(1,1,1,3,3,3-hexafluoropropoxy)dibutyltin (Found: C, 30.0; H, 3.6; Sn, 21.6; F, 38.9 %. Calc. for $\text{C}_{14}\text{H}_{20}\text{F}_{12}\text{O}_2\text{Sn}$: C, 29.6; H, 3.5; Sn, 20.9; F, 40.2 %). Infrared spectrum (liquid film): 2950 s, 2860 m, 1467 m, 1417 w, 1372 s, 1284 vs, 1257 s, 1207 vs, 1185 vs, 1131 s, 1092 vs, 1025 w, 958 w, 891 s, 855 s, 748 s, 684 s cm^{-1} . Before distillation there was a strong band at 970 cm^{-1} .

(h) Trimethyltin Chloride--A solution of trimethyltin chloride and excess H.F.A. was immiscible at 20° . The reactants were still immiscible at 120° and heating at this temperature for 12 hours resulted in no change.

(3) Reaction of 1,1,1,3,3,3-Hexafluoropropoxytrimethyltin and 1,1,1-Trifluoroacetone

An excess of the propoxytin in trifluoroacetone showed only three peaks in the ^1H n.m.r. spectrum, two, at -0.27 and -4.05

p.p.m., belonging to the unchanged propoxytin and one, at -2.11 p.p.m., belonging to the ketone. The ^{19}F n.m.r. spectrum of the propoxytin in excess trifluoroacetone showed only one peak, a well-defined doublet at -2.8 p.p.m. ($J \approx 6$ cps) from internal trifluoroacetone reference.

(4) Reaction of the 1:1 Propoxytrimethyltin-H.F.A. Complex and Trimethyltin Hydride

When excess 1:1 complex was sealed in a ^1H n.m.r. tube with trimethyltin hydride the ^1H n.m.r. spectrum showed that within two minutes after mixing at 20° the reaction was virtually complete. The trimethyltin hydride peaks disappeared and the spectrum showed two sets of septets indicating the presence of uncomplexed 1,1,1,3,3,3-hexafluoropropoxytrimethyltin.

DISCUSSION

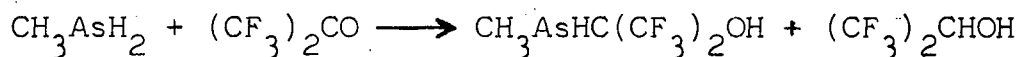
A. Arsines(1) Results

Hexafluoroacetone reacts vigorously with dimethylarsine to give the expected arsinopropanol, b.p. 124° (760 mm), in good yield.



The structure of the product is shown by the O-H infrared absorption at 3664 cm^{-1} and by its ^1H n.m.r. spectrum of only two sharp peaks, the methyl absorption at -1.16 p.p.m. and the OH absorption at -3.52 p.p.m.

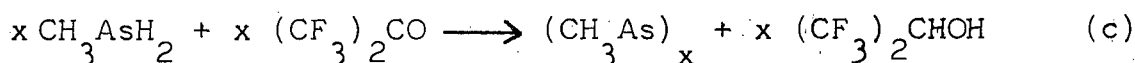
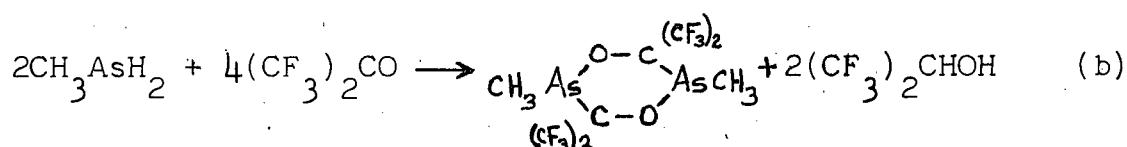
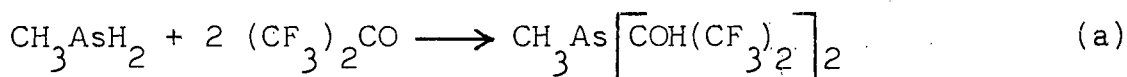
Methylarsine also reacts very readily with hexafluoroacetone. With excess arsine the product, in high yield, is hexafluoro-2-methylarsinopropan-2-ol, b.p. 117° (760 mm). Reduction of the ketone to 1,1,1,3,3,3-hexafluoropropanol, a compound which has been prepared by the reduction of hexafluoroacetone by lithium aluminum hydride²¹ and a Grignard reagent^{24,26}, also occurs to a small extent (2.5%).



The structure of the main reaction product is shown by the O-H and As-H infrared absorptions at 3620 and 2145 cm^{-1} respectively and by its ^1H n.m.r. spectrum of three peaks, the methyl absorption at -1.22 p.p.m. and the O-H and As-H absorptions overlapping at -3.6 p.p.m. with $J_{(\text{As})\text{CH}_3-(\text{As})\text{H}} = 7.5\text{ cps}$. This observed value of the coupling constant is of the same order of magnitude as $J_{(\text{As})\text{CH}_3-(\text{As})\text{H}}$ for methylarsine and dimethylarsine.

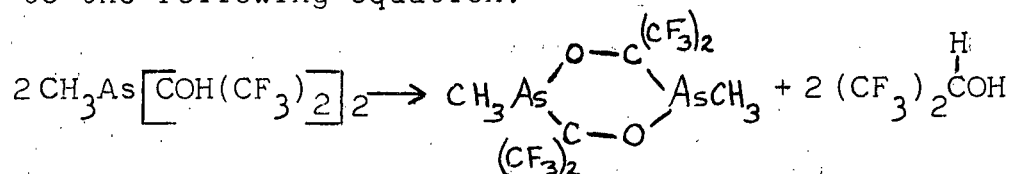
Further reaction of the remaining As-H bond with hexafluoroacetone is much slower since even in the presence of excess ketone

the 1:1 product can be isolated in 47% yield after one day at 20°. Nevertheless the 1:1 adduct eventually reacts completely with the ketone to give an unidentified, unstable, colourless solid which is insoluble in the ketone. A considerable amount of 1,1,1,3,3,3-hexafluoropropanol is also obtained. Adams and Palmer^{47,48} found that phenylarsine reacts with aldehydes in three different ways. Applying these results to the reaction of methylarsine and hexafluoroacetone the following equations are obtained.



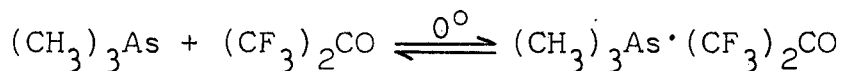
Equation (c) can be eliminated since $(\text{CH}_3\text{As})_x$ which is a red solid or yellow liquid is not formed. The stoichiometry of the reaction of the ketone to the methylarsinopropanol is 1:1, thus it appears probable that stepwise addition of hexafluoroacetone to methylarsine occurs to give the reaction product formed in equation (a).

Perfluorocyclobutanone adds to phosphine to give a 1:2 adduct which is reported to be a crystalline material²⁹. The yield of hexafluoropropanol based on equation (b) is 35%. Thus, it is possible that the product of reaction (a) decomposes slowly according to the following equation.



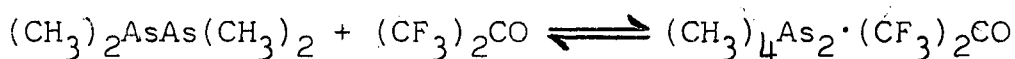
There is some experimental evidence for this proposed decomposition since formation of the crystalline solid and hexafluoropropanol occurs even after complete removal of hexafluoroacetone. These crystals oxidize immediately in air.

Trimethylarsine forms an adduct with hexafluoroacetone which solidifies at approximately -5° but appears to be completely dissociated at 20° even under high acetone pressures. The ^1H n.m.r. spectrum of a trimethylarsine-ketone solution has a sharp methyl absorption at 20° ; however at 0° the methyl peak is broad and can be resolved as a multiplet with $J \approx 0.5$ cps.

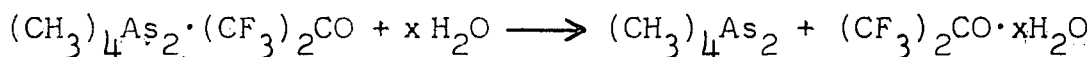


Chlorodimethylarsine does not form such an adduct with hexafluoroacetone and is immiscible with the ketone at 100° .

Hexafluoroacetone and tetramethyldiarsine react to give a compound in which there are two sets of inequivalent methyl groups and in which the trifluoromethyl groups are equivalent as shown by n.m.r. spectroscopy. The chemical shifts in hexafluoroacetone are markedly dependent on concentration. Continual pumping on a hexafluoroacetone-diarsine solution results in the gradual loss of the ketone and the appearance of the uncomplexed diarsine. This is readily shown in the ^1H n.m.r. spectrum of such a solution which shows the single diarsine peak as well as those assigned to the complex. This ^1H n.m.r. spectrum can be duplicated with a ketone-diarsine solution containing excess diarsine (such a solution also shows no carbonyl absorption in the infrared spectrum). These results indicate that the compound dissociates to some extent at 20° .

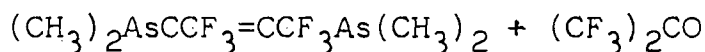
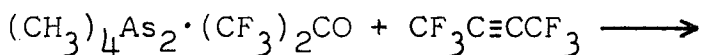


The addition of water to the 1:1 adduct gives quantitative recovery of the diarsine.



Whereas hexafluorobut-2-yne reacts with the diarsine to give an approximate 1:1 mixture of the cis- and trans-butene⁴¹, hexa-

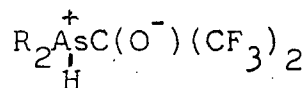
fluorobut-2-yne reacts with the 1:1 adduct to give 90% cis-isomer.



The infrared spectrum of this reaction product is almost identical with the previously described 2,3-dimethylarsinohexafluorobut-2-ene⁴¹ except that the double bond absorption at 6.3μ is much stronger indicating a predominance of the cis-isomer. The ^{19}F n.m.r. spectrum shows that the -24.3 p.p.m.^{peak} is very much enhanced and therefore this peak is assigned to the cis-isomer. The isomer distribution as determined by the relative intensities of the peaks in the ^{19}F n.m.r. spectrum is approximately 90% cis-isomer. When the butyne is reacted with the 1:1 adduct in the presence of excess hexafluoroacetone the reaction is even more stereospecific resulting in a product which is 94% cis-isomer.

(2) Proposed Mechanisms and Structures

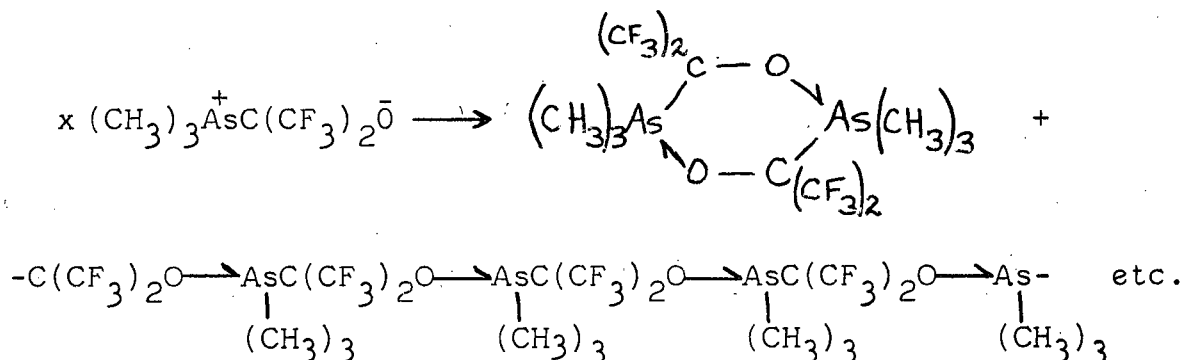
The addition of hexafluoroacetone to primary and secondary arsines is analogous to the reaction of polyfluoroketones with secondary amines^{24,25} and phosphine²⁹. The formation of the O-H bond can be explained on the basis of nucleophilic attack by the arsenic lone pair on the carbonyl carbon of the hexafluoroacetone to form a four coördinated intermediate



followed by As-H cleavage to form an OH bond by either an inter- or intramolecular mechanism. Thus the slow reaction at 20° between hexafluoroacetone and 1,1,1,3,3,3-hexafluoromethylarsinopropanol can be explained on the basis of a decrease in the availability of the arsenic lone pair due to the electronegative group $-\text{C}(\text{CF}_3)_2\text{OH}$. The inertness of chlorodimethylarsine towards

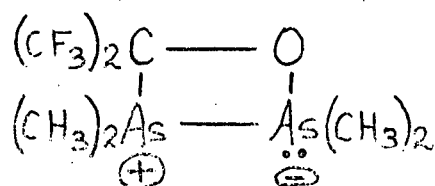
hexafluoroacetone, however, must be partially due to the As-Cl bond strength since the difference in the first ionization potentials of methylarsine (9.7 e.v.) (which reacts rapidly with hexafluoroacetone) and chlorodimethylarsine (9.9 e.v.) is only 0.2 e.v.⁴⁹

On the basis of the theory that nucleophilic attack by the arsenic lone pair occurs on the carbonyl carbon, it is proposed that the trimethylarsine-hexafluoroacetone complex has the structure $(\text{CH}_3)_3\text{As}^+\text{C}(\text{CF}_3)_2\text{O}^-$. This would explain the very small liquid range (it appears that the complex may be almost completely dissociated on melting) since it appears reasonable to assume that this monomer would be susceptible to dimerization, trimerization, etc.

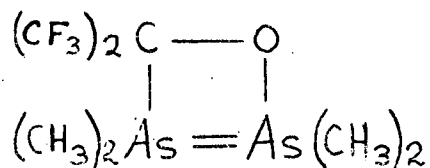


The similarity between the dimer and the proposed product from methylarsine-hexafluoroacetone reaction (equation (b)) is to be noted.

To account for the almost stereospecific reaction of the diarsine-hexafluoroacetone adduct with hexafluorobut-2-yne, the liberation of the diarsine when treated with water, the absence of any carbonyl stretching frequency in the infrared spectrum, and the n.m.r. spectra, the following structure appears most probable for the complex, $(\text{CH}_3)_2\text{AsAs}(\text{CH}_3)_2 \cdot (\text{CF}_3)_2\text{CO}$:



In this structure one arsenic atom is acting as a donor being four coördinated, and the other as an acceptor being five-coördinated if the lone pair is thought of occupying one site. Trivalent arsenic does act as an electron acceptor in the species AsCl_4^- and AsF_4^- ⁵⁰ and since the positive charge on the arsenic atom will promote delocalization of the lone pair on the adjacent arsenic atom, it is probable that the negative charge on the oxygen will be stabilized by donation to the arsenic atom. In the extreme case of complete delocalization of charge the proposed structure can be thought as having an arsenic-arsenic double bond.

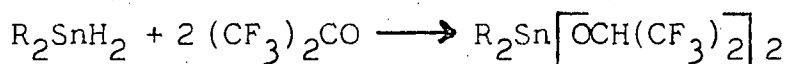
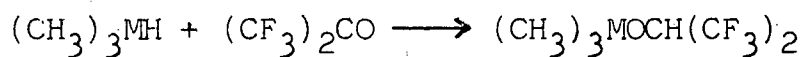


It appears that the former proposed structure at least presents a fairly significant contribution to the molecular orbitals since the chemical shift of the methyl protons is very sensitive to the presence of hexafluoroacetone. The presence of any localized charge in the complex would thermodynamically favour extensive solvolysis by a polar solvent.

B. Group IV Hydrides

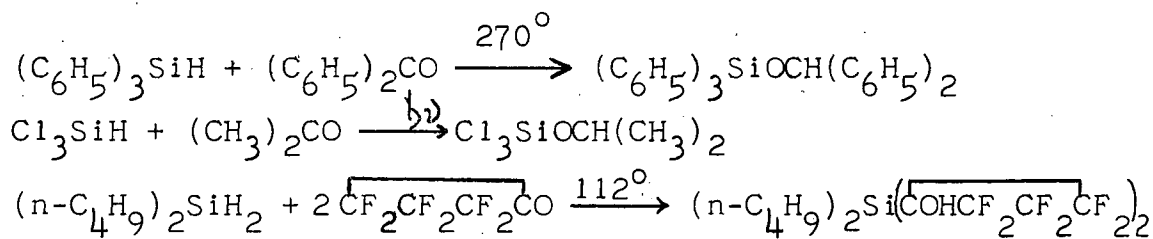
(1) Results

The addition of hexafluoroacetone to Group IV hydrides to give 1,1,1,3,3,3-hexafluoropropoxy derivatives can be represented by the following equations ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$; $\text{R} = \text{CH}_3, n\text{-C}_4\text{H}_9$)



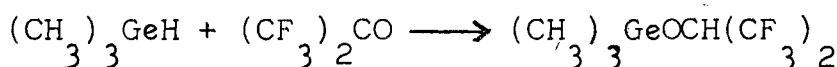
The reactions with the tin hydrides are vigorous and exothermic but addition to the silane and germane is much slower. All reactions are quantitative.

Trimethylsilane reacts with hexafluoroacetone at 20° to give 1,1,1,3,3,3-hexafluoropropoxytrimethylsilane, b.p. 86° (757 mm). It is identified by its infrared spectrum which shows no absorption in the OH region and a medium to strong absorption at 1070 cm⁻¹ attributed to the Si-O-C asymmetric stretching vibration, and by its n.m.r. spectra. The ¹H n.m.r. spectrum shows the methine absorption as a septet (J = 6.0 cps) and the ¹⁹F n.m.r. spectrum shows the trifluoromethyl absorption as a doublet (J ≈ 6 cps). Although silanes are known to react with ketones upon heating^{29,51} and upon ultraviolet irradiation⁵² to give addition products, for example



the addition of hexafluoroacetone to trimethylsilane is the first reported example of an uncatalyzed addition at 20°.

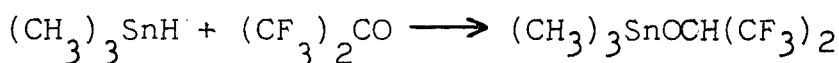
The reaction of hexafluoroacetone with excess trimethylgermane at 20° results in the quantitative preparation of 1,1,1,3,3,3-hexafluoropropoxytrimethylgermane, b.p. 117° (758 mm).



As in the silane reaction all the spectroscopic evidence clearly indicates the formation of a Ge-O bond. The ¹H n.m.r. spectrum of the product shows the methine absorption as a septet (J = 6.1 cps) and the methyl absorption as a singlet (relative intensity 1:8.9). Its ¹⁹F n.m.r. spectrum shows the trifluoromethyl absorption as a doublet (J ≈ 6 cps). The infrared absorptions which can probably be assigned to the CF stretching and CF₃ deformation frequencies of the germane, and the other hexafluoropropoxy derivatives prepared in this investigation, are given in Table I where

they are compared with the corresponding bands of 1,1,1,3,3,3-hexafluoropropanol. The similarity of the spectra is apparent.

Addition of hexafluoroacetone to excess trimethyltin hydride to form 1,1,1,3,3,3-hexafluoropropoxytrimethyltin, b.p. 76° (58 mm), occurs quantitatively below room temperature and is extremely vigorous and exothermic.



The infrared and n.m.r. spectra clearly indicate that a CH bond and not an OH bond is formed. Its ^1H n.m.r. spectrum shows the methine absorption as a septet ($J = 6.1$ cps) and the ^{19}F n.m.r. spectrum shows the trifluoromethyl absorption as a doublet ($J \approx 6$ cps). Kuivila⁵³ found that tin hydrides usually reduce ketones to alcohols, being themselves converted to ditin compounds. In the present investigations even the presence of excess tin hydride gives no trace of the reduction product 1,1,1,3,3,3-hexafluoropropanol, $\text{CF}_3\text{CH}(\text{OH})\text{CF}_3$.

TABLE I

INFRARED SPECTRA OF 1,1,1,3,3,3-HEXAFLUOROPROPOXY DERIVATIVES^a

$\text{HOCH}(\text{CF}_3)_2$	$\text{Me}_3\text{SiOCH}(\text{CF}_3)_2$	$\text{Me}_3\text{GeOCH}(\text{CF}_3)_2$	$\text{Me}_3\text{SnOCH}(\text{CF}_3)_2$	Assignment
1380 s	1378 s	1374 s	1374 s	CF stretching
1308 s	1307 vs	1304 vs	1300 vs	"
1273 vs	1270 s	1275 s	1275 s	"
1207 vs	1232 vs	1217 vs ^b	1210 vs ^b	"
	1212			
	1172 s	1153 s	1164 s	"
1112 vs	1111 s	1106 s	1101 s	"
685 m	685 m	685 m	683 m	CF_3 deformation

^a Vapour state, values in cm^{-1}

^b Broad

In a similar manner reaction of hexafluoroacetone and dialkyltin dihydrides (dimethyl and di-n-butyl) at 20° results in the addition of two moles of ketone to give bis(1,1,1,3,3,3-hexafluoropropoxy)dimethyltin, b.p. 92° (25 mm), and bis(1,1,1,3,3,3-

hexafluoropropoxy)di-n-butyltin, b.p. 75° (10^{-3} mm). The bis-(hexafluoropropoxy)dimethyltin is readily characterized by its ^1H n.m.r. spectrum of a septet at -4.57 p.p.m. ($J = 6.2$ cps) and a singlet at -0.85 p.p.m. (relative intensity 1:3.05). Its ^{19}F n.m.r. spectrum shows only the expected doublet ($J \approx 6$ cps). The di-n-butyl derivative has an infrared spectrum which is almost identical with that of the dimethyl derivative.

It was further found that the hexafluoropropoxy derivatives will complex with hexafluoroacetone. Thus hexafluoropropoxytrimethyltin and hexafluoroacetone form a stable 1:1 complex, m.p. 23° .



Its ^1H n.m.r. spectrum shows the methine absorption as a septet ($J = 6.1$ cps) and the methyl absorption as a singlet (relative intensity 1:8.5). Its ^{19}F n.m.r. spectrum gives broad absorptions at -3.1 p.p.m. and 4.4 p.p.m. (from internal hexafluoroacetone) of relative intensity 1:1 indicating two different types of trifluoromethyl groups, the hexafluoropropoxy group is at -3.1 p.p.m. and the complexed hexafluoroacetone is at 4.4 p.p.m. The ^1H n.m.r. spectrum of a mixture of the complexed and uncomplexed propoxytin compound shows two distinct septets (0.69 p.p.m. difference) but only one methyl absorption.

The ^1H and ^{19}F n.m.r. data (chemical shifts and coupling constants) of the complexed and uncomplexed hexafluoropropoxy derivatives are listed in Table II.

TABLE II

SOME ^1H AND ^{19}F CHEMICAL SHIFTS AND COUPLING CONSTANTS^a

Compound	$\delta_{\text{CH}_3}^b$ ppm.	$\delta_{\text{H}^{b,c}}$ ppm.	$J_{\text{H-F}}^d$ cps	$\delta_{\text{F(propoxy)}}^e$ ppm.	$\delta_{\text{F(complexed ketone)}}^f$ ppm.
$\text{Me}_3\text{SiOCH}(\text{CF}_3)_2$	+0.16	-3.90	6.0	-0.65 ^f	-

Compound	$\delta_{\text{CH}_3}^b$ ppm.	$\delta_{\text{H}^{\text{bc}}}$ ppm.	$J_{\text{H-F}}^d$ cps	$\delta_{\text{F(propoxy)}}^e$ ppm.	$\delta_{\text{F(complexed ketone)}}^e$ ppm.
$\text{Me}_3\text{SiOCH}(\text{CF}_3)_2 \cdot (\text{CF}_3)_2\text{CO}^g$	+0.08	-4.45	5.8	-2.51 ^h	+5.09 ^h
$\text{Me}_3\text{GeOCH}(\text{CF}_3)_2$	-0.25	-3.96	6.1	-1.65 ^f	-
$\text{Me}_3\text{GeOCH}(\text{CF}_3)_2 \cdot (\text{CF}_3)_2\text{CO}$	-0.27	-4.56	6.1	-2.9 ^{hi}	+3.4 ^h
$\text{Me}_3\text{SnOCH}(\text{CF}_3)_2$	-0.38	-4.14	6.1	-1.7 ^f	-
$\text{Me}_3\text{SnOCH}(\text{CF}_3)_2 \cdot (\text{CF}_3)_2\text{CO}$	-0.27	-4.58	6.1	-3.1 ^h	+4.4 ^h
$\text{Me}_2\text{Sn}[\text{OCH}(\text{CF}_3)_2]_2$	-0.85	-4.57	6.2	-2.07 ^{fj}	-
$\text{Me}_2\text{Sn}[\text{OCH}(\text{CF}_3)_2]_2 \cdot 2(\text{CF}_3)_2\text{CO}$	-1.03	-4.88	6.0	-2.94 ^h	+4.36 ^h

^a Spectra run on neat liquids unless otherwise indicated. Negative values of δ are downfield.

^b With respect to external tetramethylsilane.

^c Septet.

^d From ¹H spectra.

^e Doublets for uncomplexed propoxy derivatives, $J \approx 6$ cps.

^f With respect to external trifluoroacetic acid.

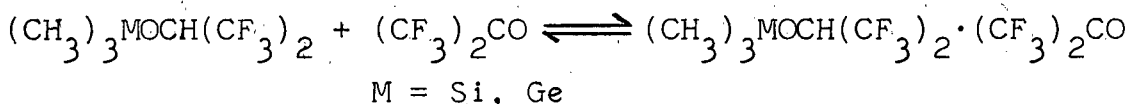
^g Solution in hexafluoroacetone.

^h With respect to internal hexafluoroacetone.

ⁱ Doublet, $J = 6$ cps, split into septet, $J = 2.5$ cps.

^j Solution in CCl_4 .

The hexafluoropropoxy-silane and -germane form easily dissociated 1:1 complexes with hexafluoroacetone at 20°.

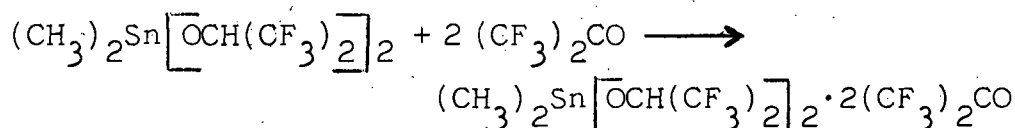


The formation of these 1:1 complexes is readily shown by ¹H n.m.r. and ¹⁹F n.m.r. spectra. The ¹H n.m.r. spectrum of a 2:1 molar hexafluoropropoxytrimethylgermane-hexafluoroacetone solution (Figure 1) shows distinct septets at -3.98 and -4.74 p.p.m. and methyl absorptions at -0.25 and -0.43 p.p.m. These peaks are assigned to the propoxygermane and its 1:1 hexafluoroacetone complex. In excess hexafluoroacetone the equilibrium shifts in favour of the 1:1 complex only one septet at -4.56 p.p.m. ($J = 6.1$ cps) and one methyl absorption at -0.27 p.p.m. are present. Hexafluoropropoxytrimethylsilane shows similar ¹H n.m.r. spectra to the germane

in hexafluoroacetone solution (Table II).

The ^{19}F n.m.r. spectra of hexafluoropropoxysilane and -germane in excess hexafluoroacetone is similar to that of the 1:1 hexafluoropropoxytrimethyltin-hexafluoroacetone complex in hexafluoroacetone, each spectrum showing two broad product peaks, one to the low field side of hexafluoroacetone and the other to the high field side (see Table II). The ^{19}F n.m.r. low field peak of the germane-hexafluoroacetone was resolved into two sets of septets with $J_{\text{H}-\text{CF}_3} = 6$ cps and $J_{\text{CF}_3-\text{CF}_3} = 2.5$ cps.

Bis(hexafluoropropoxy)dimethyltin forms a stable 1:2 complex with hexafluoroacetone at 20° .



This 1:2 complex was identified from ^1H n.m.r. and ^{19}F n.m.r.

spectra. Its ^1H n.m.r. spectrum shows a septet at -4.88 p.p.m.

($J = 6.0$ cps) and a singlet at -1.03 p.p.m. (relative intensity

1:2.9). Its ^{19}F n.m.r. spectrum shows broad peaks at -2.94 and

4.36 p.p.m. from internal hexafluoroacetone (relative intensity

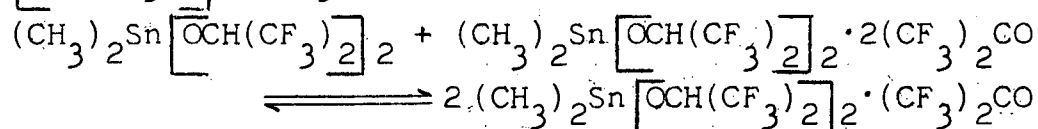
1:1). It was also found that mixing bis(hexafluoropropoxy)di-

methyltin with its 1:2 complex, $(\text{CH}_3)_2\text{Sn}[\text{OCH}(\text{CF}_3)_2]_2 \cdot 2(\text{CF}_3)_2\text{CO}$,

yields a new compound which is apparently in equilibrium with the

reactants. This new compound is believed to be the 1:1 complex,

$(\text{CH}_3)_2\text{Sn}[\text{OCH}(\text{CF}_3)_2]_2 \cdot (\text{CF}_3)_2\text{CO}$, formed by the reaction



Evidence for this comes from the ^1H n.m.r. spectra of mixtures

of the uncomplexed and dcomplexed bispropoxytin compound which

show the appearance of a third methyl peak and also the appear-

ance of another multiplet around -5 p.p.m. Table III shows that

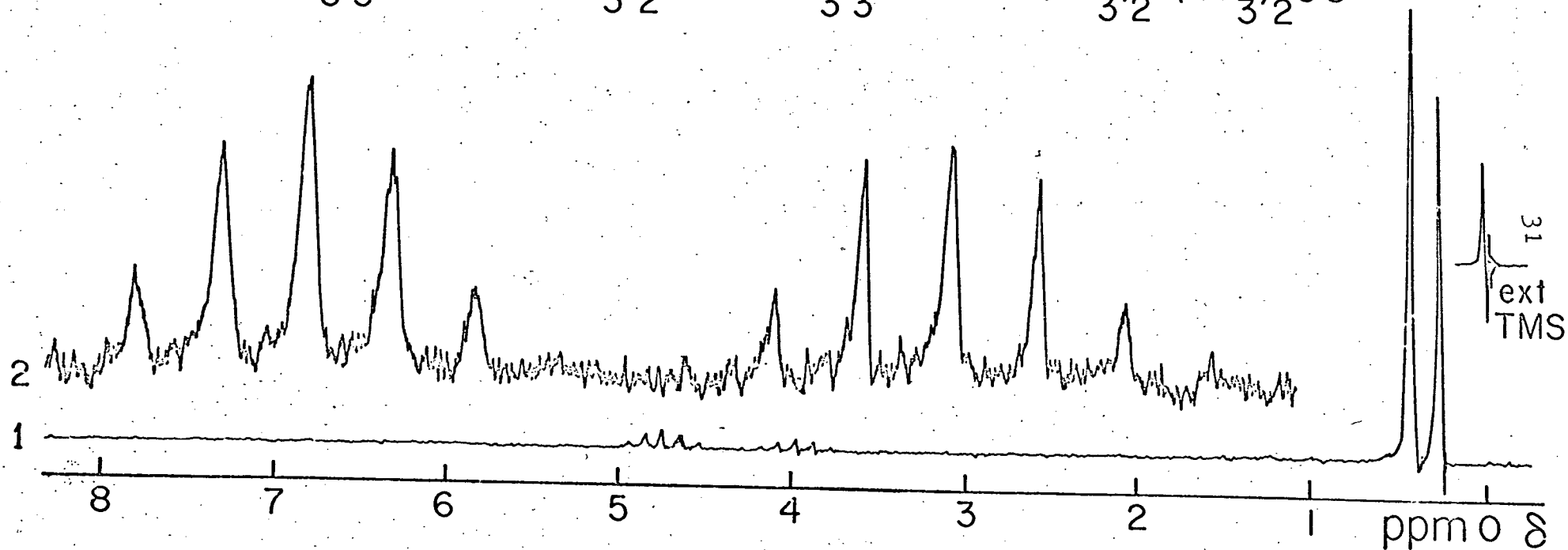
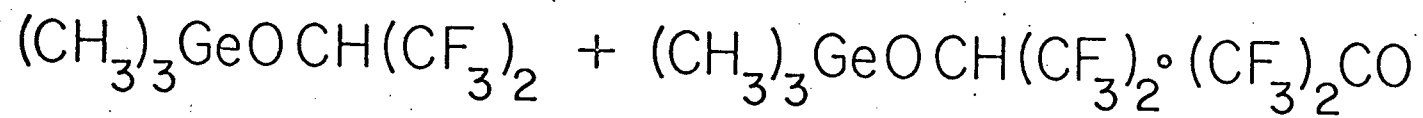


Figure 1: ^1H n.m.r. Spectrum of 2:1 Hexafluoroacetone- 1,1,1,3,3,3-Hexafluoropropoxytrimethylgermane Molar Mixture. Curve 2 is an Expansion of the Downfield Multiplets

the relative intensity of this new methyl peak varies as more of one reactant is added indicating the establishment of an equilibrium mixture^a.

TABLE III

$$^1\text{H CHEMICAL SHIFTS OF } (\text{CH}_3)_2\text{Sn}[\text{OCH}(\text{CF}_3)_2]_2$$

$$\text{AND } (\text{CH}_3)_2\text{Sn}[\text{OCH}(\text{CF}_3)_2]_2 \cdot 2(\text{CF}_3)_2\text{CO SOLUTIONS}^a$$

Mole ratio of	$\delta_{\text{CH}_3^c}$ (p.p.m.)		
$\text{Me}_2\text{SnX}_2 : \text{Me}_2\text{SnX}_2 \cdot 2(\text{CF}_3)_2\text{CO}^b$	Me_2SnX_2	$\text{Me}_2\text{SnX}_2 \cdot (\text{CF}_3)_2\text{CO}$	$\text{Me}_2\text{SnX}_2 \cdot 2(\text{CF}_3)_2\text{CO}$
0 : 1	-	-	-1.03
1 : 2	-0.78(1) ^d	-0.90(4) ^d	-1.03(4) ^d
1 : 1	-0.80(2) ^d	-0.91(5) ^d	-1.04(2) ^d
2 : 1	-0.83(7) ^d	-0.92(7) ^d	-1.05(2) ^d
1 : 0	-0.84	-	-

^a Spectra run on neat liquids. Negative values of δ are downfield.

^b $\text{X} = -\text{OCH}(\text{CF}_3)_2$.

^c With respect to external tetramethylsilane.

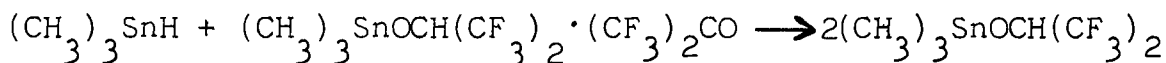
^d The approximate relative intensity of the methyl absorption for a given solution is in parenthesis after the chemical shift value.

The reaction of di-n-butyltin dihydride with excess hexafluoroacetone also gave a complex which decomposes at approximately 50° (10⁻³ mm) to give hexafluoroacetone and bis(hexafluoropropoxy)-di-n-butyltin. The complex can be identified by its infrared spectrum which gives a strong absorption at 970 cm⁻¹ characteristic of the complexed hexafluoroacetone.

It was found that trifluoroacetone would not complex with 1,1,1,3,3,3-hexafluoropropoxytrimethyltin at 20° and that hexafluoroacetone was inert to trimethyltin chloride at 120°.

^a An approximate equilibrium constant of 4.5 ± 2 can be calculated for this reaction if the relative intensities of the methyl absorption in the ¹H n.m.r. spectra are used as a measure of the concentration of the three species (Table III).

To test the reactivity of the 1:1 complex of hexafluoroacetone and propoxytrimethyltin the reaction between trimethyltin hydride and the 1:1 complex was followed by ^1H n.m.r. The results show that the tin hydride virtually disappears within two minutes with the appearance of the methine septet due to hexafluoropropoxytrimethyltin.



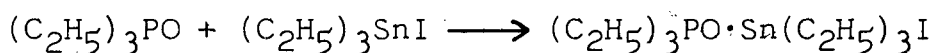
(2) Proposed Mechanisms and Structures

As described above in the reaction of hexafluoroacetone with primary and secondary arsines, amines^{24,25} and ureas²⁷, the products can be accounted for by postulating nucleophilic attack by the lone pair on the carbonyl carbon of the ketone. To account for the direction of addition of hexafluoroacetone to Group IV hydrides a reaction mechanism involving nucleophilic attack by the carbonyl oxygen on the central metal or metalloid atom is postulated. Thus a five-coordinated intermediate of the type $(\text{CH}_3)_3\text{HMO}^+(\text{CF}_3)_2$ would be first formed followed by M-H cleavage induced by the carbonyl carbon from the same intermediate (most likely) or from a second intermediate.

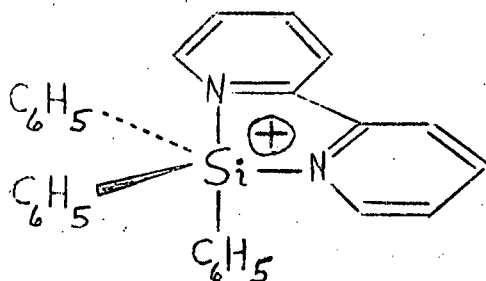
Nucleophilic attack has often been suggested as the reaction route for compounds of silicon^{54,55,56,57,58}, germanium^{57,58,59} and tin^{58,60}; it is also found that tin compounds are much more reactive to nucleophiles than silanes or germanes which is consistent with the present results. In the present investigation some evidence that a five-coordinated intermediate does occur in the hexafluoroacetone-hydride reactions comes from the result that the ketone forms complexes with the propoxy derivatives. The complexed hexafluoroacetone is almost certainly bound to the central metal or metalloid via the carbonyl oxygen.

Compounds with carbonyl groups readily form complexes with Lewis acids such as SnBr_4 , BF_3 ^{61,62,63} and $(\text{C}_4\text{H}_9)_2\text{SnCl}_2$ ⁶⁴ and it is established that bonding occurs through the oxygen atom of the carbonyl group. The infrared spectra of the tin complexes isolated in the present investigation show no carbonyl absorption, the spectra being clear above 1375 cm^{-1} except for C-H stretching bands. Thus the 1:1 propoxy-hexafluoroacetone complexes are concluded to be five-coöordinated.

In the organometallic field such coördination is well established for tin, the number of stable $\text{R}_3\text{SnX}\cdot\text{Y}$ (Y = nucleophile) complexes being large^{65,66,67,68}. Pudovik⁶⁹ and coworkers found that triethylphosphine oxide adds to triethyltin iodide to give a 1:1 adduct which can be distilled in vacuum without decomposition and which is presumably similar to the 1:1 propoxy-hexafluoroacetone complexes.



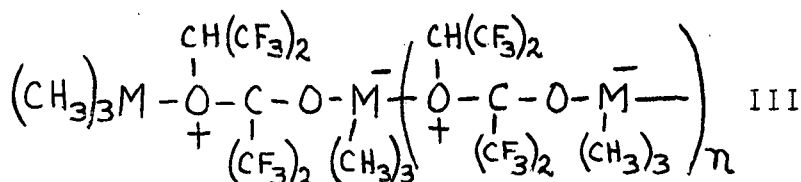
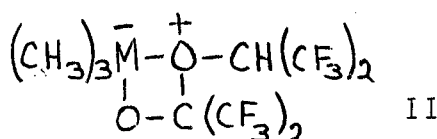
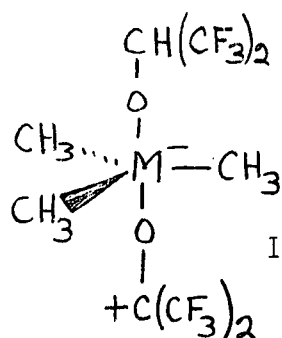
Recently five-coöordinated silicon compounds have also been isolated⁷⁰ although most of them involve three to four Si-O bonds. The only penta-coöordinated silicon species isolated containing two or more Si-C bonds is a triphenyl(bipyridyl)siliconium ion, for which the following structure is proposed⁷¹:



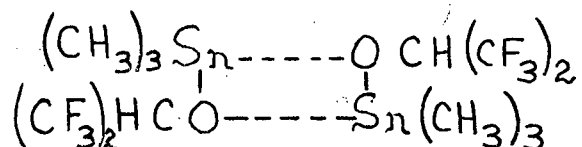
There are numerous examples of complexed germanates^{72,73,74}, but almost all are six-coöordinated and all these complexes have either Ge-X (X = halogen), Ge-O or Ge-N bonds but none have Ge-C bonds.

The formation of a six-coördinated complex $(\text{CH}_3)_2\text{Sn}[\text{OCH}(\text{CF}_3)_2]_2 \cdot 2(\text{CF}_3)_2\text{CO}$ is expected in view of the many reported six-coördinated complexes of dialkyltin dichlorides^{75,76}.

In discussing the structure of the 1:1 complexes it seems that three alternatives, I-III, should be considered.

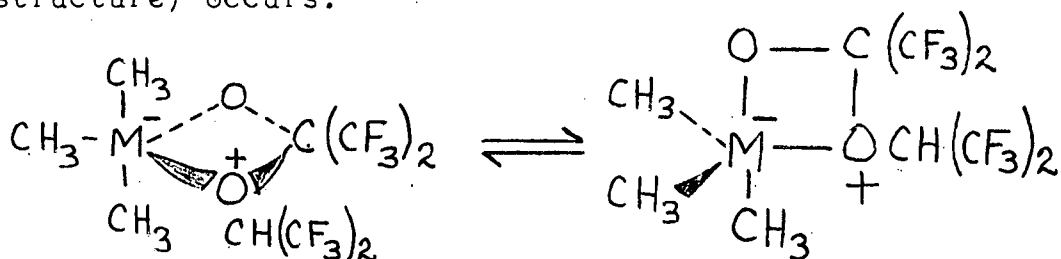


Structure I assumes almost complete localization of the positive charge since any extensive delocalization of charge through the oxygen of the complexed ketone would lead to dissociation. The carbonium ion would be unstable due to the adjacent, highly electronegative trifluoromethyl groups, and for this reason I is not favoured. There is some evidence favouring structure II and III since the propoxy oxygen appears to be a relatively good electron donor. The molecular weight of hexafluoropropoxytrimethyltin in benzene indicates dimer formation. Similar results have been obtained for trimethyltin hydroxide in carbon tetrachloride, chloroform or benzene⁷⁷. By analogy with the proposed structure for the tin hydroxide dimer the propoxytin dimer could have the following structure



Structures I and III are supported by the ^1H n.m.r. spectra of the complexes which show that the three methyl groups in a

given compound have the same chemical shift. However, this does not exclude II since the difference in chemical shifts expected for the three methyl groups could be too small to be detected. It is also possible that rapid exchange of the methyl groups from apical to the equatorial position (assuming a trigonal bipyramid as the structure) occurs.



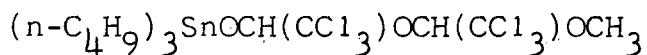
The bulk of the n.m.r. evidence suggests that I is not the structure. Firstly, in II and III the resonance due to the proton of the $-\text{CH}(\text{CF}_3)_2$ group would be expected to be downfield from that in the uncomplexed propoxy derivative because of the positive charge on the adjacent oxygen. This is found. Secondly, the same proton in I would be expected to be found upfield from the uncomplexed compound because of the negative charge on the central atom which would probably be delocalized to some extent by the propoxy oxygen. This is not found. Thirdly, the fluorine resonance due to the complexed ketone in II would be expected to be downfield from that of hexafluoroacetone because of the greater positive charge on the carbon atom resulting in an increased paramagnetic contribution. However, the resonance is in fact upfield from hexafluoroacetone. Fourthly, the peaks in the ^{19}F n.m.r. spectrum of the germanium complex are split into septets ($J \approx 2.5$ cps) which strongly suggests fluorine-fluorine coupling is present. This could occur "through space", through six bonds (as in II and III), or through eight bonds (as in I). However, if the groups in I are close enough together to couple "through space" it seems likely

that they would be close enough together for cyclization to take place to give II. The magnitude of the coupling constant appears to favour coupling "through space" or through six bonds^a. The n.m.r. evidence favours II or III and of these two structure II is favoured over III since it is thought that III would have a relatively high melting point due to its polymeric structure. On the basis of III $(\text{CH}_3)_2\text{Sn}[\text{OCH}(\text{CF}_3)_2]_2 \cdot 2(\text{CF}_3)_2\text{CO}$ would have four polymeric chains extending from the tin atom, one for each Sn-O bond (i.e. a three dimensional rather than a linear polymer), and it is then expected that the 1:2 bispropoxytin-hexafluoroacetone complex would have a higher melting point than the 1:1 propoxytrimethyltin-hexafluoroacetone complex. However, the 1:2 bispropoxytin-hexafluoroacetone complex melts at approximately 20° . Thus the melting points of the 1:1 and 1:2 tin-hexafluoroacetone complexes appear to indicate a preference for II rather than III.

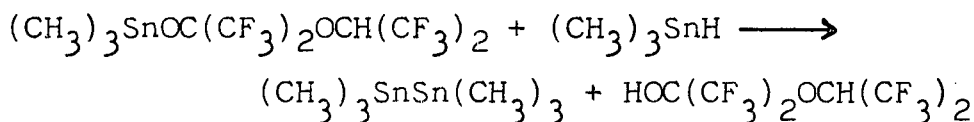
It has recently been found that chloral and other aldehydes react exothermically and reversibly with methoxytri-n-butyltin to give 1:1 addition products such as the following⁷⁸:



This 1:1 adduct will take up another mole of chloral to give a product for which the following structure is proposed:

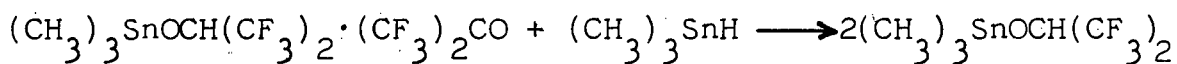


This type of structure is disregarded for the hexafluoroacetone-propoxytin complexes since the expected reaction of tin hydrides with the linear chain structure to give the reduced alcohol and the reduced ditin does not occur.



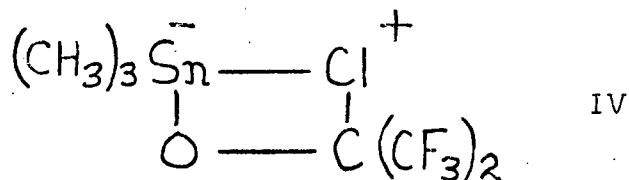
^a Coupling through eight bonds would also involve coupling through one germanium and two oxygen atoms and thus would be expected to be negligible.

As previously stated the only reaction product from trimethyltin hydride and 1:1 propoxytin-hexafluoroacetone is the propoxytin derivative.



These results coupled with the moderate stability of the trimethylarsine-hexafluoroacetone and the diarsine-hexafluoroacetone complexes seem to indicate that two criteria are necessary for stable complex formation with hexafluoroacetone. Firstly, the molecule must be able to act as a Lewis acid or base with respect to the oxygen or carbon atom of the carbonyl group and secondly, it must be able to stabilize the complex further by delocalizing the charge produced on the carbonyl group (either at the oxygen or carbon atoms) over the complexed molecule.

Since trifluoroacetone does not complex with hexafluoropropoxytrimethyltin at 20° it appears that it must be a considerably weaker nucleophile than hexafluoroacetone. This can be explained by a possible significant contribution of the tautomeric enol form, $\text{CF}_3\text{C}(\text{OH})=\text{CH}_2$ ¹⁴. It is, however, surprising to find that trimethyltin chloride is so inert toward hexafluoroacetone. Trimethyltin chloride is a compound which forms numerous complexes with Lewis bases^{66,79} and it is difficult to see why the following structure would not be stable.



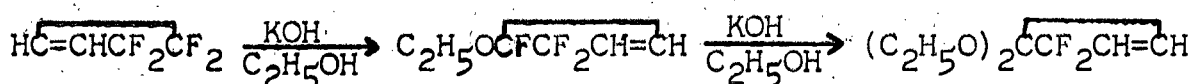
One plausible argument is that in the analogous propoxytin-hexafluoroacetone complex II the empty 2sp^3 orbital on the carbonyl carbon could be expected to overlap more efficiently with a filled 2sp^3 orbital on oxygen than with a filled 3sp^3 orbital on chlorine in the above structure IV.

CHAPTER II

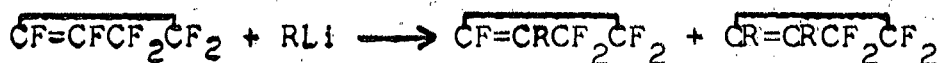
PERFLUOROCYCLOBUTENE AND 1,2-DICHLOROTETRAFLUOROCYCLOBUTENE

INTRODUCTION

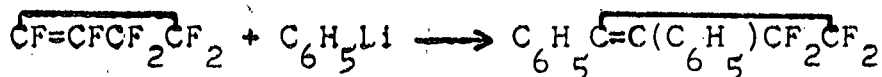
The reaction of nucleophiles with fluorinated cycloalkenes has been the subject of a number of investigations. In some of these reaction involves attack at an allylic halogen^{80,81,82} to give substitution at the allylic position.



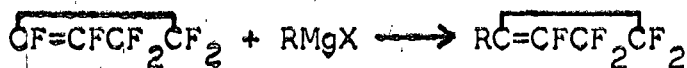
However, if a perhalocycloalkene (fluoro and chloro) is used nucleophilic attack takes place at the vinylic halogen. Dixon⁸³ studied the addition of lithium alkyl and lithium aryl reagents to perfluorocyclobutene. Lithium alkyls afforded both mono- and disubstituted products but only the disubstituted derivative was obtained from the aryl lithium reaction.



R = alkyl

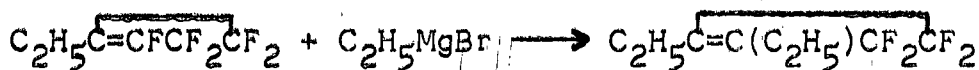


The addition of Grignard reagents to fluorinated cyclobutenes has also been studied^{84,85}. Park and Fontanelli⁸⁴ reacted both alkyl and aryl Grignard reagents with perfluorocyclobutene and 1,2-dichlorotetrafluorocyclobutene. Alkyl Grignard reagents and perfluorocyclobutene gave monosubstituted derivatives in good yield under mild conditions.



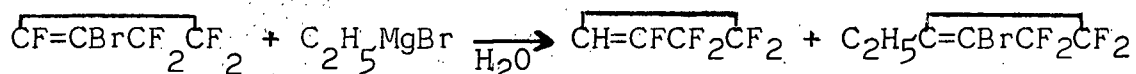
R = alkyl

Using stronger reaction conditions dialkyl derivatives were also formed in comparable yields.

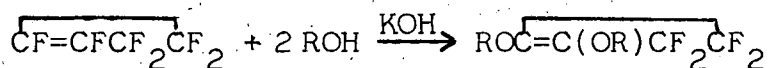


Reaction of perfluorocyclobutene with phenylmagnesium bromide

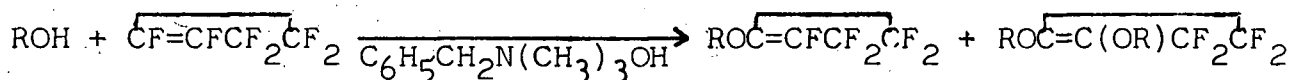
under mild conditions gave both the mono- and diphenyl derivatives. On reacting 1,2-dichlorotetrafluorocyclobutene with alkyl Grignards the monosubstituted product was readily formed. However, further substitution was more difficult in this case than for the perfluoro derivative. If bromine or iodine replaced one of the olefinic fluorine or chlorine atoms a competing reaction involving exchange of the MgBr group occurred.



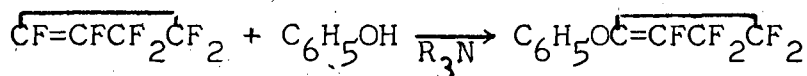
The base catalyzed reaction of alcohols with fluorinated cycloalkenes to form mono- and dialkoxy derivatives has also been studied. Park and coworkers⁸⁶ found that only the dialkoxy derivative could be obtained from perfluorocyclobutene.



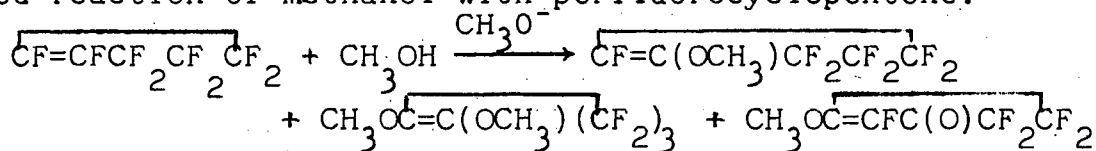
Barr and coworkers⁸⁷ found that by varying the reaction conditions both mono- and dialkoxy derivatives could be obtained with the monoalkoxy derivative predominating.



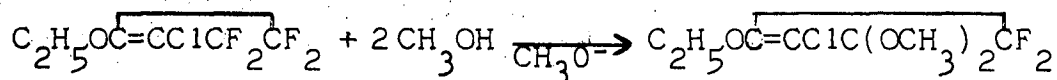
Phenol was found to give only the monophenoxy compound.



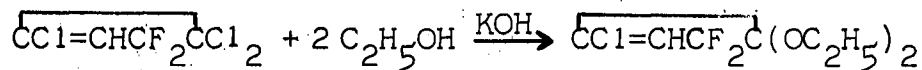
Stockel and coworkers⁸⁸ obtained both the mono- and dimethoxy derivatives as well as a methoxyketo derivative from the base catalyzed reaction of methanol with perfluorocyclopentene.



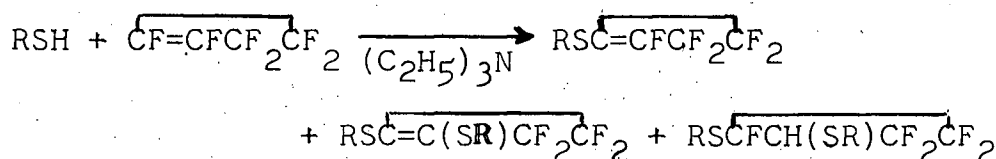
With 1,2-dichlorotetrafluorocyclobutene only the monoalkoxy derivative was obtained under normal reaction conditions⁸⁹. However, if stronger reaction conditions were used in an attempt to replace the second vinylic chlorine it was found that the allylic fluorines were attacked.



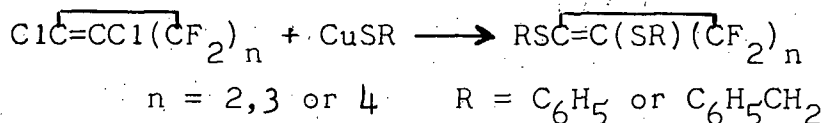
This reaction is similar to nucleophilic displacement on other related cyclobutenes^{80,81,82,90,91}, e.g.



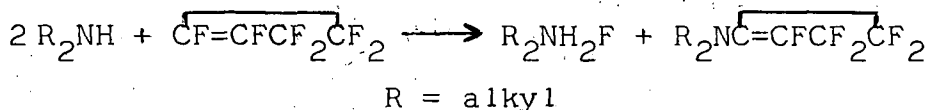
Rapp and coworkers⁹² studied the base catalyzed reaction of thiols with perfluorocyclobutene. The mono- and bismercaptocyclobutene derivatives and a diadduct (a cyclobutane) were isolated.



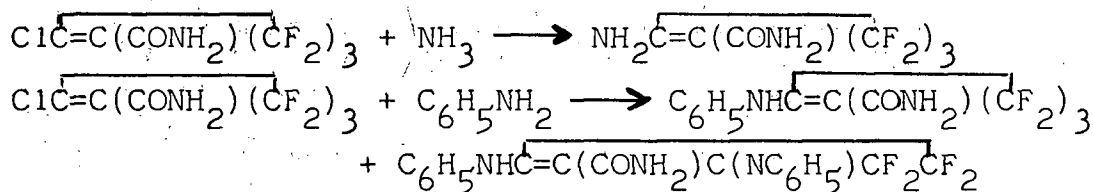
The 1,2-bismercaptocyclobutane was rather unstable and decomposed during distillation to the 1,2-bismercaptotetrafluorocyclobutene. Mercaptoderivatives of fluorocycloalkenes have also been prepared from the reaction of 1,2-dichloroperfluorocycloalkenes with cuprous mercaptides⁹³.



The reaction of primary and secondary amines with perfluorocyclobutene was studied by Pruett and coworkers⁹⁴. The results can be represented by the following equation.



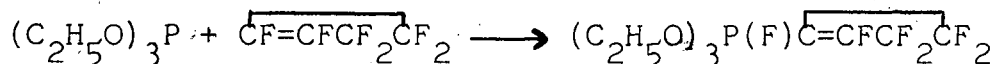
Mill and coworkers⁹⁵ and Parker⁹⁶ studied the addition of amines to 1,2-disubstituted hexafluorocyclopentene. Mill et al.⁹⁵ reacted one such cyclopentene with ammonia and aniline to get mono- and diamino derivatives.



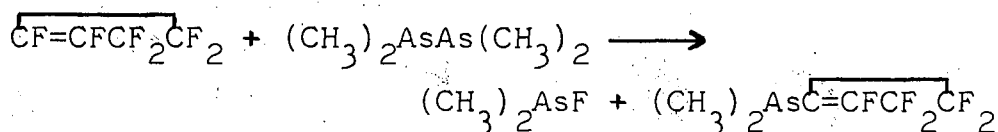
The reaction of primary amines with 1,2-dichlorohexafluorocyclopentene gave only the disubstituted product⁹⁶.



Knunyants⁹⁷ reacted triethylphosphite with perfluorocyclobutene and obtained a monosubstituted pentafluorocyclobutene containing a five coordinated phosphorus atom.

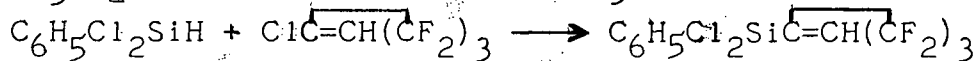
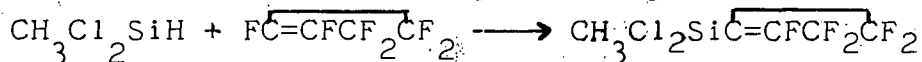
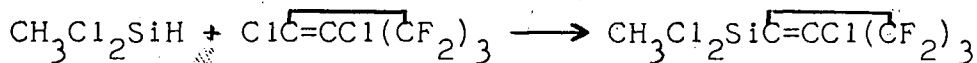


Cullen and Hota⁴¹ reacted tetramethyldiarsine with perfluorocyclobutene and obtained 1-dimethylarsinopentafluorocyclobutene.



The 1,2-dichlorotetrafluorocyclobutene and 1,2-dichlorohexafluorocyclopentene react analogously with the diarsine⁹⁸.

The only published work regarding the reaction of Group IV organometallic compounds with fluorocycloalkenes is described in a U.S. patent. Haluska⁸ reacted some chlorosilanes with a variety of 1,2-dichloroperfluorocycloalkenes and 1-chlorofluorocycloalkenes and obtained 1-silylcycloalkene derivatives.



In the present investigation a study of the reactions of some arsines and Group IV hydrides with some fluorocycloalkenes was undertaken and the results of these reactions are presented and discussed in the following section.

EXPERIMENTAL

The general experimental technique and apparatus have been previously described in Chapter I, page 6.

A. Arsines(1) Starting Materials

Perfluorocyclobutene, 1,2-dichlorotetrafluorocyclobutene, and 1,2-dichlorohexafluorocyclopentene were purchased from Peninsular Chemresearch Inc., P.O. Box 3597, Gainesville, Florida. They were used without further purification. The preparation of methylarsine and dimethylarsine is described in Chapter I, page 8. The methylphenylarsine was a gift from coworker D. S. Dawson.

(2) Reactions with the Cyclobutenes and the Cyclopentene(a) Reaction of Methylphenylarsine and Perfluorocyclobutene--

Methylphenylarsine (3.7 g) and perfluorocyclobutene (5.2 g) were heated for 17 hours at 100°. Perfluorocyclobutene (3.3 g) was recovered. The involatile product 1-methylphenylarsinopentafluorocyclobutene (2.0 g, 30%) was purified by distillation, b.p. 104° (15 mm), 58° (10⁻³ mm) (Found: C, 42.8; H, 2.1; As, 24.4; F, 30.8%. Calc. for C₁₁H₈AsF₅: C, 42.6; H, 2.6; As, 24.2; F, 30.6 %). Infra-red spectrum (liquid film): 3090 m, 3055 m, 2940 w, 1659 s, 1584 w, 1488 m, 1441 m, 1420 w, 1389 s, 1373 m, 1333 w, 1303 w (sh), 1293 w (sh), 1274 vs, 1205 s, 1115 vs, 1079 m, 1069 w (sh), 1024 m, 1001 m, 947 s, 853 m, 810 s, 735 s, 692 s, 646 m cm⁻¹. N.m.r. spectra: the ¹⁹F n.m.r. spectrum showed multiplets at 27.5, 33.7, and 39.7 p.p.m. of relative intensities 1:2:2.

(b) Reaction of Dimethylarsine and 1,2-Dichlorotetrafluorocyclobutene--

Dimethylarsine (2.4 g) and 1,2-dichlorotetrafluorocyclobutene (6.9 g) were heated at 100° for 5 days. Hydrogen chloride (0.85 g, 100%) of molecular weight 36.5 (Calc: 36.5), which went through a

-96° trap, was isolated. Unreacted butene (2.6 g) was recovered and the reaction product, 1-chloro-2-dimethylarsinotetrafluorocyclobutene (5.8 g, 97%), of known infrared spectrum⁹⁸ condensed in a -23° trap.

(c) Reaction of 1-Chloro-2-dimethylarsinotetrafluorocyclobutene and Dimethylarsine--

Dimethylarsine (2.1 g) and the dimethylarsinocyclobutene (8.0 g) were heated at 140° for 3 days. A volatile fraction was obtained which contained no As-H absorption and which when condensed into an aqueous silver nitrate solution formed a precipitate which later turned the characteristic mauve colour of silver chloride. Unreacted dimethylarsinocyclobutene (4.9 g) was recovered in a -23° trap. The involatile reaction product remaining in the Carius tube was distilled in a nitrogen atmosphere to give 1,2-bis(dimethylarsino)tetrafluorocyclobutene, b.p. 120° (47 mm), (3.5 g, 52%) (Found: C, 28.7; H, 3.4; As, 44.8; F, 23.0 %, mol. wt. (camphor), 320. Calc. for $C_8H_{12}As_2F_4$: C, 28.6; H, 3.6; As, 44.6; F, 23.2 %; mol. wt., 336). This bisarsinocyclobutene slowly oxidized in air.

Infrared spectrum (liquid film): 3000 m, 2920 m, 2810 w, 2105 w, 1913 w, 1420 s, 1329 m, 1300 vs, 1263 s, 1246 m, 1225 vs, 1154 vs, 1130 s, 1084 vs, 897 s, 859 s, 845 s, 803 s cm^{-1} .

(d) Reaction of Dimethylarsine and 1,2-Dichlorohexafluorocyclopentene--

Dimethylarsine (2.3 g) and the cyclopentene (7.9 g) were heated at 100° for 2 days. A mixture of dimethylarsine and hydrogen chloride (1.3 g) was obtained which could not be separated by trap-to-trap distillation. Unreacted dichlorohexafluorocyclopentene (5.0 g) stopped in a -46° trap. The reaction product which remained in the Carius tube was identified as 1-chloro-2-dimethylarsinohexafluorocyclopentene (3.9 g, 55%) by its known infrared spectrum⁹⁸.

(e) Reaction of Dimethylarsine and Perfluoropropene--Dimethylarsine (1.8 g) and perfluoropropene (11.0 g) were heated at 100° for 5 days. Unreacted perfluoropropene (9.3 g) which went through a -64° trap was recovered. The remaining material (3.6 g) which condensed in a -64° trap was purified by v.p.c. (5' Ucon Polar column at 110°). The reaction product, 2-H-1-dimethylarsinohexafluoropropane had a boiling point of $110-111^{\circ}$ (739 mm) (Found: C, 23.4; H, 2.8; As, 29.4; F, 44.3 %. Calc. for $C_5H_7AsF_6$: C, 23.2; H, 2.7; As, 29.3; F, 44.5 %). Infrared spectrum (vapour): 3090 w, 3030 w, 1424 w, 1381 s, 1290 s, 1212 vs, 1178 vs, 1105 s, 1077 s, 1005 w, 980 vw, 937 w, 904 w, 878 w, 854 m, 791 w, 717 m, 678 cm^{-1} .

The reaction product, 2-H-1-dimethylarsinohexafluoropropane, was heated at 180° for 21 hours. The Carius tube showed no signs of etching and the recovered arsenic compound which stopped in a -64° trap showed no trace of double bond absorption in the infrared spectrum.

(f) Reaction of the Dimethylarsinohexafluoropropane and Bromine--The arsinopropane (1.0 g), bromine (2.3 g) and carbon tetrachloride (1.8 g) were left to react at room temperature for 3 weeks. Methyl bromide (0.7 g) which went through a -96° trap was produced and was identified by its known infrared spectrum. The remaining volatile material (3.2 g) was added to mercury to remove the excess bromine. The carbon tetrachloride was removed by a -78° trap and 2-H-1-bromohexafluoropropane was identified by its known infrared spectrum⁹⁹ and its molecular weight of 227 (Calc: 231).

(3) ^1H n.m.r. Studies of Dimethylarsine and the Fluorocyclobutenes at 20°

(a) Dimethylarsine and Perfluorocyclobutene--Excess cyclobutene and dimethylarsine were sealed in an n.m.r. tube. The ^1H n.m.r. spectrum within 30 minutes after mixing showed the appearance

of a second methyl peak at -1.00 p.p.m. (the methyl absorption of $(CH_3)_2AsH$ is a doublet at -0.69 p.p.m.) which was approximately 0.5% the intensity of the dimethylarsine peaks. After 24 hours the reaction was one third complete; no downfield proton was present and a third absorption in the methyl region at -0.84 p.p.m. represented approximately 1.5% of the total methyl absorption intensity. After 4 days the reaction was 85% complete with the third methyl absorption representing 3% of the product, 1-dimethylarsinopentafluorocyclobutene, peak area.

(b) Dimethylarsine and 1,2-Dichlorotetrafluorocyclobutene--

The 1H n.m.r. study of this reaction showed that it was substantially slower at 20° being only 19% complete after 6 days and 36% complete after 12 days. The methyl absorption of the product, 1-chloro-2-dimethylarsinotetrafluorocyclobutene, was at -1.11 p.p.m. and after 12 days the methyl absorption of dimethylarsine was a singlet at -0.81 p.p.m.

B. Group IV Hydrides

(1) Starting Materials

The preparation of trimethylgermane and the tin hydrides is described in Chapter I, pages 13-14.

(2) Reactions with the Cyclobutenes and Cyclopentene

(a) Reaction of Trimethylsilane and 1,2-Dichlorotetrafluorocyclobutene--

Trimethylsilane (2.4 g) and the butene (11.5 g) were heated at 190° for 12 hours. A non-condensable gas was produced and identified as hydrogen from its molecular weight of 3 (Calc: 2.0).

Trap-to-trap distillation gave the following fractions: hydrogen chloride (0.34 g) which went through a -136° trap and which was identified by its molecular weight of 36.5 (Calc: 36.5); a mixture of trimethylsilane and tetramethylsilane (0.3 g; mol. wt., 82)

which condensed in a -136° trap and which was identified by its infrared spectrum. This latter fraction could not be separated into its separate components by further trap-to-trap distillation. A -78° fraction (8.5 g) consisting of unreacted cyclobutene and chlorotrimethylsilane could not be separated by distillation; the entire fraction boiled between 60° and 70° . This fraction was added to an aqueous solution of silver nitrate and silver chloride (1.8 g) was produced. Pure 1,2-dichlorotetrafluorocyclobutene was found to be unaffected by an aqueous silver nitrate solution. The main reaction product, 1-chloro-3,3,4,4-tetrafluorocyclobutenyltrimethylsilane (4.5 g, 60%) condensed in a -23° trap and was purified by distillation, b.p. 132° (762 mm) (Found: C, 36.1; H, 3.9; Cl, 15.5; F, 32.7 %. Calc. for $C_7H_{10}ClF_4Si$: C, 36.1; H, 3.9; Cl, 15.2; F, 32.7 %). Infrared spectrum (liquid film): 2972 m, 2905 w, 1576 s, 1419 m, 1334 vs, 1256 m (sh), 1242 vs, 1174 w (sh), 1154 w (sh), 1132 m (sh), 1116 vs, 1013 w, 948 w, 848 vs, 809 s, 764 m, 715 m, 626 cm^{-1} .

(b) Reaction of Trimethylsilane and Perfluorocyclobutene-- Trimethylsilane (7.3 g) and perfluorocyclobutene (5.5 g) were heated at 250° for 4 days. A non-condensable gas was produced which was identified as hydrogen by its molecular weight of 2.1 (Calc: 2.0). Slightly impure trimethylsilane (5.9 g) was recovered. A second fraction (5.5 g) which condensed in a -64° trap was distilled at 756 mm, the main portion coming off at 112° .

Infrared spectrum of 112° fraction (liquid film): 2995 m, 2925 w, 1398 s, 1333 s, 1281 m, 1240 vs, 1177 vs, 1167 m, 1104 m, 1037 s, 1001 s, 956 vs, 858 s, 831 m, 776 m, 766 w (sh), 700 cm^{-1} . N.m.r. spectra: the 1H n.m.r. spectrum had a singlet at 0.02 p.p.m. ($-CH_3$) and a peak at -4.93 p.p.m. which was a doublet ($J =$

52 cps) split into further peaks.

This fraction (b.p. 112° (756 mm)) could not be purified by v.p.c. (5' dinonyl phthalate at 70°) because of rapid hydrolysis of the compound. Although molecular weight measurements (Found: 237, 240; Calc. for $C_7H_{10}F_6Si$: 236) were satisfactory for 1,2,3,3,4,4-hexafluorocyclobutyltrimethylsilane, the elemental micro-analysis was not satisfactory.

A third fraction (1.3 g) which condensed in a -23° trap was shown to contain a minimum of 5 components by v.p.c. (5' dinonyl phthalate at 100°) none of which were identified.

(c) Reaction of Trimethylgermane and Perfluorocyclobutene--

The germane (1.20 g) and the cyclobutene (9.36 g) were heated at 230° for 3 days. Unreacted perfluorocyclobutene (8.05 g), which went through a -78° trap, was recovered. A second fraction (2.46 g) which condensed in a -78° trap was identified as 1,2,3,3,4,4-hexafluorocyclobutyltrimethylgermane, b.p. 118° (752 mm) (Found: C, 29.7; H, 3.8 %. Calc. for $C_7H_{10}F_6Ge$: C, 29.9; H, 3.6 %). Infra-red spectrum (vapour): 3000 w, 2930 w, 1424 w, 1398 s, 1334 s, 1282 m, 1241 vs, 1185 vs, 1163 m, 1100 m, 1035 s, 1003 s, 959 vs, 829 vs, 771 m, 753 w (sh), 714 w cm^{-1} . N.m.r. spectra: the 1H n.m.r. spectrum showed a singlet at -0.25 p.p.m. ($-CH_3$) and a peak at -5.01 p.p.m. which was a doublet ($J = 55$ cps) split into further peaks. The relative intensity of the methyl peak to the multiplet was 1:9.3 (Calc. 1:9.0).

(d) Reaction of Trimethylgermane and 1,2-Dichlorotetrafluorocyclobutene--

The germane (3.4 g) and the dichlorobutene (6.62 g) were heated at 190° for 36 hours. The more volatile fraction which went through a -46° trap showed a Ge-H infrared absorption and was transferred to a Carius tube and heated at 230° for 3 days. A

fraction (1.3 g) which condensed in a -46° trap could not be further separated by trap-to-trap distillation. The -46° fraction also could not be separated by atmospheric distillation and was separated by v.p.c. (10' silicone column at 170°). The v.p.c. spectrum showed 6 components.

The first component (20% by weight) was found to be chlorotrimethylgermane as identified by its infrared spectrum and its boiling point of 102° (lit. value 102°) (Found: C, 23.9; H, 5.9 %. Calc. for C_3H_9ClGe : C, 23.5; H, 5.9 %).

The second component (0.5% by weight) had the following 1H n.m.r. and infrared spectra. Infrared spectrum (CCl_4 solution): 3015 w, 2930 w, 1865 vw, 1825 vw, 1743 vw, 1420 w, 1333 s, 1261 s, 1168 s, 1130 m, 1117 vs, 1091 m, 903 w, 871 w, 833 s cm^{-1} . N.m.r. spectra: the 1H n.m.r. spectrum of a 20% solution in carbon tetrachloride showed a singlet at -0.33 p.p.m. ($-CH_3$) and a triplet at -6.79 p.p.m. ($J = 9.5$ cps) of relative intensity 1:8.9 (Calc. for $(CH_3)_3GeC\equiv CHCF_2CF_2$: 1:9.0).

The third component (40% by weight) was identified as 1-chlorotetrafluorocyclobutenyl-2-trimethylgermane, b.p. 78° (50 mm) (Found: C, 29.9, H, 3.7 %. Calc. for $C_7H_9ClF_4Ge$: C, 30.3; H, 3.3 %). Infrared spectrum (liquid film): 3005 w, 2925 w, 2825 vw, 1822 vw, 1576 s, 1419 m, 1380 w, 1358 w (sh), 1333 vs, 1241 vs, 1170 w (sh), 1145 w (sh), 1112 vs, 847 s, 834 m (sh), 810 m, 772 m cm^{-1} . N.m.r. spectra: the 1H n.m.r. spectrum showed a single peak at -0.21 p.p.m. ($-CH_3$).

The fourth component (4% by weight) had the following 1H n.m.r. and infrared spectra. Infrared spectrum (liquid film): 3017 w, 2950 w, 1420 w, 1354 s, 1282 m, 1261 m, 1201 s, 1164 s, 1135 s, 1099 m, 1050 m, 1010 m, 954 m, 832 s, 771 m cm^{-1} . N.m.r.

spectra: the ^1H n.m.r. spectrum of a 30% solution in carbon tetrachloride showed a singlet at -0.31 p.p.m. ($-\text{CH}_3$) and multiplets at -2.3 and -4.05 p.p.m. of relative intensity $9:0.9:1$ (Calc. for $(\text{CH}_3)_3\text{GeCH-CHClCF}_2\text{CF}_2$: $9:1:1$).

The fifth component (8% by weight) was identified as 1-chloro-3,3,4,4-tetrafluorocyclobutyl-2-trimethylgermane, b.p. $80-82^\circ$ (50 mm) (Found: C, 30.3; H, 3.8; Ge, 25.6; F, 27.4; Cl, 12.4 %. Calc. for $\text{C}_7\text{H}_{11}\text{ClF}_4\text{Ge}$: C, 30.1; H, 4.0; Ge, 26.0; F, 27.2; Cl, 12.7 %). Infrared spectrum (liquid film): 3004 w, 2930 w, 1416 w, 1351 s, 1279 m, 1244 m, 1213 s, 1163 w, 1134 s, 1082 s, 1059 w, 1025 w, 949 m, 831 s, 817 m, 769 w cm^{-1} . N.m.r. spectra: its ^1H n.m.r. spectrum showed a singlet at -0.29 p.p.m. ($-\text{CH}_3$) and multiplets at -2.57 and -4.56 p.p.m. of relative intensity $9:1:0.9$ (Calc.: $9:1:1$).

The sixth component (27% by weight), b.p. 86° (50 mm), had the following ^1H n.m.r. and infrared spectra. Infrared spectrum (CCl_4 solution): 3008 w, 2930 w, 2827 vw, 1419 w, 1356 s, 1276 m, 1250 w, 1245 s, 1219 s, 1179 s, 1145 m, 1124 s, 1105 m, 1073 m, 1030 m, 959 m, 875 s, 836 s, 690 vw cm^{-1} . N.m.r. spectra: the ^1H n.m.r. spectrum of a 20% solution in carbon tetrachloride showed a singlet at -0.49 p.p.m. ($-\text{CH}_3$) and a septet at -4.54 p.p.m. ($J = 4$ cps) of relative intensity $1:9.2$ (Calc. for $(\text{CH}_3)_3\text{GeCClCClHCF}_2\text{CF}_2$: $1:9.0$).

The material which was heated at 230° for 3 days could not be separated by vacuum or high pressure distillations. A fraction (0.22 g) which went through a -78° trap was added to an aqueous solution of silver nitrate and a curdy precipitate appeared. The -78° fraction (3.02 g) which went through a -46° trap was shown by infrared analysis to contain two absorptions in

the double bond region at 6.1μ ($\text{Cl}\overline{\text{C}=\text{CClCF}_2\text{CF}_2}$) and 6.3μ . A v.p.c. analysis of the -46° fraction (5.5 g) showed five components; the sixth component which was present in the 190° reaction was absent in this case. Components 1,2,3,4 and 5 were in ratio 5:1:10:1:2 respectively by weight.

(e) Reaction of Trimethyltin Hydride and Perfluorocyclobutene

--Trimethyltin hydride (2.4 g) and the cyclobutene (3.3 g) were left at room temperature for 4 days. The reaction mixture turned cloudy almost immediately and at the end of 4 days a solid (0.2 g) was produced. Unreacted perfluorocyclobutene (1.1 g) with a trace of 1-H-pentafluorocyclobutene, which went through a -46° trap, was recovered. The main reaction product, 1,2,3,3,4,4-hexafluorocyclobutyltrimethyltin (4.4 g), condensed in a -46° trap. Infrared spectrum (liquid film): 2985 vw, 2950 m, 1390 s, 1329 s, 1273 m, 1235 s, 1172 vs, 1150 m, 1091 m, 1056 vw, 1018 s, 999 s, 949 vs, 830 m, 782 s, 769 m, 728 w cm^{-1} . N.m.r. spectra: its ^1H n.m.r. spectrum showed a singlet at -0.28 p.p.m. ($-\text{CH}_3$) and a doublet at -5.10 p.p.m. ($J = 55$ cps) which was further split into many peaks. ^1H n.m.r. spectrum analysis also showed that a mixture of trimethyltin hydride and perfluorocyclobutene was only 0.13% reacted after 30 minutes.

The cyclobutyltrimethyltin (1.025 g) was vacuum sealed and left at 20° for 10 days. Pentafluorocyclobutene (0.20 g) was produced and identified by its molecular weight of 144 (mass spec.) and 142 (vapour) (Calc: 144). Undecomposed 1,2,3,3,4,4-hexafluorocyclobutyltrimethyltin (0.557 g) was recovered. The remaining involatile solid was identified as trimethyltin fluoride, m.p. $>320^\circ$ (lit. value decomposes $>360^\circ$) (Found: C, 20.0; H, 5.0 %. Calc. for $\text{C}_3\text{H}_9\text{FSn}$: C, 19.7; H, 4.9 %).

(f) Reaction of Triethyltin Hydride and Perfluorocyclobutene

--Triethyltin hydride (8.1 g) and the cyclobutene (14.5 g) were left at 20° for 2 months. The solution went cloudy immediately and after one day there was considerable precipitate. The fraction (13.4 g) which went through a -23° bath could not be separated any further by trap-to-trap distillation and its infrared spectrum showed two absorptions in the double bond region at 5.6 μ (CF=CFCF₂CF₂) and 5.9 μ . A second fraction (0.4 g) which condensed in a -23° trap was identified as 1,2,3,3,4,4-hexafluorocyclobutyltriethyltin by infrared analysis and had decomposed completely within one week to triethyltin fluoride, m.p. 255-257° (a sample prepared from triethyltin chloride in aqueous KF and recrystallized from ethanol gave the same melting point) (Found: C, 32.0; H, 5.9 %. Calc. for C₆H₁₅FSn: C, 32.7; H, 6.7 %). Triethyltin fluoride (8.8 g) was recovered from the original reaction.

(g) Reaction of Triethyltin Hydride and 1,2-Dichlorotetrafluorocyclobutene

Triethyltin hydride (2.9 g) and the cyclobutene (11.0 g) were heated at 100° for one day. The volatile fraction (10.9 g) contained no triethyltin group and had two infrared absorptions in the double bond region at 6.1 μ ($\overline{\text{CCl=CClCF}_2\text{CF}_2}$) and 6.3 μ . The involatile fraction was identified as triethyltin chloride (3.1 g, 91%) by its known infrared spectrum and v.p.c. analysis (5' Ucon Polar at 175°) with a retention time of 23 min. 15 sec. ((C₂H₅)₃SnCl: 23 min. 40 sec.).

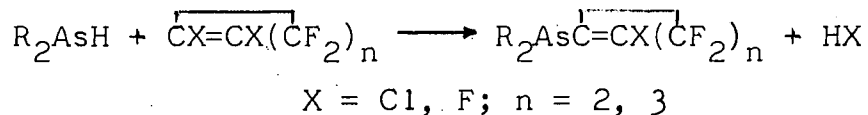
(h) Reaction of Triethyltin Hydride and 1,2-Dichlorohexafluorocyclopentene

Triethyltin hydride (3.4 g) and the cyclopentene (12.5 g) were heated at 100° for one day. Triethyltin chloride (3.7 g, 93%) was produced as identified by its infrared spectrum. The v.p.c. analysis showed only one component (5' Ucon Polar at 190°).

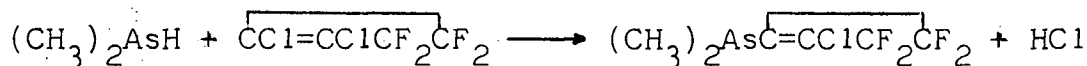
DISCUSSION

A. Arsines(1) Results

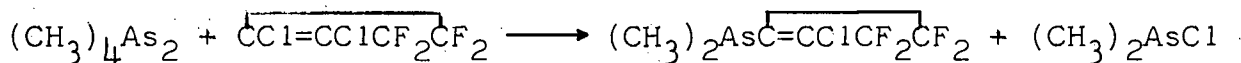
In the present investigation it was found that the reaction of arsines with fluorocyclobutenes and fluorocyclopentenenes can be represented by the general equation:



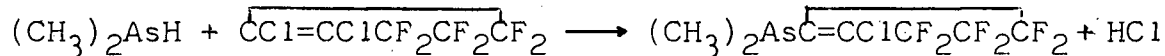
Thus dimethylarsine and 1,2-dichlorotetrafluorocyclobutene afford 1-chloro-2-dimethylarsinotetrafluorocyclobutene and hydrogen chloride both in quantitative yield at 100°.



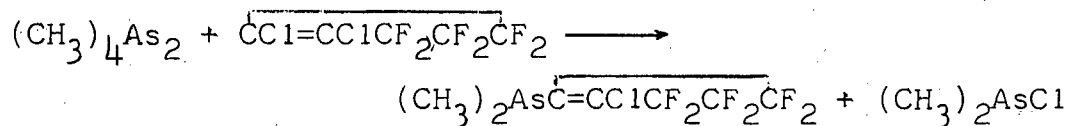
This reaction product is identical with that from cacodyl and 1,2-dichlorocyclobutene⁹⁸.



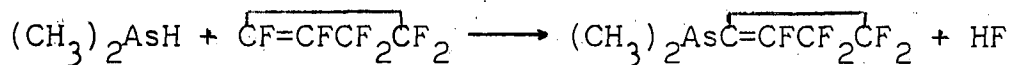
The reaction of dimethylarsine with 1,2-dichlorohexafluorocyclopentene to give the expected product, 1-chloro-2-dimethylarsinohexafluorocyclopentene, is 55% complete after two days at 100°.



As in the case of the cyclobutene derivative, this same arsino-cyclopentene has also been obtained by the reaction of cacodyl and 1,2-dichlorohexafluorocyclopentene⁹⁸.

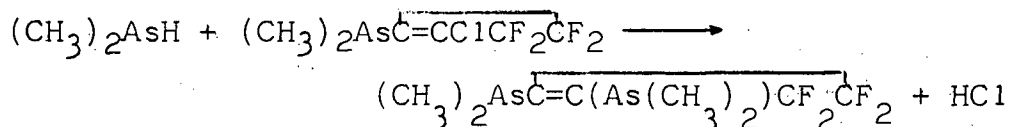


A study was made of the rates of reaction of dimethylarsine with $\overline{CX=CCF_2CF_2}$ ($X = Cl, F$) by mixing the reactants in an n.m.r. tube. The 1-dimethylarsinopentafluorocyclobutene has previously been quantitatively obtained by the reaction of dimethylarsine and perfluorocyclobutene after seven days at 20° 100°.



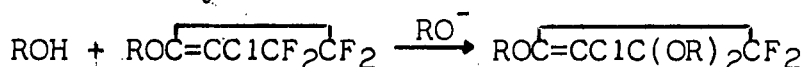
It was found that the reaction with perfluorocyclobutene is considerably faster at 20° than the reaction with 1,2-dichlorotetrafluorocyclobutene. Thus, whereas the former reaction is 35% complete after one day and 85% complete after four days, the latter reaction is only 35% complete after twelve days.

Under more forcing conditions (140°) a second mole of dimethylarsine reacts with 1-chloro-2-dimethylarsinotetrafluorocyclobutene to give the 1,2-bis(dimethylarsino)cyclobutene derivative, b.p. 120° (47 mm).

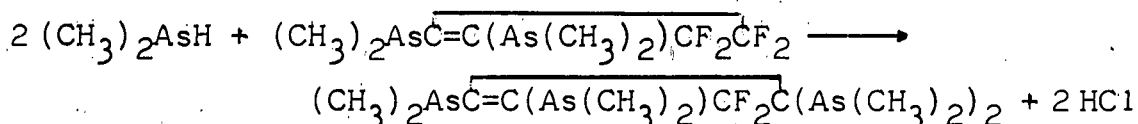


The product, 1,2-bis(dimethylarsino)tetrafluorocyclobutene, is identified by microanalysis and molecular weight. The arsine gives only a very weak absorption at 6.2 μ in the double bond region of the spectrum. On the basis of this weak infrared absorption the symmetrical 1,2-bis(dimethylarsino) derivative is favoured over the 1,3- or 1,4-bis(dimethylarsino) derivatives since these latter two compounds would be expected to have a strong infrared absorption in the double bond region similar to 1-chloro-2-dimethylarsinotetrafluorocyclobutene⁹⁸. An interesting result of this reaction is the low yield of bis(dimethylarsine) derivative (52% based on dimethylarsine) and the overall 2:1.2, dimethylarsine-dimethylarsinocyclobutene, stoichiometry of the reaction. After taking into account the yield of the bis(dimethylarsino)cyclobutene the remaining material is approximately four parts dimethylarsine to one part dimethylarsinocyclobutene. It thus appears that the allylic fluorines are attacked and from the results of Park and coworkers⁸⁹, who found that alcohols attack

the allylic fluorines of 1-alkoxy-2-chlorotetrafluorocyclobutene to form a trialkoxy



derivative, the following reaction is postulated as a possible side reaction.

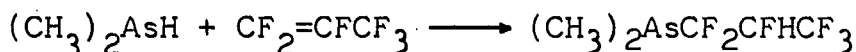


No reaction occurs between methylphenylarsine and perfluorocyclobutene after one day at 20°, and the reaction is only 30-50% complete after seventeen hours at 100°.



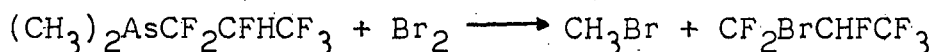
The reaction product, 1-methylphenylarsinopentafluorocyclobutene, b.p. 104° (15 mm), is identified by its ¹⁹F n.m.r. spectrum which shows peaks at 27.5, 33.7 and 39.7 p.p.m. (relative intensity 1:2:2). This is in agreement with the ¹⁹F n.m.r. spectrum of $(\text{CH}_3)_2\text{AsC}=\text{CFCF}_2\text{CF}_2$ which shows peaks at 28.9, 33.7 and 39.4 p.p.m. (relative intensity 1:2:2)¹⁰⁰. The methylphenylarsino derivative has a strong absorption in its infrared spectrum at 1659 cm⁻¹ which is assigned to the double bond. This compares favourably with a strong absorption at 1695 cm⁻¹ for 1-dimethylarsinopentafluorocyclobutene⁴¹.

At 100° the reaction of dimethylarsine with the non-cyclic fluoroolefin, hexafluoropropene, gives a quantitative yield of the addition product, 2-H-2-dimethylarsinohexafluoropropane, b.p. 110° (739 mm).



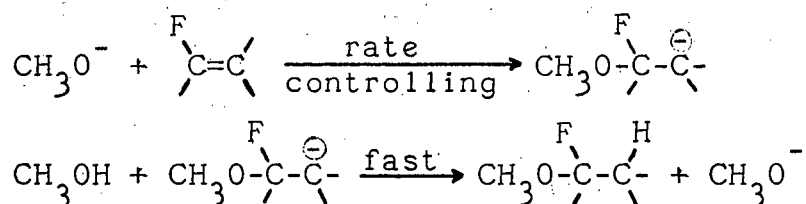
The infrared spectrum of this reaction product shows no indication of a double bond. Even upon heating to 180° this 1:1 adduct was stable. The structure of the arsine is verified by its reaction

with excess bromine to afford 2-H-1-bromohexafluoropropane and methyl bromide.

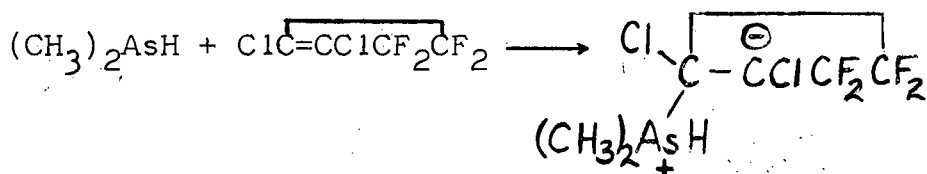


(2) Proposed Mechanisms

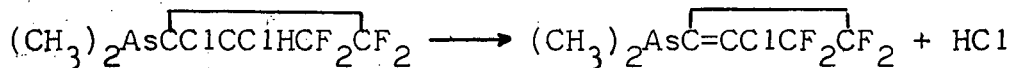
Miller and coworkers¹⁰¹ postulated the following mechanism for methoxy addition to fluoroethylenes.



A similar mechanism is favoured as the rate determining step for reaction of arsines with fluorocycloolefins, e.g.



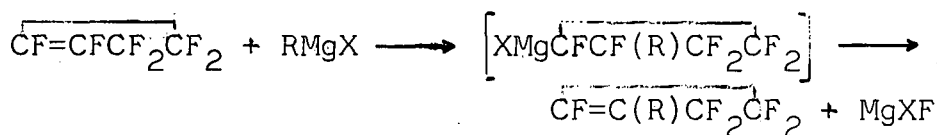
This could be followed by intramolecular As-H cleavage to form the addition product, $(\text{CH}_3)_2\text{AsCClCClHCF}_2\text{CF}_2$, followed by rapid elimination of hydrogen chloride.



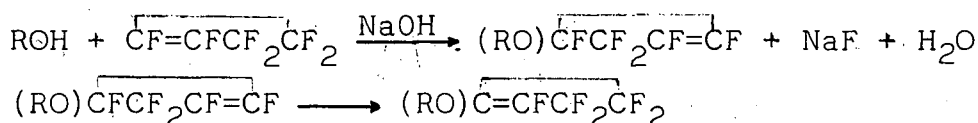
Thus, the faster reaction of dimethylarsine with perfluorocyclobutene compared with 1,2-dichlorotetrafluorocyclobutene can be explained by inductive effects, the fluorine having greater electron withdrawing power than the chlorine and leaving the vinyllic carbon more susceptible to nucleophilic attack. Also the relatively slow reaction of methylphenylarsine with perfluorocyclobutene can be explained by the decrease in availability of the arsenic lone pair due to the inductive and possible resonance effects of the phenyl group, thus making methylphenylarsine a weaker nucleophile than dimethylarsine.

This proposed mechanism involving addition followed by el-

imination is analogous to the mechanism postulated for the reaction of perfluorocyclobutene with amines⁹⁴, Grignard reagents⁸⁴, alcohols⁸⁷ and thiols⁹², e.g.



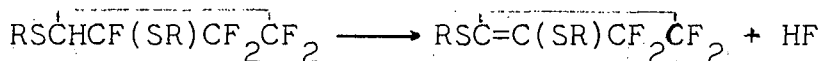
However, although Park and Fontanelli⁸⁴ favour addition followed by elimination for the reaction of Grignard reagents with perfluorocyclobutene, Park and coworkers^{86,89} have postulated a substitution mechanism for the base catalyzed reaction of alcohols with perfluorocyclobutene either by direct substitution ($\text{S}_{\text{N}}2$) at the vinylic position or substitution at an allylic position followed by rearrangement.



Possibly the best corroborating evidence is the addition of a second mole of thiol to the 1-mercaptopentafluorocyclobutene to give a 1,2-dimercaptocyclobutane⁹².



This addition product decomposed on distillation to give hydrogen fluoride and the butene derivative.



The existence of any appreciable concentration of addition product from the cyclobutene-arsine reactions does not occur as testified by the absence of any measurable CHF or CHCl proton in the ^1H n.m.r. spectra of the respective cyclobutene-arsine mixtures.

The reaction of alcohols¹⁰¹, amines¹⁰² and thiols⁹² with non-cyclic fluorinated ethylenes gives the 1:1 addition products, e.g.



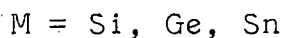
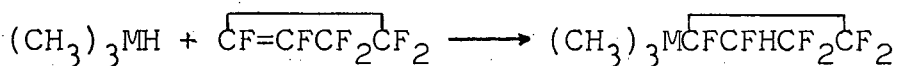
In this investigation the addition of dimethylarsine to hexafluor-

propene also only gives the 1:1 adduct and even after heating at 180° for twenty-one hours there is no sign of hydrogen fluoride or the propene derivative. This is corroborated by thermochemical data concerning the chlorination of fluoroölefins¹⁵. The enthalpy of chlorination of perfluorocyclobutene is 20 kcal/mole more than for perfluoroethylene and 10 kcal/mole more than for perfluoropropene.

B. Group IV Hydrides

(1) Results

The reaction of trimethyl-silane, -germane, and -tin hydride with perfluorocyclobutene can be represented by the following equation.



Thus perfluorocyclobutene and trimethylgermane give the addition product, 1-H-hexafluorocyclobutyl-2-trimethylgermane, b.p. 118° (752 mm), in quantitative yield after three days at 230°.



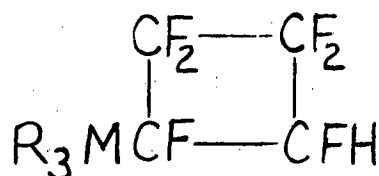
The infrared spectrum of this addition product shows no absorption in the double bond region and shows strong CF absorptions at 1398, 1334, 1241 and 1185 cm⁻¹. The structure is best shown by the ¹H n.m.r. spectrum which shows two absorptions, a single methyl peak at -0.25 p.p.m. and the methine multiplet at -5.01 p.p.m. with J_{HF_β} = 55 cps and J_{HF_α} = 22 cps, of relative intensity 1:9.3. The single methyl absorption and the methine multiplet indicate that there is only one isomer present. The configuration and conformation of this isomer and its ¹H n.m.r. spectrum are discussed in detail on page 71.

Table IV gives a list of the hexafluorocyclobutyl derivatives

prepared in this investigation with the reaction conditions under which they were formed and their respective yields. Their boiling points, pertinent ^1H n.m.r. data and the infrared absorption bands in the CF stretching region are also given. The similarity of their spectra is readily apparent.

The addition product from the trimethylsilane-perfluorocyclobutene reaction could not be analyzed, being very sensitive to air. However molecular weight measurements indicated purity of the addition product and the infrared and ^1H n.m.r. spectra confirm its structure (see Table IV).

TABLE IV
DATA CONCERNING HEXAFLUOROBUTYL DERIVATIVES



(1) Reaction Conditions of Formation, b.p., and some ^1H n.m.r. data

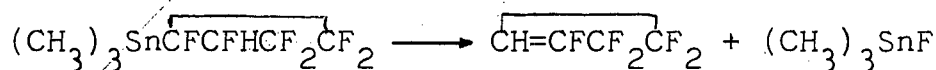
Compound	Rx.	Rx.				J_{HF}	J_{HF}	(ppm.)
R	M	Temp.	Time	Yield	b.p.	α	β	methine
						(cps)		
CH_3	Si	250°	4 days	~60%	112° (756 mm)	22	52	-4.93
CH_3	Ge	230°	3 days	100%	118° (752 mm)	22	55	-5.01
CH_3	Sn	20°	4 days	92%	decomposes	22.5	55	-5.10
C_2H_5	Sn	20°	60 days	3%	decomposes	-	-	-

(2) Infrared Spectra (Principal Absorptions)

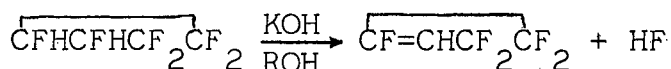
R, M	CH_3 , Si ^a	CH_3 , Ge ^b	CH_3 , Sn ^a	C_2H_5 , Sn ^{a, c}
	1398 s	1398 s	1390 s	1390 s
	1333 s	1334 s	1329 s	1330 s
	1281 m	1282 m	1273 m	1275 m
	1240 vs	1241 vs	1235 vs	1235 s
	1177 vs	1185 vs	1172 vs	1170 vs
	1037 s	1035 s	1018 s	1020 s
	1001 s	1003 s	999 s	1000 s
	956 vs	959 vs	949 vs	950 vs

^a Liquid film ^b Vapour ^c Approximate (values taken from PE 137)

The addition product from trimethyltin hydride and perfluorocyclobutene is obtained in 92% yield after four days at 20° with the remaining tin being present as trimethyltin fluoride. The structure of this 1:1 adduct is again best shown by its ¹H n.m.r. spectrum of a methyl absorption (singlet) at -0.28 p.p.m. and a multiplet at -5.10 p.p.m. Table IV shows that the infrared spectrum is very similar to its silicon and germanium analogues. The addition reaction is slow at 20° being approximately 3% complete after thirty minutes. The addition product is unstable at 20° decomposing to trimethyltin fluoride and 1-H-pentafluorocyclobutene. The decomposition



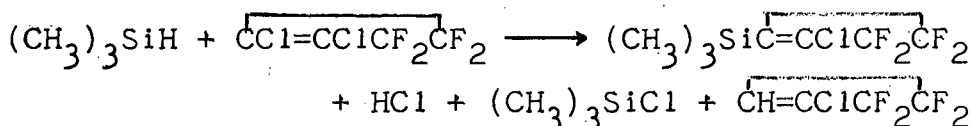
is about 46% complete after ten days. The pentafluorocyclobutene is identified by its molecular weight (vapour and mass spectrometer) and infrared spectrum which shows a double bond absorption at 5.9 μ , C-H stretch at 3.1 μ and =C-H out of plane bending at 11.7 μ . The absence of 1,2,3,4,4-pentafluorocyclobut-1-ene is consistent with the results obtained for the dehydrofluorination of 1,2,3,3,4,4-hexafluorocyclobutane^{103,104}.



The reaction of perfluorocyclobutene and triethyltin hydride after two months at 20° gives only a 3% yield of the addition product which can be identified by its infrared spectrum (see Table IV). The remaining tin is present as triethyltin fluoride. Thus, like the trimethyltin-perfluorocyclobutene adduct, the triethyltin adduct is unstable with respect to elimination of tin fluoride.

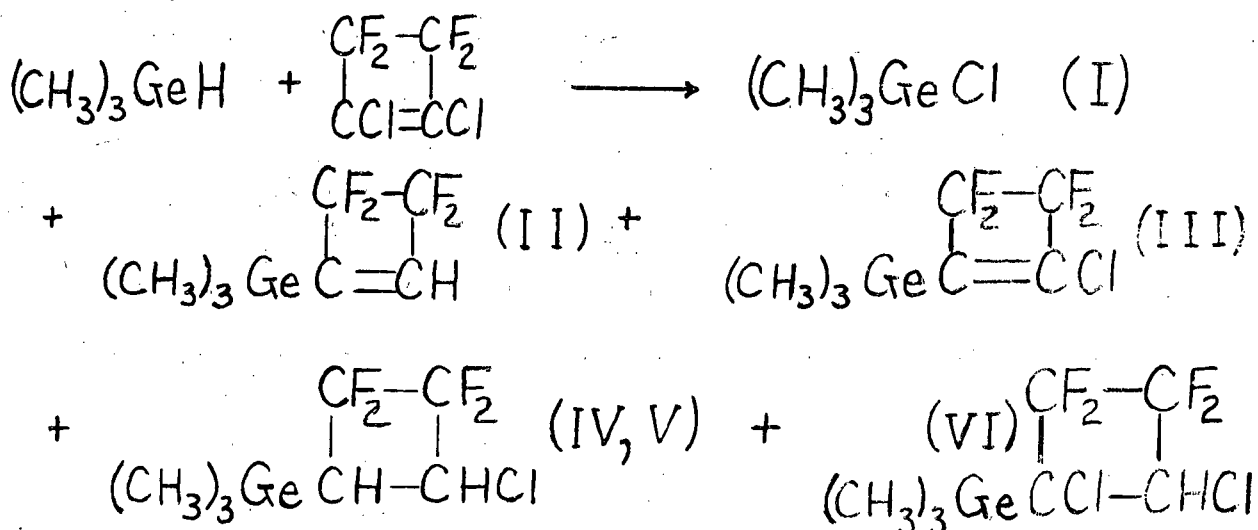
The products from the reactions of Group IV hydrides with 1,2-dichlorotetrafluorocyclobutene vary considerably with variations in the Group IV element. The slow reaction of trimethyl-

silane with 1,2-dichlorotetrafluorocyclobutene still gives a trace of unreacted trimethylsilane after twelve hours at 190°. There are two major reaction products, 1-chlorotetrafluorocyclobutenyl-2-trimethylsilane (60%), b.p. 132° (762 mm), and chlorotrimethylsilane (38%) and two minor products, hydrogen chloride and 1-H-2-chlorotetrafluorocyclobutene.



The butenyltrimethylsilane has a strong absorption in its infrared spectrum at 1576 cm^{-1} which is assigned to the double bond. The infrared spectrum of the fraction containing unreacted 1,2-dichlorotetrafluorocyclobutene shows two absorptions in the double bond region, the one at 6.3 μ being attributed to 1-H-2-chlorotetrafluorocyclobutene⁸⁰.

The reaction between trimethylgermane and 1,2-dichlorotetrafluorocyclobutene gives a relatively large number of products. The reaction is 20% complete after thirty-six hours at 190°. V.p.c. analysis of the reaction products shows the presence of six germanium compounds.



The major component (36 mole %) is 1-chlorotetrafluorocyclobutenyltrimethylgermane (III), b.p. 78° (50 mm) which is identified

by analysis, by its ^1H n.m.r. spectrum of only one sharp peak at -0.21 p.p.m. and by the strong double bond infrared absorption at 1576 cm^{-1} which occurs at the same frequency as that of analogous silane derivative. Chlorotrimethylgermane (I) (32 mole %) is the second largest component.

The least volatile component (21%) is identified as 1,2-dichloro-3,3,4,4-tetrafluorocyclobutyltrimethylgermane (VI), b.p. 86° (50 mm), by its ^1H n.m.r. spectrum of a singlet at -0.49 p.p.m. ($-\text{CH}_3$) and a septet at -4.54 p.p.m. (relative intensity 1:9.2). The ^1H n.m.r. spectrum of this molecule is discussed in detail on page 64 (see Figure 2).

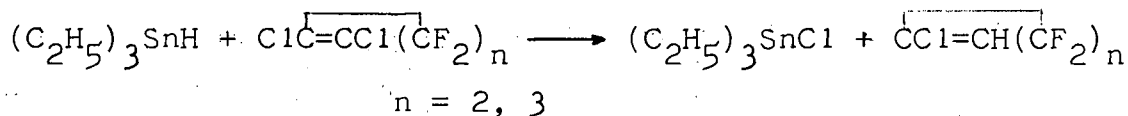
Two minor peaks (3.5 and 7%) are identified as cis and trans isomers of 1-chloro-3,3,4,4-tetrafluorocyclobutyl-2-trimethylgermane (IV, V) by their ^1H n.m.r. spectra. The ^1H n.m.r. spectrum of the trans isomer, which was analyzed, shows a methyl absorption at -0.29 p.p.m. (singlet) and unresolved multiplets at -2.57 and -4.56 p.p.m. (relative intensity 9.0:1.0:0.9) which are assigned to the methine absorptions. It is assigned the trans configuration because of the broadness of the methine multiplets, i.e. $J_{\text{HH}}^{\text{trans}} > J_{\text{HH}}^{\text{cis}}$. Again the ^1H n.m.r. spectra of these isomers are discussed in more detail on page 68. The ^1H n.m.r. spectra assigned to the cis isomer shows a methyl absorption at -0.31 ppm. and methine absorptions at -2.3 and -4.05 p.p.m. (relative intensity 9.0:0.9:1.0).

The smallest component (0.5%) is identified as 1-H-tetrafluorocyclobutenyl-2-trimethylgermane (II) by its infrared and ^1H n.m.r. spectra. Its infrared spectrum shows no double bond absorption, however, 1-H-2-dimethylarsinotetrafluorocyclobutene shows only a weak absorption at 1545 cm^{-1} ¹⁰⁰. The strong to very strong

C-F stretching absorptions in the infrared spectrum of the germane occur at 1333, 1261, 1168 and 1117 cm^{-1} and are in very good agreement with those of the arsine which occur at 1330, 1265, 1160 and 1104 cm^{-1} . The ^1H n.m.r. spectrum of the germane shows a methyl absorption at -0.33 p.p.m. and a methine absorption, a triplet, at -6.79 p.p.m. ($J = 9.5$ cps). This agrees with the ^1H n.m.r. spectrum of the arsino derivative where the methine absorption at -6.80 p.p.m. is also a triplet ($J = 10$ cps)¹⁰⁰.

When trimethylgermane and 1,2-dichlorocyclobutene are heated at 230° for three days, no trace of trimethylgermane remains. Hydrogen chloride is recovered as a reaction product. V.p.c. analysis of the reaction products shows only five germanium components with no trace of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutyltrimethylgermane (VI) and a nine-fold increase in the 1-H-tetrafluorocyclobutenyl-2-trimethylgermane (II) (5 mole %).

The reaction of triethyltin hydride with 1,2-dichlorotetrafluorocyclobutene and 1,2-dichlorohexafluorocyclopentene at 100° gives quantitative yields of triethyltin chloride.



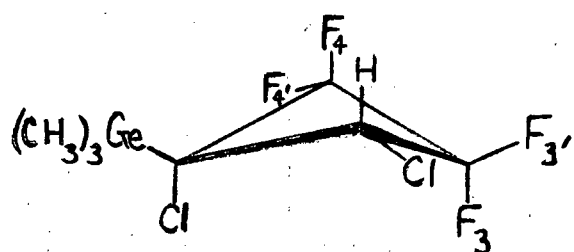
The volatile fraction from the cyclobutene reaction shows two absorptions in the double bond region of the infrared spectra which are assigned to the 1-H-cyclobutene and 1,2-dichlorocyclobutene.

(2) ^1H N.M.R. Spectra

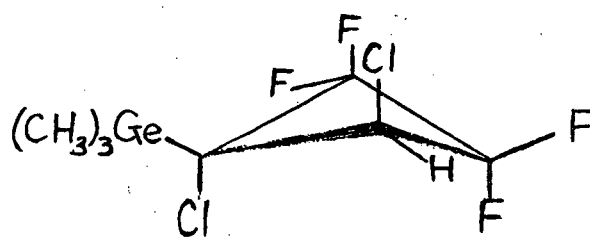
Roberts and coworkers¹⁰⁵ have studied the ^{19}F and ^1H n.m.r. spectra of 1,1-difluoro-2,2-dichloro-3-phenyl-3-methylcyclobutane, $\text{CF}_2\overline{\text{CCl}_2\text{C}(\text{C}_6\text{H}_5)(\text{CH}_3)}\text{CH}_2$, and find that the two fluorine atoms are inequivalent and that there are four very distinct vicinal H-F coupling constants. These results together with those of other

workers^{106,107} led Roberts to suggest that when a large substituent is attached to one of the carbon atoms of the cyclobutane ring then the ring is locked in a non-planar conformation. If it is assumed that a cyclobutane ring is non-planar then substituents would occupy at least partial "axial" or partial "equatorial" positions similar to those of cyclohexane. Roberts and coworkers¹⁰⁵ suggest that the degree of puckering may be considerable since the chemical shifts of the geminal fluorine atoms of 1,1-difluorocyclobutanes differ by 7-15 p.p.m. which is to be compared with a difference of 15.5 p.p.m. for 1,1-difluorocyclohexane when it undergoes slow ring inversion at -80° .

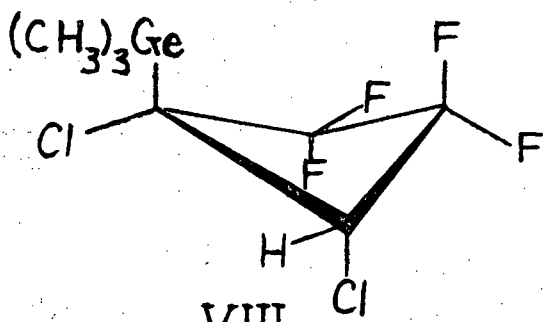
The simplest ^1H n.m.r. spectrum obtained in the present investigation is that of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutyltrimethylgermane (Figure 2). If the cyclobutane ring is puckered this compound can have one of four structures, VII, VIII, IX or X.



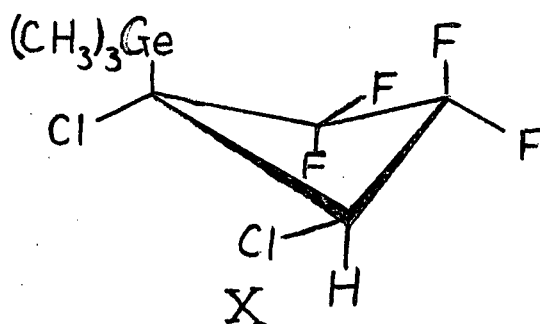
VII



IX



VIII

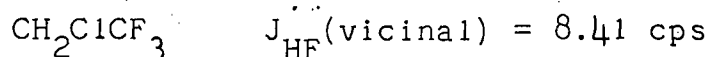
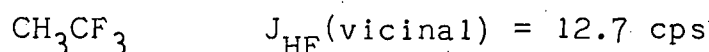
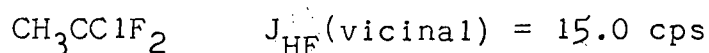
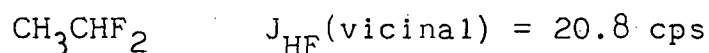


X

VII and IX are almost certain to be favoured since the bulky trimethylgermyl group would be in an "equatorial" position. It will be assumed in further discussions of the ^1H n.m.r. spectra of other cyclobutanes prepared in this investigation that the trimethyl-silyl-,germyl and -stannyl groups occupy "equatorial" positions.

To distinguish between isomers VII and IX a quantitative study of the coupling constants is necessary. Phillips¹⁰⁶ was able to assign coupling constants for 1-phenyl-3,3,4,4-tetrafluorocyclobutane on a first-order basis since there is no measurable coupling between the vicinal fluorines. Figure 2 gives an assignment of the coupling constants for 1,2-dichloro-3,3,4,4-tetrafluorocyclobutyltrimethylgermane on a first-order basis. The fact that first-order assignments correctly account for the spacings and intensities in the ^1H n.m.r. spectrum of the germane appears to indicate that second order effects are small.

The assigned vicinal "axial-axial" H-F coupling of 12 cps is justified from the assignment of 20.5 cps for the same coupling in 1,1-difluoro-2-dichloro-3-phenyl-3-methylcyclobutane¹⁰⁵ and electronegativity effects. Abraham and Cavalli¹⁰⁸ have studied extensively the dependence of vicinal H-F coupling in ethanes on the electronegativities of the remaining substituents and have found that as the electronegativities of the substituents increase the vicinal H-F coupling decreases, e.g.



In view of these results the assigned value of J_{HF_3} of 12 cps (Fig-

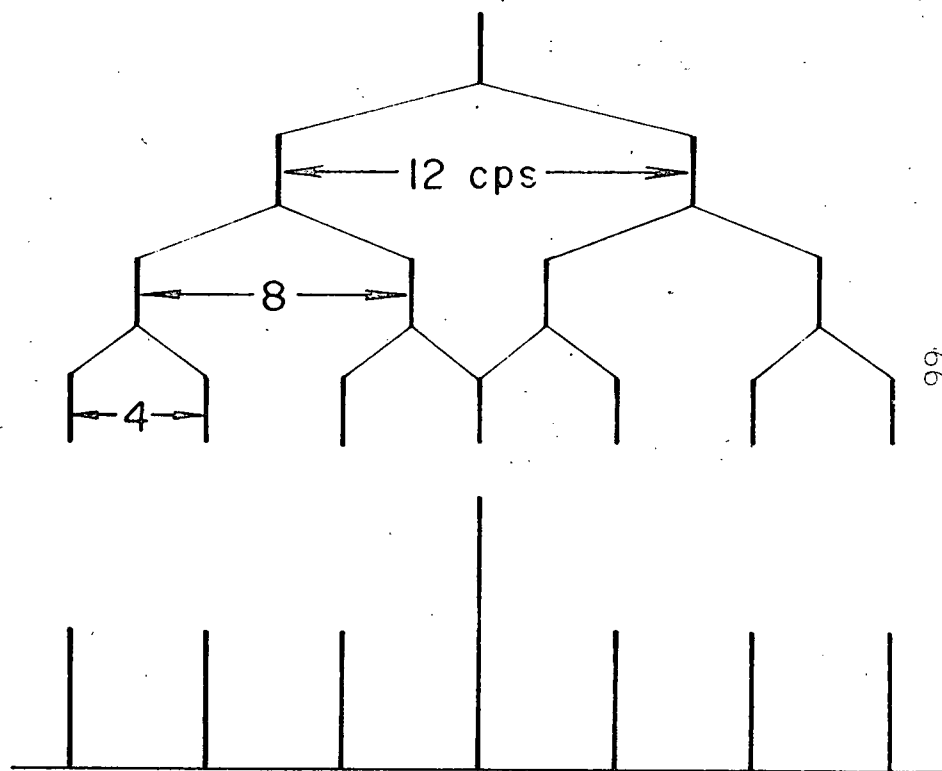
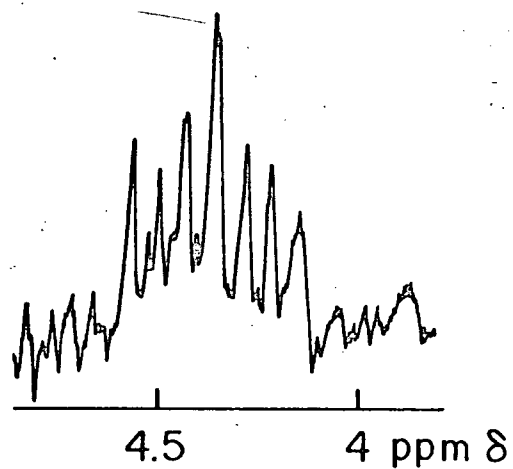
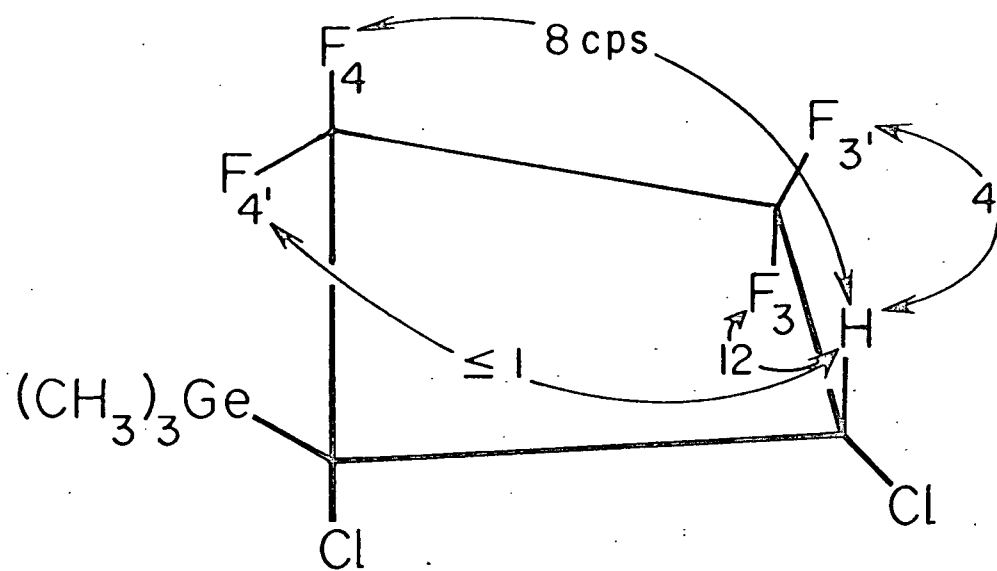


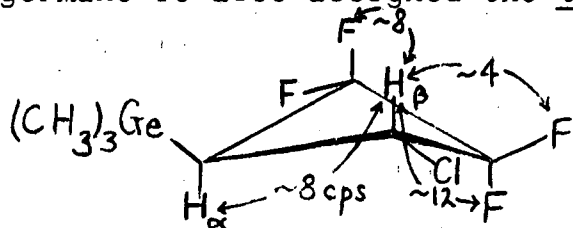
Figure 2: ¹H n.m.r. Spectrum of 1,2-Dichlorotetrafluorocyclobutyltrimethylgermane

ure 2) appears reasonable.

Hall and Mansville¹⁰⁹ find that for fluorinated sugars the vicinal "axial-axial" H-F coupling is two to three times that of vicinal "axial-equatorial" H-F coupling. Thus J_{HF_3} is assigned a value of 4 cps. The assigned value of the same coupling constant for 1,1-difluoro-2,2-dichloro-3-phenyl-3-methylcyclobutane is 9.4 cps¹⁰⁵, and in view of Abraham's and Cavalli's¹⁰⁸ results the decrease from 9.4 to 4 cps for J_{HF_3} on going from the 1,1-difluorocyclobutane to the germane does not appear unreasonable. The 8 cps coupling assigned to the "axial-axial" H-F coupling, J_{HF_4} , seems to be reasonable in view of the value of 2.1 cps for "axial-axial" CH_3 -F coupling in 1,1-difluoro-2,2-dichloro-3-phenyl-3-methylcyclobutane¹⁰⁵.

The H-F coupling constants for vicinal "equatorial H-equatorial F" and "equatorial H-axial F" conformations in 1,1-difluoro-2,2-dichloro-3-phenyl-3-methylcyclobutane are 1.8 and 13.7 cps respectively¹⁰⁵. Because of the increase of the electronegativities of the substituents these coupling constants could be expected to be of the order of 1 and 8 cps for the germanium derivative. If the germanium derivative is assigned structure IX this would mean that J_{HF_4} and $J_{HF_4'}$ must be assigned values of 12 and 4 cps which appears to be very unreasonable. Thus on the basis of the coupling constants 1,2-dichloro-3,3,4,4-tetrafluorocyclobutyltrimethylgermane is assigned the trans configuration.

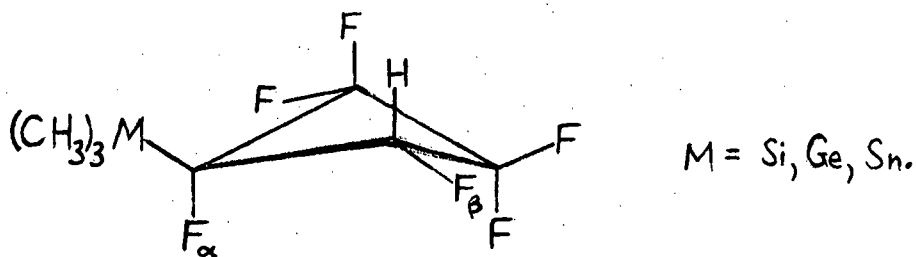
The major isomer of 1-chloro-3,3,4,4-tetrafluorocyclobutyl-2-trimethylgermane is also assigned the trans configuration.



The downfield proton at -4.56 p.p.m. is assigned to H_β since this proton is expected to be more deshielded than H_α . The resolution of the ^1H n.m.r. spectrum of the chlorocyclobutylgermane is not sufficient to measure coupling constants. However, the width of the spectrum of H_β allows for an approximate assignment of 8 cps for $J_{H_\alpha H_\beta}$ if it is assumed that the remaining coupling constants are approximately equal to the coupling constants assigned to the 1,2-dichlorocyclobutylgermane (Figure 2). This coupling, $J_{H_\alpha H_\beta} \sim 8$ cps, is the order expected for vicinal "axial-axial" proton coupling¹¹⁰.

The ^1H n.m.r. spectra of the monochlorocyclobutylgermane isomers show that there is no 1-chloro-3,3,4,4-tetrafluorocyclobutyl-1-trimethylgermane formed since the difference in chemical shift between "axial" and "equatorial" geminal protons is expected to be of the order of 0.5 p.p.m.¹⁰⁵ whereas the measured difference in the relevant spectra is approximately 2 p.p.m.

The configuration of the group IV hydride-perfluorocyclobutene adducts is given below (see also Figures 3 and 4).



The assigned coupling constants for all three 1:1 adducts are compiled in Table V. The ^1H n.m.r. spectrum of all three adducts show the presence of only one isomer. The geminal coupling constants, J_{HF_β} , are readily assigned from results obtained by other workers. Hall and Mansville¹⁰⁹ find that geminal H-F coupling in some fluorinated sugars (six-membered saturated ring systems),

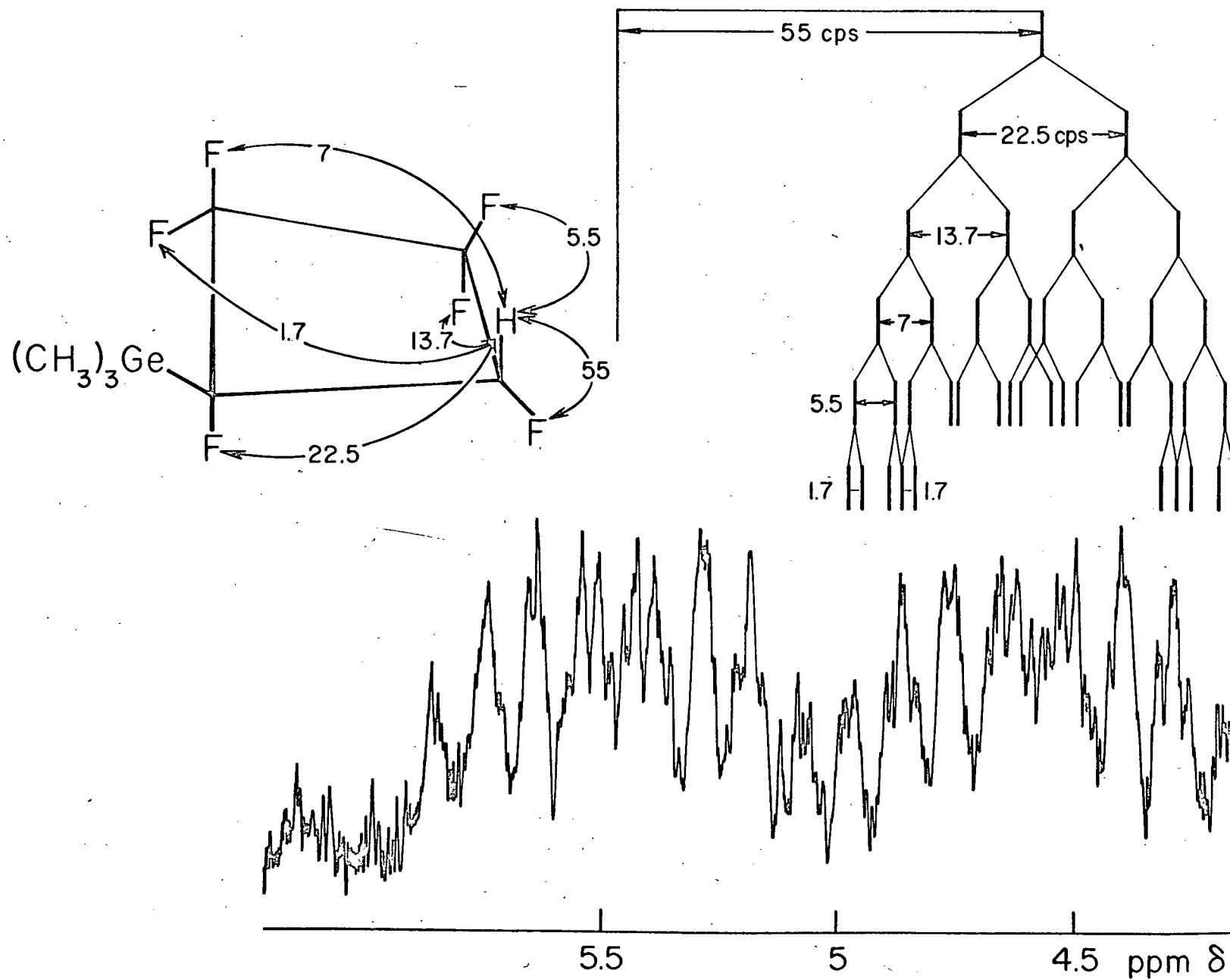


Figure 3: ¹H n.m.r. Spectrum of 1-H-Hexafluorocyclobutyl-2-trimethylgermane

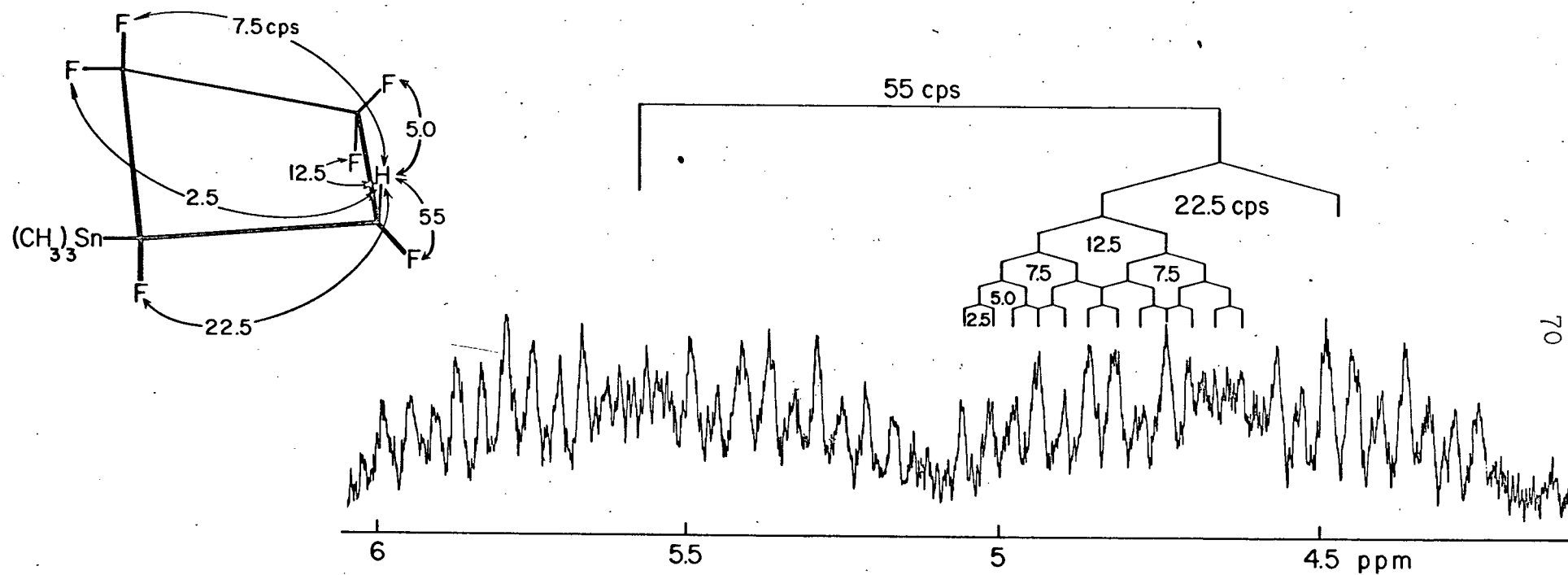
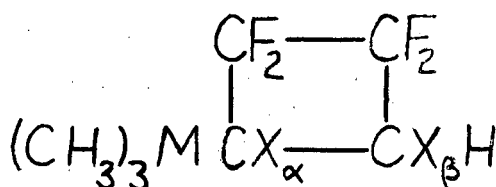


Figure 4: ^1H n.m.r. Spectrum of 1-H-Hexafluorocyclobutyl-2-trimethyltin

with remaining substituents of comparable electronegativity to that of the $-\text{CF}_2-$ and $-\text{CFM}(\text{CH}_3)_3-$ groups, varies from 51.9 to 53.4 cps. Clark and coworkers¹¹¹ assign a value of 57 cps for the geminal HF coupling in 1,1,2,2-tetrafluoroethyltrimethyltin, $(\text{CH}_3)_3\text{SnCF}_2\text{CF}_2\text{H}$. These results indicate that the J_{HF_e} assignments of 52 (silane), 55 (germane) and 55 cps (tin) are correct.

TABLE V

H-F COUPLING CONSTANTS OF THE 1:1 FLUOROCYCLOBUTENE-HYDRIDE ADDUCTS^a



Compound M	X	Vicinal ^b J_{HF_α}	Geminal ^b J_{HF_e}	Vicinal ^b		Through 4 bonds ^b	
				Ax-Ax	Ax-Eq	Ax-Ax	Ax-Eq
Si	F	22	52	~13	~6	~7	~1.5
Ge	F ^c	22	55	13.7	5.5	7.0	1.7
Sn	F ^d	22.5	55	12.5	5.0	7.5	2.5
Ge	Cl ^e	-	-	12	4.0	8.0	~1

^a From ^1H n.m.r. spectra

^b cps

^c Figure 3

^d Figure 4

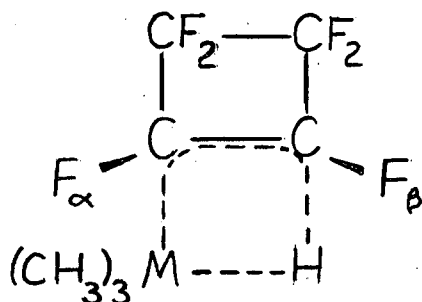
^e Figure 5

When the ^1H n.m.r. spectrum of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutyltrimethylgermane is compared with that of the perfluorocyclobutene-hydride adducts (Table V) it is readily seen that the coupling of 22-22.5 cps can be assigned to J_{HF_α} . Hall and Mansville¹⁰⁹ find that the vicinal "axial-axial" HF coupling in fluorinated sugars varies from 23.4 to 25.4 cps. The vicinal "axial-equatorial" H-F coupling is considerably less (8.0 to 11.7 cps). Thus the adducts are assigned the trans HF_α configuration and the "axial-axial" HF_α conformation. The remaining coupling constants of the perfluorocyclobutene adducts are assigned in an analogous

manner to the coupling constants that were assigned to 1,2-dichloro-3,3,4,4-tetrafluorocyclobutyltrimethylgermane (Figure 2).

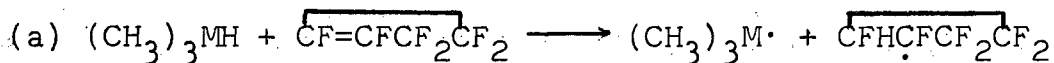
(3) Proposed Mechanisms

The ^1H n.m.r. spectra of the 1:1 perfluorocyclobutene-hydride adducts indicate that they have a trans "axial-axial" H-F configuration such as would be formed by cis addition of the trimethyl-silane, -germane and trimethyltin hydride across the double bond. It appears on this basis that a four-centre mechanism is most reasonable with a transition state as follows:

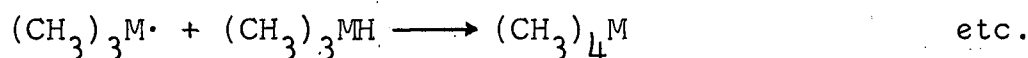
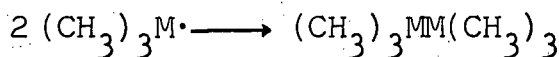
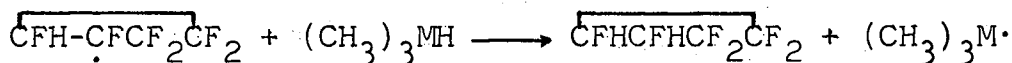


M = Si, Ge, Sn

A free radical mechanism could also account for the cis addition, viz.

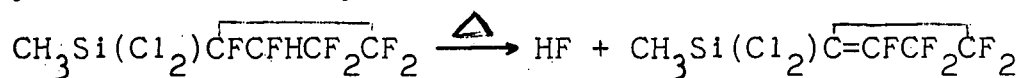


In equation (b) $(\text{CH}_3)_3\text{MH}$ would attack the pseudo "equatorial" position and the hydrogen would be in a pseudo "axial" position to give a trans "axial-axial" H-F configuration. However, the radical mechanism does not explain the quantitative yield of the germane or tin derivatives (the latter subsequently slowly decomposes after forming) since it seems that additional products would be formed by the following reactions:

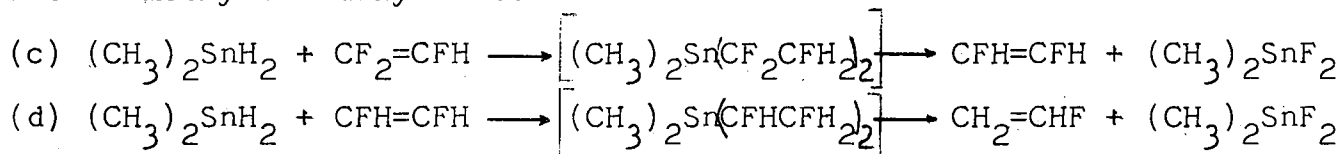


The stability of the 1:1 perfluorocyclobutene-silane and

-germane adducts at 250 and 230° respectively agrees with the results obtained by Haluska⁸ who found that heating to 350-600° was necessary to eliminate hydrogen fluoride from 1-H-hexafluorocyclobutyl-2-dichloromethylsilane.



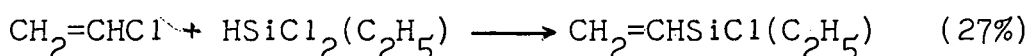
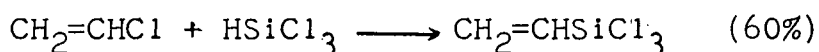
The decomposition of the 1:1 perfluorocyclobutene-tin adducts to tin fluorides is to be expected in view of the results of related studies. Clark and coworkers¹² obtained dimethyltin difluoride from the reactions of trifluoroethylene and 1,2-difluoroethylene with dimethyltin dihydride.



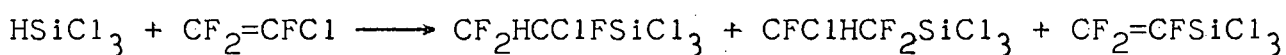
These workers obtained some evidence that the reactions proceed, as indicated, by addition followed by elimination although the addition products could not be isolated and conclusively identified. They found, however, that the addition products, $(\text{CH}_3)_2\text{Sn}(\text{H})\text{CF}_2\text{CF}_2\text{H}$ and $(\text{CH}_3)_2\text{Sn}(\text{CF}_2\text{CF}_2\text{H})_2$, from the reaction of tetrafluoroethylene and dimethyltin dihydride are stable with respect to the elimination of tin fluorides. Thermochemical data obtained by Swarts¹¹² indicate that it requires approximately 10 kcal/mole more energy to break a C-F bond in the $-\text{CF}_2-$ group than the C-F bond in the $-\text{CFH}-$ group. Thus the stability of compounds such as $(\text{CH}_3)_2\text{Sn}(\text{CF}_2\text{CF}_2\text{H})_2$ and $(\text{CH}_3)_2\text{Sn}(\text{H})\text{CF}_2\text{CF}_2\text{H}$ and the instability of $(\text{CH}_3)_2\text{Sn}(\text{CFHCFH}_2)_2$ and $(\text{CH}_3)_2\text{Sn}(\text{H})\text{CFHCFH}_2$ would be expected. However the instability of $(\text{CH}_3)_2\text{Sn}(\text{CF}_2\text{CFH}_2)_2$ to form tin fluoride and the olefin, $\text{CFH}=\text{CFH}$, is unexpected. Clark and coworkers¹² do not commit themselves as to the direction of addition (the postulated intermediate $(\text{CH}_3)_2\text{Sn}(\text{CF}_2\text{CFH}_2)_2$ is the author's choice based on dipole moments), but regardless of whether the intermediate addition product is $(\text{CH}_3)_2\text{Sn}(\text{CFHCF}_2\text{H})_2$ or $(\text{CH}_3)_2\text{Sn}(\text{CF}_2\text{CFH}_2)_2$ or

whether an addition product is actually formed the reaction product $\text{CFH}=\text{CFH}$ and not $\text{CF}_2=\text{CH}_2$ (equation c) appears to have no thermodynamic basis.

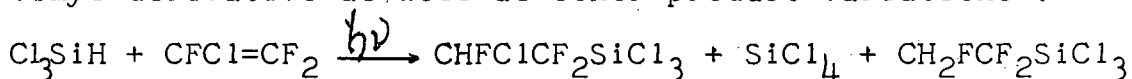
The dehydrochlorination of chloroalkylsilanes has been extensively investigated¹¹³. Bases such as quinoline^{114,115,116} catalyze this elimination. Substitution of alkyl groups for chlorine on the silane leads to a lower yield of the vinyl derivative, e.g.



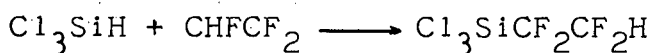
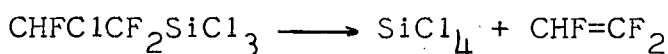
The reaction of polyfluoroolefins containing chlorine has also been investigated. The addition of trichlorosilane to trifluoro-chloroethylene resulted in saturated as well as vinyl derivatives⁸.



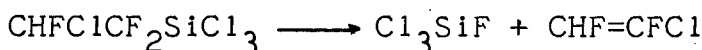
These same reactants under different conditions are reported to give no vinyl derivative as well as other product variations⁹.



Although Haszeldine and Young⁹ proposed a chain of radical reactions to account for $\text{CH}_2\text{FCF}_2\text{SiCl}_3$ and SiCl_4 their presence can also be explained by an elimination followed by an addition reaction.



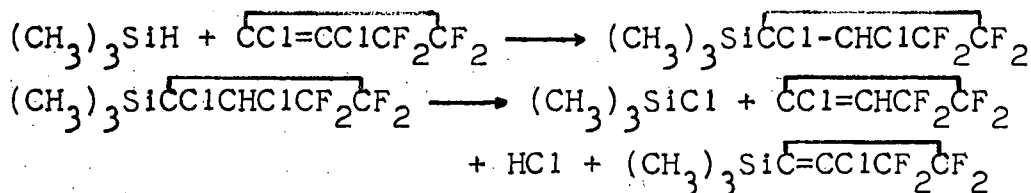
However, somewhat anomalous results are reported for 1,1,2-trifluoro-2-chloroethyl-1-trichlorosilane when it is heated to 250° ⁹. Fluorotrichlorosilane and chloro-1,2-difluoroethylene are the major products.



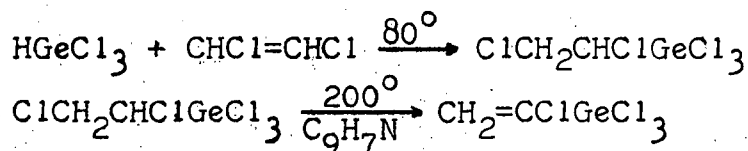
This appears to be inconsistent in view of the thermodynamic stability of the $-\text{CF}_2-$ group¹¹² and the absence of SiF eliminated prod-

ucts in the results of other workers¹¹³.

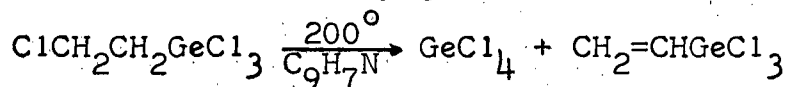
On the basis of these previous investigations the reaction of trimethylsilane with 1,2-dichlorotetrafluorocyclobutene in the present investigation is thought to be an addition followed by competing elimination reactions.



The dehydrochlorination of chloroalkylgermanes in the presence of base or aluminum trichloride has been observed¹¹⁷.

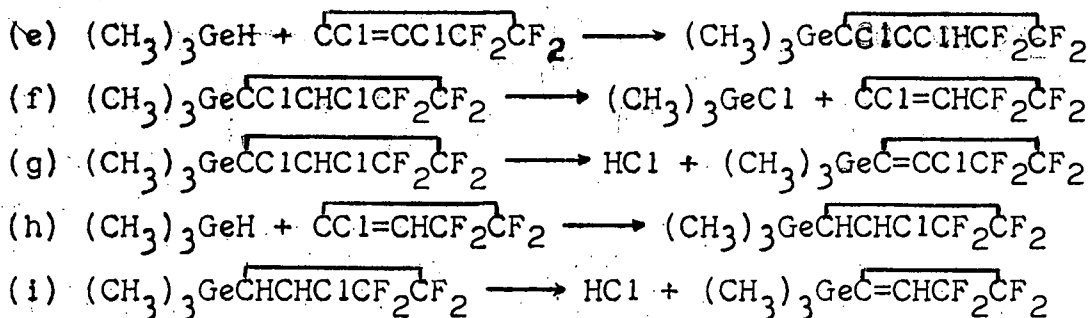


Competing elimination products similar to some results obtained from the chloroalkylsilanes reactions described above has also been observed for chloroalkylgermanes¹¹⁸.



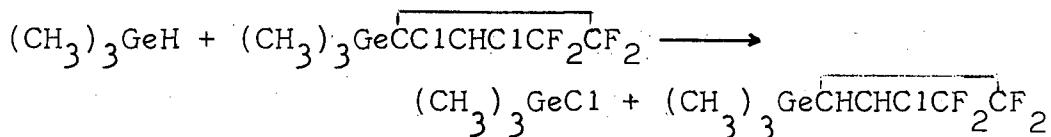
It is also to be noted that the formation of germanium tetrachloride in this reaction involves 1,2 elimination. No examples of fluoroolefins reacting with germanes have been published at present.

The product formation of the 1,2-dichlorotetrafluorocyclobutene-trimethylgermane reaction indicates the following reaction scheme:

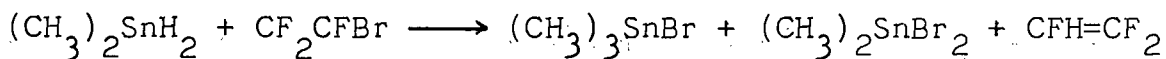


The complete absence of the original 1:1 adduct (equation (e))

from the thermal reaction at 230° and its presence in the thermal reaction at 190° appear to indicate its formation followed by decomposition according to (f) and (g). Equations (h) and (i) are merely repetitions of (e) and (g) to account for the product formation. The ^1H n.m.r. results (page 64) indicate that 1,2-dichloro-3,3,4,4-tetrafluorocyclobutyltrimethylgermane has a trans configuration which would involve a cis addition of the germane to the double bond. A four centre mechanism accounts for this cis addition and is favoured in the present investigation. The apparent presence of both cis- and trans-isomers for 1-chloro-3,3,4,4-tetrafluorocyclobutyl-2-trimethylgermane can not be explained on the basis of a four-centre mechanism. However, it is possible that a secondary reaction between trimethylgermane and 1,2-dichloro-3,3,4,4-tetrafluorocyclobutyltrimethylgermane to form the cis- and trans-chlorocyclobutylgermane derivative without the intermediate formation of 1-H-2-chlorotetrafluorocyclobutene may occur.



By analogy with the reactions described above it appears reasonable to assume that addition followed by elimination also accounts for the formation of tin chlorides from the 1,2-dichlorocyclobutene and -pentene reactions with tin hydride. There are no known examples of dehydrochlorination of chloroalkyltin compounds but the possible elimination of tin bromides from bromo-fluoroalkyltin compounds has been reported¹².



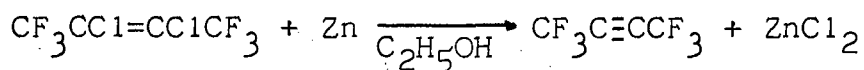
Although the addition products could not be isolated there was evidence suggesting their presence.

CHAPTER III

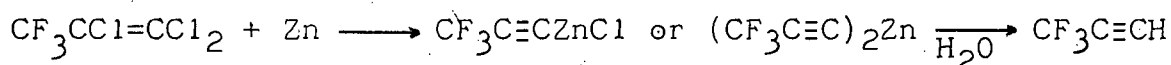
FLUOROACETYLENES

INTRODUCTION

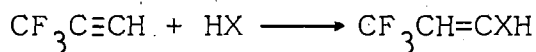
The fluoroacetylenes, 1,1,1-trifluoropropyne and hexafluorobut-2-yne were first prepared about fifteen years ago; the butyne by dechlorination of 2,3-dichlorohexafluorobut-2-ene with zinc¹¹⁹



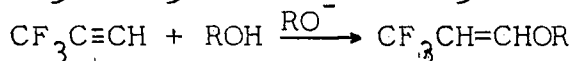
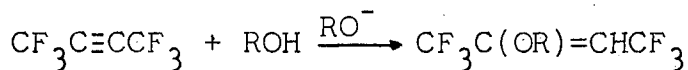
and the propyne by the dehydrohalogenation of 1,1,1-trifluoro-3-halopropene¹²⁰. The butyne is now commercially available and the propyne is more conveniently prepared from the commercially available 1,1,1-trifluorotrichloropropene as follows¹²¹.



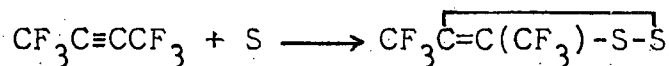
Haszeldine¹²² studied the addition of hydrogen halides to hexafluorobut-2-yne and 1,1,1-trifluoropropyne. Addition to 1,1,1-trifluoropropyne was found to be anti Markovnikov.



Investigation of the reactions of Group VI compounds with these fluoroacetylenes has been mainly restricted to alcohols. Haszeldine¹²² added methane and ethanol in the presence of the respective alkoxides to hexafluorobut-2-yne and 1,1,1-trifluoropropyne.

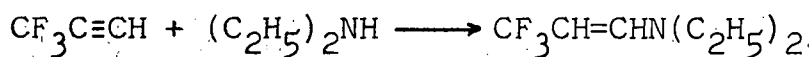
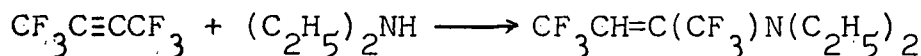


Chaney¹²³ obtained both the mono- and diadducts from the addition of ethanol and glyoxal to hexafluorobut-2-yne. There are two examples of the reaction of sulphur or sulphur compounds to the butyne. Krespan and coworkers¹²⁴ reacted hot sulphur vapour and hexafluorobut-2-yne and obtained as one of the products a disulphide group across the triple bond.

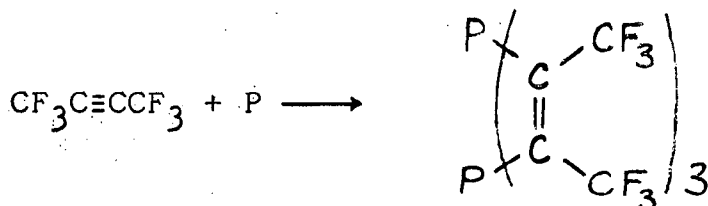


The other reported example is the x-ray catalyzed addition of hydrogen sulphide to hexafluorobut-2-yne to give the mono-adduct¹²⁵.

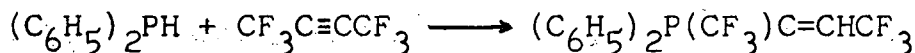
By comparison, studies of the reactions of hexafluorobut-2-yne with Group V compounds have been relatively numerous. Hazeldine¹²² reacted secondary amines with 1,1,1-trifluoropropyne and hexafluorobut-2-yne and obtained the monoadducts.



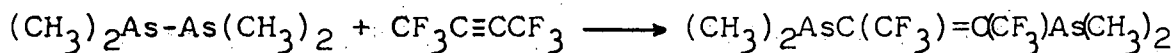
Krespan¹²⁴ reacted the butyne with red phosphorus at 200° in the presence of iodine and obtained a cyclic olefinic compound.



The monoadduct, 2,3-bis(diphenylphosphino)hexafluorobut-2-ene was obtained when tetraphenyldiphosphine and hexafluorobut-2-yne were heated to 130°¹²⁶. The butyne adds to diphenylphosphine at 20° to give the monoadduct¹²⁶.



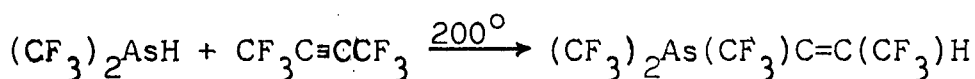
Cullen and Hota⁴¹ found that a reaction between tetramethyldiarsine and hexafluorobut-2-yne occurs rapidly and quantitatively at room temperature.



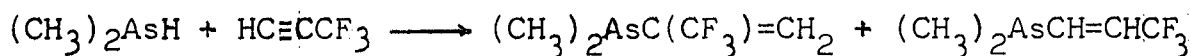
The butyne does not react with tetrakis(trifluoromethyl)diarsine even when heated to 100°.

A number of secondary arsines have been reacted with hexafluorobut-2-yne by Cullen and coworkers¹²⁶. Dimethylarsine and the butyne react immediately on mixing to give 2-dimethylarsino-1,1,1,4,4,4-hexafluorobut-2-ene, phenylmethylarsine adds slowly to

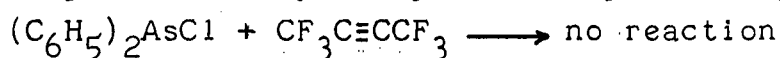
the butyne at 20°, and bis(trifluoromethyl)arsine requires heating to give the arsinobutene.



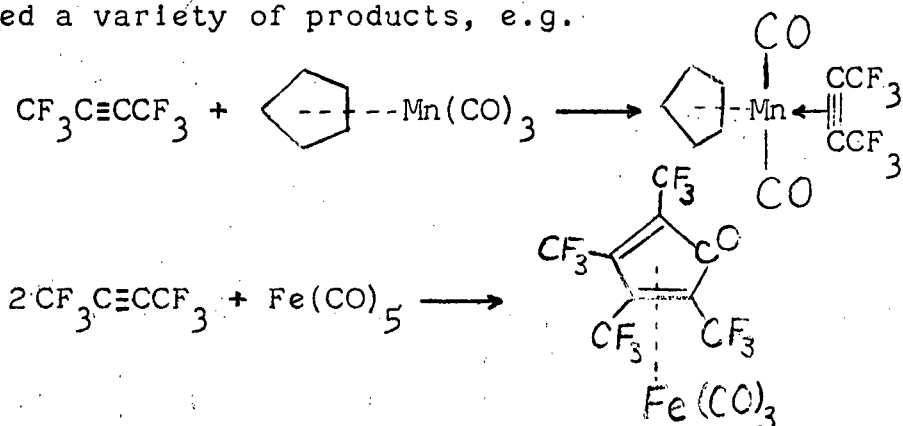
Dimethylarsine reacts readily with 1,1,1-trifluoropropyne to give an isomeric mixture of butenes¹²⁶.



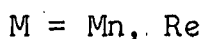
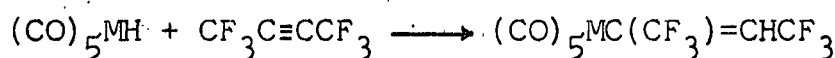
Upon ultraviolet irradiation or heating hexafluorobut-2-yne will add to chlorodimethylarsine but little or no reaction occurs with various other chloroarsines¹²⁷.



The reaction between hexafluorobut-2-yne and transition metal compounds, in particular transition metal carbonyls, has been investigated by two groups of workers. Wilkinson and coworkers^{128,129} reacted the butyne with a number of transition metal carbonyls and transition metal carbonyl cyclopentadienyl compounds and obtained a variety of products, e.g.



Stone and coworkers^{130,16} found that hexafluorobut-2-yne will add to manganese pentacarbonyl hydride and rhenium pentacarbonyl hydride to give the respective butenes.



In the following experimental and discussion sections the

reaction of hexafluorobut-2-yne and 1,1,1-trifluoropropyne with some Group IV and Group V organometallic compounds is described.

EXPERIMENTAL

The general experimental technique and apparatus has been previously described in Chapter I, page 6.

A. Group IV Hydrides(1) Starting Materials

Hexafluorobut-2-yne was purchased from Peninsular Chemresearch, and its purity was checked by its infrared spectrum. The 1,1,1-trifluoropropyne was a gift from coworker M. Woollends.

(a) Triethylgermane--Bromotriethylgermane was prepared by heating tetraethylgermane (0.1 mole excess) and bromine at 100° for one day. After removal of the volatile material the resulting bromotriethylgermane and tetraethylgermane mixture was used for the preparation of triethylgermane. This mixture was dissolved in 1M hydrobromic acid and reduced by sodium borohydride⁴⁴. The work-up necessitated repeated extractions with diethyl ether and then drying over calcium chloride for two days. Triethylgermane was purified by distillation, b.p. 120-125° (lit. value 124-125°) (12% yield) and its purity was checked by its infrared spectrum.

(b) Tin Hydrides--The preparation of trimethyltin hydride has been previously described in Chapter I, page 14. Triethyltin hydride was similarly prepared in diethyl ether and purified by trap-to-trap distillation and its purity checked by its infrared spectrum. Dibutyltin dihydride was also similarly prepared from the corresponding dichloride in diethyl ether. The solvent was distilled off and the remaining liquid was taken as dibutyltin dihydride. Tributyltin hydride was prepared by the addition of ammonium chloride to a solution of tributyltin sodium in liquid ammonia¹³¹. Tributyltin chloride was added to sodium-liquid am-

monia solution for the preparation of tributyltin sodium. Tributyltin hydride was purified by distillation, b.p. 75° (2 mm) (lit. value $65-67^{\circ}$ (0.6 mm))^a and its purity checked by its infrared spectrum.

(2) Reactions with Fluoroacetylenes

(a) Reaction of Trimethylsilane and Excess Hexafluorobut-2-yne

--Trimethylsilane (2.1 g) and hexafluorobut-2-yne (11.1 g) were irradiated with ultraviolet light for 11 days. Unreacted butyne (7.45 g) which went through a -96° trap was recovered. The main product, 1,1,1,4,4,4-hexafluorobutenyltrimethylsilane (5.1 g, 73%), b.p. $97-98^{\circ}$ (754 mm), which went through a -23° trap and condensed in a -96° trap (Found: C, 35.3; H, 4.2; F, 47.9 %. Calc. for $C_7H_{10}F_6Si$: C, 35.6; H, 4.2; F, 48.3 %). Infrared spectrum (liquid film): 2995 w, 2912 w, 1421 w, 1354 s, 1300 m, 1257 vs, 1141 vs, 948 m, 883 m, 849 s, 771 m, 693 m, 659 w, 641 m cm^{-1} . N.m.r. spectra: the 1H n.m.r. spectrum showed a broad methyl absorption at 0.10 p.p.m. and an olefinic proton absorption at -6.38 p.p.m. as a quartet of quartets ($J = 8.8$ and 2.5 cps) of relative intensity 1:9.0 (Calc. 1:9.0).

A -23° fraction (2.0 g) had 7 components according to v.p.c. analysis (5' Ucon Polar at 110°). The main component, approximately 65% by weight, was collected and identified as a hexafluorobutenebis(trimethylsilane), b.p. 79° (38 mm) (Found: C, 38.7; H, 6.5; F, 36.9 %; mol. wt. (camphor), 307. Calc. for $C_{10}H_{20}F_6Si_2$: C, 38.7; H, 6.5; F, 36.8 %; mol. wt., 310). Infrared spectrum (liquid film): 2988 m, 2920 m, 1423 m, 1367 s, 1335 m, 1285 s, 1259 s, 1239 m, 1181 w (sh), 1165 w (sh), 1146 s, 1071 s,

^a The Sn-H infrared absorptions and the boiling points of some tin hydrides are tabulated in a recent review¹³².

1028 m, 886 m, 844 s, 777 m, 762 w, 741 m, 693 m cm^{-1} . N.m.r. spectra: the ^1H n.m.r. spectrum showed a broad methyl absorption at 0.10 p.p.m. and a methine multiplet at -1.66 p.p.m. of relative intensity 1:8.8 (Calc. 1:9.0). The ^{19}F n.m.r. spectrum showed doublets at -21.8 p.p.m. ($J = 13$ cps) and -23.6 p.p.m. ($J = 12$ cps) of equal intensity.

(b) Reaction of Excess Trimethylsilane with Hexafluorobut-2-yne

--The silane (3.5 g) and the butyne (2.1 g) were irradiated for 11 days. Unreacted trimethylsilane (2.1 g) which went through a -78° trap was recovered. The monoadduct, 1,1,1,4,4,4-hexafluorobutenyltrimethylsilane (1.4 g), and the diadduct (2.0 g) were produced and identified by their infrared spectra.

A second experiment of excess trimethylsilane (7.76 g) and hexafluorobut-2-yne (4.06 g) produced the monoadduct (3.52 g) and the diadduct (2.02 g) after 7 days irradiation with ultraviolet light.

(c) Reaction of Trimethylsilane and the Monoadduct--Trimeth-

ylsilane (3.55 g) and 1,1,1,4,4,4-hexafluorobutenyltrimethylsilane (1.85 g) were irradiated for 11 days. Unreacted trimethylsilane (3.5 g) and monoadduct (1.65 g) were recovered. Some diadduct (0.25 g) was produced and identified by its infrared spectrum.

(d) Thermal Reaction of Trimethylsilane and Excess Hexafluorobut-2-yne--

Trimethylsilane (0.82 g) and the butyne (6.26 g) were heated at 235° for 7 hours. Unreacted butyne (4.06 g) which went through a -78° trap was recovered. The monoadduct (1.73 g) was produced as identified by its infrared and ^1H n.m.r. spectra. N.m.r. spectra: the ^1H n.m.r. spectrum showed methyl absorptions at 0.16 and 0.10 p.p.m. (relative intensity 1:15.6) and olefinic proton multiplets at -5.72 p.p.m. ($J = 8.3$ and ≤ 0.6 cps) and -6.32 p.p.m.

(J = 8.6 and 2.5 cps).

A -23° fraction (1.29 g) was found to contain nine components by v.p.c. analysis (10' silicone at 180°). None of these was identified.

(e) Thermal Reaction of Excess Trimethylsilane and Hexafluorobut-2-yne--

Trimethylsilane (5.70 g) and the butyne (2.77 g) were heated at 235° for 7 hours. An unidentified fraction (0.1 g) which contained C-F bands and which went through a -96° trap was produced. A -96° fraction (4.16 g) which went through a -78° trap was found to contain a mixture of tetramethylsilane and trimethylsilane (identified by infrared and ^1H n.m.r. spectra) along with a small amount of impurity. The mixture was analyzed quantitatively by ^1H n.m.r. to contain trimethylsilane (2.2 g) and tetramethylsilane (1.8 g). The butenyltrimethylsilane (cis:trans, 1:10 by ^1H n.m.r. analysis) (2.94 g) was recovered in a -78° trap and identified by its infrared and ^1H n.m.r. spectra. The diadduct, the butenebis-trimethylsilane (1.27 g), was also produced. The diadduct was heated at 235° for 7 hours and was recovered quantitatively after this period of heating.

(f) Thermal Reaction of Trimethylsilane and Trans-1,1,1,4,4,4-Hexafluorobutenyltrimethylsilane--

Trimethylsilane (3.34 g) and the butenylsilane (3.02 g) were heated at 235° for 7 hours. Unreacted trimethylsilane (3.34 g) was recovered. The recovered monoadduct (2.95 g) was in a cis-trans ratio of 1:6.1 from ^1H n.m.r. analysis.

The cis-trans ratio of the monoadduct was unchanged after 3 days of ultraviolet irradiation with or without the presence of either trimethylsilane or hexafluorobut-2-yne. After 4 days heating at 235° a cis-trans ratio of 1:6 of the monoadduct was unchanged.

Similarly after 20 hours at 235° the trans monoadduct from the ultraviolet reaction was less than 15% converted to the cis-isomer.

(g) Reaction of Triethylgermane and Hexafluorobut-2-yne--Triethylgermane (1.2 g) and the butyne (4.1 g) were irradiated for one week. Unreacted hexafluorobutyne (2.8 g) was the only volatile fraction. The involatile fraction (2.4 g) was distilled to give 1,1,1,4,4,4-hexafluorobutenyltriethylgermane, b.p. 82° (26 mm) (Found: C, 37.8; H, 4.7 %. Calc. for $C_{10}H_{16}GeF_6$: C, 37.2; H, 5.0 %). Infrared spectrum (liquid film): 2930 m, 1466 w, 1435 w, 1383 w, 1369 w, 1341 s, 1293 m, 1257 vs, 1142 vs, 1020 w (sh), 1010 m, 973 w, 880 w, 850 w, 720 w, 706 m cm^{-1} . N.m.r. spectra: the 1H n.m.r. spectrum showed a peak at -0.87 p.p.m. ($-C_2H_5$) and multiplets at -5.82 p.p.m. (quartet, $J = 8$ and ≤ 1 cps) and -6.59 p.p.m. ($J = 8.0$ and 2.5 cps). The relative intensity of the ethyl peak to the downfield peaks is 1:15.9 (Calc. 1:15.0) and the relative intensity of the two downfield multiplets is 1:11.

After heating this isomeric mixture of the butenylgermane for 45 hours at 220° there was little or no change in the isomer distribution although considerable decomposition had occurred.

(h) Reaction of Trimethyltin Hydride and Hexafluorobut-2-yne--Trimethyltin hydride (2.9 g) and the butyne (6.9 g) gave an exothermic reaction immediately on mixing. Unreacted butyne (4.1 g) which went through a -78° trap was recovered. The reaction product (5.9 g) which condensed in a -78° trap was identified as the known compound, 1,1,1,4,4,4-hexafluorobutenyltrimethyltin, b.p. 124° (751 mm), by means of its infrared and 1H n.m.r. spectra (see also (2)(a) page). N.m.r. spectra: the 1H n.m.r. spectrum showed a peak at -0.15 p.p.m. ($-CH_3$) and a multiplet at -6.57 p.p.m. ($J = 7.5$ and 2.3 cps) of relative intensity 1:8.8 (Calc.

1:9.0), and also showed that only one isomer was present.

(i) Reaction of Triethyltin Hydride and Hexafluorobut-2-yne--

Triethyltin hydride (5.7 g) and the butyne (8.25 g) gave an immediate exothermic reaction on mixing. Unreacted butyne (3.3 g) was recovered. The remaining fraction (10.3 g) was identified as 1,1,1,4,4,4-hexafluorobutenyltriethyltin, b.p. 86° (24 mm) (Found: C, 32.5; H, 4.0; Sn, 32.0; F, 30.9 %. Calc. for $C_{10}H_{16}F_6Sn$: C, 32.5; H, 4.3; Sn, 32.2; F, 30.9 %). Infrared spectrum (liquid film): 2930 m, 2900 w (sh), 2860 w (sh), 2820 w (sh), 1469 m, 1454 m, 1382 m, 1368 w (sh), 1352 w, 1326 s, 1290 m, 1253 vs, 1190 w (sh), 1137 vs, 1005 m, 961 m, 848 m, 717 w, 675 m cm^{-1} . N.m.r. spectra: the 1H n.m.r. spectrum showed peaks at -1.01 and -1.05 p.p.m. ($-C_2H_5$) and a multiplet at -6.61 p.p.m. ($J = 7.5$ and 2.4 cps). The relative intensity of the ethyl absorption to the multiplet is 1:14 (Calc. 1:15).

The cis-trans isomer ratio is 1:50 from v.p.c. analysis (5' Ucon Polar at 150°).

(j) Reaction of Tributyltin Hydride and Hexafluorobut-2-yne--

Tributyltin hydride (7.1 g) and the butyne (8.85 g) gave a vigorous exothermic reaction immediately on mixing. Unreacted butyne (5.0 g) was recovered. The involatile fraction (11.0 g) was identified as 1,1,1,4,4,4-hexafluorobutenyltrimethyltin, b.p. 72° (10^{-3} mm) (Found: C, 42.0; H, 6.3; Sn, 26.4; F, 25.7 %; mol. wt., 238. Calc. for $C_{16}H_{28}F_6Sn$: C, 42.4; H, 6.2; Sn, 26.2; F, 25.2 %; mol. wt., 253). Infrared spectrum (liquid film): 2982 s, 2917 s, 2870 m, 1470 m, 1426 w, 1382 m, 1356 w, 1330 s, 1295 m, 1255 vs, 1144 vs, 1075 m, 1048 w, 1024 w, 1001 w, 962 w, 881 m, 850 m, 717 w, 674 m cm^{-1} . N.m.r. spectra: the 1H n.m.r. spectrum showed a multiplet at -6.60 p.p.m. ($J = 7.5$ and 2.3 cps) and the ^{19}F n.m.r.

spectrum showed a peak at -10.9 p.p.m. and a broad doublet at -11.3 p.p.m. ($J \sim 7$ cps).

The cis-trans isomer ratio is 1:12 from v.p.c. analysis (5' Ucon Polar at 105°).

(k) Reaction of Dibutyltin Dihydride and Hexafluorobut-2-yne--

The dihydride (3.1 g) and hexafluorobutyne (16.8 g) reacted immediately on mixing. Unreacted butyne (13.7 g) was recovered as the only volatile fraction. The involatile fraction (6.2 g) gave a white solid on standing indicating the presence of impurity in the bis(1,1,1,4,4,4-hexafluorobutenyl)dibutyltin, b.p. 63° (10^{-3} mm). An analytical sample was obtained by v.p.c. (5' Ucon Polar at 160°) (Found: C, 34.2; H, 3.3; Sn, 20.3; F, 40.5 %. Calc. for $C_{16}H_{20}F_{14}Sn$: C, 34.4; H, 3.6; Sn, 21.2; F, 40.8 %). Infrared spectrum (liquid film): 2981 m, 2915 m, 2875 m, 1468 m, 1425 w, 1382 m, 1358 w, 1329 s, 1295 m, 1255 vs, 1139 vs, 1078 m, 1048 w, 1025 w, 998 w, 960 w, 920 w, 883 m, 718 w, 670 m cm^{-1} . N.m.r. spectra: the 1H n.m.r. spectrum shows a downfield olefinic proton at -6.64 p.p.m. ($J = 7$ and ~ 1.5 cps). The relative intensity of this multiplet to the upfield butyl peaks is 1:9.4 (Calc. 1:9.0).

(l) Reaction of Trimethyltin Hydride and Excess 1,1,1-Trifluoropropyne --

Trimethyltin hydride (5.75 g) and the propyne (4.65 g) were left at 20° for one day. Unreacted propyne (2.35 g) which went through a -96° trap was recovered. Unreacted trimethyltin hydride (1.7 g) which went through a -46° trap condensed in a -96° trap. The monoadduct, 1,1,1-trifluoropropenyltrimethyltin (3.9 g), b.p. 129° (756 mm), condensed in a -46° trap (Found: C, 27.6; H, 4.2 %. Calc. for $C_6H_{11}F_3Sn$: C, 27.8; H, 4.3 %). Infrared spectrum (liquid film): 3005 w, 2932 w, 1619 w, 1356 w, 1313 m, 1278 vs, 1215 s,

1203 m (sh), 1183 w, 1151 w (sh), 1117 vs, 985 m, 968 vw, 838 w, 771 s, 719 w, 689 w cm^{-1} . N.m.r. spectra: the ^1H n.m.r. spectrum (Figure 5) showed methyl absorption at 0.00 and -0.05 p.p.m. and two discernible downfield olefin proton patterns; the trans isomer showed absorptions at -5.82 (H_β) and -6.81 p.p.m. (H_α) with $J_{\text{HH}} = 19.2$ cps, $J_{\text{H}_\beta\text{CF}_3}$ (geminal) = 5.3 cps, and $J_{\text{H}_\alpha\text{CF}_3}$ (vicinal) = 1.9 cps; the iso isomer showed absorptions at -5.48 and -6.18 p.p.m. with $J_{\text{HH}} = 1.5$ and $J_{\text{HCF}_3} = 2.3$ and ≤ 1 cps. The relative intensity of the methyl absorptions to the downfield olefinic absorptions is 4.6:1 (Calc. 4.5:1). The isomer distribution by ^1H n.m.r. spectrum of the monoadduct did not change after distillation. Although three different columns were used, 10' Ucon Polar, 10' silicone, and 10' Apiezon J, the isomers could not be separated by v.p.c.

An involatile fraction (2.4 g), b.p. 108° (29 mm), analyzed as the diadduct, 1,1,1-trifluoro-3,3-bis(trimethyltin)propane (Found: C, 25.4; H, 4.6 %. Calc. for $\text{C}_9\text{H}_{21}\text{F}_3\text{Sn}_2$: C, 25.5; H, 5.0%). Infrared spectrum (liquid film): 3000 m, 2930 m, 1447 m, 1385 w, 1362 m, 1311 m, 1279 w, 1259 s, 1213 s, 1193 w (sh), 1133 s, 1110 m, 1078 s, 1050 w, 1022 m, 893 m, 828 m, 812 w, 761 s, 714 m, 677 w cm^{-1} . N.m.r. spectra: the ^1H n.m.r. spectrum showed a peak at -0.20 p.p.m. ($-\text{CH}_3$) and a multiplet at -2.58 p.p.m. ($-\text{CH}_2$) ($J = 8.0$ and 10.5 cps). The relative intensity of the methylene absorption to the methyl absorption was 1:10 (Calc. 1:9).

(m) Reaction of Excess Trimethyltin Hydride and 1,1,1-Tri-fluoropropyne--

Trimethyltin hydride (2.0 g) and trifluoropropyne (1.05 g) were left at 20° for 4 days. Unreacted acetylene (0.5 g) and unreacted trimethyltin hydride (0.4 g) were recovered. The monoadduct (1.1 g) and the diadduct (1.0 g) were produced and identified by

their infrared spectra.

(n) Reaction of Trimethyltin Hydride and 1,1,1-Trifluoropropenyltrimethyltin--

The hydride (2.2 g) and the monoadduct (1.6 g) were left at 20° for 2 days. The monoadduct (1.6 g), 8% cis isomer by ¹H n.m.r. analysis, and trimethyltin hydride (2.0 g) were recovered. An involatile fraction (0.2 g) showed only weak C-F absorptions in the infrared spectrum.

(o) Reaction of Dimethylamine and 1,1,1-Trifluoropropyne--

Dimethylamine (1.2 g) and the propyne (6.0 g) gave a vigorous exothermic reaction immediately on mixing. Unreacted propyne (4.1 g) which went through a -96° trap was recovered. A -96° fraction (2.1 g) which could not be further separated was identified as the 1:1 adduct, b.p. 118° (759 mm) (Found: C, 43.0; H, 5.7; F, 41.0; N, 10.3 %. Calc. for C₅H₈F₃N: C, 43.2; H, 5.8; F, 41.0; N, 10.1 %). Infrared spectrum (liquid film): 2915 m, 2820 w, 1736 w, 1660 vs, 1488 w, 1447 m, 1362 s, 1307 s, 1258 s, 1229 s, 1154 vw (sh), 1102 w, 1076 vs, 960 s, 888 s, 845 m, 739 m, 678 s cm⁻¹. N.m.r. spectra: the ¹H n.m.r. spectrum showed a peak at -2.29 p.p.m. (-CH₃) and multiplets of equal intensity at -3.66 and -6.17 p.p.m. (J_{HH} = 13.0 cps and J_{HCF₃} = 6.5 and 1.5 cps). The relative intensity of the olefinic multiplets to the methyl absorption is 1:3 (Calc. 1:3).

An involatile fraction (0.9 g) which remained in the Carius tube had the same general infrared spectrum as the decomposition product from the distillation of the 1:1 adduct--the recovery of the 1:1 adduct was approximately 25% upon distillation.

B. Metal-Metal Bonds

(1) Starting Materials

(a) Hexaethyldigermane--Bromotriethylgermane and sodium were

heated at 290° in a Carius tube for one day¹³³. Distillation of the involatile liquid gave a 35% yield of hexaethyldigermane, b.p. 80° (0.5 mm) (lit. value $69-72^{\circ}$ (0.1 mm))¹³⁴.

(b) Hexamethylditin--Tetramethyltin was prepared by adding stannic chloride to an excess of methylmagnesium iodide in di-n-butyl ether, stannic bromide was prepared by dropping a carbon tetrachloride-bromine solution onto finely divided tin¹³⁵, and trimethyltin bromide was prepared by the addition of tetramethyltin (3 moles) to stannic bromide (1 mole)¹³⁶. The trimethyltin bromide was added to a sodium-liquid ammonia solution and the resulting hexamethylditin was purified by distillation, b.p. 122° (132 mm) (lit. value 182° (756 mm))¹³⁷ and its purity checked by its infrared spectrum.

Hexabutyliditin was purchased from Columbia Organic Chemicals and its purity checked by microanalysis (Found: C, 49.5; H, 9.1; Sn, 40.0 %. Calc. for $C_{24}H_{54}Sn_2$: C, 49.7; H, 9.3; Sn, 40.9 %).

The tetrakis(trifluoromethyl)diarsine was a gift from W. R. Cullen.

(2) Reactions with Hexafluorobut-2-yne

(a) Hexamethylditin--The ditin (5.2 g) and the butyne (8.0 g) were immiscible at 20° . Heating at 100° for 2 days resulted in considerable reaction with unreacted butyne (6.5 g) being recovered. The remaining liquid showed only weak C-F absorptions in the infrared spectrum. The remaining solid in the Carius tube was extracted with ether and recrystallized from acetic acid. The solid was identified as trimethyltin fluoride (0.5 g) by its infrared spectrum and X-ray powder photograph.

When the ditin compound (6.2 g) and the acetylene (6.1 g) were irradiated with ultraviolet light for 2 days one liquid phase was

produced. Unreacted hexafluorobut-2-yne (3.0 g) was recovered. The involatile colourless liquid residue (9.3 g) distilled at 10^{-3} mm with some decomposition. A fraction boiling at $29-30^{\circ}$ (10^{-3} mm) was identified as hexamethylditin. A fraction boiling at 53° (10^{-3} mm) was identified as the expected 1:1 adduct, hexafluoro-2,3-bis(trimethylstannyl)but-2-ene (Found: C, 24.7; H, 3.8; F, 23.0; Sn, 48.4 %. Calc. for $C_{10}H_{18}F_6Sn_2$: C, 24.5; H, 3.7; F, 23.3; Sn, 48.5 %). Infrared spectrum (liquid film): 2960 m, 2885 m, 1685 m, 1308 w, 1261 m, 1235 vs, 1185 m, 1130 vs, 1015 m, 847 w, 767 s, 692 w, 642 m cm^{-1} . N.m.r. spectra: the 1H n.m.r. spectrum of a 25% solution in acetone showed a broad absorption at -0.34 p.p.m. ($J \sim 0.8$ cps). The ^{19}F n.m.r. spectrum showed only one broad peak at -21.8 p.p.m.

Qualitative base hydrolysis of the 1:1 adduct (70° for 4 days) gave only a trace of a mixture of cis- and trans-1,1,1,4,4,4-hexafluorobutene of known infrared spectrum. A sample of the 1:1 adduct was heated at 150° for 18 hours. The decomposition products were worked up by trap-to-trap distillation. A -78° fraction (0.35 g) which went through a -46° trap contained mostly tetramethyltin as identified by its molecular weight of 181 (Calc: 179) and its v.p.c. retention time (Apiezon J at 100° : $(CH_3)_4Sn$, 17 min. 50 sec.; sample, 17 min. 55 sec.). V.p.c. analysis of a -46° fraction (1.25 g) (Apiezon J at 120°) showed 5 components. The first component was an unidentified fluorocarbon, and the third component, the main decomposition product (~ 1.0 g), was identified as 1,1,1,4,4,4-hexafluorobutenyltrimethyltin (Found: C, 25.8; H, 3.0; Sn, 36.0; F, 35.1 %. Calc. for $C_7H_{10}F_6Sn$: C, 25.7; H, 3.1; Sn, 36.3; F, 34.9 %). Infrared spectrum (liquid film): 2990 w, 2900 w, 1731 vw, 1417 w, 1392 vw, 1351 vw, 1328 s,

1291 m, 1255 vs, 1227 vw (sh), 1210 vw (sh), 1200 vw (sh), 1140 vs, 919 vw, 879 m, 849 m, 782 s, 728 w, 634 s cm^{-1} .

(b) Hexabutylditin--The ditin (11.5 g) and the butyne (15.0 g) were irradiated with ultraviolet light for 5 days. The volatile fraction (13.4 g) contained a number of fluorocarbons and was not further separated. The involatile fraction (12.4 g) was distilled at 10^{-3} mm and gave a small amount of material which came over at $61-63^{\circ}$ and was identified as bis(1,1,1,4,4,4-hexafluorobutenyl)di-n-butylditin (Found: C, 34.0; H, 3.4; F, 41.4 %. Calc. for $\text{C}_{16}\text{H}_{20}\text{F}_{12}\text{Sn}$: C, 34.4; H, 3.6; F, 40.8 %). A large portion of the remaining involatiles distilled at $70-100^{\circ}$ (10^{-3} mm). The infrared spectra of various cuts showed a steady increase in C-H intensity and a decrease in C-F intensity with decreasing volatility. The infrared spectra were somewhat similar to the tin hydride-hexafluorobut-2-yne adducts.

In a second experiment after irradiation for 28 hours distillation of the involatiles at 10^{-3} mm resulted in the formation of tributyltin fluoride in the still pot. The fluoride was identified by comparison of its melting point with that of an authentic sample prepared from tributyltin chloride and an aqueous solution of potassium fluoride. A fraction which boiled at $63-65^{\circ}$ (10^{-3} mm) was analyzed by v.p.c. (Ucon Polar at 140°) and found to contain 9 components. The main component, the last peak (50% by weight), had a downfield quartet ($J \sim 8$ cps) at -5.88 p.p.m. in its ^1H n.m.r. spectrum. The infrared spectrum of this component was almost identical with that of the reaction product obtained from dibutyltin dihydride and hexafluorobut-2-yne with a slight difference in the CF region and the appearance of two weak bands at 5.77 and 6.10μ . The ^1H n.m.r. spectrum of the first 4 components also showed the presence of downfield protons as quartets ($J \sim 8$ cps).

(c) Tetrakis(trifluoromethyl)diarsine--The diarsine (1.4 g) and hexafluorobut-2-yne (1.7 g) were irradiated for 4 days and the 1:1 adduct, 2,3-bis(bistrifluoromethylarsino)hexafluorobut-2-ene (0.6 g) was obtained (Found: C, 16.4; F, 58.0; As, 25.7 %. Calc. for $C_8As_2F_{18}$: C, 16.3; F, 58.2; As, 25.5 %). Infrared spectrum (liquid film): 1329 w, 1314 w, 1253 vs, 1191 s, 1173 vs, 1154 vs, 1132 s, 1120 vs, 1070 vs, 870 w, 808 w, 731 s, 711 w, 657 m cm^{-1} .

On measuring the vapour pressure of the compound as a function of temperature the following data were obtained for the arsinobutene:

$T^{\circ}K$	p cm	log p	$\frac{1}{T} \times 10^3 \text{ } ^{\circ}K^{-1}$
297	0.30	-0.52	3.37
311	0.758	-0.12	3.21
325	1.529	+0.18	3.08
339	2.789	+0.44	2.95
353	5.280	+0.72	2.83
360	6.922	+0.84	2.78

A linear plot of log p against $\frac{1}{T}$ was obtained for this narrow range. This was used to give

$$\text{b.p.} = 156^{\circ} \pm 2^{\circ}$$

$$\Delta H_v = 10.3 \pm 0.5 \text{ kcal/mole}$$

$$\text{Trouton's const.} = 24 \pm 1.5 \text{ e.u.}$$

Some decomposition was taking place on the mercury surface at higher temperatures, thus only a narrow range of pressures were recorded.

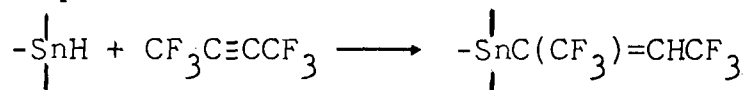
Qualitative base hydrolysis of the adduct at 100° gave only trans-1,1,1,4,4,4-hexafluorobut-2-ene.

(d) Hexaethyldigermene--The digermene (2.4 g) and hexafluorobut-2-yne (7.6 g) were irradiated for 2 days. Unreacted butyne (7.6 g) was recovered. The remaining liquid showed no C-F absorptions in the infrared.

DISCUSSION

A. Group IV Hydrides(1) Results

The reaction of hexafluorobut-2-yne with tin hydrides to give the hexafluorobutenyltin compounds can be represented by the general equation

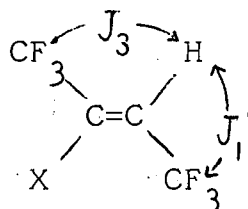
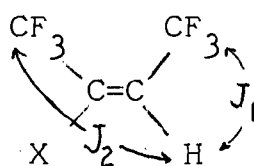


The addition occurs spontaneously and quantitatively below room temperature. Thus hexafluorobut-2-yne adds to trimethyltin hydride to give 1,1,1,4,4,4-hexafluorobutenyltrimethyltin, b.p. 124° (751 mm). The product is best identified by its ^1H n.m.r. spectrum of two sets of peaks, the methyl absorption, a singlet at -0.15 p.p.m., and an olefinic proton at -6.57 p.p.m. (relative intensity 1:8.8). Its ^1H n.m.r. spectrum also shows that only the trans-isomer is present. The quartet of quartets at -6.57 p.p.m., with coupling constants 2.3 and 7.5 cps arises because of the trans configuration; 7.5 cps is the geminal CF_3 -H coupling and 2.3 cps is the vicinal cis CF_3 -H coupling. These assignments follow from the results of previous investigations. Wilford and Stone¹⁶ for $(\text{CO})_5\text{ReC}(\text{CF}_3)=\text{CHCF}_3$ assign coupling of 9.1 cps for geminal CF_3 -H and 2.5 cps for vicinal cis CF_3 -H. Cullen¹²⁶ found that for dimethylarsino-1,1,1,4,4,4-hexafluorobutene the geminal CF_3 -H coupling for both cis- and trans-isomers is 8.3 cps and that the vicinal CF_3 -H coupling for the trans- and cis-isomers is 2 and ≤ 1 cps respectively. In all cases of butyne addition to Group IV hydrides to give the hexafluorobutenyl derivatives the trans-isomer predominates. Table VI lists the products obtained in this investigation and gives the pertinent ^1H n.m.r. data, the isomer distribution and the boiling points of these hexafluorobutenyl compounds.

The isomer distribution was analyzed either by v.p.c. or by ^1H n.m.r. spectroscopy. In the latter case the trans-isomer is distinguished from the cis-isomer by the relatively large vicinal $\text{CF}_3\text{-H}$ coupling.

TABLE VI

DATA CONCERNING HEXAFLUOROBUTENYL DERIVATIVES



X	δ^a	J_1 (cps)	J_2	δ'	J_1' (cps)	J_3	Trans	b.p.
$(\text{CH}_3)_3\text{Si}$	-5.72	8	≤ 0.6	-6.38	8.8	2.5	100% ^b	98° (754 mm)
$(\text{C}_2\text{H}_5)_3\text{Ge}$	-5.82	8.0	≤ 1	-6.59	8.0	2.5	92% ^b	82° (26 mm)
$(\text{C}_2\text{H}_5)_3\text{Sn}$	-	-	-	-6.61	7.5	2.5	98% ^c	86° (24 mm)
$(n\text{-C}_4\text{H}_9)_3\text{Sn}$	-	-	-	-6.60	7.5	2.3	92% ^c	72° (10^{-3} mm)
$(n\text{-C}_4\text{H}_9)_2\text{Sn}^d$	-	-	-	-6.64	7	1.5	-	63° (10^{-3} mm)
$(\text{CH}_3)_3\text{Sn}$	-	-	-	-6.57	7.5	2.3	100% ^b	124° (751 mm)
$(\text{CH}_3)_2\text{As}^{126}$	-5.48	8.3	≤ 1	-6.50	8.3	2.0	86% ^b	

^a Chemical shift of olefin proton.

^b ^1H n.m.r. determination

^c V.p.c. determination

^d $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{C}(\text{CF}_3)=\text{CHCF}_3)_2$

Some characteristic absorptions for the hexafluorobutenyl derivatives which are attributed to C-F stretching modes and an olefinic C-H deformation mode are given in Table VII. The similarity of the spectra is readily apparent. Bellamy¹³⁸ gives a range of $790\text{-}840\text{ cm}^{-1}$ for the strong CH out-of-plane deformation band in the infrared spectrum. However in the spectra of the hexafluorobutenyl derivatives there are only very weak absorptions in this region ($790\text{-}840\text{ cm}^{-1}$); consequently, the medium absorption

at $849\text{--}850\text{ cm}^{-1}$ is assigned to the CH out-of-plane deformation vibration. Strong absorptions in the $1000\text{--}1400\text{ cm}^{-1}$ region are characteristic of fluorocarbon derivatives and can be assigned to C-F stretching vibrations¹³. An interesting observation is that these trans hexafluorobutenyl derivatives do not give a double bond absorption in the infrared spectra. This appears to indicate that the dipole moment of the C-H bond is the same as that of the M-C (M = Si, Ge, Sn) bond and that the electronegativities of Si, Ge and Sn are almost identical. The electronegativities of these three elements has been calculated to be very similar in a number of investigations¹³⁹.

TABLE VII

SOME CHARACTERISTIC INFRARED ABSORPTIONS OF
THE 1,1,1,4,4,4-HEXAFLUOROBUTENYL DERIVATIVES^a

XC(CF ₃)=CHCF ₃					
X	C-F stretching				
(CH ₃) ₃ Si	1354 s	1300 m	1257 vs	1141 vs	- ^b
(C ₂ H ₅) ₃ Ge	1341 s	1293 m	1257 vs	1142 vs	850 m ^c
(CH ₃) ₃ Sn	1328 s	1291 m	1255 vs	1140 vs	849 m ^c
(C ₂ H ₅) ₃ Sn	1328 s	1292 m	1255 vs	1139 vs	850 m ^c
(C ₄ H ₉) ₃ Sn	1330 s	1295 m	1255 vs	1143 vs	850 m ^c
(C ₄ H ₉) ₂ Sn ^d	1329 s	1295 m	1255 vs	1139 vs	850 m ^c

^a Liquid film.

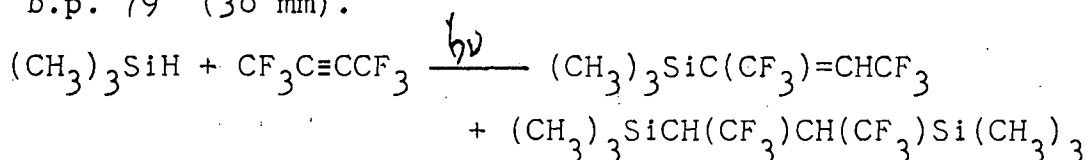
^b Hidden by (CH₃)₃Si rocking absorption at 849 cm^{-1} .

^c C-H (-C=CH) out of plane deformation.

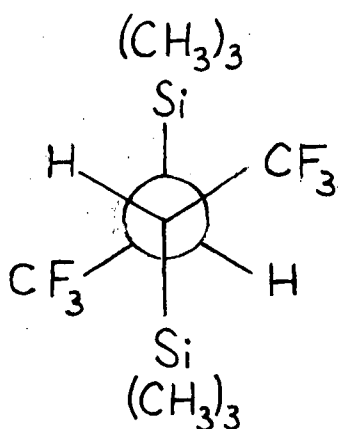
^d (C₄H₉)₂Sn(C(CF₃)=CHCF₃)₂

A reaction between triethylgermane and hexafluorobut-2-yne does not occur in the dark at 20° but gives the 1:1 adduct, 1,1,1,4,4,4-hexafluorobutenyltriethylgermane, b.p. 82° (26 mm), upon ultraviolet irradiation. The product is identified by its infrared

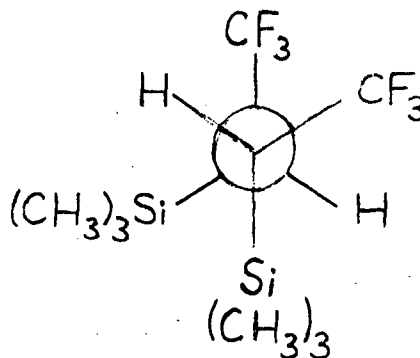
spectrum (Table VII) and its ^1H n.m.r. spectrum (Table VI). The reaction of trimethylsilane and-hexafluorobut-2-yne under the influence of ultraviolet light affords both the 1:1 adduct, 1,1,1,4,4,4-hexafluorobutenyltrimethylsilane, b.p. 98° (754 mm), and the 1:2 adduct, 1,1,1,4,4,4-hexafluorobutene-2,3-bis(trimethylsilane), b.p. 79° (38 mm).



The 1:1 adduct is identified by its infrared spectrum (Table VII) and its ^1H n.m.r. spectrum (Table VI). The 1:2 adduct is identified by its ^1H n.m.r. spectrum of a broad methyl absorption at 0.10 p.p.m. and a multiplet at -1.66 p.p.m. (relative intensity 9.0:1), and by its ^{19}F n.m.r. spectrum of broad doublets of equal intensity at -21.8 p.p.m. ($J = 13$ cps) and -23.6 p.p.m. ($J = 12$ cps). The ^{19}F n.m.r. spectrum can be explained on the basis of a 1:1 mixture of the meso- and racemic d,l isomers of the following structures.



meso

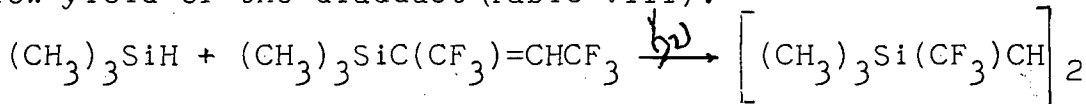


d, l

The coupling of 12 and 13 cps can be assigned to the geminal $\text{CF}_3\text{-H}$ coupling and the broadening assigned to the vicinal $\text{CF}_3\text{-CF}_3$ and $\text{CF}_3\text{-H}$ couplings. The two skew conformations shown above would

probably be the highest populated conformations of each structure because of steric considerations. If the diadduct were the unsymmetrical 2,2-bis(trimethylsilyl)butane, $((\text{CH}_3)_3\text{Si})_2\text{C}(\text{CF}_3)\text{CH}_2\text{CF}_3$, then the ^{19}F n.m.r. spectra would consist of a broad singlet and a triplet. This is not found.

The ratio of the 1:1 adduct, 1,1,1,4,4,4-hexafluorobutenyl-trimethylsilane, to the 1:2 adduct in the product can be varied by varying the ratio of the reactants as shown in Table VIII. It is readily seen that the ratio of the 1:1 adduct to the 1:2 adduct decreases as the ratio of trimethylsilane to butyne increases. To check if the diadduct forms by the addition of butyne to the 1:1 adduct a mixture of the two reactants were irradiated. It is found that addition of trimethylsilane to the 1:1 adduct gives only a low yield of the diadduct (Table VIII).



The addition of trimethylsilane to hexafluorobut-2-yne to give the mono- and diadduct also occurs upon heating. The results of this reaction are also tabulated in Table VIII.

TABLE VIII

FORMATION OF 1:1 AND 1:2 TRIMETHYLSILANE-BUTYNE ADDUCTS

(1) Reaction of Trimethylsilane and Hexafluorobut-2-yne

millimoles reactant $(\text{CH}_3)_3\text{SiH}$ $\text{CF}_3\text{C}\equiv\text{CCF}_3$		reaction conditions	millimoles product 1:1 adduct(cis:trans) ^a	1:2 adduct
28	69	$h\nu$ (11 days)	21.6 (0:1)	4.2
47	13	"	5.9 (0:1)	6.5
105	25	"	15.0 (0:1)	6.5
11	39	235° (7 hr.)	7.3 (1:15)	-
77	17	"	12.5 (1:10)	4.1

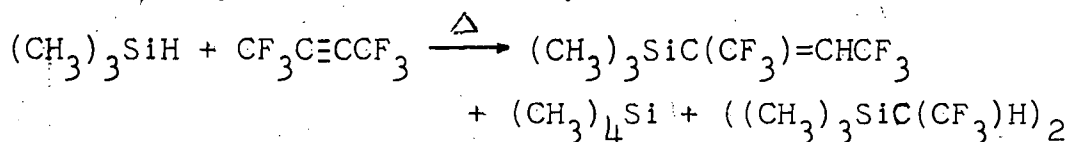
(2) Reaction of Trimethylsilane and the 1:1 Adduct

$(\text{CH}_3)_3\text{SiH}$ 1:1 adduct

48	7.9 (trans)	$h\nu$ (11 days)	7.0 (0:1)	0.8
45	12.8 (trans)	235° (7 hr.)	12.5 (1:6)	-

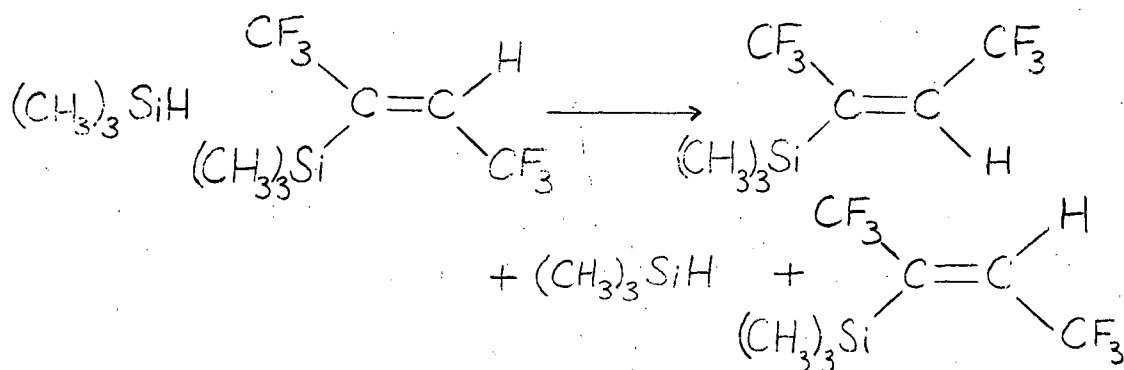
^a ^1H n.m.r. analysis.

The reaction of excess butyne with trimethylsilane gives a fraction of low volatility which contains nine components (v.p.c. analysis) and its infrared spectrum indicates that little or no diadduct is formed. Excess trimethylsilane and the butyne when heated to 235° give a 26% yield of 1:1 adduct, an 18% yield of diadduct and a 44% yield of tetramethylsilane.



In view of the high yield of tetramethylsilane and the low yield of the diadduct it was thought that the diadduct might slowly decompose at 235° . However, after seven hours at 235° the diadduct is quantitatively recovered. The 1:1 adduct from the irradiated reactions is 100% trans-isomer whereas the 1:1 adduct from the thermal reactions has a cis-isomer concentration which varies from 6 to 14%.

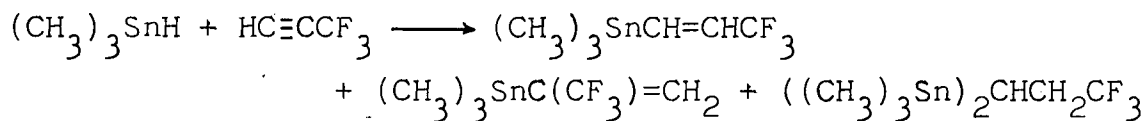
Although no measurable addition of trimethylsilane to the trans 1:1 adduct occurs after seven hours at 235° it is found that the cis-isomer concentration increases to 14%.



However, if the trans 1:1 adduct is heated alone, then conversion to the cis-isomer does not occur. The 1:1 adduct is also unaffected by ultraviolet light even in the presence of trimethylsilane or hexafluorobut-2-yne.

It was originally thought that because of the polarity of the

tin hydride bond ($\overset{\delta+}{\text{Sn}}-\overset{\delta-}{\text{H}}$) and the polarity of the acetylenic carbon hydrogen bond ($\overset{\delta-}{\text{C}}\equiv\overset{\delta+}{\text{C}}-\text{H}$) that the reaction of 1,1,1-trifluoropropyne with trimethyltin hydride might produce hydrogen and the propynyltin derivative, $(\text{CH}_3)_3\text{SnC}\equiv\text{CCF}_3$, but this does not occur. The reaction between trimethyltin hydride and the propyne at 20° is similar to the trimethylsilane-hexafluorobut-2-yne reaction described above in that both 1:1 and 1:2 adducts are produced.



The 1:1 adduct is identified by its ^1H n.m.r. spectrum of methyl absorptions at -0.05 and 0.00 p.p.m., four downfield quartets, two centred at -5.82 p.p.m. and two centred at -6.81 p.p.m., which are assigned to the trans-isomer, and a doublet at -5.48 p.p.m. and two quartets at -6.18 p.p.m. which are assigned to the iso-isomer. The relative intensity of the downfield absorptions to the methyl absorptions is 2:9.2. Figure 5 shows the ^1H n.m.r. spectrum and the assignments of the chemical shifts and coupling constants for the trans- and iso-isomers. It appears that the remaining downfield olefinic peaks may be assigned to the cis-isomer if J_{HH} is of the same order as the chemical shift between these protons. This situation would give large second order effects. On the basis of the ^1H n.m.r. spectrum the 1:1 adduct analyzes to be 65% trans-, 13% cis- and 22% iso-isomer. This isomer distribution does not measurably alter after distillation of the 1:1 adduct.

Figure 6 gives the ^1H n.m.r. spectrum of the 1:1 dimethylarsine-1,1,1-trifluoropropyne adducts¹²⁶. A comparison of Figure 5 with Figure 6 shows the similarity of the spectra of the respective trans-isomers. The H-H coupling constant of the iso-arsine

isomer is negligible whereas that of the iso-tin isomer is 1.5 cps but beyond this the similarity of the respective iso-isomers is readily apparent.

The 1:2 adduct, $((\text{CH}_3)_3\text{Sn})_2\text{CHCH}_2\text{CF}_3$, is identified by its ^1H n.m.r. spectrum of one methyl absorption at -0.20 p.p.m. and a methylene absorption at -2.58 p.p.m. consisting of two quartets with vicinal H-H coupling of 8.0 cps and geminal CF_3 -H coupling of 10.5 cps. The relative intensity of the methylene absorption to the methyl absorption is 1:10. The methine absorption is probably obscured by the tin methyl side bands since it would be expected to be at higher field than the methylene absorption. The 1,2-trimethyltin adduct, $(\text{CH}_3)_3\text{SnCH}(\text{CF}_3)\text{CH}_2\text{Sn}(\text{CH}_3)_3$, would be expected to show two methyl absorptions and the methylene absorption would be expected to show two quartets with $J_{\text{HH}} \sim 8$ cps and $J_{\text{CF}_3\text{H}} \sim 2$ cps.

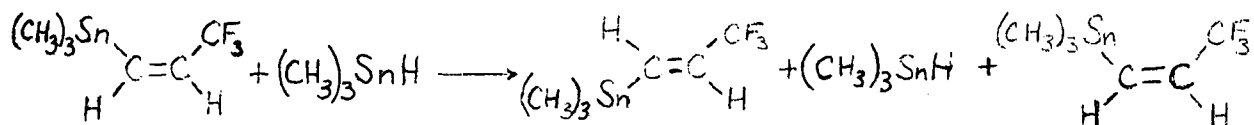
The ratio of monoadduct to diadduct varies with the trimethyltin hydride-propyne ratio as indicated in Table IX.

TABLE IX

REACTION OF TRIMETHYLTIN HYDRIDE AND 1,1,1-TRIFLUOROPROPYNE

millimoles reactants			reaction conditions	millimoles products		
$(\text{CH}_3)_3\text{SnH}$	$\text{CF}_3\text{C}\equiv\text{CH}$	ratio		1:1 adduct	1:2 adduct	ratio
35	49	1:1.4	20° (1 day)	15	5.7	2.6:1
12	11	1:0.9	20° (4 days)	4.2	2.4	1.8:1

The diadduct is not produced when trimethyltin hydride and the 1:1 adduct are left for two days at 20° although the cis-isomer concentration of the 1:1 adduct decreases from 13 to 8%.



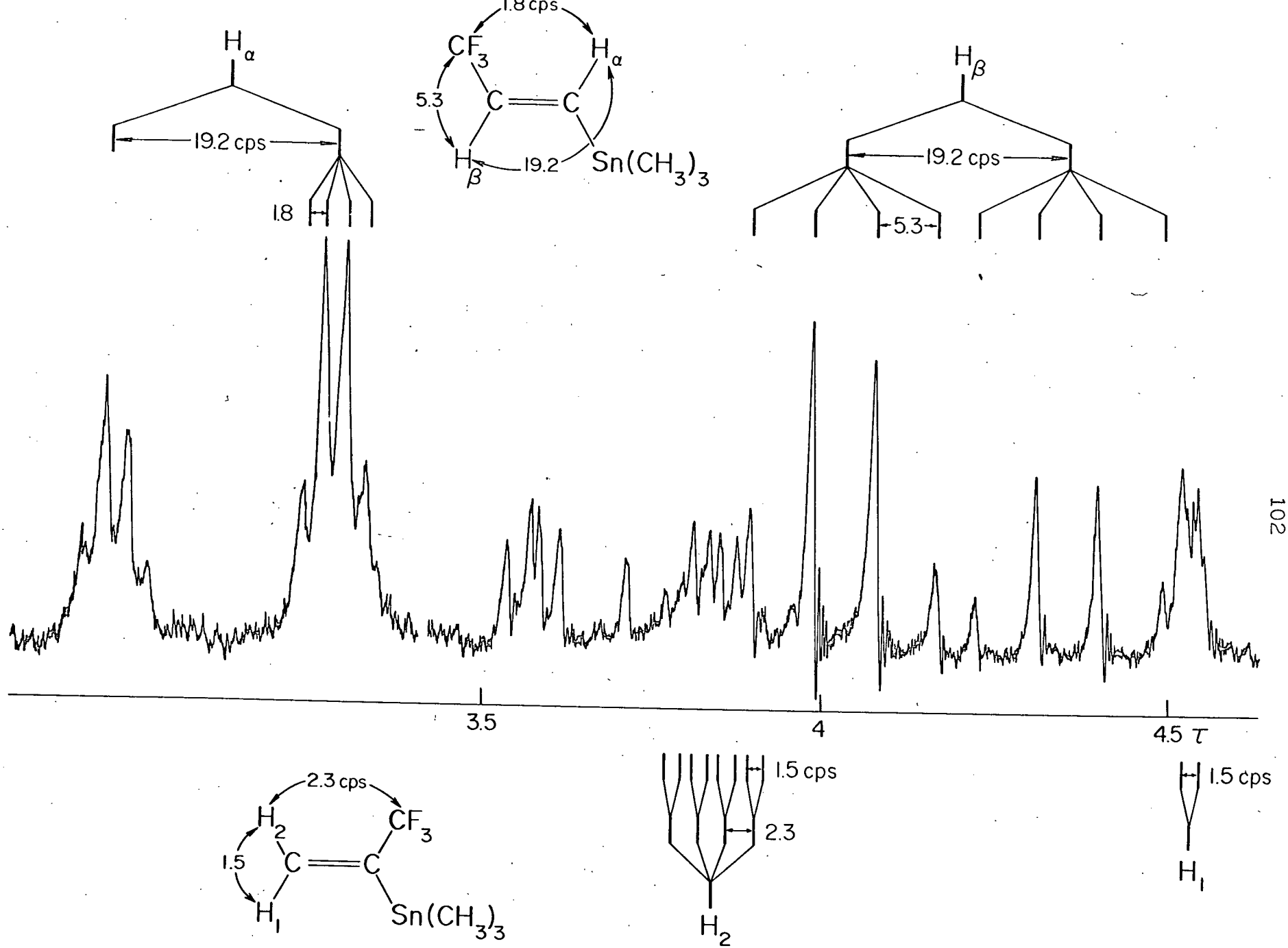
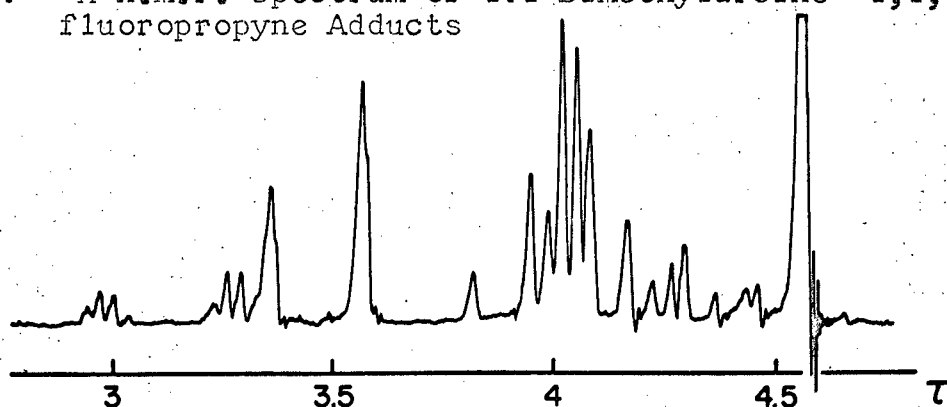


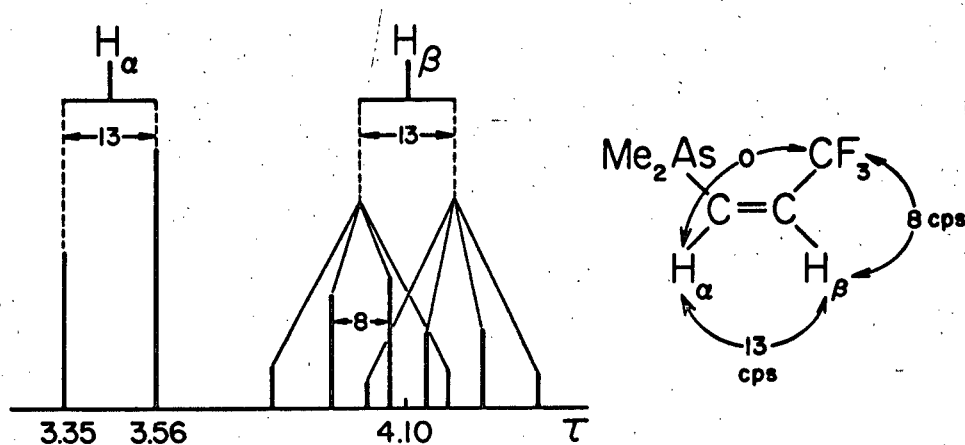
Figure 5: ^1H n.m.r. Spectrum of 1:1 Trimethyltin Hydride-1,1,1-Trifluoropropyne Adducts

Figure 6: ^1H n.m.r. Spectrum of 1:1 Dimethylarsine- 1,1,1-Tri-fluoropropyne Adducts

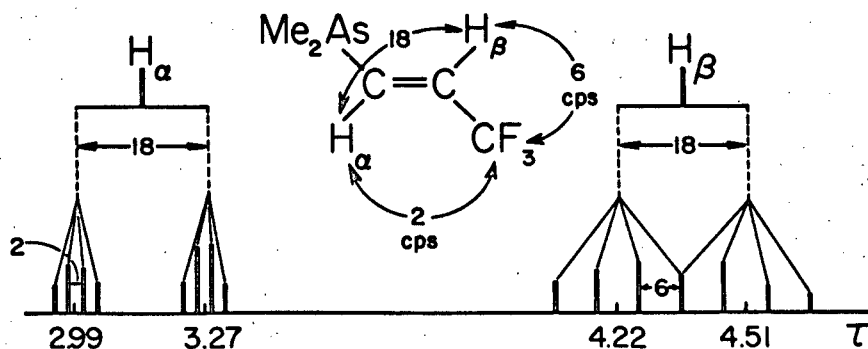
(a)



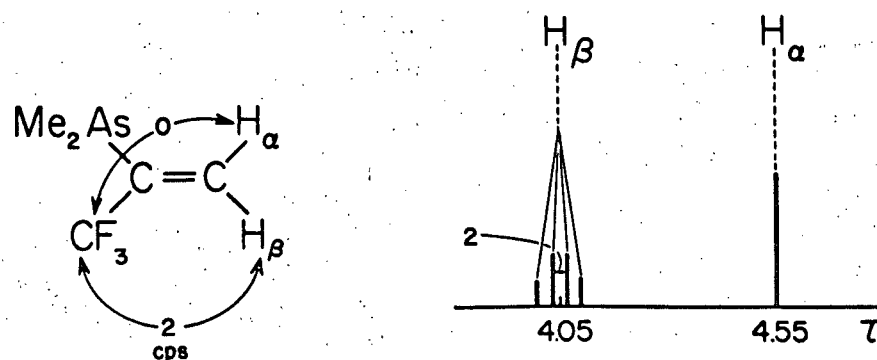
(b)



(c)



(d)



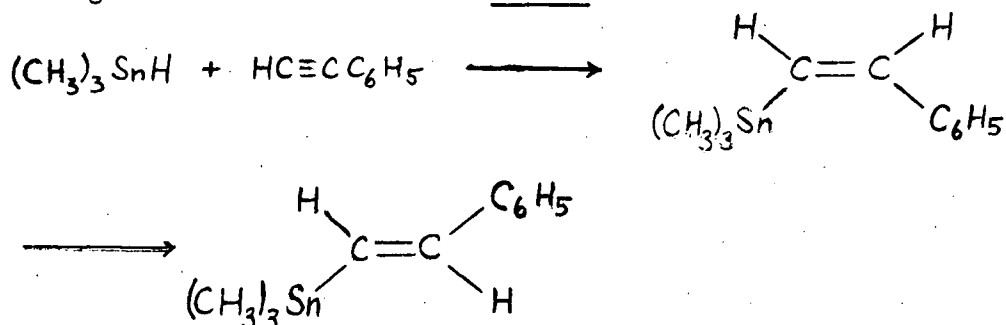
The isomer distribution of the 1:1 adduct from the reaction of dimethylamine and 1,1,1-trifluoropropyne is strikingly different from the isomer distribution of the 1:1 adduct obtained from the reaction of the same acetylene with dimethylarsine or trimethyltin hydride. The 1:1 adduct, 3-dimethylamino-1,1,1-trifluoropropene, b.p. 118° (759 mm), is obtained in 57% yield from the reaction of the amine and the propyne.



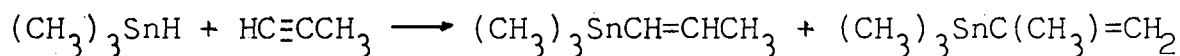
This 1:1 adduct can be assigned the trans configuration from a comparison of its ^1H n.m.r. spectrum with Figure 6. Two quartets at -6.17 p.p.m. with $J_{\text{HH}} = 13$ cps and $J_{\text{CF}_3\text{H}} = 1.5$ cps can be assigned to H_α and the overlapping quartets at -3.66 p.p.m. with $J_{\text{CF}_3\text{H}} = 6.5$ cps can be assigned to H_β . The relative intensity of the olefinic protons to the methyl peak is 1:3. Its infrared spectrum shows strong bands at 960 and 1307 cm^{-1} which can be assigned to the trans -HC=CH- "out-of-plane" and "in-plane" bending vibrations respectively¹³³. The ^1H n.m.r. spectrum shows no signs of any other isomer. The trans-1-dimethylamino-3,3,3-trifluoropropene is unstable to distillation (760 mm), although the isomer distribution in the undecomposed distillate remains unchanged.

(2) Proposed Mechanism of Hydride-Fluoroacetylene Reactions

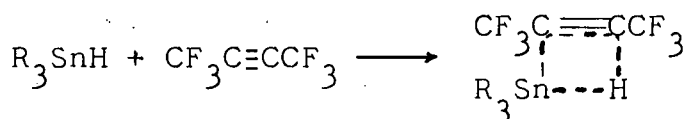
(a) Tin Hydrides--Fulton¹⁴⁰ found that tin hydrides add trans to phenylacetylene to give the cis-isomer which rearranges on warming to the more stable trans-isomer.



The presence of any iso-isomer was not observed by Fulton. The reaction of trimethyltin hydride and methylacetylene is reported to give all three isomers, trans-, cis- and isopropenyltrimethyltin in a ratio of 68:28:4¹⁴¹.



In the present investigation the reaction of tin hydrides with hexafluorobut-2-yne produces almost completely trans-isomer (Table VI). A four-centre mechanism, as shown, would not account for predominance of the trans-isomer.

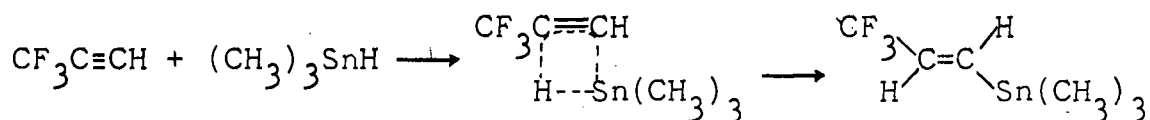


The speed of this reaction is also against such a mechanism since the orientation necessary for a four-centre addition is not expected to allow a reaction to be complete within seconds.

There appear to be two reasonable mechanisms involving either hydride nucleophilic attack or tin electrophilic attack on the acetylene. A general rule of trans nucleophilic addition to alkynes has been postulated¹⁴². Burnelle¹⁴³ has also calculated that a trans distortion of the alkyne is to be expected on the approach of an electrophile, thus leading to trans electrophilic additions. The speed of the tin hydride-hexafluorobut-2-yne reaction in which the acetylene carbon atoms have the highly electron withdrawing $-\text{CF}_3$ groups attached, and the slowness of the tin hydride-methylacetylene reaction which is only 30% complete after eighteen hours at 100° ¹⁴¹ indicate nucleophilic attack. Hazeldine¹²² found that hexafluorobut-2-yne is very susceptible to nucleophilic attack but requires catalysts to react with electrophilic reagents.

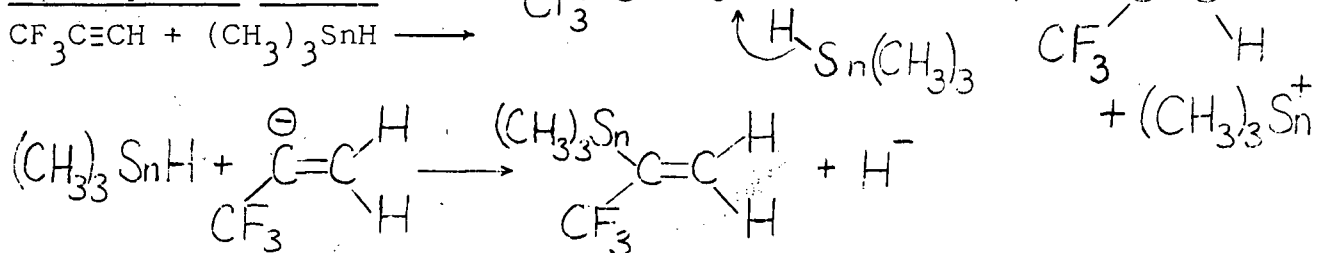
The reaction of 1,1,1-trifluoropropyne and trimethyltin hydride

is 80% complete after four days at 20° and gives predominantly the trans 1:1 adduct. The major product can be explained by the following four-centre addition.

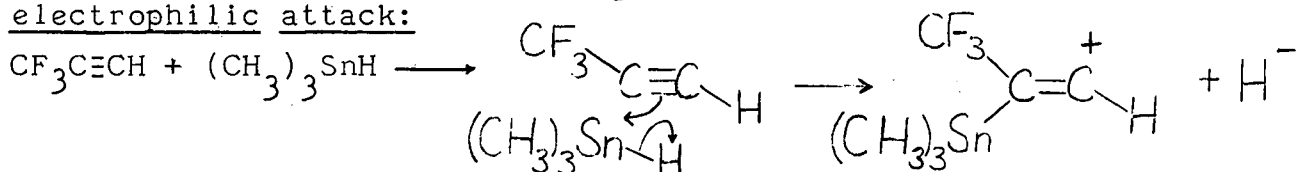


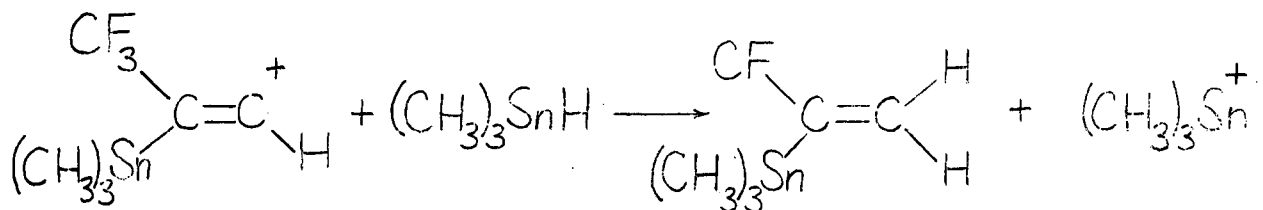
However, an alternate mechanism to account for trans-1,1,1-trifluoropropenyl-3-trimethyltin involves trans nucleophilic addition to give the cis-isomer followed by isomerization. Fulton¹⁴⁰ describes the trimethyltin hydride catalyzed isomerization of cis- β -styryltrimethyltin to the trans-isomer. In the present investigation there was tin hydride remaining in the propyne-trimethyltin hydride reaction consequently a similar result might be anticipated. Indeed it is found trimethyltin hydride does catalyze the isomerization of cis-1,1,1-trifluoropropenyl-3-trimethyltin to the trans-isomer. Haszeldine¹²² found that both electrophilic and nucleophilic reagents add readily to 1,1,1-trifluoropropyne; electrophiles attack at the central carbon and nucleophiles attack at the terminal acetylenic carbon. On this basis electrophilic attack by the tin atom of trimethyltin hydride and nucleophilic attack by the hydride group on trimethyltin hydride would give the iso-isomer, viz.

nucleophilic attack:

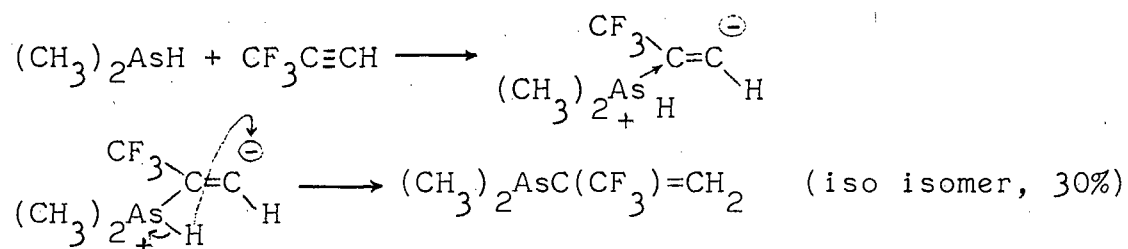


electrophilic attack:

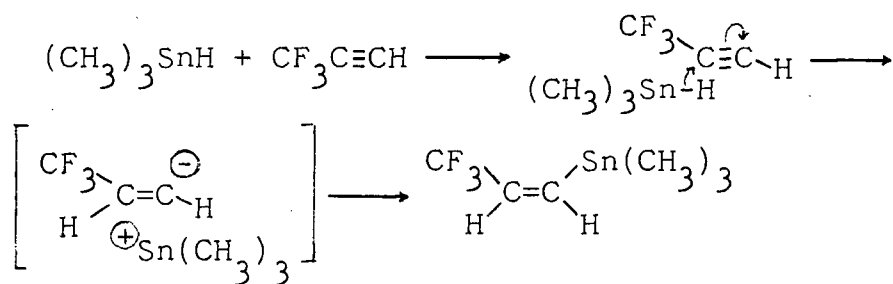




In both the reaction schemes described above a second trimethyltin hydride molecule might not be involved, the reaction mechanism probably being more concerted than is indicated. Cullen and Dawson¹²⁶ observed that the reaction of 1,1,1-trifluoropropyne and dimethylarsine gives a 30% yield of the *iso*-isomer, the remaining 1:1 adduct (70%) being a mixture of *cis*- and *trans*-3-dimethylarsino-1,1,1-trifluoropropene. Since the mechanism of formation of the 1:1 arsine-propyne adduct probably involves nucleophilic attack by the arsenic lone pair it appears that nucleophilic attack can occur at the central carbon atom of 1,1,1-trifluoropropyne.

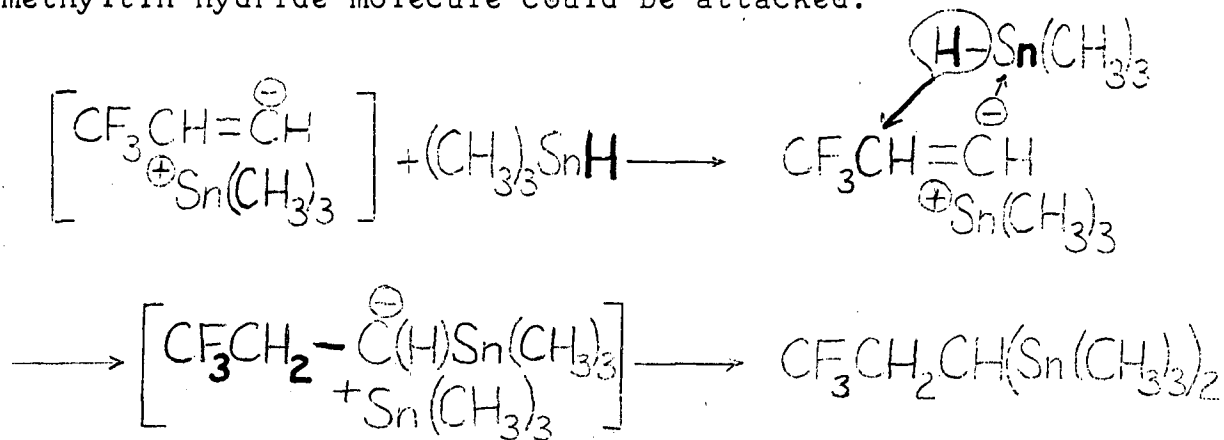


Thus, from the arsine-propyne results a similar nucleophilic attack would explain the formation of *trans*-1,1,1-trifluoropropenyltrimethyltin.



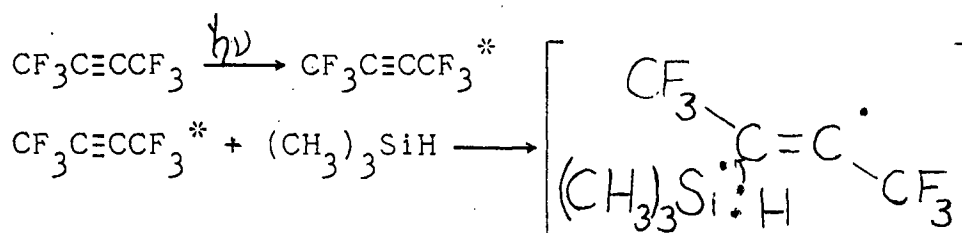
The reaction of 1,1,1-trifluoropropyne and trimethyltin hydride also gives a considerable yield of the diadduct, 1,1,1-trifluoro-3,3-bis(trimethylstannyl)propane. Since the tin hydride does not add to the 1:1 adduct at 20° in the dark it seems that

the mechanism to form the diadduct is concerted. If the postulated intermediate for the formation of the 1:1 adduct, $\text{CF}_3\text{CH}=\bar{\text{C}}\text{H}$, has a finite lifetime then it seems probable that a second trimethyltin hydride molecule could be attacked.



Haszeldine¹²² obtained some 2,2-dialkoxybutane from the base catalyzed reaction of hexafluorobut-2-yne and alcohols at 0° and observed that a second mole of alcohol does not add to the monoalkoxybutene under the same conditions.

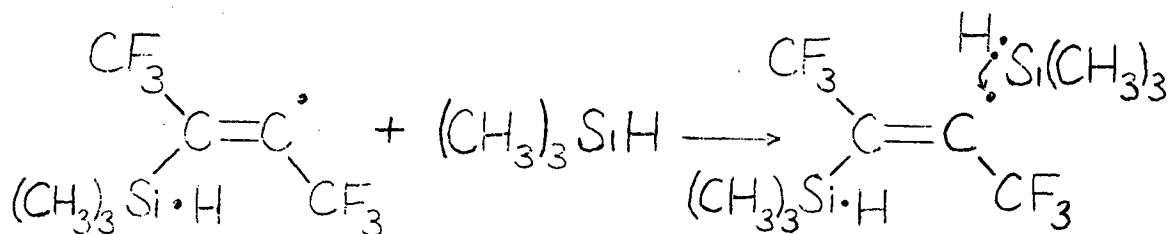
(b) Silanes and Germanes--The ultraviolet initiated reactions of trimethylsilane and triethylgermane with hexafluorobut-2-yne also afford the 1:1 adduct of predominantly trans configuration (Table VI). This might be expected since acetylene is trans bent in its first singlet excited state¹⁴³. However, a rather bewildering point is that above 3000 Å there does not appear to be any ultraviolet absorption by hexafluorobut-2-yne. Nevertheless in thick-walled Pyrex tubes, which do not transmit any significant amount of light below 3000 Å, the reactions do proceed upon irradiation to give the 1:1 trans addition products. Assuming that the butyne does absorb some radiation to give a singlet excited state it seems probable that on collision the excited butyne could fall to a lower lying triplet state and combine with a trimethylsilane or triethylgermane molecule to give a radical intermediate.



This intermediate could then form the 1:1 adduct by intramolecular or intermolecular proton abstraction.

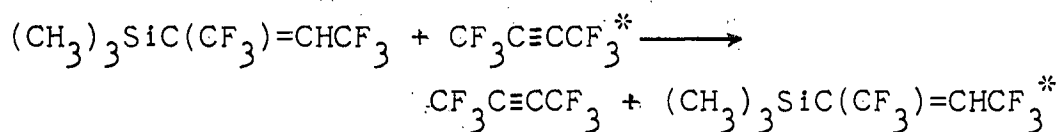
In the thermal reaction of trimethylsilane and hexafluorobut-2-yne, since trimethylsilane catalyzes the isomerization of the trans 1:1 adduct to the cis-isomer, the isomer distribution of the 1:1 adduct changes with the concentration of trimethylsilane and duration of heating. It seems probable that the initial reaction involves a trans nucleophilic addition similar to that postulated for the formation of the 1:1 tin hydride-butyne adducts. However a radical mechanism cannot be disregarded especially in view of the high yield of tetramethylsilane (44%) in the butyne-excess trimethylsilane reaction.

The symmetrical butene-2,3-bistrimethylsilane is obtained from the trimethylsilane-hexafluorobut-2-yne reaction both on heating and irradiation. If the silane-hexafluorobut-2-yne radical intermediate, $(\text{CH}_3)_3\text{Si}(\text{H})\text{C}(\text{CF}_3)=\dot{\text{C}}\text{CF}_3$, postulated above has a finite lifetime then it seems probable that another silicon atom on a second trimethylsilane molecule could be attacked.



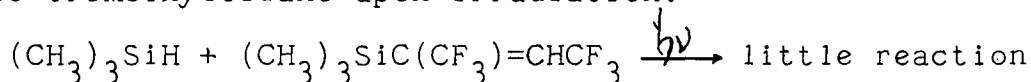
This second intermediate could then afford the diadduct by intramolecular proton transfer. Another possibility which would account for the diadduct formation would involve energy transfer

by the butyne to the 1:1 adduct as follows:

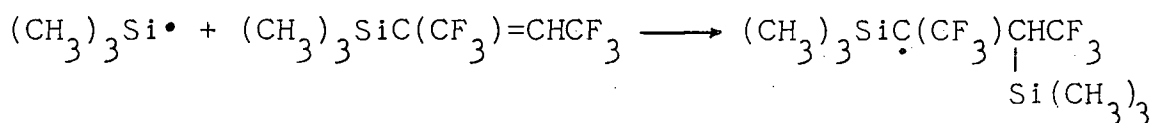


The excited 1:1 adduct could add to a second silane molecule.

It is necessary to postulate the excited 1:1 adduct before assuming addition since the experimental results of this investigation have established that the 1:1 adduct does not add appreciably to trimethylsilane upon irradiation.



The main reaction product from the thermal reaction of trimethylsilane and hexafluorobut-2-yne is tetramethylsilane. This suggests the presence of the radical $(\text{CH}_3)_3\text{Si}\cdot$ and this radical, if formed, could afford the diadduct on attack of the 1:1 adduct.



A concerted mechanism involving nucleophilic attack on the acetylene would probably afford the 2,2-bistrimethylsilane, $((\text{CH}_3)_3\text{Si})_2\text{C}(\text{CF}_3)\text{CH}_2\text{CF}_3$, since the unsymmetrical dialkoxybutene, $\text{CF}_3\text{C}(\text{OR})_2\text{CH}_2\text{CF}_3$, was obtained from the base-catalyzed reaction of hexafluorobut-2-yne and alcohol¹²².

Benkeser and coworkers¹⁴⁴ found that a diadduct, in addition to the monoadduct, forms when trichlorosilane is reacted with t-butylacetylene in the presence of benzoyl peroxide. It was also found that trichlorosilane adds to the cis 1:1 t-butylacetylene-silane adduct in the presence of benzoyl peroxide but not to the trans 1:1 adduct. In the present investigation, however, it was found that although trimethylsilane catalyzes the conversion of trans- to cis-isomer it does not add even to the cis-butenylsilane.

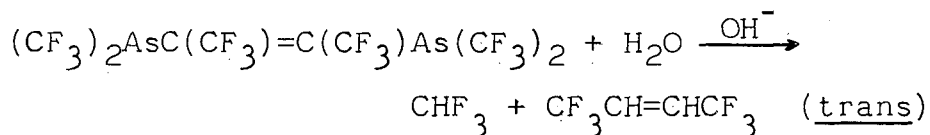
B. Metal-Metal Bonds

(1) Results

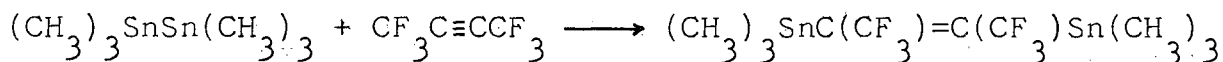
Hexafluorobut-2-yne and tetrakis(trifluoromethyl)diarsine react on ultraviolet irradiation to give the 1:1 adduct, 2,3-bis-(bistrifluoromethylarsino)hexafluorobut-2-ene, b.p. 156° (760 mm).



The absence of any absorption in the C=C stretching region indicates that the product is mainly the trans-isomer. The product is identified by elemental analysis. It has been reported that tetrakis(trifluoromethyl)diarsine and the butyne do not react at 100° ⁴¹ although the butyne does react with tetramethyldiarsine at 20° to give an approximate 1:1 mixture of the cis- and trans-isomers of $(\text{CH}_3)_2\text{AsC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{As}(\text{CH}_3)_2$. Qualitative base hydrolysis of 2,3-bis(bistrifluoromethylarsino)hexafluorobut-2-ene gives trifluoromethane and only trans-1,1,1,4,4,4-hexafluorobut-2-ene.



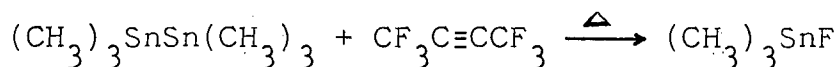
The butyne and hexamethylditin react on ultraviolet irradiation to give a 1:1 adduct, hexafluoro-2,3-bis(trimethylstannyl)but-2-ene, b.p. 53° (10^{-3} mm), which is rather unstable in air.



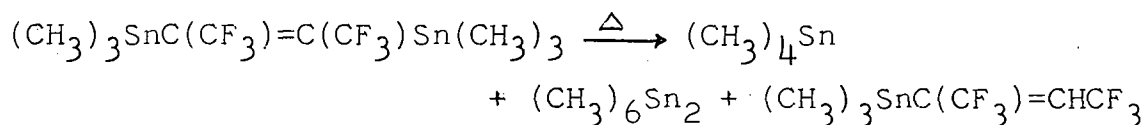
The adduct is identified by elemental analysis. The ^1H n.m.r. spectrum of this ditin adduct consists of a single methyl peak which is split into a multiplet with $J \sim 0.8$ cps. This splitting is assigned to $\text{CF}_3\text{-CH}_3$ interaction. Its ^{19}F n.m.r. spectrum consists of only one broad peak indicating the presence of only one isomer. The broadness of the single line in the ^{19}F n.m.r. spectrum is probably a consequence of weak $\text{CH}_3\text{-CF}_3$ coupling which is expected to be of the order of 1 cps¹³⁰. The absence of any C=C stretching frequency in the infrared spectrum suggests that the

ditin adduct is the trans-isomer. The use of infrared spectra for assigning structures of this type appears to be reliable since the compound, $(\text{CH}_3)_2\text{AsSC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{SAs}(\text{CH}_3)_2$, which without doubt has the cis-structure, has a strong band at 1535 cm^{-1} ¹⁴⁵. The 1:1 mixture of $(\text{CH}_3)_2\text{AsC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{As}(\text{CH}_3)_2$ has a weak band at 1570 cm^{-1} ⁴¹, and when its preparation is carried out with the 1:1 complex, $(\text{CH}_3)_4\text{As}\cdot(\text{CF}_3)_2\text{CO}$, the yield of cis-isomer is very much increased with a corresponding increase in the intensity of the 1570 cm^{-1} band (see Chapter I, page 23).

The 1:1 ditin adduct is not obtained on heating hexamethylditin and the butyne; trimethyltin fluoride was the only tin containing reaction product isolated from this reaction.



The 1:1 ditin adduct does decompose on heating to tetramethyltin, hexamethylditin, 1,1,1,4,4,4-hexafluorobutenyltrimethyltin, and numerous other unidentified liquids and solids.



Base hydrolysis of the ditin adduct gives a cis-trans mixture of 1,1,1,4,4,4-hexafluorobutene; thus, it does not appear that there is retention of configuration upon hydrolysis.

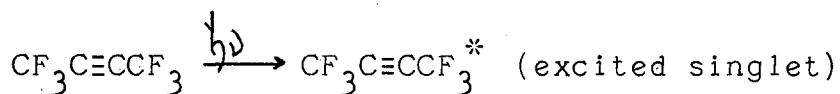
Although there is a reaction between hexabutylditin and hexafluorobut-2-yne on ultraviolet irradiation, it is rather complicated. The only product that was identified is dibutylbis(1,1,1,4,4,4-hexafluorobutenyl)tin, $(\text{C}_4\text{H}_9)_2\text{Sn}(\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H})_2$, b.p. $60-63^\circ$ (10^{-3} mm). This has the same boiling point as the diadduct formed from dibutyltin dihydride and the butyne (page 95), although the infrared spectrum shows some slight differences in the C=C stretching region which are probably due to a difference in

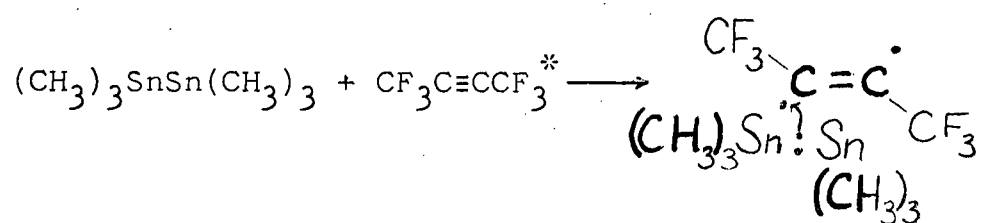
isomer distribution. Its ^1H n.m.r. spectrum shows a downfield quartet, $J \sim 8$ cps, typical of the group $-\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}$. Other fractions isolated from the reaction suggest the presence of other compounds of the type $(\text{C}_4\text{H}_9)_n\text{Sn}(\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H})_{4-n}$. If it is assumed, and it appears reasonable, that the 1:1 adduct is originally formed followed by decomposition then the presence of the compound with $n = 3$ could be expected in view of the results from the thermal decomposition of $(\text{CH}_3)_3\text{SnC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{Sn}(\text{CH}_3)_3$.

It was found that hexaethyldigermene is stable to hexafluorobut-2-yne on ultraviolet irradiation. This is expected in view of the increasing M-M bond strength in the compounds R_3MMR_3 as the group is ascended.

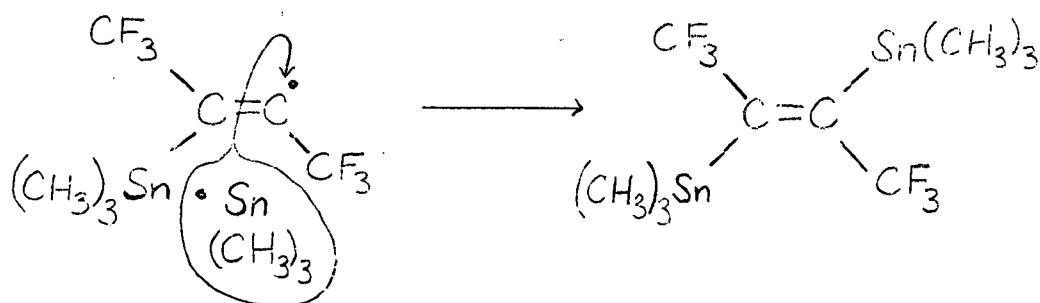
(2) Proposed Mechanism of Metal-Metal Addition to Hexafluorobut-2-yne

Tin hydrides, tetramethylarsine⁴¹ and amines¹²² add vigorously to hexafluorobut-2-yne at 20° , and in these reactions the most probable mechanism involves nucleophilic attack on the acetylenic carbons of the butyne. For the reactions involving the irradiation of the butyne and tetrakis(trifluoromethyl)diarsine or the ditin compounds the same mechanism is very unlikely. Tetrakis(trifluoromethyl)diarsine is probably a weak nucleophile because of the inductive effect of the trifluoromethyl groups and it is unlikely that any nucleophilic character can be attributed to the tin atoms of the ditin compounds. The predominant formation of the trans-isomer for the addition of hexafluorobut-2-yne to hexamethylditin and the diarsine is consistent with the trans addition of trimethylsilane and triethylgermane to the butyne on irradiation and therefore a mechanism involving a similar intermediate





followed by intramolecular trimethyltin transfer is proposed.



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