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THE REACTION OF GROUP IV HYDRIDES WITH PERHALOCYCLOBUTENES*

W. R. CULLEN AND G. E. STYAN
Chemistry Department, University of British Columbia, Vancouver 8, B.C. (Canada)

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INTRODUCTION

It has been established[1,2] that cyclobutenyl derivatives such as $(CH_3)_2As\overline{C{=}CFCF_2CF_2}$ can be obtained by reacting the fluoroolefin $\overline{CF{=}CFCF_2CF_2}$ with suitable arsenicals as follows:

$$(CH_3)_2AsH + \overline{CF{=}CFCF_2CF_2} \longrightarrow (CH_3)_2As\overline{C{=}CFCF_2CF_2} + HF \tag{1}$$

$$(CH_3)_2As\text{-}As(CH_3)_2 + \overline{CF{=}CFCF_2CF_2} \longrightarrow (CH_3)_2As\overline{C{=}CFCF_2CF_2} + FAs(CH_3)_2 \tag{2}$$

$$(CH_3)_2AsMgBr + \overline{CF{=}CFCF_2CF_2} \longrightarrow (CH_3)_2As\overline{C{=}CFCF_2CF_2} + MgBrF \tag{3}$$

It seemed desirable to try to prepare similar derivatives of other metals and metalloids since at the time of starting this investigation only two silicon containing analogues had been reported[3,4].

$$CF_2{=}CFCl + CH_2{=}CClSi(CH_3)_3 \xrightarrow{200^\circ} (CH_3)_3Si\overline{CClCFClCF_2CH_2} \xrightarrow{Zn} (CH_3)_3Si\overline{C{=}CFCF_2CH_2} \tag{4}$$

$$(CH_3)Cl_2SiH + \overline{CF{=}CFCF_2CF_2} \xrightarrow{\sim 500^\circ} (CH_3)Cl_2Si\overline{C{=}CFCF_2CF_2} + HF \tag{5}$$

Haluska[4] also claimed to have obtained compounds of the type $(CH_3)Cl_2Si\text{-}\overline{C{=}CClCF_2CF_2CF_2}$ from $(CH_3)Cl_2SiH$ and $\overline{ClC{=}CClCF_2CF_2CF_2}$ and stated that the mechanism of reaction appeared to be the addition of the silane across the double bond with subsequent elimination of hydrogen halide. Recently Stone and coworkers[5] have found that carbonylmetal anions react with certain fluoroolefins in a manner analogous to the arsinomagnesium bromide in eqn. (3), *e.g.*

$$(CO)_5Mn^- + \overline{CF{=}CFCF_2CF_2} \longrightarrow (CO)_5Mn\overline{C{=}CFCF_2CF_2} + F^- \tag{6}$$

The present paper is concerned with attempts to prepare perhalocyclobutenyl derivatives of silicon, germanium, and tin, the corresponding compounds of carbon

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being well known[6]. In preliminary experiments it was found that hexamethylditin and perfluorocyclobutene do not react at temperatures up to 100° (*cf.* eqn. 2) and that trimethyltin towards lithium and the same olefin yield an intractable gum (*cf.* eqn. 6)[7]. Therefore, in view of Haluska's success (eqn. 5)[4], the reactions of trialkyl derivatives R_3MH (M = Si, Ge, Sn) with the cyclic fluoroolefins $\overline{CX{=}CXCF_2CF_2}$ (X = F or Cl) were investigated.

Unsuccessful attempts to prepare cyclobutenylgermanes by allowing triethyl(3,3,3-trifluoropropynyl)germane to react with fluoroolefins have been described[5].

RESULTS

The reaction of trimethylsilane, -germane and -tin hydride with perfluorocyclobutene can be represented by the following equation (M = Si, Ge, Sn).

$$(CH_3)_3MH + \overline{CF{=}CFCF_2CF_2} \longrightarrow (CH_3)_3M\overline{CFCFHCF_2CF_2} \qquad (7)$$

Triethyltin hydride reacts similarly, and the conditions are summarized in Table 1. It is seen that both tin compounds are unstable. The addition product from trimethyltin hydride is obtained in 92 % yield after four days at 20° and the remaining tin is present as trimethyltin fluoride. The addition reaction, which can be followed by NMR, is slow at 20°, being approximately 3 % complete after thirty minutes. The addition product slowly decomposes to trimethyltin fluoride and 1-H-pentafluorocyclobutene, a reaction which is about 41 % complete after 10 days at 20°.

TABLE 1

DATA FOR THE REACTION $R_3MH + \overline{CF{=}CFCF_2CF_2} \longrightarrow R_3M\overline{CFCFHCF_2CF_2}$

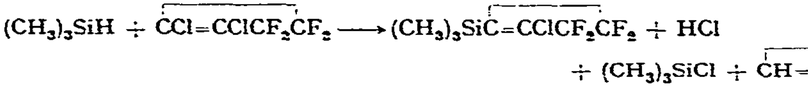
Compound		*Reaction*	*Reaction*	*Yield (%)*	*B.p. (°C)*
R	*M*	*temp. (°C)*	*time (days)*		
CH_3	Si	250	4	~ 60	112 (756 mm)
CH_3	Ge	230	3	86	118 (752 mm)
CH_3	Sn	20	4	92	decomposes
C_2H_5	Sn	20	60	3	decomposes

$$(CH_3)_3Sn\overline{CFCFHCF_2CF_2} \longrightarrow \overline{CH{=}CFCF_2CF_2} + (CH_3)_3SnF \qquad (8)$$

The reaction of triethyltin hydride gives only a 3 % yield of the addition product after two months at 20°. The remaining tin is present as triethyltin fluoride, so apparently the adduct is again unstable with respect to elimination of tin fluoride.

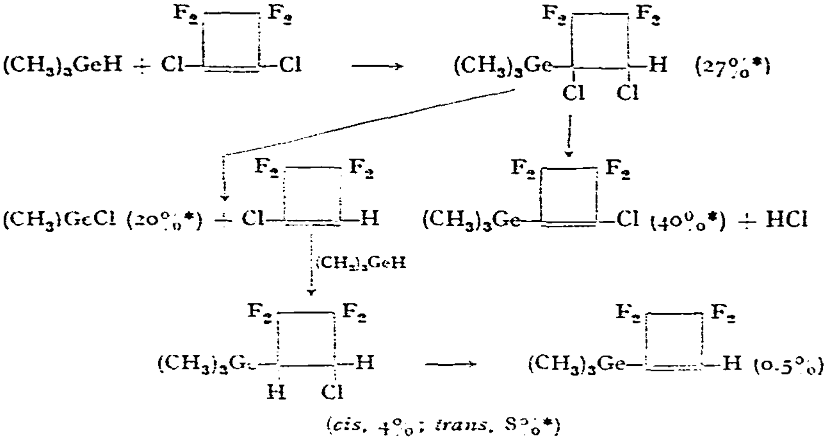
The products from the reaction of 1,2-dichlorotetrafluorocyclobutene with the Group IV hydrides vary considerably with the Group IV element. The slow reaction of trimethylsilane with the dichlorocyclobutene is not complete after twelve hours at 190°. There are two major silicon containing products, 2-chlorotetrafluorocyclobutenyl-1-trimethylsilane (60 %) and chlorotrimethylsilane (38 %), in addition to hydrogen chloride and 1-H-2-chlorotetrafluorocyclobutene.

Trimethylgermane and 1,2-dichlorotetrafluorocyclobutene give a number of products in a reaction which is 20 % complete after 36 h at 190°. VPC analysis shows



$$(CH_3)_3SiH + \overline{CCl{=}CClCF_2CF_2} \longrightarrow (CH_3)_3Si\overline{C{=}CClCF_2CF_2} + HCl + (CH_3)_3SiCl + \overline{CH{=}CClCF_2CF_2} \quad (9)$$

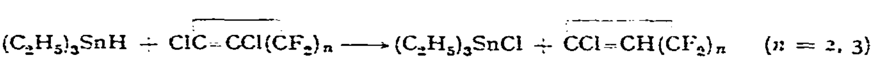
the presence of six germanium compounds, with the major components being (2-chlorotetrafluorocyclobutenyl)trimethylgermane (~ 36 %) and chlorotrimethylgermane (~ 32 %). These products and the other minor components of the reaction mixture are shown in eqn. (10) which is set out to show possible means of their formation.



(10)

The approximate yields are given and analytical data were obtained for the compounds marked by an asterisk. Although the hydrogen chloride and 1-H-2-chlorotetrafluorocyclobutene were identified, no yields were obtained.

Triethyltin hydride and 1,2-dichlorotetrafluorocyclobutene interact at 100° to give a quantitative yield of triethyltin chloride. The latter is also obtained when the hydride reacts with 1,2-dichlorohexafluorocyclopentene under the same conditions.



$$(C_2H_5)_3SnH + \overline{ClC{=}CCl(CF_2)_n} \longrightarrow (C_2H_5)_3SnCl + \overline{CCl{=}CH(CF_2)_n} \quad (n = 2, 3) \qquad (11)$$

DISCUSSION

Structures of the new compounds

The available evidence (see refs. 9 and 10 and references therein) indicates that a cyclobutane ring will accommodate a substituent by puckering in such a way as to minimize non-bonded interactions. From studies of NMR spectra of molecules such as those shown in Fig. 1 Lambert and Roberts[9,10] have suggested that they exist as an equilibrium mixture of conformers with the phenyl group in either the "axial" or "equatorial" position. The "axial" form of the phenyl methyl compound (A) is almost planar but the phenyl bromo compound (B) apparently exists in two distinct non-planar conformations as is shown in Fig. 1. At 30° both equilibria lie in favor of the left hand side with the bulky phenyl group in the "equatorial" position. Cyclobutenes appear to be planar[9,10].

$(CH_3)_3M\overline{CFCFHCF_2CF_2}$ (M = Si, Ge, Sn). These molecules are the products described in eqn. (7). Even though an elemental analysis was obtained only for the germane, the very close similarity of the infrared spectra of these compounds, Table 2, suggests that they all have the same structure. The decomposition of the tin compound to trimethyltin fluoride and 1-H-pentafluorocyclobutene (eqn. 8) is also good supporting evidence for this. The purity of the compounds and probably the presence of only one isomer is indicated by the single sharp $(CH_3)_3M$ peaks in their ^1H NMR spectra (M = Si at 0.02, Ge at −0.25, and Sn at −0.25 ppm). The downfield ^1H NMR spectrum of the germane is shown in Fig. 2 and the spectra of the tin and silicon analogues are essentially the same. The derived coupling constants from the spectrum

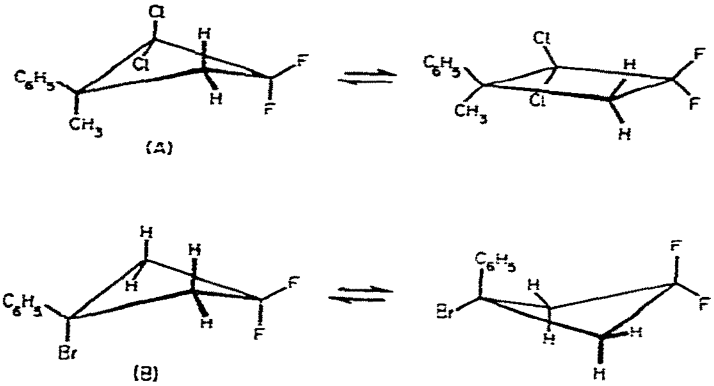


Fig. 1. Conformational equilibria for cyclobutanes.

TABLE 2

INFRARED SPECTRA OF THE COMPOUNDS $R_3M\overline{CFCFHCF_2CF_2}$[a]

$(CH_3)_3Si$	$(CH_3)_3Ge$	$(CH_3)_3Sn$	$(C_2H_5)_3Sn$[b]
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 s	1235 m
1177 vs	1185 vs	1172 vs	1170 vs, broad
1167 vs	1163 m	1150 m	
1104 m	1100 m	1091 m	1090 m
1037 s	1035 s	1018 s	1020 s
1001 s	1003 s	999 s	1000 s
956 vs	959 vs	949 vs	950 vs
831 m	829 vs	830 m	830 m
776 m	771 m	782 s	775 s

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[a] Bands associated with, for example, C–H stretching and CH_3–Si rocking frequencies are present in the spectra in their usual positions and are not given. The bands listed are presumably those associated with the $-\overline{CFCFHCF_2CF_2}$ group. [b] Approximate frequencies taken from PE 137 instrument.

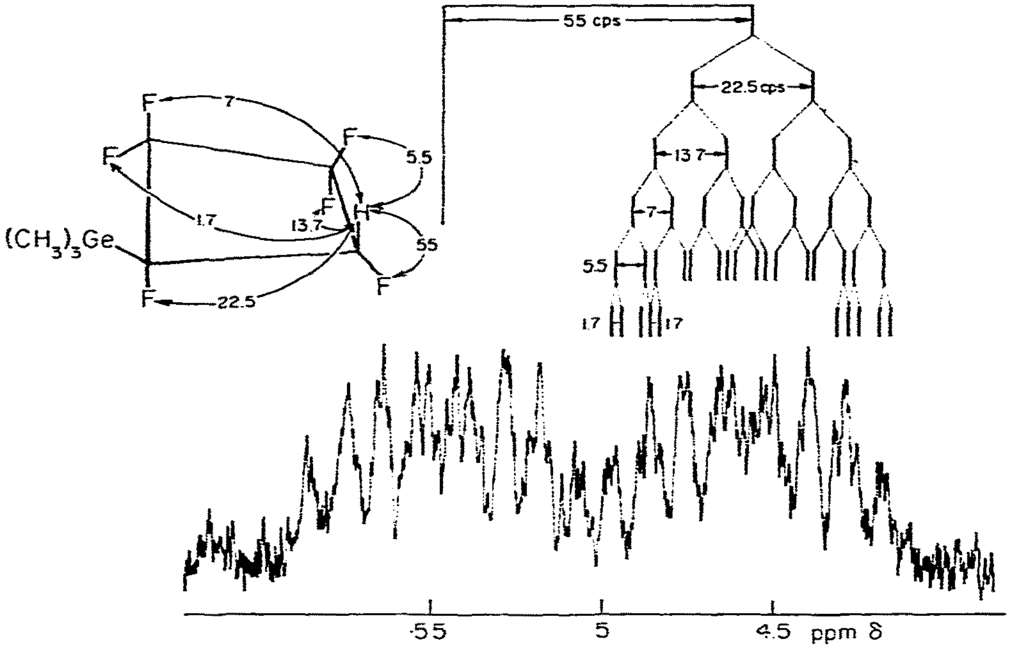


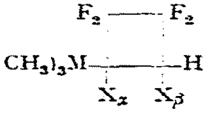
Fig. 2. ¹H NMR spectrum of $(CH_3)_3GeCFCFHCF_2CF_2$.

of Fig. 2 are shown in the figure and are listed in Table 3 together with the derived constants for the tin and silicon compounds and for $(CH_3)_3GeCClCClHCF_2CF_2$ (*q.v.*). The assignments were made on a first order basis which seems to account correctly for the observed spacings and intensitites. The ¹H NMR spectra of A and B (Fig. 1) are not first order[9,10].

In molecules such as $(CH_3)_3MCFCFHCF_2CF_2$ it seems reasonable to assume that the equilibrium will favor the conformer in which the bulky $(CH_3)_3M$ group occupies an "equatorial" position as is shown in Fig. 2. The largest coupling, ~ 50 cps, is assigned to the geminal H–F interaction. This correlation is well established and in the related compound $(CH_3)_3SnCF_2CF_2H$ it is 57 cps[11]. The coupling of 22 cps is

TABLE 3

H–F COUPLING CONSTANTS FOR THE 1:1 ADDUCTS



Compound		Vicinal	Geminal	Vicinal		Through 4 bonds	
M	*X*	*J(H–Fα)*	*J(H–Fβ)*	*Ax–Ax*	*Ax–Eq*	*Ax–Ax*	*Ax–Eq*
Si	F	22	52	~ 13	~ 6	~ 7	~ 1.5
Ge	F	22	55	13.7	5.5	7.0	1.7
Sn	F	22.5	55	12.5	5.0	7.5	2.5
Ge	Cl			12.0	4.0	8.0	⩽ 1

assigned to a vicinal H–F interaction as is the next largest coupling of 13 cps. However, since a coupling of 12 cps is present in $(CH_3)_3Ge\overline{CClCClHCF_2CF_2}$ (Table 3 and Fig. 3) the 22 cps splitting is assigned to $J(H–F_x)$. The magnitude of this interaction indicates that both the hydrogen and fluorine atoms are in "axial" positions. The vicinal "axial–axial" H–F couplings in fluorinated sugars[12] and in cyclobutanes such as A (Fig. 1) are of the order of 23 cps[10]. The vicinal "axial–equatorial" H–F couplings are considerably less (~ 12 cps).

Thus the adducts are assigned the *trans*-HF_x configuration and the "axial–axial" HF_x conformation which is consistent with the assumption that the $(CH_3)_3M$ groups are in an "equatorial" position. The remaining coupling constants listed in Table 3 are assigned analogously to those of $(CH_3)_3Ge\overline{CClCClHCF_2CF_2}$.

$(CH_3)_3Ge\overline{CClCClHCF_2CF_2}$. The structure of this molecule (eqn. 10) follows from its analysis and from its simple ^1H NMR spectrum. The downfield region of the latter is shown in Fig. 3 together with the derived coupling constants (see also Table 3).

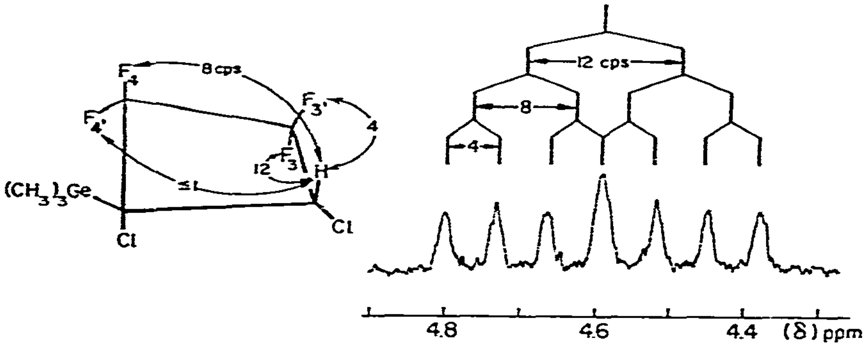


Fig. 3. ^1H NMR spectrum of $(CH_3)_3Ge\overline{CClCClHCF_2CF_2}$.

If it is again assumed that the trimethylgermyl group occupies an "equatorial" position, the greatest coupling of 12 cps can be assigned to the *trans* "axial–axial" H–F coupling, $J(H–F_3)$, on the basis that the greatest H–F coupling will be "axial–axial"[10] and that a similar value is found in the compounds described above (Table 3) Although in compound A (Fig. 1) the analogous coupling constant is 21 cps[10] substitution of a hydrogen for a chlorine (or fluorine) as in the cyclobutylgermanes would be expected to reduce the value considerably[13]. It has been found for fluorinated sugars and certain cyclobutanes such as A, that the vicinal "axial–axial" H–F coupling is two to three times the vicinal "axial–equatorial" H–F coupling. Thus $J(H–F'_3)$ is assigned the value 4 cps which leaves the 8 cps coupling to be assigned to $J(H–F_4)$. The latter should be greater than $J(H–F'_4)$[10], and 8 cps seems to be a reasonable value in view of the 2.1 cps found for a similar "axial–axial" CH_3–F coupling in A (Fig. 1)[14].

It should be emphasized that these assignments are only tentative and that especially in the case of $(CH_3)_3Ge\overline{CClCClHCF_2CF_2}$ the coupling constants could be interpreted as arising from conformers in an equilibrium of the type illustrated for B (Fig. 1), and that the hydrogen could possibly be *trans* to the trimethylgermyl group[10].

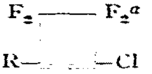
However, since the latter group is probably more bulky than a chlorine atom the suggested structure is probably correct. The internal consistency of the coupling constants (Table 3) also supports this conclusion.

$(CH_3)_3GeCHCHClCF_2CF_2$. Eqn. (10) shows that two isomers of this compound were obtained. One isomer, possibly with the hydrogen atoms *trans* to each other, was identified by analysis. The ^1H NMR spectrum of each isomer shows the expected three regions of absorption. In both cases the absorption due to the $(CH_3)_3Ge$ group is a singlet indicating the purity of the compounds. The difference in chemical shift of the two multiplets associated with the other hydrogen atoms is ~ 2 ppm in both compounds indicating that the hydrogen atoms are not geminal as they would be in the isomer $(CH_3)_3GeCClCH_2CF_2CF_2$. In this compound the chemical shift difference would probably be ~ 0.5 ppm[10]. Other isomers would involve a –CFH– group with J(H–F) ~ 50 cps. The analyzed isomer can be assigned the *trans* structure on the basis that the methine multiplets of this compound are broader than those of the other as would be expected for $J(\text{H–H})_{trans} > J(\text{H–H})_{cis}$.

$(CH_3)_3MC{=}CClCF_2CF_2$ ($M = Si$, Ge). The structures of these compounds (eqns. 9 and 10) follow from their analysis and from comparison of their infrared spectra with those of related arsenic derivatives (Table 4). It is seen that there is a very good correlation in a large number of bands and that the C=C stretching frequency is almost constant at 1576 cm^{-1} indicating very little difference in the electronic effects of the groups in the 1-position. The ^{19}F NMR spectrum of the germanium compound shows two bands of equal intensity at +110.1 and +115.3 ppm in good agreement with the arsines which show bands at ~ 108 and ~ 114 ppm[1].

TABLE 4

INFRARED DATA FOR



$R = (CH_3)_3Si$	$R = (CH_3)_3Ge$	$R = (CH_3)_2As^b$	$R = (CH_3)(C_6H_5)As^b$
1570 s	1570 s	1576 vs	1575 s
1419 m	1419 m	1420 s	1422 w
1334 vs	1333 vs	1328 vs	1329 vs
1242 vs	1241 vs	1245 vs	1240 vs
1174 w (sh)	1170 w (sh)	1172 w (sh)	1157 w (sh)
1154 w (sh)	1145 w (sh)	1150 m (sh)	1150 m (sh)
1110 vs	1112 vs	1115 vs	1121 vs
848 vs	847 s	855 s	855 s
809 s	810 m	810 s	810 m

[a] Bands associated with for example, C–H stretching and CH_3–Si rocking frequencies were present in the expected regions and are not listed. [b] From ref. 1.

$(CH_3)_3GeC{=}CHCF_2CF_2$. The infrared spectrum of this germane (eqn. 10) shows no double bond absorption, however, the corresponding arsine[15] has only a weak absorption at 1545 cm^{-1} and the C–F stretching bands of the germane occur at 1333, 1261, 1168, and 1117 cm^{-1} in good agreement with the 1330, 1265, 1160, and 1104 cm^{-1} bands of the arsine. The ^1H NMR spectrum of the germane shows a sharp singlet

due to the $(CH_3)_3Ge$ group, indicating the purity of the compound, and a downfield triplet ($J = 10.5$ cps) at -6.79 ppm in good agreement with the arsine which shows a triplet at -6.68 ppm ($J = 10$ cps).

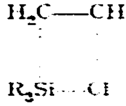
The reactions

The addition of the hydrides of silicon, germanium, and tin to olefins is well known (refs. 16 and 17 and references therein, refs. 18–21) and the generally accepted mechanism seems to involve free radical attack on the olefin. However, it has been suggested[17] that some of the thermally initiated additions of silanes may go by some other path, and recently it has been found[22] that the hydrostannation of acrylonitrile proceeds partly via a polar mechanism. Unfortunately little can be said about the mechanism of the addition reactions described by eqns. (7) and (10) since any of a number of possible mechanisms could give rise to the moderately well substantiated *cis*-addition. In one case apparently both *cis*- and *trans*-adducts are formed (eqn. 10).

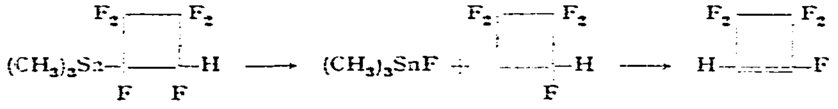
Clark and coworkers[23] obtained dimethyltin difluoride from the reaction of dimethyltin dihydride with either 1,2-difluoroethylene or trifluoroethylene. There is some evidence that these reactions proceed by addition followed by elimination although the addition products were not identified.

$$(CH_3)_2SnH_2 + CF_2{=}CFH \longrightarrow [(CH_3)_2Sn(C_2F_3H_2)_2] \longrightarrow CFH{=}CFH + (CH_3)_2SnF_2 \quad (12)$$

Similar reactions involving, for example, trimethyltin hydride and (fluorovinyl)tin compounds have recently been reported[24]. In the present investigation it has been found that the interaction of trimethyltin hydride with hexafluorocyclobutene can be represented by the sum of eqns. (7) and (8). Thus an intermediate is formed in this case. The elimination reaction (eqn. 8) is of interest in that if the cyclobutane intermediate has the configuration and conformation indicated (Fig. 2), then the type of four-center intermediate proposed for the unimolecular β-halo elimination from silyl compounds[25–27], *e.g.* (I), would be unlikely.


(I)

Thus the elimination is probably either bimolecular or involves a carbene intermediate which rearranges to give the olefin.


(13)

A similar mechanism has been proposed to explain the thermal decomposition of some fluoroalkylsilanes[21,26,27], and is certainly very likely for the tin compound since α-fluorine abstraction by tin occurs very easily[28].

The addition–elimination mechanism also seems likely for the tin hydride reductions described by eqn. (11), and for the silane and germane reactions of eqns. (9) and (10).

EXPERIMENTAL

Hexafluorocyclobutene, 1,2-dichlorotetrafluorocyclobutene, and trimethylsilane were obtained from Peninsular ChemResearch Inc. Tin hydrides were prepared from the appropriate chloride by reduction with lithium aluminium hydride[29]. Trimethylgermane was obtained by reducing trimethylgermanium bromide (from tetramethylgermane and bromine[30]) with sodium borohydride[31]. Volatile reagents and products were manipulated in a vacuum system using standard techniques. Reactions were done in sealed Pyrex tubes.

Infrared spectra were run on a Perkin–Elmer Model 21 instrument (NaCl optics) and NMR spectra on Varian A60, HR60, and HA100 spectrometers. Chemical shifts are reported in parts per million (ppm) from external tetramethylsilane (^{1}H spectra) and external trichlorofluoromethane (^{19}F spectra), positive values being to higher field. Analyses were done by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. and by the Microanalytical Laboratory, University of British Columbia.

Reactions of hexafluorocyclobutene

(*a*) *With trimethylgermane.* The germane (1.20 g) and the cyclobutene (9.36 g) were heated at 230° (3 days) to give (1,2,3,3,4,4-hexafluorocyclobutyl)trimethylgermane, b.p. 118° (752 mm) (2.46 g; 86 % yield). (Found: C, 29.7; H, 3.8. $C_7H_{10}F_6Ge$ calcd.: C, 29.9; H, 3.6 %.) Infrared spectrum: Table 2. ^{1}H NMR spectrum: Fig. 2 and Table 3.

(*b*) *With trimethyltin hydride.* When the tin hydride (2.4 g) and the cyclobutene (3.3 g) were left at 20° for 4 days a small amount of white solid (0.2 g) was produced. Perfluorocyclobutene (1.1 g) which contained a trace of 1-H-pentafluorocyclobutene was recovered. The main reaction product was a colorless liquid which condensed in a trap at —46°, and which was identified as (1,2,3,3,4,4-hexafluorocyclobutyl)trimethyltin (4.4 g; 94 % yield), by means of its infrared and NMR spectra (Tables 2 and 3).

The cyclobutyltrimethyltin compound (1.025 g) was left at 20° (10 days) to give 1-H-pentafluorocyclobutene (0.20 g), identified by its molecular weight of 144 (mass spec.) (calcd.: 144) and known infrared spectrum[32]; unchanged tin compound (0.557 g); and an involatile solid which was identified as trimethyltin fluoride, m.p. > 320°. (Found: C, 20.0; H, 5.0. C_3H_9FSn calcd.: C, 19.7; H, 4.9 %.)

(*c*) *With trimethylsilane.* Trimethylsilane (7.3 g) and the butene (5.5 g) were heated to 250° (4 days). Hydrogen was produced of molecular weight 2.1 (calcd.: 2.0) and trap-to-trap distillation gave slightly impure trimethylsilane (5.9 g) and a fraction (5.5 g) which condensed in a trap at —64° and which on distillation in an atmosphere of nitrogen gave a main cut b.p. 112° (756 mm). This was identified as (1,2,3,3,4,4-hexafluorocyclobutyl)trimethylsilane by its molecular weight of 237 (calcd.: 236) and infrared and NMR spectra (Tables 2 and 3). The compound was unstable to air and a satisfactory analysis was not obtained.

A third fraction from the original reaction (1.3 g) which condensed in a trap at —23° was found to contain at least 5 components by VPC (5 ft. dinonyl phthalate column at 100°), none of which were identified.

Reactions of 1,2-dichlorotetrafluorocyclobutene.

(*a*) *With trimethylsilane.* The silane (2.4 g) and the butene (11.5 g) were heated at 190° (12 h) to give hydrogen of molecular weight 3 (calcd.: 2.0); hydrogen chloride (0.34 g), molecular weight 36.5 (calcd.: 36.5); a mixture of trimethylsilane and tetramethylsilane (0.3 g; mol. wt., 82) of known infrared spectrum; and a mixture of unreacted cyclobutene and chlorotrimethylsilane (8.5 g) which distilled in the range 60–70° (760 mm) and which gave 1.8 g of silver chloride on being added to aqueous silver nitrate. (Pure cyclobutene does not react with aqueous silver nitrate.) The main reaction product, (2-chloro-3,3,4,4-tetrafluorocyclobutenyl)trimethylsilane (4.5 g; 60 % yield) condensed in a trap at −23° and was purified by distillation, b.p. 132° (760 mm). (Found: C, 36.1; H, 3.9; Cl, 15.5; F, 32.7. $C_7H_{10}ClF_4Si$ calcd.: C, 36.1; H, 3.9; Cl, 15.2; F, 32.7 %.) Infrared spectrum: Table 4.

(*b*) *With triethyltin hydride.* After 2.9 g of the tin hydride and 11.0 g of the cyclobutene were heated at 100° for one day, the volatile fraction (10.9 g) contained no triethyltin compounds but did contain a mixture of unchanged butene and 1-H-2-chlorotetrafluorocyclobutene of known infrared spectra. The involatile liquid left in the tube was identified as triethyltin chloride (3.1 g, 91 %) of known infrared spectrum and retention time on a 5 ft. Ucon Polar VPC column at 175°.

(*c*) *With trimethylgermane.* The germane (3.4 g) and the cyclobutene (6.62 g) were heated at 190° (36 h). The more volatile fraction which did not condense in a trap at −46° showed Ge–H infrared absorption and was further heated at 230° (3 days). The fraction which condensed at −46° (1.3 g) could not be separated further by trap-to-trap distillation or distillation at atmospheric pressure. However, separation was achieved by VPC (10 ft. silicone column at 160°) into 6 components as follows (in order of elution, percentages were determined from the area of the peak on the chromatogram):

(*i*) (20 %) identified as chlorotrimethylgermane, b.p. 102° (lit.[33] 102°) of known infrared spectrum. (Found: C, 23.9; H, 5.9. C_3H_9ClGe calcd.: C, 23.5; H, 5.9 %.)

(*ii*) (0.5 %) identified as (3,3,4,4-tetrafluorocyclobutenyl)trimethylgermane by means of its infrared and ^1H NMR spectrum. The latter (CCl_4 solution) consisted of a singlet at −0.33 ppm [$(CH_3)_3Ge$] and a triplet at −6.79 ppm ($J = 9.5$ cps) of relative area, singlet to triplet, 8.9:1 (calcd.: 9:1). Infrared spectrum (CCl_4 solution, main bands only): 1333 s, 1261 s, 1168 s, 1130 m, 1117 vs, 1091 m, 833 s, cm^{-1}.

(*iii*) (40 %) identified as (2-chloro-3,3,4,4-tetrafluorocyclobutenyl)trimethyl germane, b.p. 78° (50 mm). (Found: C, 29.9; H, 3.7. $C_7H_9ClF_4Ge$ calcd.: C, 30.3; H, 3.3 %.) ^1H NMR spectrum a singlet at −0.21 ppm [$(CH_3)_3Ge$]. ^{19}F NMR spectrum: two multiplets of equal intensity at +110.1 and +115.3 ppm. Infrared spectrum: Table 4.

(*iv*) (4 %) identified as an isomer of (2-chloro-3,3,4,4-tetrafluorocyclobutyl)-trimethylgermane by means of its ^1H NMR spectrum (CCl_4 solution) of a singlet at −0.31 ppm [$(CH_3)_3Ge$] and multiplets at −2.3 and 4.05 ppm of relative area 9:0.9:1 (calcd. 9:1:1). Infrared spectrum (liquid film, main bands only): 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}.

(*v*) (8 %) identified as an isomer of (2-chloro-3,3,4,4-tetrafluorocyclobutyl)-trimethylgermane, b.p. 80–82° (50 mm). (Found: C, 30.3; H, 3.8; Cl, 12.4; F, 27.4; Ge, 25.6. $C_7H_{11}ClF_4Ge$ calcd.: C, 30.1; H, 4.0; Cl, 12.7; F, 27.2; Ge, 26.0 %.) ^1H NMR spectrum: a singlet at −0.29 ppm [$(CH_3)_3Ge$] and multiplets at −2.57 and −4.56 ppm of relative area 9:1:0.9 (calcd.: 9:1:1).

(*vi*) (27 %) a solid, m.p. ~ 23°, identified as (1,2-dichloro-3,3,4,4-tetrafluorocyclobutyl)trimethylgermane, b.p. 86° (50 mm), by means of analysis and its NMR and infrared spectra. (Found: C, 26.4; H, 3.23. $C_7H_{10}Cl_2F_4Ge$ calcd.: C, 26.8; H, 3.19 %.) Infrared spectrum (CCl_4 solution, main bands only): 1356 s, 1276 m, 1245 s, 1219 s, 1179 s, 1145 m, 1124 s, 1105 m, 1073 m, 1030 m, 959 m, 875 s, 863 s, cm^{-1}. ^1H NMR spectrum (CCl_4 solution): singlet at −0.49 ppm [$(CH_3)_3Ge$] and a septet at −4.60 ppm (J = 4 cps) of relative intensity 1:9.2 (calcd.: 1:9) (see Fig. 3).

The material which was heated at 230° for 3 days contained hydrogen chloride, unreacted dichlorocyclobutene, 1-H-2-chlorotetrafluorocyclobutene of known infrared spectra, and again a fraction which condensed at −46°. VPC examination showed that except for component (*vi*) the same compounds were present as described above in the ratio (*i*):(*ii*):(*ii*):(*iv*):(*v*) = 5:1:10:1:2.

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SUMMARY

The compounds $(CH_3)_3MH$ (M = Si, Ge, Sn) react with $FC{=}CFCF_2CF_2$ to give the 1:1 adducts $(CH_3)_3MCFCFHCF_2CF_2$. The tin compound decomposes at 20° to $(CH_3)_3SnF$ and $HC{=}CFCF_2CF_2$. The main products from the interaction of $(CH_3)_3MH$ (M = Si, Ge) with $ClC{=}CClCF_2CF_2$ are $(CH_3)_3MCl$ and $(CH_3)_3MC{=}CClCF_2CF_2$, other minor products have been obtained from the germane reaction. $(C_2H_5)_3SnH$ and $ClC{=}CCl(CF_2)_n$ (n = 2, 3) yield $(C_2H_5)_3SnCl$ and $HC{=}CCl(CF_2)_n$. The structures of the new compounds are discussed.

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