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FLUOROCYCLOPROPENYL DERIVATIVES OF GERMANIUM AND TIN

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SUMMARY

The perfluoroalkynyl derivatives of germanium and tin $(CH_3)_nM(C\equiv CR_f)_{4-n}$ ($M = Ge, Sn$; $R_f = CF_3, CF_2CF_3, CF(CF_3)_2$; $n = 3, 2$; but not all combinations) react with trimethyl-trifluoromethyltin at 150° to give the cyclopropenyl derivatives $(CH_3)_nM(\overline{C{=}C(R_f)CF_2})_{4-n}$. The reaction probably involves the addition of difluorocarbene to the carbon–carbon triple bond, and the carbene is probably produced in the singlet state by thermolysis of the tin compound, since it adds stereospecifically to the double bond of *cis*- and *trans*-butene-2. The carbene also adds to the double bond of trimethylvinylsilane, but not to the double bond of the cyclopropenyl derivatives. Spectroscopic properties of the new compounds are discussed.

INTRODUCTION

The addition of carbenes and carbenoids across unsaturated bonds is well-known[1–6]. It seems that trimethyl-trifluoromethyltin acts as a source of difluorocarbene when heated at 150°[7],

$$(CH_3)_3SnCF_3 \xrightarrow{150^\circ} (CH_3)_3SnF + CF_2$$

and we have previously reported that difluorocarbene from this source adds to alkynes and olefins to yield cyclopropenes and cyclopropanes[8–10]. The present paper describes an extension of this earlier work and is mainly concerned with the addition of the carbene to fluoroalkynyl derivatives of germanium and tin, and its stereospecific addition to olefins. Other workers have added difluorocarbene to the carbon–carbon triple bond of hexafluorobutyne-2 to give both the cyclo-

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[*] See Ref. 9 for a preliminary communication of part of this work.

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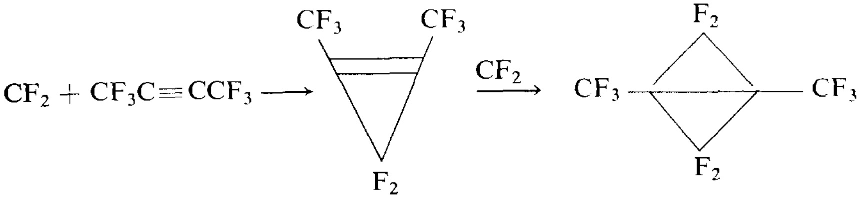
propene and the bicyclobutane[11] (in this case tris-trifluoromethylphosphorus difluoride was the carbene source), and to the triple bond of a steroid derivative[12].



In the latter case, the carbene was generated by the thermolysis of chlorodifluoroacetic acid, and again both cyclopropene and bicyclobutane derivatives were obtained.

EXPERIMENTAL

The perfluoroalkynyl derivatives of germanium and tin, triethyl-2-trifluoromethyl-3,3-difluorocyclopropenylgermane, and trimethyl-trifluoromethyltin were prepared as described in the literature[7,8,13]. The *cis*- and *trans*-butene and trimethylvinylsilane were obtained commercially. Volatile reactants and products were manipulated using standard vacuum techniques. A specially-designed apparatus[14] was used in handling potentially air-sensitive, toxic, highly-reactive, or low-boiling compounds—particularly during vapour phase chromatographic (VPC) analysis. Unless otherwise indicated, reactions were carried out in thick-walled Carius tubes. Molecular weights were determined by Regnault's method. Micro-boiling points were determined using Siwoloboff's method[15], and are reported, uncorrected, at atmospheric pressure. Infrared spectra were obtained in the gas phase using Perkin–Elmer model 21 and 457 instruments. The NMR spectra were obtained using either Varian A-60 or Jeolco C-60H instruments both operating at 60 MHz. The ^{19}F spectra were obtained using a Varian HA-100 spectrometer operating at 94.07 MHz. The ^1H spectra are reported in parts per million (ppm) relative to external $(CH_3)_4$ Si, and the ^{19}F NMR spectra in ppm relative to either internal or external $CFCl_3$. Negative values of chemical shifts are to low field for all spectra. 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 Engelskirchin, West Germany.

Reactions of trimethyl-trifluoromethyltin

General

In all the reactions the tin compound was present in excess, and its thermal decomposition products were always found, including, in varying amounts: $(CH_3)_3SnF$, SiF_4, cyclo-C_3F_6, CHF_3 and, in some cases, $CF_2{=}CF_2$. The latter four products were always found among the most volatile products. Trimethyltin fluoride was observed as white crystals on the walls of the Carius tube.

Reaction with Group IV perfluoroalkynyl derivatives

Table I tabulates these reactions. As an example, the reaction between trimethyl-trifluoromethyltin and trimethyl-3,3,3-trifluoropropynylgermane is described in detail. The germane (1.062 g, 5.08 mmoles) and tin compound (1.723 g, 7.4 mmoles) were heated at 145° for 21 h. The major product, trimethyl-2-trifluoromethyl-3,3-difluorocyclopropenylgermane (1.095 g, 84% yield), condensed in a trap at —78° and was purified by VPC using a 20% silicone GE–SS–96 column at 105°. It was identified on the basis of its analysis and spectroscopic properties (Tables 2–4).

Reaction with trans-*butene-2*

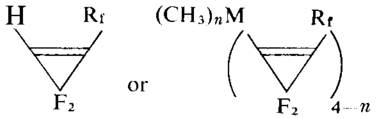
Trans-butene-2 (0.538 g, 9.61 mmoles) and trimethyl-trifluoromethyltin (1.258 g, 5.4 mmoles) were heated at 150° for 22.5 h. The volatile contents of the reaction tube were passed twice through a —78° bath and once through a —84° bath. VPC analysis of the combined fractions (20% SF–96 at 112°) showed a single major product with *ca.* 2% impurity. The major product was identified as *trans*-1,1-difluoro-2,3-dimethylcyclopropane (0.522 g, 91% yield). Anal: Found, C, 56.35; H, 7.64%. Calc. for $C_5H_8F_2$, C, 56.60; H, 7.55%. Molecular weight found: 107 (Calc. for $C_5H_8F_2$: 106). Infrared spectrum (vapour): 3022(m), 2975(m), 2940(m), 2887(m), 1479(s(br)), 1330(m), 1325(m), 1268(s), 1219(s), 1162(m), 1067(m), 1032(s), 979(m), 936(m), 888(m), 811(m) cm^{-1}. The ^1H NMR spectrum showed three complex multiplets in the region —0.83 to —0.93 ppm. The ^{19}F NMR spectrum (external $CFCl_3$) showed an unsymmetrical multiplet of at least 30 peaks centred at 142.3 ppm. The extrapolated vapour pressure curve gave the following data: b.p. (760 mm Hg) 52.5 ± 1°; latent heat of vapourization = 6.9 kcal $mole^{-1}$; Trouton's constant = 21.2 e.u.

Reaction with cis-*butene-2*

Cis-butene-2 (0.51 g, 9.25 mmoles) and trimethyl-trifluoromethyltin (0.786 g, 3.37 mmoles) were heated for 22.5 h at 150°. *Cis*-butene-2 (0.34 g), which passed through a trap at —84°, was recovered. The remainder was identified as *cis*-1,1-difluoro-2,3-dimethylcyclopropane (0.333 g, 93.5% yield). An analytical sample was obtained by VPC (20% SF–96 at 115°). Molecular weight found: 109 (Calc. for $C_5H_8F_2$: 106). Anal: Found, C, 56.63; H, 7.36%. Calc. for $C_5H_8F_2$, C, 56.60; H, 7.55%. Infrared spectrum (vapour): 3040(m), 2989(m), 2940(m), 2985(m), 1481(s), 1455(m), 1295(s), 1210(s), 1120(m), 1018(m), 911(m), 905(m(sh)) cm^{-1}. The ^{19}F NMR spectrum showed an AB pattern with absorptions centred at 128.1 and 157.2 ppm. (Figure 1). The extrapolated vapour pressure curve gave the following data: b.p. (760 mm Hg), 59.7° ± 2°; latent heat of vapourization = 6.59 kcal $mole^{-1}$; Trouton's constant = 19.8 e.u.

TABLE 1

PERFLUOROALKYL-3,3-DIFLUOROCYCLOPROPENES AND SOME OF THEIR GROUP IV DERIVATIVES

$HC{\equiv}CR_f$ or $(CH_3)_nM(C{\equiv}CR_f)_{4-n}$	+	$(4-n)(CH_3)_3SnCF_3$ (CF_2source)	Reaction temp. °C (Reaction time)		B.p.°C[a] (atm)	Yield %
$R_f = CF_3$						
$HC{\equiv}CCF_3$	+	CF_2	$\xrightarrow[(24\ h)]{143°}$	$HC{=}C(CF_3)CF_2$	—	15
$(CH_3)_3GeC{\equiv}CCF_3$	+	CF_2	$\xrightarrow[(21\ h)]{145°}$	$(CH_3)_3GeC{=}C(CF_3)CF_2$	93.2[d]	84
$(CH_3)_2Ge(C{\equiv}CCF_3)_2$	+	$2CF_2$	$\xrightarrow[(21\ h)]{145°}$	$(CH_3)_2Ge(C{=}C(CF_3)CF_2)_2$	—	low
$(CH_3)_3SnC{\equiv}CCF_3$	+	CF_2	$\xrightarrow[(20\ h)]{143°}$	$(CH_3)_3SnC{=}C(CF_3)CF_2$	135.0[d]	39
$(CH_3)_2Sn(C{\equiv}CCF_3)_2$	+	$2CF_2$	$\xrightarrow[(20\ h)]{145°}$	$(CH_3)_2Sn(C{=}C(CF_3)CF_2)_2$	—	low
$R_f = CF_2CF_3$						
$HC{\equiv}CCF_2CF_3$	+	CF_2	$\xrightarrow[(24\ h)]{150°}$	$HC{=}C(CF_2CF_3)CF_2$	—	23
$(CH_3)_3GeC{\equiv}CCF_2CF_3$	+	CF_2	$\xrightarrow[(24\ h)]{150°}$	$(CH_3)_3GeC{=}C(CF_2CF_3)CF_2$	128.5[b]	31
$(CH_3)_2Ge(C{\equiv}CCF_2CF_3)_2$	+	$2CF_2$	$\xrightarrow[(24\ h)]{150°}$	$(CH_3)_2Ge(C{=}C(CF_2CF_3)CF_2)$	—	64[c]
$(CH_3)_3SnC{\equiv}CCF_2CF_3$	+	CF_2	$\xrightarrow[(24\ h)]{150°}$	$(CH_3)_3SnC{=}C(CF_2CF_3)CF_2$	—	36
$R_f = CF(CF_3)_2$						
$HC{\equiv}CCF(CF_3)_2$	+	CF_2	$\xrightarrow[(24\ h)]{150°}$	$HC{=}C(CF(CF_3)_2)CF_2$	—	8
$(CH_3)_3GeC{\equiv}CCF(CF_3)_2$	+	CF_2	$\xrightarrow[(44\ h)]{150°}$	$(CH_3)_3GeC{=}C(CF(CF_3)_2)CF_2$	138.5[b]	38

[a] Unless otherwise noted boiling points are recorded, uncorrected, at atmospheric pressure.
[b] Micro-boiling point.
[c] Estimated from VPC integration.

TABLE 2

ANALYTICAL DATA FOR GROUP IV CYCLOPROPENYL DERIVATIVES

	Purification	Found% C	H	F	Calculated% C	H	F
$(CH_3)_3GeC=C(CF_3)CF_2$[a]	20% silicone GE–SS–96 at 105°	32.43	3.41	36.10	32.31	3.45	36.45
$(CH_3)_2Ge(C=C(CF_3)CF_2)_2$	20% silicone GE–SS–96 at 75°	30.90	1.71	48.51	30.86	1.54	48.86
$(CH_3)_3SnC=C(CF_3)CF_2$[b]	20% silicone GE–SS–96 at 100°	27.38	2.91	30.39	27.40	2.76	38.72
$(CH_3)_2Sn(C=C(CF_3)CF_2)_2$	20% silicone GE–SS–96 at 100°	27.96	—	43.50	27.61	—	43.71
$(CH_3)_3GeC=C(CF_2CF_3)CF_2$	20% silicone GE–SS–96 at 85°	31.03	2.84		30.90	2.95	
$(CH_3)_2Ge(C=C(CF_2CF_3)CF_2)_2$	20% Kel-F grease at 110°	29.72	1.42	54.11	29.45	1.23	54.45
$(CH_3)_3SnC=C(CF_2CF_3)CF_2$	20% silicone GE–SS–96 at 120°	27.18	2.64		26.90	2.52	
$(CH_3)_3GeC=C(CF(CF_3)_2)CF_2$	20% Kel-F grease at 90°	30.22	2.62	47.08	29.97	2.49	47.37

[a] Ge analysis: Found, 27.86. Calc., 27.86.

[b] Sn analysis: Found, 38.88. Calc., 38.72.

TABLE 3

INFRARED SPECTRA OF SOME PERFLUOROALKYL-3,3-DIFLUOROCYCLOPROPENES AND SOME OF THEIR GROUP IV DERIVATIVES[a]

$HC=C(CF_3)CF_2$[b]	1730	1353	1264	1189	1113								
$(CH_3)_3SiC=CCF_3CF_2$[c]	1758	1355	1285	1181	1100								
$(CH_3)_3GeC=C(CF_3)CF_2$	1752	1344	1285	1178	1095								
$(CH_3)_2Ge(C=C(CF_3)CF_2)_2$	1749	1342	1280	1183	1090								
$(CH_3)_3SnC=C(CF_3)CF_2$	1741	1344	1285	1179	1096								
$(CH_3)_2Sn(C=C(CF_3)CF_2)_2$	1729	1339	1280	1192	1090								
$HC=C(CF_2CF_3)CF_2$[b]	1737	1347		1231	1172	1126	1046						
$(CH_3)_3GeC=C(CF_2CF_3)CF_2$	1748	1340	1260	1230	1158	1122	1100	1010					
$(CH_3)_2Ge(C=C(CF_2CF_3)CF_2)_2$	1737	1333	1253	1224	1155	1117		1000					
$(CH_3)_3SnC=C(CF_2CF_3)CF_2$	1733	1342	1258	1227	1159	1120	1099	1009					
$HC=C(CF(CF_3)_2)CF_2$[b]	1732	1360	1318	1287	1252	1190	1125	1059	992	728			
$(CH_3)_3GeC=C(CF(CF_3)_2)CF_2$	1738	1338	1319	1280	1259	1244	1204	1120	1093	1009	985	838	729

[a] Main bands only in cm^{-1}.

[b] From Ref. 10.

[c] From Ref. 8.

TABLE 4

^{1}H AND ^{19}F NMR CHEMICAL SHIFTS (δ) AND COUPLING CONSTANTS OF SOME CYCLOPROPENES[a]

	^{1}H[b]		^{19}F							
Cyclopropene	$\delta(CH_3)$	$\delta(CF_2{}^f)$	$\delta(CF_3)$	$\delta(CF_2)$	$\delta(CF)$	$J(CF_2{}^f-CF_3)$	$J(CF_2{}^f-CF_2)$	$J(CF_2{}^f-CF)$	$J(CF_2-CF_3)$	$J(CF-CF_3)$
$HC=C(CF_3)CF_2$[e]		102.8	63.3			2.8				
$(CH_3)_3GeC=C(CF_3)CF_2$	-0.20[d]	103.4[c,d]	63.25			3.6				
$(CH_3)_2Ge(C=C(CF_3)CF_2)_2$	-0.15[d]	102.8	63.90			3.9				
$(CH_3)_3SnC=C(CF_3)CF_2$	-0.21[d]	101.3	63.50			3.75				
$(CH_3)_2Sn(C=C(CF_3)CF_2)_2$	-0.20[d]	101.3[c,d]	63.4			3.6				
$HC=C(CF_2CF_3)CF_2$[e]		104.6	85.85	115.8		0.9	5.2		2.55	
$(CH_3)_3GeC=C(CF_2CF_3)CF_2$	-0.34	103.6	85.79	115.0		0.9	6.4		2.75	
$(CH_3)_2Ge(C=C(CF_2CF_3)CF_2)_2$	-0.7	103.3	85.60	115.2		0.8	6.0		2.2	
$(CH_3)_3SnC=C(CF_2CF_3)CF_2$	-0.3	102.0	85.61	115.4		0.9	6.5		2.8	
$HC=C(CF(CF_3)_2)CF_2$[e]		104.9	77.05		182.2	0.9		6.8		9.2
$(CH_3)_3GeC=C(CF(CF_3)_2)CF_2$	-0.35	104.2	79.35		181.1	1.0		8.6		9.6

[a] $CFCl_3$ solution unless otherwise indicated — J values in Hz.
[b] With respect to external TMS.
[c] With respect to external $CFCl_3$.
[d] Neat.
[e] From Ref. 10.
[f] CF_2 in bridge.

Reaction with Group IV cyclopropenyl derivatives

Difluorocarbene from trimethyl-trifluoromethyltin failed to add to the double bond of either of the derivatives $R_3Ge\overline{C=C(CF_3)CF_2}$ ($R = C_2H_5$, CH_3) when a mixture of the particular germane and the tin compound was heated at 145° for 24 h.

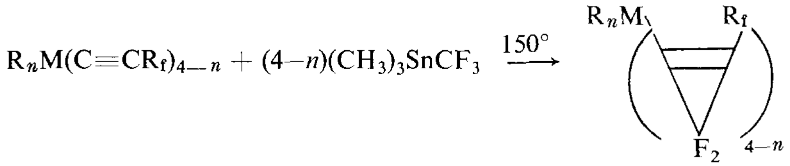
Reaction with trimethylvinylsilane

The silane (0.912 g, 9.12 mmoles) and the tin compound (3.13 g, 13.5 mmoles) were heated at 130° for 21.5 h. VPC purification (20% silicone GE–SS–96 at 75°) of the −64° fraction, yielded 2,2-difluorocyclopropyltrimethylsilane (0.30 g, 41%) Anal: Found, C, 48.2; H, 7.8; F, 25.1%. Calc. for $C_6H_{12}F_2Si$, C, 48.0; H, 8.0; F, 25.3%.

DISCUSSION AND RESULTS

Preparation of Group IV cyclopropenyl derivatives

The novel class of organometallic compounds in which a Group IV element, other than carbon, is σ-bonded to a cyclopropene ring at a vinylic position can be prepared, in general, by the reaction of trimethyl-trifluoromethyltin in the gas phase at *ca.* 150° with a Group IV perfluoroalkynyl derivative.



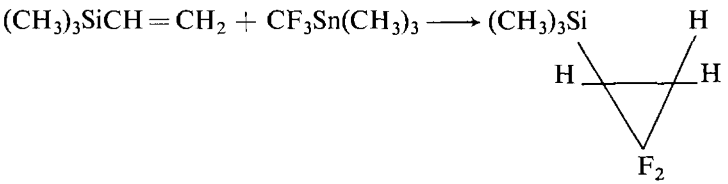
(3)

($R = CH_3$; M = Ge, Sn; $R_f = CF_3$, C_2F_5, $CF(CF_3)_2$; $n = 2, 3$)

Two similar derivatives of silicon and germanium and one of arsenic are known[8]. As mentioned in the Introduction, the reaction probably takes place by first thermally inducing the elimination of difluorocarbene from $(CH_3)_3SnCF_3$; the carbene then adding across the triple bond to form the cyclopropenyl derivative. The Group IV cyclopropenyl derivatives which have been prepared in this investigation are listed in Table 1. The analytical and spectroscopic data (Tables 2–4) leave no doubt concerning the proposed structures. The data on the parent cyclopropenes[10] has been included for reference.

Difluorocarbene from the same source does not add to the double bond of the cyclopropenes, $R_3Ge\overline{C=C(CF_3)CF_2}$ ($R = CH_3$, C_2H_5) in the gas phase at 150°. As mentioned in the Introduction, this contrasts with two published reports which describe the addition of CF_2 (from other sources) to the double bond of a cyclopropenyl derivative[11,12]. The failure to produce a bicyclobutane product in the present case may be related to (a) the method of generation of the carbene, since it is known that different sources of the same carbene produce carbene species of different reactivity[16,17], or (b) the electrophilic character of CF_2, and the reduced electron density of the $C=C$ group caused by some form of $p\pi$–$d\pi$ bonding between the $C=C$ group and the germanium d orbitals. Seyferth and Dertouzos[18] have utilized the tin compound as a source of CF_2 in reactions, in solution, with various olefins and Group IV vinylic compounds, and have found that vinylsilanes were less reactive towards CF_2 than similar unsubstituted olefins. The reduced reactivity has been attributed to reduced electron density in the vinylsilane caused by $p\pi$–$d\pi$ interactions.

Both the gas phase method of CF_2 transfer from trimethyl-trifluoromethyltin used in this investigation and the solution method employed by Seyferth *et al.* seem equally good as sources of CF_2. Seyferth *et al.*[19] obtained a 52% yield of $(C_2H_5)_3Si\overline{CH-CH_2-CF_2}$ from $(C_2H_5)_3SiCH=CH_2$ in solution, while a 44% yield of $(CH_3)_3Si\overline{CH-CH_2-CF_2}$ was obtained during this investigation from $(CH_3)_3SiCH=CH_2$ and CF_2 in the gas phase at 150°.


$(CH_3)_3SiCH=CH_2 + CF_3Sn(CH_3)_3 \longrightarrow (CH_3)_3Si$

*Stability of the Group IV perfluoroalkyl-*3,3*-difluorocyclopropenyl derivatives*

The trimethylgermyl derivatives $(CH_3)_3Ge\overline{C=C(R_f)CF_2}$ ($R_f = CF_3$, CF_2CF_3 and $CF(CF_3)_2$) are both thermally and hydrolytically stable at 20°, and can be stored for long periods without apparent decomposition, although some slight discolouration does take place. The bis-(cyclopropenyl)germanium derivatives, $(CH_3)_2Ge(\overline{C=C(R_f)CF_2})_2$ ($R_f = CF_3$, CF_2CF_3), on the other hand, decompose slowly at room temperature. In contrast both the mono- and bis-(alkynyl)germanium precursors are stable to heat[13].

Of the three tin cyclopropenyl derivatives, only $(CH_3)_3Sn\overline{C=C(CF_3)CF_2}$ is thermally stable, even at 150°. The other two cyclopropenyl tin derivatives, $(CH_3)_2Sn(\overline{C=C(CF_3)CF_2})_2$ and $(CH_3)_3Sn\overline{C=C(CF_2CF_3)CF_2}$, both slowly decompose in sealed tubes at 20°. This order of thermal stability is similar to the order of thermal decomposition established previously for the tin perfluoroalkynyl derivatives[13], *i.e.*, the thermal stability decreases as the number of fluorocarbon substituents bonded to tin increase, and as the size of the R_f group attached to the unsaturated bond increases.

The derivative $(CH_3)_3Sn\overline{C=C(CF_3)CF_2}$ is quantitatively hydrolyzed at room temperature to give $H\overline{C=C(CF_3)CF_2}$. The other tin derivatives are presumably hydrolyzed in a similar way.

Spectroscopic results

All the cyclopropenes listed in Table 3 show strong bands near 1745 cm^{-1} due to a vibration which we will write as $\nu(C=C)$. This designation is used in the realization that in cyclopropenes the "double-bond stretching vibration" cannot be treated as a group frequency as it involves considerable contributions from normal skeletal modes and substituent vibrations[20, 21]. The other bands in Table 3 are probably associated with C–F vibrations. The pattern of bands for each derivative, and especially for the 2-trifluoromethyl compounds, is very characteristic.

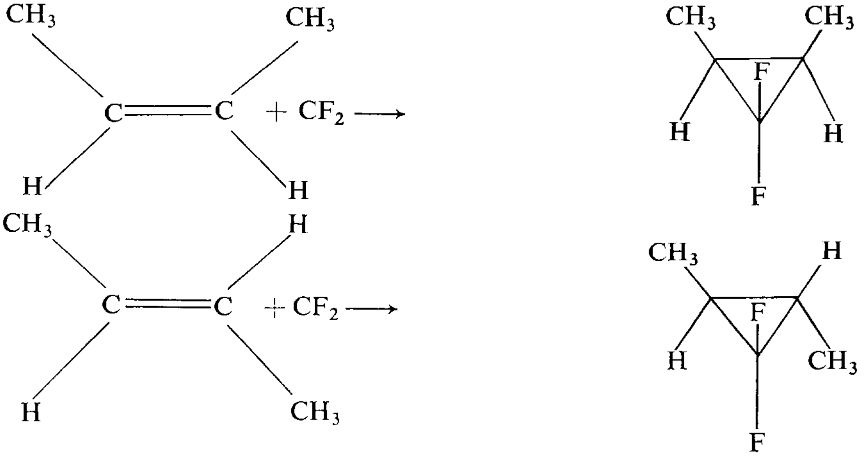
The NMR data for these compounds are listed in Table 4. The ^1H spectra all show singlet absorptions for the methyl groups, and the ^{19}F spectra are analyzable on a first-order basis and confirm the proposed structures. The chemical shifts and coupling constants are internally consistent. The magnitude of the coupling between the bridging fluorine atoms and the fluorine on the vinylic carbon increases as the latter are substituted by CF_3 groups. This same effect is observed in the cyclopropenes $H\overline{C=CR_fCF_2}$, as seen in Table 4, and can be taken as an indication of the lower electronegativity of the CF_3 group[10].

The frequency of $\nu(C=C)$ in these and related cyclopropenes show some interesting trends. It seems that in a given series in Table 3 the frequency of $\nu(C=C)$ decreases as the atomic number of the Group IV element increases, and also as the size of the fluorocarbon group decreases. These trends are probably due to mass effects. It is worth noting, however, that replacement of a vinylic hydrogen atom by a bulky $(CH_3)_3M$ group can result in an increase of $\nu(C=C)$. Examination of the double-bond frequencies of simpler cyclopropenes containing only H, CH_3, CF_3 or F as substituents[22] reveals that substituents in a vinylic position cause an increase in the frequency of $\nu(C=C)$ in the order $H < CH_3 < CF_3 < F$. The great influence of fluorine is probably due to strong coupling with the C–F mode. Coupling effects probably also outweigh mass effects in the case of CF_3 (and $(CH_3)_3M$) substitution. Similar effects account for the high $\nu(C=C)$ absorption of fluoroacetylene[23]. In the case of the cyclo-olefins, the larger exocyclic angles (which would allow stronger coupling) also account for the larger substituent effects than are found in non-cyclic olefins. The same survey[22] reveals that substituents in the 3-position in cyclopropenes cause an increase in $\nu(C=C)$ in the order $F < CF_3 < CH_3 < H$, the reverse of that found for the vinylic substituent effect.

The multiplicity of difluorocarbene and the mechanism of its addition to multiple bonds

The multiplicity of a carbene species, singlet or triplet, can be determined by spectroscopic techniques. However, it has also been concluded that, in general, the multiplicity of a carbene species can be deduced from the stereochemistry of the cyclopropane product formed by adding the carbene across the $C=C$ bond of an olefin of known geometry[1,2,24]. In particular, stereospecific addition is considered to involve a singlet carbene and concerted bond formation via a three-centred transition state.

In the present investigation we find that CF_2 from $(CH_3)_3SnCF_3$ adds stereospecifically in the gas phase at 150° to *cis*- and *trans*-butene-2 to give *cis*- and *trans*-1,1-difluoro-2,3-dimethylcyclopropane, respectively. The yield of cyclopropane product is greater than 90% in each case, and only one isomer is obtained from a particular reaction.



The ^{19}F NMR spectrum of *cis*-1,1-difluoro-2,3-dimethylcyclopropane is shown in Fig. 1. An AX (J(F–F) = 156 Hz) pattern is displayed due to the inequivalence of the fluorine atoms on the different sides of the ring. The splitting patterns are centred at 128.1 and 157.2 ppm. Mitch[25] obtained a similar ^{19}F n.m.r. spectrum for the cyclopropane product derived from difluorodiazirine and *cis*-butene-2 with absorptions at 127.8 and 157.1 ppm and with J(F–F) = 157.6 Hz. We assign the low- and high-field fluorine absorptions to the fluorine atoms *cis* and *trans* to the methyl groups, respectively. This assignment is based upon the now well-established rule that, in fluorinated cyclopropanes the magnitude of the vicinal fluorine–hydrogen coupling is J(F–H(*cis*)) > J(F–H(*trans*))[26]. In the present case J(F–H(*cis*)) = 14.1 Hz and J(F–H(*trans*)) = 0 Hz. The coupling constants of the fluorines with the methyl groups are also descernible (J(F–CH_3(*cis*)) = 0.13 Hz; J(F–CH_3(*trans*)) = 0.3 Hz). The ^{19}F NMR spectrum of the *trans*-1,1-difluoro-2,3-dimethylcyclopropane consists of a broad multiplet (31 Hz) centred at 142.3 ppm. This chemical shift value is the same as that reported by Mitch[25] for the ^{19}F NMR signal of the adduct obtained by adding CF_2 from difluorodiazirine to the double bond of *trans*-butene-2.

On the basis that the addition reactions are stereospecific, it can be concluded that if free CF_2 is produced from the thermolysis of trimethyl-trifluoromethyltin, it is produced in the singlet state. Other workers[27,28], with one exception[29], also describe the multiplicity of CF_2 as a singlet. Indeed it seems that dihalocarbenes

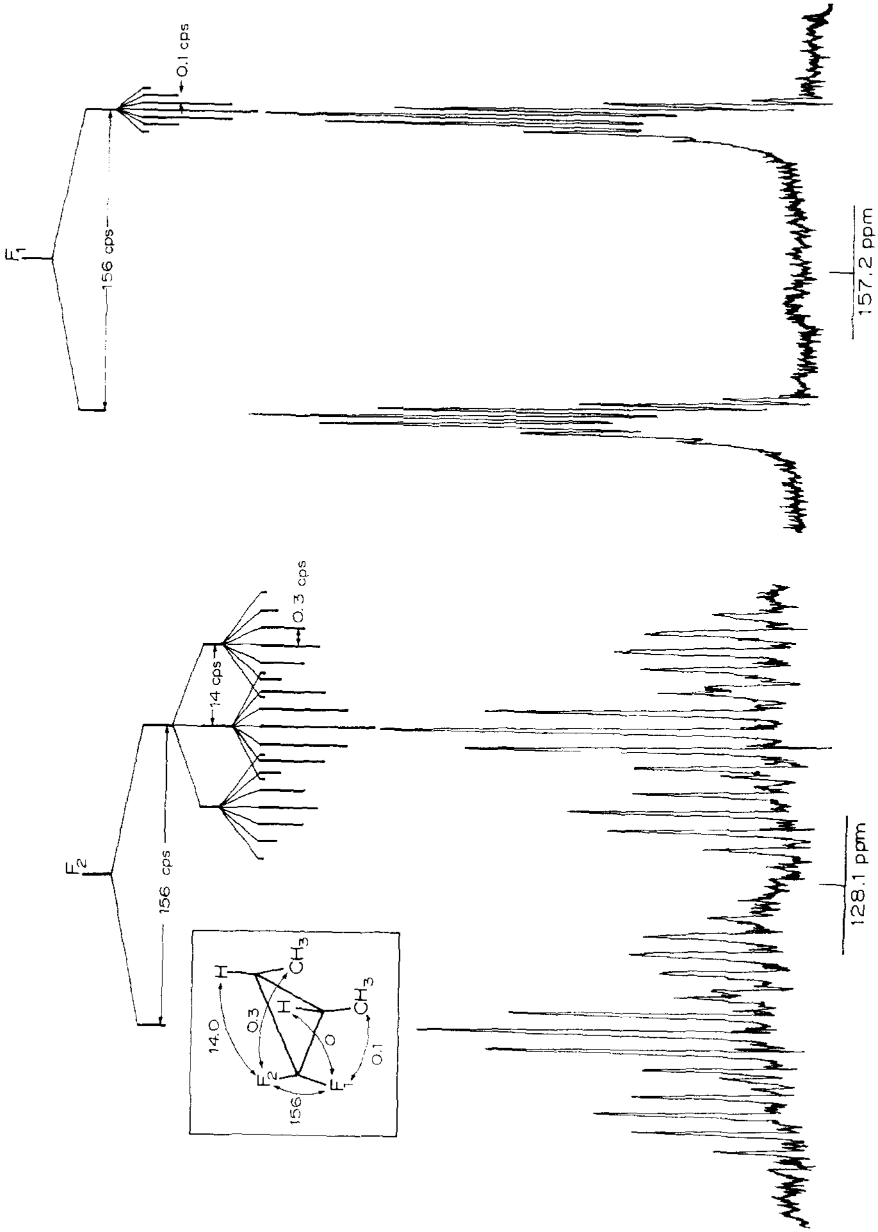


Fig. 1. The ^{19}F NMR spectrum of *cis*-1,1-difluoro-2,3-dimethylcyclopropane.

in general are in this state when they react with olefins. Thus, it seems probable that the additions of CF_2, from the tin source, to carbon–carbon multiple bonds takes place via a three-centre transition state, with concerted formation of both bonds during the production of cyclopropanes or cyclopropenes.

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