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PERFLUOROALKYNYL DERIVATIVES
II. THE PREPARATION OF SOME GROUP IV COMPOUNDS

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SUMMARY

Group IV organometallic halides, $(CH_3)_nMX_{4-n}$, (M = Si, Ge, Sn; n = 0–3, X = usually Cl but also Br), react with $R_fC{\equiv}CMgY$ (R_f = CF_3, CF_2CF_3, $CF(CF_3)_2$) to give the appropriate Group IV perfluoroalkynyl derivatives, $(CH_3)_nM(C{\equiv}CR_f)_{4-n}$, (not all combinations of R_f, n, and M are described). CH_3SiCl_3 is an exception in that it yields only $(CH_3)_2Si(C{\equiv}CCF_3)_2$ and not the expected product $CH_3Si(C{\equiv}CCF_3)_3$. The silicon and germanium derivatives are hydrolytically and thermally stable: the tin derivatives are not. Some spectroscopic properties of the new derivatives are described and discussed.

INTRODUCTION

Research into the preparation and properties of fluoro-organometallic derivatives has, until recently, been mainly confined to aliphatic [1–3] and olefinic systems [1–5]. Fluoroalkynyl derivatives have been largely unexplored although a large number of non-fluorinated alkynyl derivatives of metals and metalloids have been described [6, 7]. Apart from our previous paper in this series [8] describing some Group IV and V derivatives of 3,3,3-trifluoropropyne, and a recent report describing tetrakis-(3,3,3-trifluoropropynyl)silane [9], little work has been reported concerning fluoroalkynyl derivatives of the Main Group elements [10]. We now report an extension of our earlier investigations [8] to include the preparation of Group IV derivatives of the alkynes $HC{\equiv}CR_f$ (R_f=CF_2CF_3 and $CF(CF_3)_2$). Preliminary reports of some of this work have been published [11].

EXPERIMENTAL

The following chemicals were purchased: CF_3I, CF_3CF_2I, $(CF_3)_2CFI$, $GeCl_4$ from Peninsular ChemResearch Inc.; $(CH_3)_2GeCl_2$, CH_3GeCl_3, $(CH_3)_4Sn$,

$(CH_3)_2SnCl_2$, $SnCl_4$ from Alfa Inorganics Ltd.; $CF_3CCl{=}CCl_2$ from Columbia Organic Chemicals; $(CH_3)_2SiCl_2$, CH_3SiCl_3 from Dow–Corning Chemicals Inc. All these compounds were found to be at least 99% pure, except $(CH_3)_2GeCl_2$ which contained 15% of an impurity believed to be CH_3GeCl_3. Nevertheless the $(CH_3)_2GeCl_2$ was used without further purification.

The following were prepared according to procedures described in the literature: $CF_3C{\equiv}CH$ [12], $CF_3CF_2C{\equiv}CH$ [13], $(CF_3)_2CFC{\equiv}CH$ [14], $(CH_3)_3GeBr$ [15] (*via* $(CH_3)_4Ge$ [16]), and $(CH_3)_3SnCl$ [17].

Volatile reactants and products were manipulated using standard vacuum techniques. A specially designed apparatus [18] was used in handling potentially air-sensitive, toxic, or low-boiling compounds, particularly during analysis by vapour phase chromatography (VPC). Unless otherwise indicated, reactions were carried out in thick-walled Carius tubes. Molecular weights of gases were determined by Regnault's method. Micro-boiling points were determined using Siwoloboff's method [19] and are reported at atmospheric pressure.

Infrared spectra were obtained using Perkin–Elmer model 21 and 457 instruments. The ^1H NMR spectra were obtained using either Varian A-60 or Jeolco C-60H instruments both operating at 60 MHz. The ^{19}F NMR spectra were obtained using a Varian HA-100 spectrometer operating at 94.07 MHz.

Elemental analyses were carried out by Mr. P. Borda of this department, Schwarzkopf Microanalytical Laboratory, Woodside, New York, Drs. F. and E. Pascher, Bonn, West Germany, and Dr. Alfred Bernhardt, Elbach Uber Engelskirchen, West Germany.

Preparation of perfluoroalkynyl derivatives

The perfluoroalkynyl Grignard reagents were prepared by an exchange reaction between the appropriate alkyne and a Grignard reagent prepared from either an alkyl (usually methyl) or aryl halide. Previously reported procedures [8, 11] have involved carrying out this reaction in a sealed tube. This procedure is, however, inherently dangerous because of the methane or ethane usually evolved during the reaction, and so a safer procedure was developed.

The preparation of trimethyl-3,3,3-trifluoropropynylgermane is described as an example. A 250 ml flask was equipped with a magnetic stirrer, a bubbler which extended to the bottom of the flask, a dropping funnel with a pressure-equalizing arm, and a low-temperature condenser cooled to —78°. A portable trap, also cooled to —78° was connected in line between the low-temperature condenser and a paraffin-oil bubbler. The 3,3,3-trifluoropropyne (9.0 g, 95.8 mmole), contained in a Carius tube equipped with a Teflon valve, was bubbled slowly into the flask containing a slight molar excess of a diethyl ether solution of CH_3MgI (105.5 mmole). After the addition of the propyne was complete the solution was stirred vigorously for ~ 15 min. The low-temperature condenser was then replaced by a water-cooled condenser, and the mixture was heated under reflux for 5-10 min.

When the flask had cooled, trimethylgermanium bromide (12 g, 60.8 mmole), dissolved in a small quantity of ether, was slowly added with vigorous stirring, and the mixture was refluxed for 3 h. The excess Grignard was then decomposed with a saturated aqueous ammonium chloride solution*.

The ether layer was separated and the aqueous layer extracted with small portions of ether. The combined ether solution was dried over $CaCl_2$, and most of the ether was distilled off at atmospheric pressure. The remaining volatiles were removed under vacuum with heating. Distillation of this fraction at atmospheric pressure gave a fraction, b.p. 112–114°, which was purified by VPC.

In the cases of $CH_3Ge(C{\equiv}CCF_3)_3$ and $Ge(C{\equiv}CCF_3)_4$, which are solids at room temperature, purification was accomplished by vacuum sublimation on to a probe cooled to $-78°$, followed by recrystallization from hot hexane. The purification of $(CH_3)_2Ge(C{\equiv}CCF_3)_2$ was complicated by the presence of a large number of by-products. Two main fractions were obtained from the initial distillation of b.p. 118–125° and 137–138° respectively. VPC purification gave $(CH_3)_2Ge(C{\equiv}CCF_3)_2$ as one of the two main components of the lower boiling fraction.

RESULTS AND DISCUSSION

The reaction of a perfluoroalkynyl Grignard reagent with a Group IV organometallic halide has been found to be a successful synthetic route to the preparation of Group IV perfluoroalkynyl derivatives. The reaction sequence can be represented as follows:

$$RY + Mg \rightarrow RMgY \qquad (1)$$

$$RMgY + HC{\equiv}CR_f \rightarrow YMgC{\equiv}CR_f \qquad (2)$$

$$(CH_3)_nMX_{4-n} + (4-n)\,YMgC{\equiv}CR_f \rightarrow (CH_3)_nM(C{\equiv}CR_f)_{4-n} + (4-n)\,MgXY \qquad (3)$$

(X = usually Cl, also Br; M = Si, Ge, or Sn; $R_f = CF_3$, C_2F_5, or $CF(CF_3)_2$).

The new compounds so prepared are listed in Table 1. Similar reactions have been used to prepare perfluoroalkyl and perfluorovinyl derivatives of the Group IV metals [1–5].

The compounds $YMgC{\equiv}CCF_3$ (Y = Br, I) (eq. (2)) can be prepared by the reaction of $HC{\equiv}CCF_3$ with $C_6H_5CH_2MgBr$, C_6H_5MgBr, or C_6H_5MgI. Preparation of the propynyl Grignard reagent *via* CH_3MgI or C_2H_5MgBr has been

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* Only during the preparation of the germanium derivatives could the reaction mixture be treated with an aqueous ammonium chloride solution. In the cases of the silicon and tin derivatives complete decomposition of the metal–alkynyl derivative took place. One of the decomposition products was the free alkyne which was collected in the portable trap.

reported previously[8,20,21]. We find that methyl iodide is the best starting halide in that it gives better yields and allows easier purification of the final products. The acetylenic hydrogen atoms of the fluoroalkynes $HC{\equiv}CCF_2CF_3$ and $HC{\equiv}CCF(CF_3)_2$, like that of $HC{\equiv}CCF_3$, are also sufficiently acidic to displace methane from CH_3MgI. All these alkynyl Grignard reagents seem to be stable in refluxing diethyl ether. Perfluoroalkyl and perfluoroalkynyl Grignard reagents are less stable[1–5].

It can be seen from Table 1 that all the Group IV halides produced the corresponding alkynyl derivatives, with the exception of CH_3SiCl_3, which yielded, surprisingly, $(CH_3)_2Si(C{\equiv}CCF_3)_2$. None of the expected product was detected. It seems likely that a re-distribution reaction takes place within the reaction mixture as follows:

$$2CH_3Si(C{\equiv}CCF_3)_3 \rightarrow (CH_3)_2Si(C{\equiv}CCF_3)_2 + Si(C{\equiv}CCF_3)_4 \qquad (4)$$

TABLE 1

PREPARATION OF THE GROUP IV PERFLUOROALKYNYL DERIVATIVES (ALL NEW COMPOUNDS)

Starting Halide (RY)	Perfluoroalkynyl Grignard Reagent	+	Metal Halide	→	Metal Perfluoroalkynyl Derivative[a]	B.p.°C (atm)[f] (m.p.°C)	% Yield
Derivatives of $HC{\equiv}CCF_3$							
CH_3I	$IMgC{\equiv}CCF_3$	+	$(CH_3)_2SiCl_2$	→	$(CH_3)_2Si(C{\equiv}CCF_3)_2$	111[g]	11
CH_3I	$IMgC{\equiv}CCF_3$	+	CH_3SiCl_3	→	$(CH_3)_2Si(C{\equiv}CCF_3)_2$	111[g]	~5
CH_3I	$IMgC{\equiv}CCF_3$	+	$(CH_3)_3GeCl$	→	$(CH_3)_3GeC{\equiv}CCF_3$	94[g]	14.5
C_2H_5Br	$BrMgC{\equiv}CCF_3$	+	$(CH_3)_2GeCl_2$	→	$(CH_3)_2Ge(C{\equiv}CCF_3)_2$	126[g]	10
CH_3I	$IMgC{\equiv}CCF_3$	+	CH_3GeCl_3	→	$CH_3Ge(C{\equiv}CCF_3)_3$	132–133.5[g] (47)	7[e]
CH_3I	$IMgC{\equiv}CCF_3$	+	$GeCl_4$	→	$Ge(C{\equiv}CCF_3)_4$	(101.5–102.5)	10
CH_3I	$IMgC{\equiv}CCF_3$	+	$(CH_3)_3SnCl$	→	$(CH_3)_3SnC{\equiv}CCF_3$	125[h]	64[b,d]
C_2H_5Br	$BrMgC{\equiv}CCF_3$	+	$(CH_3)_2SnCl_2$	→	$(CH_3)_2Sn(C{\equiv}CCF_3)_2$	156[g]	21[c]
Derivatives of $HC{\equiv}CCF_2CF_3$							
CH_3I	$IMgC{\equiv}CCF_2CF_3$	+	$(CH_3)_3GeBr$	→	$(CH_3)_3GeC{\equiv}CCF_2CF_3$	104[g]	74
CH_3I	$IMgC{\equiv}CCF_2CF_3$	+	$(CH_3)_2GeCl_2$	→	$(CH_3)_2Ge(C{\equiv}CF_2CF_3)_2$	138[g]	67
CH_3I	$IMgC{\equiv}CCF_2CF_3$	+	$(CH_3)_3SnCl$	→	$(CH_3)_3SnC{\equiv}CCF_2CF_3$	131[g]	20
Derivative of $HC{\equiv}CCF(CF_3)_2$							
CH_3I	$IMgC{\equiv}CCF(CF_3)_2$	+	$(CH_3)_3GeBr$	→	$(CH_3)_3GeC{\equiv}CCF(CF_3)_2$	113.1[g]	77

[a] Only one product was isolated and identified in each reaction.

[b] C_2H_5Br and C_6H_5Br both gave much lower yields ~ 5%.

[c] C_6H_5Br and C_6H_5I both gave much lower yields and the products could not be isolated.

[d] Best yield of three attempts using CH_3I. Other yields: 10% and 13%.

[e] The yield was probably considerably higher.

[f] Boiling points are recorded, uncorrected, at atmospheric pressure.

[g] Micro-boiling point.

[h] By distillation.

TABLE 2

ANALYTICAL DATA FOR THE GROUP IV PERFLUOROALKYNYL DERIVATIVES

	Purification Procedure	Found % C	H	F	M	Calculated % C	H	F	M
$(CH_3)_2Si(C\equiv CCF_3)_2$	VPC; 20% silicone GE-SS-96 at 55°	39.19	2.28	46.41		39.35	2.48	46.68	
$(CH_3)_3GeC\equiv CCF_3$	VPC; 20% SE-30 at 103° or 20% dinonyl phthalate at 85°	33.83	4.35			34.19	4.28		
$(CH_3)_2Ge(C\equiv CCF_3)_2$	VPC; Apiezon-J at 120° followed by dinonyl phthalate at 125°	33.22	2.41	40.23		33.31	2.09	39.5	
$CH_3Ge(C\equiv CCF_3)_3$	sublimation	32.99	0.99	46.40		32.75	0.82	46.63	
$Ge(C\equiv CCF_3)_4$	sublimation	32.60		51.00		32.41		51.26	
$(CH_3)_3SnC\equiv CCF_3$	distillation	28.22	3.82	22.20	46.09	28.06	3.53	22.19	46.21
$(CH_3)_2Sn(C\equiv CCF_3)_2$	VPC; 20% silicone GE-SS-96 at 158°	28.55	1.85	33.81	35.51	28.67	1.81	34.05	35.45
$(CH_3)_3GeC\equiv CCF_2CF_3$	VPC; 20% Kel-F grease at 85°								
$(CH_3)_2Ge(C\equiv CCF_2CF_3)_2$	VPC; 20% Kel-F grease at 115° followed by 20% silicone GE-SS-96 at 110°	30.69	1.55			30.90	1.56		
$(CH_3)_3SnC\equiv CCF_2CF_3$	VPC; 20% silicone GE-SS-96 at 75°	27.42	3.10	30.69		27.40	2.96	30.96	
$(CH_3)_3GeC\equiv CCF(CF_3)_2$	VPC; 20% Kel-F grease at 80°	30.89	2.91	42.90	23.13	30.93	2.91	42.79	23.63

TABLE 3

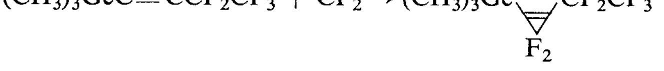
PARTIAL INFRARED SPECTRA OF THE PARENT FLUOROALKYNES AND GROUP IV PERFLUOROALKYNYL DERIVATIVES[a]

$HC\equiv CCF_3$[c]	3330	2165	1254	1222	1182			
$(CH_3)_3SiC\equiv CCF_3$[d]		2205	1262	1222	1165			
$(CH_3)_2Si(C\equiv CCF_3)_2$		2221	1250	1222	1179			
$(CH_3)_3GeC\equiv CCF_3$		2201	1261	1219	1163			
$(CH_3)_2Ge(C\equiv CCF_3)_2$		2208	1251	1221	1179			
$CH_3Ge(C\equiv CCF_3)_3$[b]		2223	1241	1218	1166			
$Ge(C\equiv CCF_3)_4$[b]		2225	1241	1219	1155			
$(CH_3)_2Sn(C\equiv CCF_3)_2$		2195	1242	1220	1172			
$(CH_3)_3SnC\equiv CCF_3$		2188	1252	1219	1164			
$HC\equiv CCF_2CF_3$	3339	2160	1348	1237	1205	1150	1052	
$(CH_3)_3GeC\equiv CCF_2CF_3$		2195	1339	1225	1200	1130	1050	
$(CH_3)_2Ge(C\equiv CCF_2CF_3)_2$		2200	1340	1226	1207	1137	1051	
$(CH_3)_3SnC\equiv CCF_2CF_3$		2182	1346	1231	1208	1133	1054	
$HC\equiv CCF(CF_3)_2$	3340	2155	1319	1282	1259	1189	1160	1079
$(CH_3)_3GeC\equiv CCF(CF_3)_2$		2182	1312	1272	1245	1182	1158	1077

[a] Main bands only (in cm^{-1}) in the C–H, $C\equiv C$, and C–F stretching regions taken from vapor spectra unless otherwise indicated.
[b] Mull.
[c] From Reference 28.
[d] From Reference 8.

The compound $Si(C\equiv CCF_3)_4$ has been recently reported as a solid[9] and would not have been detected using the present methods of isolation and purification. Some support for eq. (4) comes from the report that the tetra-organosilanes $C_2H_5Si(CH_3)_3$ and $C_2H_5Si(C_6H_5)_3$ both thermally disproportionate to give $(C_2H_5)_2SiR_2$ products[22]. However, these latter reactions take place under rather extreme conditions (300° and 100 atm).

The analytical and spectroscopic data for the new compounds listed in Tables 2–4 leave no doubt concerning their proposed structures. Only one compound, $(CH_3)_3GeC\equiv CCF_2CF_3$, failed to give good microanalytical results, in spite of appearing to be pure as judged by its chromatographic behaviour and spectroscopic properties. Confirmation of its structure was obtained from the complete characterization, including a good microanalysis, of the cyclopropene $(CH_3)_3Ge\overline{C{=}C(CF_2CF_3)C}F_2$, formed by the addition of a molecule of difluorocarbene (from $(CH_3)_3SnCF_3$) across the triple bond[11, 23].



$$(CH_3)_3GeC\equiv CCF_2CF_3 + CF_2 \rightarrow (CH_3)_3Ge\underset{F_2}{\triangledown}CF_2CF_3 \qquad (5)$$

Although the carbanion $CF_3C\equiv C^-$ is expected to be unusually stable, in keeping with the high acidity of alkynes and the large stabilizing effect of the very electronegative fluorine atoms, only the tin perfluoroalkynyl derivatives are unusually unstable with respect to hydrolysis. The silicon derivative, $(CH_3)_2Si(C\equiv CCF_3)_2$, is both hydrolytically and thermally stable in air at 20°. The stability

TABLE 4

NMR PARAMETERS OF THE PARENT FLUOROALKYNES AND GROUP IV PERFLUOROALKYNYL DERIVATIVES

	^{1}H spectra[a,f]			^{19}F spectra[f]					
	δ(H)	$J(^{117}Sn\text{-}CH_3)$	$J(^{119}Sn\text{-}CH_3)$	$\delta(CF_3)$	$\delta(CF_2)$	δ(CF)	J(F–F)	$J(F^{\alpha}\text{-}H)$	$J(F^{\beta}\text{-}H)$
$HC\equiv CCF_3$	−1.88			55.55[b]				3.5	
$(CH_3)_3SiC\equiv CCF_3$	+0.20[e]			49.95[e]					
$(CH_3)_2Si(C\equiv CCF_3)_2$	−0.10			53.41[b]					
$(CH_3)_3GeC\equiv CCF_3$	−0.17			51.35[b]					
$(CH_3)_2Ge(C\equiv CCF_3)_2$	−0.39			52.6[b]					
$CH_3Ge(C\equiv CCF_3)_3$	−1.07			52.85[c,d]					
$Ge(C\equiv CCF_3)_4$				53.35[c,d]					
$(CH_3)_3SnC\equiv CCF_3$	−0.26	58.2	61.0	50.25[b]					
$(CH_3)_2Sn(C\equiv CCF_3)_2$	−0.49	68.6	72.7	51.54[b]					
$HC\equiv CCF_2CF_3$	−2.23			88.7[b]	105.9		3.6	5.3	0.5
$(CH_3)_3GeC\equiv CCF_2CF_3$	−0.16			86.65[b]	101.9		4.1		
$(CH_3)_2Ge(C\equiv CCF_2CF_3)_2$	−0.47			86.9[b]	103.7		3.8		
$(CH_3)_3SnC\equiv CCF_2CF_3$	−0.22	59.0	61.7	86.43	101.1		4.1		
$HC\equiv CCF(CF_3)_2$	−2.35			90.7[b]		171.8	9.9	6.0	0.4
$(CH_3)_3GeC\equiv CCF(CF_3)_2$	−0.18			73.0[c]		166.0	10.6		

[a] Chemical shift, δ, in ppm with respect to external $(CH_3)_4Si$.

[b] Chemical shift, δ, in ppm with respect to external $CFCl_3$.

[c] Chemical shift, δ, in ppm with respect to internal $CFCl_3$ in solution with sample.

[d] $CDCl_3$ solution.

[e] From Reference 8. The original value of −26.6 ppm downfield from CF_3COOH has been converted to a chemical shift relative to $CFCl_3$ by using $\delta(CF_3COOH) = +76.6$ ppm upfield from $CFCl_3$. (J. J. BURKE AND T. R. KRUGH, *A table of ^{19}F chemical shifts for a variety of compounds*, Mellon Institute, Pittsburgh, Penn., (U.S.A.)).

[f] Coupling constants J in Hz.

of other silicon alkynyls varies, although most are cleaved by strong nucleophilic agents. It is particularly interesting that the analogous compound $(CH_3)_2Si(C{\equiv}CC_6H_5)_2$ is stable to hot water[24].

All the germanium derivatives are both hydrolytically and thermally stable at 20°. In addition, the compound $(CH_3)_2Ge(C{\equiv}CCF_3)_2$ yields only a trace of propyne after heating with water for 24 h at 105°. This stability is in keeping with the stability of tetra-alkyl and tetra-arylgermanes which are stable in air even at quite high temperatures[25]. The solid germanes, $CH_3Ge(C{\equiv}CCF_3)_3$, and $Ge(C{\equiv}CCF_3)_4$, are both stable to impact and rapid heating. The stability of the tetra-substituted derivative contrasts with that of $Ge(C{\equiv}CH)_4$, which detonates explosively on impact[26].

The tin derivatives $(CH_3)_3SnC{\equiv}CR_f$ ($R_f = CF_3$, C_2F_5) and $(CH_3)_2Sn(C{\equiv}CCF_3)_2$ are all both hydrolytically and thermally unstable. Furthermore, relative to each other, their stability is found to decrease as the size of the R_f group increases and as the number of perfluoroalkynyl substituents increases. Thus, $(CH_3)_3SnC{\equiv}CCF_3$ is thermally stable in the absence of air at 20°, $(CH_3)_3SnC{\equiv}CCF_2CF_3$, under the same conditions, is stable only at 0°, and $(CH_3)_2Sn(C{\equiv}CCF_3)_2$, under the same conditions, decomposes at 0°. All three tin compounds are readily cleaved by water at 25° to give the starting fluoroalkyne. After 24 h at 25° $(CH_3)_3SnC{\equiv}CCF_3$ yields 98% of the expected amount of $HC{\equiv}CCF_3$, while $(CH_3)_2Sn(C{\equiv}CCF_3)_2$ yields 76%. Hydrolysis of $(CH_3)_3SnC{\equiv}CCF_2CF_3$ is slower (72% after 28 days at 25°). This neutral hydrolysis should be compared with the reaction[27],

$$2R'C{\equiv}CH + R_3SnOSnR_3 \rightarrow 2R'C{\equiv}CSnR_3 + H_2O \tag{6}$$
$$(R' = C_6H_5,\ CH_3O,\ CH_2{=}CH,\ NC{-}C{\equiv}C;\ R = C_2H_5,\ C_4H_9,\ \text{or}\ C_6H_5)$$

The difference can be explained on the basis of the effect of the fluorine atoms, which, being highly electronegative, shift the electron density along the internuclear axis and leave a polarized tin–carbon bond which makes the tin atom sufficiently electrophilic to undergo attack by the water molecule.

Spectroscopic Results

The main bands in the infrared spectra of the derivatives of 3,3,3-trifluoropropyne (Table 3) can all be assigned. The absorption at 2225–2201 cm^{-1} is due to the $C{\equiv}C$ stretching vibration. The strong bands at 1250 ± 11 cm^{-1} and 1157 ± 22 cm^{-1} can be assigned to the approximately fundamental C–F symmetric and asymmetric stretching modes, respectively; the corresponding bands in the spectrum of $HC{\equiv}CCF_3$ occur at 1254 and 1182 cm^{-1} [28]. The band at 1218 ± 4 cm^{-1} is of medium strength and is probably an overtone of the fundamental mode associated with the $-CF_3$ deformation[28].

Assigning the bands in the infrared spectra of the derivatives of the other acetylenes is less simple than above. Included, as expected, in the spectra of all derivatives is a band in the region 2200–2182 cm^{-1} due to the $C{\equiv}C$ stretching vibration. The pattern of C–F stretching bands for each derivative is very similar to that of the parent acetylene. However, because there is a large amount of coupling in this region between C–F and C–C vibrations a complete assignment of the bands is difficult, although some attempts have been made for related compounds[29,30]. When the frequencies of $\nu(C{\equiv}C)$ of all the known compounds $(CH_3)_nM(C{\equiv}CR_f)_{4-n}$ are compared, some interesting trends are apparent. Firstly, in those compounds where n and R_f are constant, $\nu(C{\equiv}C)$ decreases as M changes from Si to Ge to Sn. A similar decrease in the frequency of $\nu(C{\equiv}C)$ has been observed for the series $(CH_3)_3MC{\equiv}CH$[31,32], $(CH_3)_3MC{\equiv}CCl$[33] and $(CH_3)_3MC{\equiv}CCH_3$[34]. This decrease is to be expected as the mass of M increases; it seems that in the case of hydrocarbons, however, other effects such as π-bonding need to be invoked to explain the magnitudes of the decreases, especially from $M = C$ to $M = Si$[31,32,35]. However, it is worth pointing out that the $C{\equiv}C$ bond length in the compounds $(CH_3)_3MC{\equiv}CCl$ does *not* change significantly in the series $M = C$, Si, and Ge[35].

Secondly, in those compounds where M and n are constant, $\nu(C{\equiv}C)$ decreases as the size of the R_f group increases. This may be related to the mass of the R_f groups and/or the strong electronegativity of the R_f group, which seems to increase in the sequence $CF_3 < CF_2CF_3 < CF(CF_3)_2$[36].

Thirdly, in those compounds where M and R_f are constant, $\nu(C{\equiv}C)$ increases as n decreases. The cause of this trend is not understood.

Using, as above, the general formula $(CH_3)_nM(C{\equiv}CR_f)_{4-n}$ as a basis, the following two trends are observed in the ^1H and ^{19}F spectroscopic results. Firstly, in those compounds where n and R_f are constant, both the chemical shift values of the hydrogen and the fluorine atoms successively shift to lower field as M changes from Si to Ge to Sn, and secondly, in those compounds where M and R_f are constant the chemical shift values of the hydrogens shift downfield, and those of the fluorines shift upfield, as n decreases ($3 \rightarrow 0$). These trends may be related to the increasing electropositive character of the metal and/or the decreasing $d\pi$–$p\pi$ bonding as the series is descended, and to the enhanced electron-withdrawing effect of the R_f groups as the number of these is increased. The NMR trends seem to be related to the infrared trends.

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REFERENCES

1 P. M. TREICHEL AND F. G. A. STONE, *Advan. Organometal. Chem., 1* (1964) 143.
2 H. C. CLARK, *Advan. Fluorine Chem., 3* (1963) 19.
3 R. E. BANKS AND R. N. HASZELDINE, *Advan. Inorg. Chem. Radiochem., 3* (1961) 337.
4 M. I. BRUCE AND F. G. A. STONE, *Angew. Chem., Intern. Edn., 7* (1968) 747.
5 W. R. CULLEN, *Fluorine Chem. Rev., 3* (1969) 73.
6 W. E. DAVIDSOHN AND M. C. HENRY, *Chem. Rev., 66* (1967) 73.
7 F. L. BOWDEN AND A. B. P. LEVER, *Organometal. Chem. Rev. A, 3* (1968) 227.
8 W. R. CULLEN AND W. R. LEEDER, *Inorg. Chem., 6* (1966) 1004.
9 B. C. PANT AND R. E. SACHER, *Inorg. Nucl. Chem. Letters, 5* (1969) 549.
10 M. I. BRUCE AND W. R. CULLEN, *Fluorine Chem. Rev., 4* (1969) 79.
11 W. R. CULLEN AND M. C. WALDMAN, *Inorg. Nucl. Chem. Letters, 4* (1968) 205; *6* (1969) 205.
12 W. G. FINNEGAN AND W. P. NORRIS, *J. Org. Chem., 28* (1963) 1139.
13 R. N. HASZELDINE AND K. LEEDHAM, *J. Chem. Soc.,* (1952) 3483.
14 W. R. CULLEN AND M. C. WALDMAN, *Can. J. Chem., 47* (1969) 3093.
15 M. P. BROWN AND G. W. A. FOWLES, *J. Chem. Soc.,* (1958) 2811.
16 E. R. LIPPINCOTT AND M. C. TOBIN, *J. Amer. Chem. Soc., 75* (1953) 4141.
17 J. G. A. LUITJEN AND G. J. M. VAN DER KERK, *Investigations in the Field of Organotin Chemistry,* Tin Research Institute, Greenford, Middlesex, England 1955.
18 M. C. WALDMAN, *J. Chem. Educ., 46* (1969) 364.
19 A. I. VOGEL, *Practical Organic Chemistry,* Wiley, New York, N.Y., 3rd. edn., 1956, p. 85.
20 M. I. BRUCE, D. A. HARBOURNE, F. WAUGH, AND F. G. A. STONE, *J. Chem. Soc., (A),* (1968) 356.
21 A. L. HENNE AND M. NAGER, *J. Amer. Chem. Soc., 74* (1952) 650.
22 B. DOLGOV AND YU. VOLNOV, *Zh. Obshch. Khim., 1* (1931) 91; *Chem. Abstr., 25* (1931) 4535.
23 W. R. CULLEN AND M. C. WALDMAN, to be published.
24 S. D. IBERKIVE AND M. J. NEWLANDS, *J. Chem. Soc.,* (1965) 4608.
25 F. GLOCKING AND K. A. HOOTON, in A. G. MACDAIRMID (ed.), *The Bond to Carbon,* Vol. 1, Part II, Marcel Dekker, New York, N.Y., 1968, p. 59.
26 W. DAVIDSOHN AND M. C. HENRY, *J. Organometal. Chem., 5* (1966) 29.
27 W. P. NEUMANN AND F. G. KLEINER, *Tetrahedron Letters,* (1964) 3779.
28 C. V. BERNEY, L. R. COUSINS, AND F. A. MILLER, *Spectrochim. Acta, 19* (1963) 2019.
29 P. KLABOE AND J. R. NIELSEN, *J. Chem. Phys., 30* (1959) 1375.
30 R. D. CHAMBERS, W. K. R. MUSGRAVE, AND J. SAVORY, *J. Chem. Soc.,* (1962) 1993.
31 E. A. KASTILOVOCH, D. N. SHIGOUN, AND N. V. KOMAROV, *J. Opt. Spect., 16* (1964) 24.
32 R. WEST AND C. S. KRAIHANZEL, *Inorg. Chem., 1* (1962) 967.
33 W. STEINGROSS AND W. ZEIL, *J. Organometal. Chem., 6* (1966) 109.
34 W. STEINGROSS AND W. ZEIL, *J. Organometal Chem., 6* (1966) 464.
35 W. ZEIL, J. HAASE, AND M. DAKKOURI, *Discuss. Faraday Soc., 47* (1969) 149.
36 W. R. CULLEN, J. R. SAMS, AND M. C. WALDMAN, *Inorg. Chem., 9* (1970) 1682.