CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER, BRITISH COLUMBIA, CANADA

Trifluoropropynyl Derivatives. I. Their Preparation and Reaction with Difluorocarbene[1]

BY W. R. CULLEN AND W. R. LEEDER

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The trifluoropropynyl derivatives $(CH_3)_2AsC{\equiv}CCF_3$, $CH_3As(C{\equiv}CCF_3)_2$, $(CH_3)_3SiC{\equiv}CCF_3$, and $(C_2H_5)_3GeC{\equiv}CCF_3$ can be prepared from $CF_3C{\equiv}CMgI$ and the appropriate organometallic halide. They react with CF_2 [from $(CH_3)_3SnCF_3$] yielding the novel cyclopropenyl derivatives $R_nM\overline{C{=}C(CF_3)C}F_2$ [$R_nM = (CH_3)_2As$, $(CH_3)_3Si$, or $(C_2H_5)_3Ge$]. $(CH_3)_2AsC{\equiv}CCF_3$ is also obtained by the reaction of $CF_3C{\equiv}CH$ with compounds with As—N, As—S, As—As, and As—O bonds. $CF_3CH{\equiv}CH$ and $ClAs(CH_3)_2$ afford a little $(CH_3)_2AsC{\equiv}CCF_3$, but the main products are the isomers of the 1:1 adduct $(CH_3)_2AsC(CF_3){=}CHCl$.

Although a considerable amount is now known about the chemistry of fluoroalkyl derivatives of the metals and metalloids, most of this concerns saturated aliphatic systems.[2] Studies on unsaturated systems have been confined largely to perfluorovinyl compounds,[2] however recently some more novel olefinic compounds have been described.[3] Derivatives of fluoroacetylenes have been investigated even less, and, apart from the compounds to be described below, only $CF_3C{\equiv}CAg$, $CF_3C{\equiv}CCu$, $(CF_3C{\equiv}C)_2Hg$,[4] $CF_3C{\equiv}CMgBr$,[5] and $(CF_3C{\equiv}C)_2Zn$ (or $CF_3C{\equiv}CZnCl$)[6] are known. The zinc compound is probably an intermediate in the convenient synthesis of 3,3,3-trifluoropropyne.[6]

$$\begin{array}{l} CF_3CCl_2CCl_3 + Zn \longrightarrow [(CF_3C{\equiv}C)_2Zn \text{ or } CF_3C{\equiv}CZnCl] \quad (1) \\ \qquad\qquad\qquad\qquad\qquad\qquad \Big\downarrow H_2O \\ \qquad\qquad\qquad\qquad\qquad\quad CF_3C{\equiv}CH \end{array}$$

The present investigation was undertaken because of our general interest in the reactions of fluoroacetylenes[7] and, more specifically, because of a desire to extend the knowledge of the chemistry of fluoroalkynyl derivatives of the elements.

Experimental Section

$(CH_3)_3SiCl$, $(C_2H_5)_4Ge$, and most of the fluorocarbons used were obtained from Peninsular ChemResearch Inc., $(CH_3)_4Sn$ from M and T Chemicals, $CH_3AsO(OH)_2$ and $(CH_3)_2AsO(OH)$ from the Ansul Chemical Co., and $CF_3CCl_2CCl_3$ from Columbia Organic Chemicals. The following reagents were prepared as described in the literature: $CF_3C{\equiv}CH$,[6] $(CH_3)_3SiSC_2H_5$,[8a] $(C_2H_5)_3GeBr$,[7d] $[(C_2H_5)_3Ge]_2O$,[8b] $(CH_3)_3SnCF_3$,[9] CH_3AsCl_2,[10a] $(CH_3)_2AsI$,[10b] $[(CH_3)_2As]_2O$,[10c] $(CH_3)_2As{-}As(CH_3)_2$,[10d] $(CH_3)_2AsSC_2H_5$,[10e] $(CH_3)_2AsN(CH_3)_2$,[10f] $(CH_3)_2AsC(CF_3){=}C(CF_3)H$.[7b]

Volatile reactants and products were manipulated in a vacuum system. Reactions were carried out in sealed Pyrex tubes unless otherwise indicated. Infrared spectra were recorded using a Perkin-Elmer Model 21 instrument (NaCl optics), and nmr spectra were run using Varian A-60 and H.R.-60 spectrometers. Chemical shifts are given in ppm with respect to external tetramethylsilane (^1H spectra) and external trifluoracetic acid (^{19}F spectra), negative values being to low field. Analytical and spectroscopic data for new compounds are listed in Tables II and III and in the text below. Microanalyses were done by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim (Ruhr), West Germany, and by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Preparation of 3,3,3-Trifluoropropynyl Derivatives. (a) The Grignard Method.—The preparation of dimethyl-3,3,3-trifluoropropynylarsine is described as an example. Trifluoropropyne (5.8 g) was condensed onto the Grignard reagent made from 1.5 g of magnesium turnings and 8.5 g of methyl iodide in 30 ml of anhydrous ether. The tube was warmed cautiously while the methane was produced. The noncondensable gas was pumped away and 13.9 g of iododimethylarsine was condensed into the tube which was then sealed and shaken at 20° for 2 hr. Trap-to-trap distillation gave a least volatile fraction which was distilled in a nitrogen atmosphere to give the propynylarsine. In a similar way dichloromethylarsine gave methylbis(3,3,3-trifluoropropynyl)arsine and chlorotrimethylsilane gave trimethyl-3,3,3-trifluoropropynylsilane. In the latter case di-*n*-butyl ether was used as solvent and the propynylsilane was separated by vpc only with difficulty from unreacted chlorosilane. Because of the low volatility of bromotriethylgermane the solution of the propynylmagnesium iodide was slowly added (20°) to a stirred ethereal solution of the bromogermane, the reaction flask being attached to the vacuum system.

(b) Reaction of Chlorodimethylarsine with 3,3,3-Trifluoropropyne.—The chloroarsine (3.1 g) and the propyne (4.1 g) were heated to 155° (4 days). The volatile contents of the tube were taken into the vacuum system. A small amount of a tar which contained C=C and C≡C units remained behind. The least volatile fraction (2.7 g), which condensed at −78°, was examined by vpc (12-ft dinonyl phthalate column at 135°) and found to contain four components. These were identified as follows (in order of elution): dimethyl-3,3,3-trifluoropropynylarsine, of known infrared spectrum; *trans*-1-dimethylarsino-3,3,3-

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TABLE I

SYNTHESIS OF TRIFLUOROPROPYNYL COMPOUNDS FROM 3,3,3-TRIFLUOROPROPYNE

Reactants	Conditions	Products identified[a]	Yield of propynyl compd, %
$(CH_3)_2As—As(CH_3)_2$ (1.6 g) $CF_3C≡CH$ (1.4 g)	20° (18 hr)	$CF_3C≡CAs(CH_3)_2$ *trans*-$(CH_3)_2AsCH=CHCF_3$	~80
$(CH_3)_2As—N(CH_3)_2$ (1.3 g) $CF_3C≡CH$ (2.27 g)	20° (18 hr)[b]	$CF_3C≡CAs(CH_3)_2$ *trans*-$(CH_3)_2NCH=CHCF_3$	~100
$(CH_3)_2As—SC_2H_5$ (1.6 g) $CF_3C≡CH$ (2.0 g)	125° (24 hr)[c]	$CF_3C≡CAs(CH_3)_2$	Trace
$[(CH_3)_2As]_2O$ (1.4 g) $CF_3C≡CH$ (1.7 g)	20° (7 days)	$CF_3C≡CAs(CH_3)_2$	44
$(CH_3)_3Si—SC_2H_5$ (0.85 g) $CF_3C≡CH$ (1.8 g)	100° (2 days)[d]	. . .[e]	0
$[(C_2H_5)_3Ge]_2O$ (6.5 g) $CF_3C≡CH$ (10.2 g)	120° (7 days)[f]	. . .	0

[a] Identified, after isolation, by means of known infrared and nmr spectra. [b] Vigorous reaction on mixing well below 20°. [c] No reaction at 20° (10 days). [d] No reaction at 20° (2 days). [e] Some reaction but no $(CH_3)_3SiC=CCF_3$ produced. [f] No reaction at 20° (7 days) or 80° (7 days).

trifluoropropene, of known infrared and ^1H nmr spectra.[7b] The third and fourth peaks were produced by isomers (III and IV) of the 1:1 adduct $(CH_3)_2AsC(CF_3)=CHCl$. The relative area of the peaks on the chromatogram was 12:2:9:77.

Anal. Calcd for $(CH_3)_2AsC_3HClF_3$: C, 25.6; H, 2.98; As, 31.9; Cl, 15.1; F, 21.2; mol wt, 235. Found for isomer IV: C, 25.7; H, 2.87; As, 31.9; Cl, 15.0; F, 24.9; mol wt (Rast), 240. Found for isomer III: C, 25.8; H, 3.04; Cl, 15.2. Infrared data (main bands only, liquid film): isomer III, 1588 (s), 1290 (s), 1260 (s, br) (1160, 1125) (s, br), 855 (m), 828 (m), 690 (m) cm^{-1}; isomer IV, 1598 (s), 1426 (m), 1327 (s), 1220 (s), 1140 (s, br), 855 (m), 830 (m), 780 (m), 750 (m) cm^{-1}. Nmr data: isomer III, multiplet at -1.1 ppm ($J \sim 1$ cps) and quartet at -7.46 ppm ($J = 2.1$ cps); isomer IV, singlets at -1.09 and -6.44 ppm.

The more volatile fraction from this experiment (1.85 g) consisted of unreacted propyne (1.65 g) together with a fraction (0.2 g) which condensed at −98° and which was identified as 3,3,3-trifluoro-1-chloroprop-1-ene by means of its ^1H nmr spectrum. The coupling constants and isomer distribution are shown in I and II.

In other experiments it was found that the propyne and chloroarsine react on ultraviolet irradiation[11] or on heating at 110°. The propynylarsine is not produced under these conditions and is only obtained when the initial reaction products are distilled at 760 mm. The mixture of isomers III and IV, which is the main product, boils at 142–144°.

Isomer IV was little changed (darkened in color) after heating to 155° (2 days) but after 18 hr at 180° small amounts of III were present. In the presence of air, isomerization of IV takes place at 140°. Both III and IV are stable at 140° in the absence of air.

(c) **Other Reactions Using 3,3,3-Trifluoropropyne.**—The results of a number of experiments are summarized in Table I.

Preparation of Cyclopropenyl Derivatives.—Using the arsenic compound again as an example, dimethyl-3,3,3-trifluoropropynylarsine (1.72 g) and a slight excess of trimethyltrifluoromethyltin (2.02 g) were heated at 140° (20 hr). Trimethyltin fluoride deposited on the tube walls. The volatile contents of the tube were taken into the vacuum system and then the less volatile fraction (1.60 g), which condensed at −78°, was separated into its constituents by vpc (12-ft dinonyl phthalate column at 140°). In a similar way the silicon and germanium analogs were prepared and isolated by vpc using a 12-ft silicone column, at 65° for the silane and at 170° for the germane.

Reactions of the Trifluoropropynyl Derivatives. (a) **Dimethyltrifluoropropynylarsine.**—The arsine (0.45 g) and water (2 ml) were immiscible at 20° and after 4 months no reaction had occurred. Similarly there was no reaction after 5 days at 110°. The arsine reacted with 10% aqueous NaOH (5 days, 20°) giving 3,3,3-trifluoropropyne (29% yield). The arsine became slightly colored on exposure to ultraviolet light[11] and darkened on heating to 155° (2.5 days) and 180° (2.5 days), but in no case was the extent of decomposition very significant as judged by infrared and nmr spectra of the samples.

The arsine (0.41 g) and hexafluoropropene (2.26 g) were heated to 155° (2.5 days) and 180° (2 days) without reaction. The arsine and the propene failed to react after ultraviolet irradiation for 5 days in a Pyrex tube or 3 days in a quartz tube.

(b) **Methylbis(trifluoropropynyl)arsine.**—The arsine was stable to water (8 days, 20°) but reacted with 10% aqueous NaOH (3.5 days, 20°) to give trifluoropropyne (36% yield). The arsine had almost completely decomposed to a black solid after 2.5 days at 140° and became discolored very quickly on exposure to ultraviolet irradiation (2 hr).[11] After 2.5 days of irradiation the sample was black.

(c) **Triethyltrifluoropropynylgermane.**—The germane was stable to water at 20° (2 weeks) and to 10% aqueous NaOH (1 week, 20°).

The germane (1.67 g) and tetrafluoroethylene (4.5 g) did not react after 1 day at 140°. The same mixture was heated to 245° (2 days) and some tar was produced, but the least volatile liquid was only unreacted germane. Similarly, the germane failed to react with chlorotrifluoroethylene at 140° (12 hr), 140° (7 days), and 210° (7 days), and with 1,1-dichloro-2,2-difluoroethylene at 210° (7 days).

Reaction of 2-Dimethylarsino-1,1,1,4,4,4-hexafluorobutene with Trimethyltrifluoromethyltin.—The arsine (>90% *trans* isomer, 1.50 g) and the tin compound (1.48 g) were heated to 140° (20 hr) to give a 10% yield of 1-dimethylarsino-1,2-bis(trifluoromethyl)-3,3-difluorocyclopropane, which was separated from unreacted starting material by vpc (12-ft dinonyl phthalate column at 120°). *Anal.* Calcd for $(CH_3)_2AsC_5HF_5$: C, 26.5; H, 2.21; As, 23.6; F, 47.9. Found: C, 26.5; H, 2.33; As, 23.5; F, 47.7. The ^1H nmr spectrum consists of a multiplet at -1.22 ppm ($J \sim 2$ cps) due to $(CH_3)_2As$– and a complex multiplet at -2.70 ppm, area ratio = 6.1:1.

Discussion

Preparation of 3,3,3-Trifluoropropynyl Derivatives.—The synthetic route to 3,3,3-trifluoropropyne (eq 1) suggested that trifluoropropynyl derivatives might be produced if compounds such as iododimethylarsine or chlorotrimethylsilane were substituted for the water. However, this approach was unsuccessful. The first successful synthesis of this type of compound used a conventional Grignard procedure as follows [R_nMX = $(CH_3)_2AsI$, $(CH_3)_3SiCl$, $(C_2H_5)_3GeBr$]

$$CH_3MgI + CF_3C≡CH \longrightarrow CF_3C≡CMgI + CH_4 \qquad (2)$$

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(11) G.E. lamp (100-w) placed 10 cm from the tube.

TABLE II

ANALYTICAL DATA FOR CYCLOPROPENYL AND PROPYNYL DERIVATIVES

Compound	Bp, °C	Yield, %	Calcd, %				Found, %			
			C	H	M	F	C	H	M	F
$(CH_3)_2As\overline{C{=}C(CF_3)CF_2}$	~120[a]	~50[b]	29.0	2.42	30.2	38.4	29.2	2.55	30.1	38.5
$(C_2H_5)_3Ge\overline{C{=}C(CF_3)CF_2}$	160	~90[b]	39.8	4.96	23.8	31.4	39.5	4.96	24.2	31.3
$(CH_3)_3Si\overline{C{=}C(CF_3)CF_2}$	...	~90[b]	38.8	4.17	...	43.9	37.6	4.20	...	42.0
$(CH_3)_2AsC{\equiv}CCF_3$	98	35[c]	30.3	3.01	37.8	28.8	30.3	3.21	37.7	28.7
$(C_2H_5)_3GeC{\equiv}CCF_3$	98–100 (105 mm)	62[c]	42.9	5.93	...	...	42.7	6.16	...	...
$(CH_3)_3SiC{\equiv}CCF_3$	73[e]	18[d]	43.4	5.42	...	34.3	43.2	5.60	...	34.2
$CH_3As(C{\equiv}CCF_3)_2$	122–124	15[c]	30.4	1.10	27.4	41.3	30.4	1.07	27.1	41.5

[a] With decomposition. [b] Estimated by vpc. [c] Middle cut of distillation. [d] Estimated from nmr spectrum of mixture with $(CH_3)_3SiCl$. [e] Extrapolated from vp curve.

$$CF_3C{\equiv}CMgI + R_nMX \longrightarrow R_nMC{\equiv}CCF_3 + MgIX \quad (3)$$

$$2CF_3C{\equiv}CMgI + CH_3AsCl_2 \longrightarrow CH_3As(C{\equiv}CCF_3)_2 + 2MgIX$$

Trifluoropropynylmagnesium bromide had been prepared previously by a method analogous to that of eq 2.[5]

The new compounds, listed in Table II, were not obtained in good yield; however, this could be improved by changing the conditions. Nevertheless it seemed desirable to investigate other synthetic routes to the propynyl compounds, especially those which would use the propyne directly. One such possibility would be to allow the propyne to react with a metal hydride in the hope of eliminating hydrogen. This, apparently, is one of the ways in which phenylacetylene reacts with compounds with Al–H and B–H bonds,[12] but, although the propyne reacts with hydrides of tin or arsenic, addition of the hydride to the unsaturated system is all that occurs[7b,7d]

$$(CH_3)_3SnH + HC{\equiv}CCF_3 \longrightarrow (CH_3)_3SnCH{=}CHCF_3\ (\textit{cis}\text{ and }\textit{trans}) + (CH_3)_3SnC(CF_3){=}CH_2 + [(CH_3)_3Sn]_2CHCH_2CF_3 \quad (4)$$

$$(CH_3)_2AsH + HC{\equiv}CCF_3 \longrightarrow (CH_3)_2AsCH{=}CHCF_3\ (\textit{cis}\text{ and }\textit{trans}) + (CH_3)_2AsC(CF_3){=}CH_2 \quad (5)$$

Another possibility would be to allow the propyne to react with a metal halide in the hope of eliminating hydrogen halide. One such reaction, that with chlorodimethylarsine, has been investigated in the present work. At 155° some propynylarsine is obtained but the main product is a 1:1 adduct which is a mixture of the two isomers III and IV.

$$(CH_3)_2AsCl + HC{\equiv}CCF_3 \longrightarrow (CH_3)_2AsC{\equiv}CCF_3\ (12\%) + (CH_3)_2AsCH{=}CHCF_3\ (2\%) + (CH_3)_2AsC(CF_3){=}CClH\ (86\%) + CF_3CH{=}CHCl \quad (6)$$

The isomer formed by *trans* addition predominates as has been found for the 1:1 adduct obtained from chlorodimethylarsine and hexafluorobut-2-yne.[7c]

When the reaction is carried out at 100° or on ultraviolet irradiation no propynylarsine is obtained. However, if the reaction product is then distilled, the propynylarsine is produced. This suggests that the chloroarsine can also attack the other end of the triple bond to give the isomer $(CH_3)_2AsCH{=}C(CF_3)Cl$, probably by *trans* addition, which on heating eliminates HCl. In the reaction at 150° the HCl adds to the excess propyne

$$HCl + CF_3C{\equiv}CH \longrightarrow CF_3CH{=}CHCl \quad (7)$$

The origin of the *trans*-$(CH_3)_2AsCH{=}CHCF_3$ (eq 6) is less certain. This could arise by elimination of dimethylarsine from isomer III assisted by (or followed by) reaction with the propyne to give the 1:1 adduct.

$$(CH_3)_2AsC(CF_3){=}CClH \longrightarrow (CH_3)_2AsH + CF_3C{\equiv}CCl \quad (8)$$

The assisted path seems to be the more likely since only the *trans* isomer (the more thermodynamically stable of the *cis–trans* pair[7b]) is produced and no iso compound (*cf.* eq 5). The $CF_3C{\equiv}CCl$ which would be the other product was not identified.

Recently it has been found that tin compounds containing Sn–N,[13] Sn–O,[14] and Sn–Sn[15] bonds react readily with compounds containing active hydrogen. In particular acetylenes give alkynyltin derivatives as in the example[13]

$$R_3Sn{-}N(CH_3)_2 + HC{\equiv}CC_6H_5 \longrightarrow R_3SnC{\equiv}C_6CH_5 + HN(CH_3)_2 \quad (9)$$

It seemed reasonable to expect the analogous compounds of arsenic to react similarly, and the results are shown in Table I. The As–S bond is not very reactive but the As–N bond reacts quite rapidly. The diarsine is intermediate in reactivity. The oxide method is potentially the most economic since the eliminated water does not add to the acetylene. These reactions probably proceed through initial addition of the arsenic compound across the triple bond followed by elimination of the appropriate arsine, amine, sulfide, or hydroxide as in the examples

$$\begin{gathered}(CH_3)_2As{-}As(CH_3)_2 + HC{\equiv}CCF_3 \longrightarrow [(CH_3)_2AsCH{=}C(CF_3)As(CH_3)_2] \\ \Big\downarrow \qquad\qquad (10) \\ (CH_3)_2AsC{\equiv}CCF_3 + HAs(CH_3)_2\end{gathered}$$

$$(CH_3)_2AsH + HC{\equiv}CCF_3 \longrightarrow (CH_3)_2AsCH{=}CHCF_3 \quad (11)$$

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TABLE III

SPECTROSCOPIC DATA FOR CYCLOPROPENYL AND PROPYNYL DERIVATIVES

	Nmr, ppm		Infrared, cm^{-1}				
	δ(H)	δ(F)					
$(CH_3)_2As\overline{C{=}C(CF_3)CF_2}$	−1.05	. . .[a]	1754	1337	1291	1181	1100
$(C_2H_5)_3Ge\overline{C{=}C(CF_3)CF_2}$	−0.82[b]	. . .	1745	1335	1289	1155	1100
$(CH_3)_3Si\overline{C{=}C(CF_3)CF_2}$	+0.15	. . .	1758	1355	1285	1181	1100
$(CH_3)_2AsC{\equiv}CCF_3$	−1.08	−27.9	2210	1257	1216	1161	
$(C_2H_5)_3GeC{\equiv}CCF_3$	−0.80[b]	−27.6	2205	1259	1218	1140	
$(CH_3)_3SiC{\equiv}CCF_3$	+0.20	−26.6	2205	1262	1222	1165	
$CH_3As(C{\equiv}CCF_3)_2$	−1.44	−26.4	2210	1250	1222	1150	

[a] ^{19}F spectrum: quartet at +25.0 and triplet at −16.5 ppm (J_{F-F} = 3.82 cps). [b] Main peak of complex multiplet (see ref 30).

$$[(CH_3)_2As]_2O + HC{\equiv}CCF_3 \longrightarrow [(CH_3)_2AsCH{=}C(CF_3)OAs(CH_3)_2] \quad (12)$$
$$\downarrow$$
$$(CH_3)_2AsC{\equiv}CCF_3 + HOAs(CH_3)_2$$

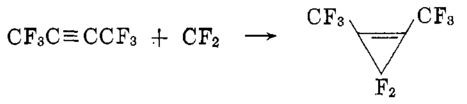
$$2(CH_3)_2AsOH \longrightarrow [(CH_3)_2As]_2O + H_2O \quad (13)$$

The eliminations are probably assisted at least for the arsine and amine since the arsine gives only *trans*-$(CH_3)_2AsCH{=}CHCF_3$ (eq 11) and not the mixture described in eq 5. Some justification for the initial step comes from the results that compounds with As–As[7a] and As–N[16] bonds add across the triple bond of hexafluorobut-2-yne.

The Ge–O bond is much less susceptible to attack by the propyne than is the As–O. However, compounds with Ge–N bonds should react.[17]

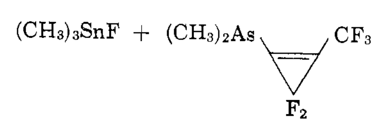
Preparation of Cyclopropenyl Derivatives.—Although dichlorocarbene has been added to acetylenes the dihalocyclopropene intermediates have not been isolated. They were immediately hydrolyzed to give, in low yield, the cyclopropenones.[18]

Mahler[19] has shown that hexafluorobut-2-yne reacts with difluorocarbene at 100° yielding the cyclobutene. The source of the CF_2 was $(CF_3)_3PF_2$.



(14)

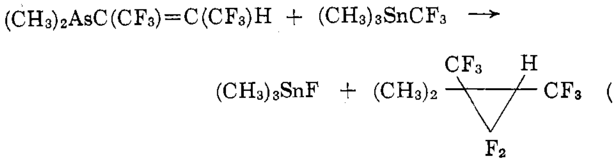
Clark and Willis[9a] found that $(CH_3)_3SnCF_3$ decomposes at 150° with elimination of CF_2, so the new propynyl compounds were heated with the trifluoromethyltin compound at 140°. The results in Table II show that good yields of the cyclopropenyl compounds can be obtained.



(15)

These compounds are the first to be prepared with a cyclopropene ring attached to a metal. They are stable indefinitely at 20° and appear to be moderately stable on heating, the germanium compound being unchanged after being heated to 160° in air for a few minutes.

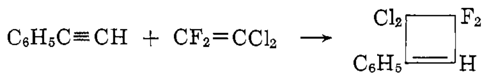
We have also found that difluorocarbene reacts with a vinylarsine to give the appropriate arsinocyclopropane.



(16)

This reaction of an olefin with a dihalocarbene to give a cyclopropane is well known.[20] However, only a few cyclopropanes have been prepared in which the ring is directly bonded to a metal or metalloid.[20,21]

Other Properties of Propynyl Derivatives.—Mahler[19] also found that heating tetrafluoroethylene with hexafluorobut-2-yne affords a low yield of 1,2-bis(trifluoromethyl)tetrafluorocyclobutene. It had been found earlier[22] that phenylacetylene and 1,1-dichloro-2,2-difluoroethylene also give a cyclobutene. Cyclobutenyl derivatives of the metals and metalloids are little known[3a,3b,23] and consequently attempts were made to prepare them by allowing the propynyl compounds to react with fluoroolefins such as $CF_3CF{=}CF_2$, $CF_2{=}CF_2$, $CF_2{=}CFCl$, and $CF_2{=}CCl_2$. A variety of conditions were used but in no case was there any sign of the anticipated cyclobutene.



Other properties of the trifluoropropynylarsines, such as thermal and hydrolytic stability, seem to be about the same as those of the corresponding arsines.[24]

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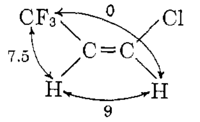
The propynylgermane appears to be more stable in these respects than the one investigated trifluoromethyl compound.[25]

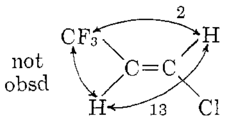
Structures of the New Compounds.—The analytical and spectroscopic data listed in Tables II and III leave no doubt that the propynyl and cyclopropenyl derivatives are as claimed. The only analytical figures which differ significantly from the expected values are those of the cyclopropenylsilane; however, the linearity of the plot of log (vapor pressure) against $1/T$ and the presence of only one $Si(CH_3)_3$ peak in its ^1H nmr spectrum attest to its purity. The acetylenes show similar infrared spectra and all have a strong $C{\equiv}C$ stretching band near 2210 cm^{-1}. The ^{19}F nmr spectra show the expected single peak. Only in the parent compound, $HC{\equiv}CCF_3$, is there any H—F coupling with $J = 3.7$ cps.[26] The cyclopropenyl compounds also have very similar infrared spectra and the double bond is seen as a strong band near 1750 cm^{-1}. The C=C stretching frequency of $CF_3\overline{C{=}C(CF_3)CF_2}$ (eq 14) is 1820 cm^{-1},[19] but the frequency of this band seems to be very dependent on the nature of the substituents on the ring.[27] Apart from the C=C and $C{\equiv}C$ vibrations the other bands listed in Table III are probably due to C—F stretching. The ^{19}F nmr spectrum of the arsinocyclopropene shows the expected triplet due to the CF_3 group and quartet due to the CF_2 group, the peaks being of the correct relative area.

The ^1H nmr spectrum of the product of eq 7 shows the couplings and isomer distributions given in I and II



17 parts

I

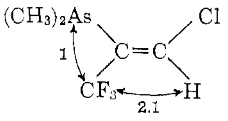


3 parts

II

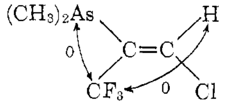
(couplings in cps). These assignments are based on the now well-established result that for this type of system J_{CF_3-H} (*trans*) ~ 0, J_{CF_3-H} (*cis*) ~ 2, and J_{CF_3-H} (*gem*) ~ 8 cps.[7b,7d,28] Furthermore they result in the usual relationship of J_{H-H} (*cis*) being less than J_{H-H} (*trans*). Haszeldine[29] had earlier found that HCl adds to the propyne in the direction indicated but was not able to determine the isomer distribution.

The major products of eq 6 are two compounds which analyze to be 1:1 adducts of $ClAs(CH_3)_2$ and $HC{\equiv}CCF_3$. That they are *cis–trans* isomers follows from the result that they can be interconverted on heating (faster in the presence of oxygen) and, as described in the preceding paragraph, from the magnitudes of the CF_3–H couplings in their ^1H nmr spectra. The couplings and suggested structures are given in III and IV. The point of attachment of the arsenic is not



1 part

III



9 parts

IV

completely certain, and these structures are based on the observation that the nmr spectra of compounds of the type $(CH_3)_2AsR_f$ (R_f is a fluorocarbon group) show splitting of the peak due to the methyl groups only when the structural unit $(CH_3)_2\substack{As\\CF_3}{>}C{=}$ is present[7]. Structure III is indicated because of the CF_3–CH_3 coupling and structure IV follows because of the isomerization.

In connection with this CF_3–CH_3 coupling, it should be noted that the ^1H nmr spectrum of the cyclopropane product of eq 16 also shows some splitting of the peak due to the $(CH_3)_2As$– group. However, some caution must be used since the addition of the difluorocarbene may not have been stereospecific, resulting in two compounds with similar nmr spectra. This possibility seems unlikely and the steric course of these additions is being further investigated. Seyferth[20] has given evidence which strongly suggests that dichlorocarbene adds stereospecifically to vinylsilanes.

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