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REACTION OF GROUP IV HYDRIDES WITH FLUOROACETYLENES

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INTRODUCTION

During the course of studies on the reactions of hexafluoro-2-butyne with organometallic substances[1-3] it was found[1] that $(CH_3)_3SnC(CF_3)=C(CF_3)Sn(CH_3)_3$, from $(CH_3)_3Sn\text{-}Sn(CH_3)_3$ and $CF_3C{\equiv}CCF_3$, decomposes on heating to give, amongst other products, the hexafluorobutenyl compound, $(CH_3)_3SnC(CF_3)=C(CF_3)H$. Since $CF_3C{\equiv}CCF_3$ had been found to add to the M–H bond of transition metal[4,5] and Group V hydrides[3] it was to be expected that the butenyltin compound would also be produced from trimethyltin hydride and the butyne. Since the reactions of Group IV hydrides with fluoroacetylenes had not been studied, the present investigation was undertaken.

EXPERIMENTAL

Hexafluoro-2-butyne, tetraethylgermane, and trimethylsilane were obtained from Peninsular ChemResearch, Inc. Triethylgermane was prepared in low yield by reducing bromotriethylgermane, from tetraethylgermane and bromine at 100° in a sealed tube, with sodium borohydride[6]. Tin hydrides were prepared by the reduction of the appropriate tin chloride with lithium aluminium hydride[7]. The tin chlorides were the gift of M & T Chemicals. Trifluoropropyne was prepared from 1,1,1-trifluoro-2,2,3,3,3-pentachloropropane as described by Finnegan and Norris[8].

Volatile reagents and products were manipulated in a standard vacuum system. Reactions were carried out in sealed Pyrex tubes. Infrared spectra were recorded on a Perkin–Elmer Model 21 spectrophotometer (NaCl optics). Fluorine and ^{1}H NMR spectra were obtained using Varian H.R.60 and A60 instruments. Chemical shifts are reported in ppm relative to external tetramethylsilane (^{1}H spectra) and external trifluoracetic acid (^{19}F spectra). Analytical data for new compounds are given in Table 1.

(1) *Reaction of hexafluoro-2-butyne with tin hydrides*

The reaction with trimethyltin hydride is described as an example. Trimethyltin hydride (2.9 g) and the butyne (6.9 g) reacted exothermically immediately on mixing well below 20°. Unreacted butyne (4.1 g) was recovered and the reaction product (5.9 g), which condensed in a trap at −78°, was identified as the known compound (1,1,1,4,4,4-hexafluorobutenyl)trimethyltin, b.p. 124° (751 mm) by means of its infrared and ^{1}H NMR spectra[1].

(2) Reaction of hexafluoro-2-butyne with triethylgermane

The germane (1.2 g) and the butyne (4.1 g) did not react in the dark at 20°. However, when the reactants were irradiated with UV light for 7 days only 3.8 g of the butyne could be recovered. The involatile fraction (2.4 g) was identified as (1,1,1,4,4,4-hexafluorobutenyl)triethylgermane. The new germane was heated to 220° for 45 h and there was little or no change in the original isomer distribution although considerable decomposition, had occurred.

(3) Reaction of hexafluoro-2-butyne with trimethylsilane

The silane (2.1 g) and excess butyne (11.1 g) were irradiated for 11 days. Unreacted butyne (7.45 g) was recovered. The main product (1,1,1,4,4,4-hexafluorobutenyl)trimethylsilane (5.1 g, 73% yield) went through a trap at —23°. The fraction which condensed at —23° (2.0 g) contained 7 components by VPC analysis (5′ Ucon Polar at 110°). The main component, approximately 65%, was collected and identified as 1,1,1,4,4,4-hexafluoro-2,3-bis(trimethylsilyl)butane. Infrared spectrum (strong bands, liquid film): 1367, 1285, 1295, 1146, 1071, 844 cm^{-1}. NMR data: ^{1}H spectrum showed a broad singlet at 0.10 ppm, $[Si(CH_3)_3]$ and a multiplet at —1.66 ppm of relative area 1:8.8 (calcd. 1:9.0). The ^{19}F spectrum showed doublets at —21.8 ($J = 13$ cps) and —23.6 ppm ($J = 12$ cps) of equal intensity. The results of this experiment and other runs using trimethylsilane are summarized in Table 5.

Reaction of trimethyltin hydride with 3,3,3-trifluoropropyne

The hydride (5.75 g) and the propyne (4.65 g) were left at 20° (1 day). Unreacted

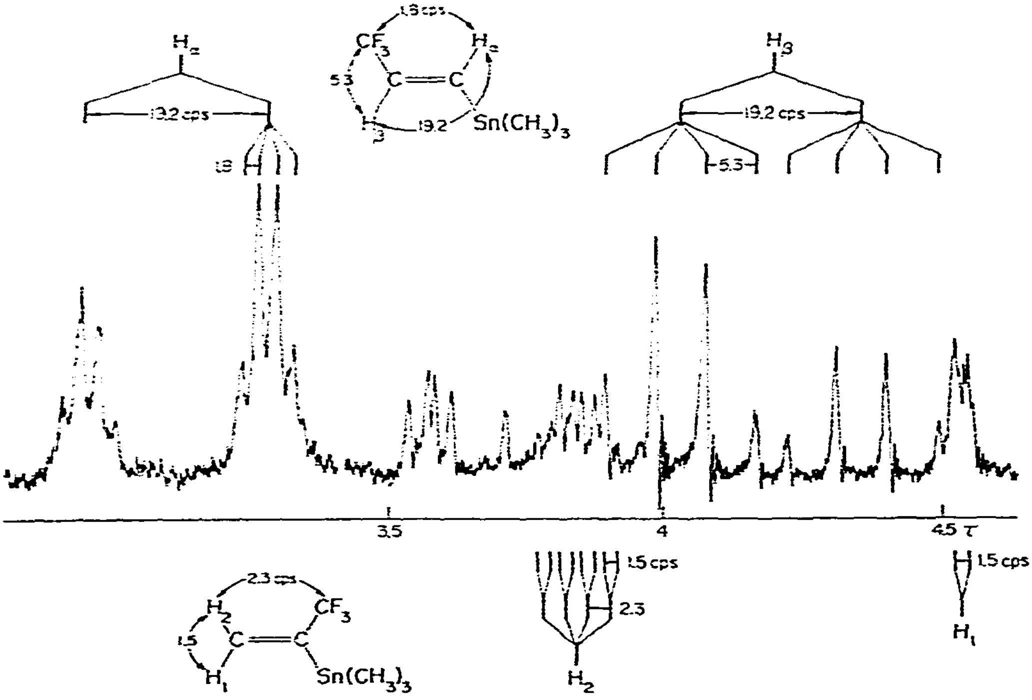

Fig. 1. Downfield ^{1}H NMR spectrum of the 1:1 adduct $(CH_3)_3SnH \cdot CF_3C{\equiv}CH$.

propyne (2.35 g) and trimethyltin hydride (1.7 g) were recovered by trap-to-trap distillation. The monoadduct (3,3,3-trifluoropropenyl)trimethyltin (3.9 g) condensed in a trap at —46°. The least volatile liquid was the diadduct, 1,1,1-trifluoro-3,3-bis-(trimethyltin)-propane (2.4 g) Infrared data (strong bands, liquid films): monoadduct: 1278, 1215, 1117, 771 cm^{-1}; diadduct: 1259, 1213, 1133, 1078, 761 cm^{-1}. ^{1}H NMR data: monoadduct: the down field region is shown in Fig. 1, in addition there are singlets at 0.00 and —0.05 ppm [$Sn(CH_3)_3$]; diadduct: singlet at —0.20 ppm [$Sn(CH_3)_3$], and a doublet ($J = 8.0$ cps) of quartets ($J = 10.5$ cps) at —2.58 ppm (CH_2). The relative area of CH_3 to CH_2 is 1:10 (calcd. 1:9).

The monoadduct distilled unchanged in isomer distribution. The isomers could not be separated by VPC using column of Ucon Polar, silicone, or Apiezon J.

In another experiment the tin hydride (2.0 g) and the propyne were left for 4 days at 20° to give monoadduct (1.1 g) and diadduct (1.0 g).

Reaction of trimethyltin hydride with (3,3,3-trifluoropropenyl)trimethyltin

The hydride (2.2 g) and the monoadduct (1.6 g, 13% *cis*-isomer by NMR) were left at 20° for 2 days. The monoadduct (1.6 g 8% *cis*-isomer by NMR) and trimethyltin hydride (2.0 g) were recovered. An involatile fraction (0.2 g) showed only weak C–F absorption in its infrared spectrum.

DISCUSSION

Addition of tin hydrides

The results of the present investigation can be represented by the following equations ($R = CH_3, C_2H_5$, n-C_4H_9)

$$R_3SnH + CF_3C{\equiv}CCF_3 \rightarrow R_3SnC(CF_3){=}C(CF_3)H \quad (I)$$

$$(C_4H_9)_2SnH_2 + CF_3C{\equiv}CCF_3 \rightarrow (C_4H_9)_2Sn[C(CF_3){=}C(CF_3)H]_2 \quad (II)$$

$$(CH_3)_3SnH + HC{\equiv}CCF_3 \rightarrow (CH_3)_3SnCH{=}CHCF_3 \ (III) + H_2C{=}C(CF_3)Sn(CH_3)_3 \ (IV) +$$
$$[(CH_3)_3Sn]_2CHCH_2CF_3 \ (V)$$

The quantitative reactions producing (I) and (II) are exothermic and occur below 20° in the presence of excess butyne. The reaction of trimethyltin hydride with the propyne is much slower being incomplete after 4 days at 20°. Analytical data for compounds (I)–(V) are given in Table 1. The similarity of (I) and (II) is shown by the infrared spectral data in Table 2. The bands listed are probably due to C–F stretching with the exception of the bands near 850 cm^{-1} which may be due to C–H out-of-plane deformations[9]. Bands of similar intensity and position are also present in the spectra of other hydride adducts of the butyne[3–5]. One difference does arise in the presence of weak C=C stretching frequencies in the Group V hydride adducts[3] and their absence in (I) and (II). In fact the presence of the double bond in (I) and (II) is best established by the down field proton in the ^{1}H NMR spectrum of these compounds, and the chemical shifts and coupling constants for this proton are given in Table 3. Data for some related compounds are also listed. The assignments of the geometry of

TABLE 1

ANALYTICAL DATA FOR NEW COMPOUNDS[a]

Compound	B.p. [°C(mm)]	Calcd.				Found			
		C	H	M	F	C	H	M	F
$(CH_3)_3SiC(CF_3)=C(CF_3)H$	98	35.6	4.2		48.3	35.3	4.2		47.9
$[(CH_3)_3SiC(CF_3)H\text{–}]_2$[b]	79(38)	38.7	6.5		36.8	38.7	6.5		36.9
$(C_2H_5)_3GeC(CF_3)=C(CF_3)H$	82(26)	37.2	5.0			37.8	4.7		
$(C_2H_5)_3SnC(CF_3)=C(CF_3)H$	86(24)	32.5	4.3	32.2	30.9	32.5	4.0	32.0	30.9
$(C_4H_9)_3SnC(CF_3)=C(CF_3)H$	72(10^{-3})	42.4	6.2	26.2	25.2	42.0	6.3	26.4	25.7
$(C_4H_9)_2Sn[C(CF_3)=C(CF_3)H]_2$	63(10^{-2})	34.4	3.6	21.2	40.8	34.2	3.3	20.3	40.5
$(CH_3)_3SnH\cdot CF_3C\equiv CH$	129	27.8	4.3			27.6	4.2		
$[(CH_3)_3Sn]_2CHCH_2CF_3$	108(29)	25.5	5.0			25.4	4.6		

[a] Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. and Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim (Ruhr), West Germany. [b] Mol. wt. calcd. 310, found 307 (Rast).

TABLE 2

SOME CHARACTERISTIC INFRARED ABSORPTION OF THE 1,1,1,4,4,4-HEXAFLUOROBUTENYL DERIVATIVES $MC(CF_3)=C(CF_3)H$[a]

M					
$(CH_3)_3Si$	1354s	1300m	1257vs	1141vs	[b]
$(C_2H_5)_3Ge$	1341s	1293m	1257vs	1142vs	850m[c]
$(CH_3)_3Sn$	1328s	1291m	1255vs	1140vs	849m[c]
$(C_2H_5)_3Sn$	1328s	1292m	1255vs	1139vs	850m[c]
$(C_4H_9)_3Sn$	1330s	1295m	1255vs	1143vs	850m[c]
$(C_4H_9)_2Sn$[d]	1329s	1295m	1255vs	1139vs	850m[c]

[a] Values in cm^{-1}. [d] Hidden by $(CH_3)_3Si$ rocking absorption at 849 cm^{-1}. C–H (of C=CH) out-of-plane deformation. [d] $(C_4H_9)_2Sn[C(CF_3)=C(CF_3)H]_2$.

the products in Table 3 are based on the now fairly well established results that J_1 and J_1' are of the order of 8.0 cps and that J_3 ($\sim$ 2 cps) is usually greater than J_2 ($\lesssim$ 1 cps)[3,5]. In a recent analysis of the spectrum of 3,3,3-trifluoropropene, J_1, J_2 and J_2 were found to be +6.28, +0.03, and −2.22 cps respectively[10]. [However, as is seen in Table 3, J_3 for the compound $(CH_3)_3NC(CF_3)=C(CF_3)H$ is less than the usual value.] Thus on the basis of their NMR spectra the compounds (I) are almost completely *trans*-isomers*.

Because of the broadness of the peaks in the ^1H NMR spectrum of (II) the isomer distribution cannot be assigned with certainty, however, it seems that a *trans-trans* configuration of the two fluorocarbon groups is most likely in view of the infrared and NMR data (Tables 2 and 3).

The reaction products from trimethyltin hydride and 3,3,3-trifluoropropyne are structurally more interesting; both 1:1 and 1:2 adducts are obtained. The 1:1 adduct could be present as the *cis*- and *trans*-isomers of (III) and the *gem*-compound (IV). The down field region of the ^1H NMR spectrum of the 1:1 adduct is shown in Fig. 1.

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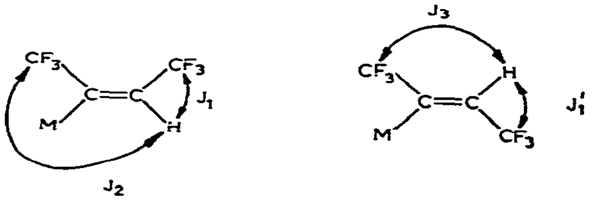
* In this paper compounds of the type $R'RC=CRR''$ are designated *cis*- or *trans*- isomers on the basis of the orientation of the groups R. R is either CF_3 or H, whichever is appropriate.

TABLE 3

^{1}H NMR DATA FOR HEXAFLUOROBUTENYL DERIVATIVES[a]



M	δ[b]	J_1	J_2	δ'	J'_1	J_3	*trans*-Isomer (%)[c]
$(CH_3)_3Si$	−5.72	8.0	⩽0.6	−6.38	8.8	2.5	100[d], 84–92[e]
$(C_2H_5)_3Ge$	−5.82	8.0	⩽1	−6.59	8.0	2.5	92[d]
$(CH_3)_3Sn$				−6.57	7.5	2.3	100[f]
$(C_2H_5)_3Sn$				−6.61	7.5	2.5	>98[f,g]
$(C_4H_9)_2Sn$				−6.64	7.0	1.5	[h]
$(CH_3)_2As$	−5.48	8.3	⩽1	−6.50	8.3	2.0	86[g]
$(CH_3)(C_6H_5)As$	−5.40	8.5	⩽1	−6.36	8.5	2.0	92[g,i]
$(CF_3)_2As$				−6.93	7.5	1.5	100[i,j]
$(CH_3)_2N$	−4.16	9.1	⩽1	−4.62	9.1	⩽1	86[g,i]
$(CO)_5Mn$					9.6	2.3	~ 100[g,k]
$(CO)_5Re$					9.1	2.5	~ 100[g,k]

[a] J values in cps. [b] Chemical shift of olefinic proton. [c] From ^{1}H NMR spectrum unless as in [f]. [d] UV reaction. [e] Dark reaction at 235° (see Table 5). [f] Estimated from VPC of compounds; NMR gives ~ 100%. [g] Dark reaction $T \leqslant 20°$. [h] $(C_4H_9)_2Sn[C(CF_3)=C(CF_3)H]_2$. [i] Ref. 3. [j] Dark reaction at 210°. [k] Ref. 4 and 5.

The assigments given for *trans*-(III) and for (IV) are based on the similarity of the spectra to those of the known compounds *trans*-$(CH_3)_2AsCH{=}CHCF_3$ and $(CH_3)_2AsC(CF_3){=}CH_2$[3]. The remaining peaks in the spectrum are presumably due to the *cis*-isomer of (III), although the coupling constants involved are not obvious. The presence of this *cis*-isomer can be inferred from the results that the mixture analyzes for the 1:1 adduct, and that in the ^{1}H NMR spectrum the ratio of the overall area of the down field peaks to the area of the two up field $[Sn(CH_3)_3]$ peaks is 2:9.2 (the calculated ratio being 2:9.0). On this basis the 1:1 adduct consists of 65% *trans*-(III), 13% *cis*-(III), and 22% (IV).

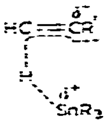
The 1:2 adduct (V) is identified by its ^{1}H NMR spectrum of one $Sn(CH_3)_3$ absorption and a methylene absorption consisting of two quartets with J(H–H) (vicinal) = 8.0 cps and $J(CF_3$–H) (geminal) = 10.5 cps. The relative intensity of the methylene absorption to the methyl is 1:10 as expected. The methine absorption was not seen. The alternative structure, $(CH_3)_3SnCH(CF_3)CH_2Sn(CH_3)_3$, would be expected to show two $Sn(CH_3)_3$ absorptions and the absorption of the CH_2 group would be expected to appear as two quartets with J(H–H) ~ 8 cps and $J(CF_3$–H) ~ 2 cps.

As described above the tin hydride–hexafluoro-2-butyne adducts (I) and (II) have predominantly the *trans*-configuration. This results is in agreement with the direction of addition to the butyne found for amines, arsines, and transition metal hydrides[3–5]. The reaction of tin hydrides with other disubstituted acetylenes has been little investigated but the results obtained from the reaction (R = alkyl)[11]

$$R_3SnH + C_2H_5OOCC{\equiv}CCOOC_2H_5 \rightarrow C_2H_5OOCC(SnR_3){=}CHCOOC_2H_5$$

indicate that the *trans*-isomer is again the major product (*trans*/*cis* ~ 9:1). Since a general rule of *trans*-nucleophilic addition to alkynes has been postulated whenever mobile protons are available[12,13] it is tempting to state that the mechanism of the hydride additions involves nucleophilic attack. However, it has recently been found that an amine such as aziridine can add to diethyl acetylenedicarboxylate to give a predominantly *cis*-product[14,15]. Thus it seems unwise to speculate on the mechanism of the hydride additions on the basis of the *cis*-*trans*-isomer distribution of the products. This is especially true if, as has been found by Fulton[16], *cis*- *trans*-isomerization of the products can be catalyzed by tin hydride. In the present investigation it seems that trimethyltin hydride catalyses the isomerization of *cis*- and *trans*-(III).

It has been pointed out[11] that it seems unlikely that the mechanism of the non-terminal addition of tin hydrides to RC≡CH involves free radical attack as has been suggested for additions to olefins[17–19]. It has recently been demonstrated that tin hydrides can act in a nucleophilic[20] or electrophilic[21] manner and some evidence that the additions to alkynes involve some degree of nucleophilic attack comes from the result that trimethyltin hydride reacts faster with hexafluoro-2-butyne than with 1,1,1-trifluoropropyne. Haszeldine[22] has shown that the butyne is more susceptible to nucleophilic attack than the propyne. Further support for this suggestion is shown in Table 4. Since nucleophilic attack by the hydride to give the non-terminal adduct could involve an intermediate of type (VI) or in the limit, (VII),


(VI)

$H_2C{=}\bar{C}R'$ (VII)

the amount of non-terminal addition would be dependent on how well the group R′ could stabilize the partial (or full) negative charge in the non-terminal carbon atom.

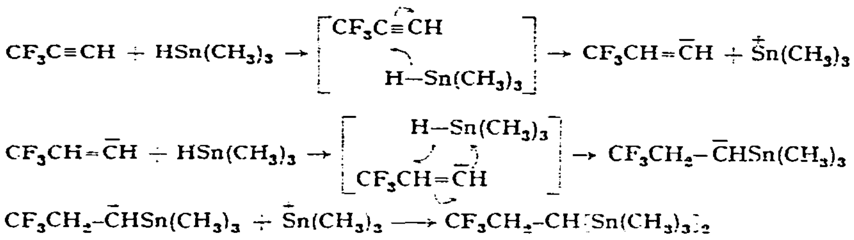
TABLE 4

DISTRIBUTION OF ISOMERS FOR THE REACTION $R_3SnH + HC{\equiv}CR' \rightarrow R_3SnCH{=}CHR' + H_2C{=}CR'SnR_3$

R	*R′*	*Terminal adduct (cis and trans)*	*Non-terminal adduct*	*Ref.*
CH_3	CN	0	100	11
C_2H_5	CN	0	100	11
n-C_4H_9	CN	0	100	11
CH_3	$COOCH_3$	19	81	11, 26
C_2H_5	$COOCH_3$	42	58	11, 20
n-C_3H_7	$COOCH_3$	69	31	11, 26
C_2H_5	CH_2OH	75	25	11
CH_3	CF_3	78	22	
CH_3	CH_3	96	4	27
C_2H_5	C_4H_9	preponderant	trace	11
CH_3	C_6H_5	preponderant	trace	11, 16

The order found, $CN > COOR > CH_2OH \sim CF_3 > CH_3 \sim C_6H_5$, is what might be expected since the first two groups not only are electronegative[11] but can delocalize the negative charge through resonance. The CF_3 group is similar in that it is electronegative and can delocalize the charge through hyperconjugation as in $C{=}C{=}CF_2F^-$[*].

The 2:1 adduct is also produced when the propyne reacts with trimethyltin hydride. It may be significant that this is not produced when the 1:1 adduct mixture is treated with trimethyltin hydride, although the proportion of the 1:2 adduct in the final reaction product depends on the initial trimethyltin hydride–propyne ratio. This suggests that an intermeidate in the formation of the 1:1 adduct is stable enough to react with a second molecule of trimethyltin hydride *e.g.*,



$$CF_3C{\equiv}CH + HSn(CH_3)_3 \rightarrow \left[\begin{array}{l} CF_3C{\equiv}CH \\ \quad\quad H{-}Sn(CH_3)_3 \end{array}\right] \rightarrow CF_3CH{=}\bar{C}H + \overset{+}{S}n(CH_3)_3$$

$$CF_3CH{=}\bar{C}H + HSn(CH_3)_3 \rightarrow \left[\begin{array}{l} \quad\quad H{-}Sn(CH_3)_3 \\ CF_3CH{=}\bar{C}H \end{array}\right] \rightarrow CF_3CH_2{-}\bar{C}HSn(CH_3)_3$$

$$CF_3CH_2{-}\bar{C}HSn(CH_3)_3 + \overset{+}{S}n(CH_3)_3 \longrightarrow CF_3CH_2{-}CH[Sn(CH_3)_3]_2$$

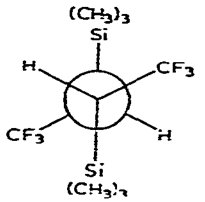
This mechanism makes the not unreasonable assumption that nucleophilic attack is also responsible for terminal addition to the propyne. It should be pointed out that electrophilic attack by the tin leads to non-terminal addition.

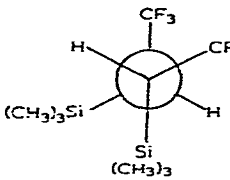
Addition of trimethylsilane and triethylgermane

The butyne and triethylgermane do not react in the dark at 20°, however, on ultraviolet irradiation the *trans*-adduct is formed in good yield (Tables 1, 2, 3). Ultraviolet irradiation of trimethylsilane and the butyne affords both the *trans*-1:1 adduct and a 1:2 adduct which can be formulated as 1,1,1,4,4,4-hexafluoro-2,3-bis-(trimethylsilyl)butane.

$$(CH_3)_3SiH + CF_3C{\equiv}CCF_3 \rightarrow (CH_3)_3SiC(CF_3){=}CHCF_3 + (CH_3)_3SiCH(CF_3)CH(CF_3)Si(CH_3)_3$$

The structure of the 1:2 adduct is best established by its NMR spectra. The proton spectrum shows a single broad $(CH_3)_3Si$ signal and a downfield multiplet of the expected relative intensity (9:1). The ^{19}F spectrum shows two broad doublets of equal intensity which can be explained on the basis of a 1:1 mixture of the *meso*- and racemic D,L-isomers of the following structures:





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[*] *Note added in proof*. It has recently been found (A. J. LEUSINK AND J. W. MARSMAN, *Rec. Trav. Chem.*, 84 (1965) 1123) that non-terminal addition of tin hydride to strongly electrophilic acetylenes such as $HC{\equiv}CCOOCH_3$ involves nucleophilic attack of the organotin hydride hydrogen. However, terminal addition seems to involve a free radical mechanism. The hydrostannation of acrylonitrile appears to be similar (A. J. LEUSINK AND J. G. NOLTES, *Tetrahedron letters*, (1966) 335).

The coupling of 12 and 13 cps can be assigned to the geminal CF_3–H interaction and the broadening to the vicinal CF_3–CF_3 and CF_3–H interactions. The two skew conformations shown would probably be the highest populated conformations of each structure because of steric considerations.

It is seen from Table 5 that the ratio of the 1:1 adduct to the 1:2 adduct decreases as the ratio of trimethylsilane to butyne increases, and that on irradiating a mixture of the 1:1 adduct and trimethylsilane only a low yield of the 1:2 adduct is obtained. The same products are obtained from the thermal reaction (235°) of the silane with the butyne although side reactions become more important. Some *cis*-isomer is produced. The high yield of tetramethylsilane obtained in one of the experiments does not result from decomposition of either the 1:1 or 1:2 adducts since it was found that these are stable under the reaction conditions.

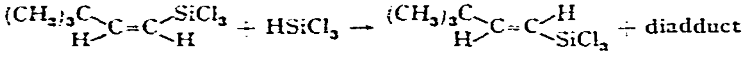
TABLE 5

REACTIONS OF SOME SILYL COMPOUNDS

Reactants (mmoles)		*Reaction conditions*	*Products (mmoles)*	
$(CH_3)_3SiH$	$CF_3C{\equiv}CCF_3$		*1:1 adduct (cis:trans)*	*1:2 adduct*
28	69	*hν*, 11 days	21.6 (0:1)	4.2
47	13	*hν*, 11 days	5.9 (0:1)	6.5
105	25	*hν*, 11 days	15.9 (0:1)	6.5
11	39	235°, 7 h	7.3 (1:15)	[a]
37	17	235°, 7 h	12.5 (1:10)	4.0[b]
48	7.9(*trans*)[c]	*hν*, 11 days	7.0 (0:1)	0.8
48	12.8(*trans*)[c]	235°, 7 h	12.5 (1:6)	

[a] The least volatile fraction contained at least 9 components by VPC analysis, however, the infrared spectrum showed that little, if any, 1:2 adduct was present. [b] A 44% yield of tetramethylsilane was also obtained. [c] $(CH_3)_3SiC(CF_3)=C(CF_3)H$.

Apart from one exception, it seems that silyl hydrides add to alkynes to give olefinic products which are predominantly obtained by *trans*-addition, in the case of peroxide catalysis, or *cis*-addition, in the case of catalysis by transition metals and their compounds[23]. In one case the peroxide catalyzed reaction has been found to yield a diadduct of unknown structure and it was shown that the diadduct resulted from the addition of the silane to the *cis*-adduct.



$$\frac{(CH_3)_3C}{H}\!>C{=}C<\!\frac{SiCl_3}{H} + HSiCl_3 \rightarrow \frac{(CH_3)_3C}{H}\!>C{=}C<\!\frac{H}{SiCl_3} + \text{diadduct}$$

The *trans*-adduct does not even isomerize under the same reaction conditions. It is suggested that the peroxide-catalyzed reactions involve free radicals.

In the present investigation the thermal addition reactions of trimethylsilane are probably also free radical in nature and thus fit into the general pattern of *trans*-addition. However, the mechanism of the UV-catalyzed reaction of the butyne with the silane and germane is not at all certain. Neither the butyne nor the hydrides have a detectable absorption above 3000Å yet the reactions take place in thick-walled Pyrex tubes.

Thermal addition of germanium hydrides to alkynes has been reported[24,25] although no information about the geometry of the adducts seems to be available.

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SUMMARY

Hexafluoro-2-butyne reacts easily with the tin hydrides R_3SnH (R = alkyl) to give mainly *trans*-$R_3SnC(CF_3){=}C(CF_3)H$. The dihydride, $(n\text{-}C_4H_9)_2SnH_2$, reacts similarly. $(CH_3)_3SiH$ and $(C_2H_5)_3GeH$ add to the butyne on UV irradiation. In the case of the silane a 1:2 adduct, $(CH_3)_3SiCHCF_3CHCF_3Si(CH_3)_3$, is also produced. Heating $(CH_3)_3SiH$ and $CF_3C{\equiv}CCF_3$ yields both 1:1 and 1:2 adducts. $(CH_3)_3SnH$ and $CF_3C{\equiv}CH$ give the non-terminal adducts $(CH_3)_3SnC(CF_3){=}CH_2$ and the *cis*- and *trans*-isomers of the terminal adducts.

The mechanism of these reactions is discussed and evidence is presented suggesting that tin hydride additions to alkynes involve some degree of nucleophilic attack by the hydride.

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