SOME REACTIONS OF HEXAFLUORO-2-BUTYNE WITH COMPOUNDS OF ARSENIC AND TIN*

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Hexafluoro-2-butyne has been found to react with the As–As bonds of arsenic metal[1] and tetramethyldiarsine[2] to give compounds containing $AsC(CF_3)=C(CF_3)As$ units, for example:

$$(CH_3)_2As\text{—}As(CH_3)_2 + CF_3C\equiv CCF_3 \longrightarrow (CH_3)_2AsC(CF_3)=C(CF_3)As(CH_3)_2$$

The addition to the diarsine takes place smoothly at 20° giving an approximately 1:1 mixture of the *cis*- and *trans*-isomers It has also been reported[2] that tetrakis(trifluoromethyl)diarsine and the butyne do not react at 150°.

It has now been found that the butyne and tetrakis(trifluoromethyl)diarsine react on ultraviolet irradiation to give the expected adduct, b.p. 156°.

$$(CF_3)_2As\text{—}As(CF_3)_2 + CF_3C\equiv CCF_3 \longrightarrow (CF_3)_2AsC(CF_3)=C(CF_3)As(CF_3)_2$$

The absence of any absorption in the C=C stretching region indicates that in this case the product is mainly the *trans*-isomer. Similarly the butyne and hexamethylditin react on ultraviolet irradiation to give an unstable 1:1 adduct, $(CH_3)_3SnC(CF_3)=C(CF_3)Sn(CH_3)_3$, b.p. 53° ($10^{-3}$ mm). The ^{19}F NMR spectrum of this compound consists of only one broad peak indicating the presence of only one isomer and the absence of any C=C stretching frequency in the infrared spectrum suggests that it is the *trans*-isomer. The use of infrared spectra for assigning structures of this type seems to be reliable since the compound $(CH_3)_2AsSC(CF_3)=C(CF_3)SAs(CH_3)_2$, which without doubt has the *cis*-structure, has a strong band[3] at 1535 cm^{-1}. The 1:1 mixture of isomers of $(CH_3)_2AsC(CF_3)=C(CF_3)As(CH_3)_2$ has a weak band[2] at 1570 cm^{-1}, and when the preparation of this last compound is carried out in the presence of hexafluoroacetone the yield of the *cis*-isomer is very much increased with a corresponding increase in the intensity of the 1570 cm^{-1} band[4].

The ^1H NMR spectrum of the ditin adduct consists of a single methyl peak which is split into a multiplet with $J \approx 0.8$ cps. Splitting of the CH_3 resonance has been previously observed for methyl tin hydrides[5,6] but a single methyl peak was found for compounds of the type $(CH_3)_2Sn(CF_2CF_2H)_2$[6]. However, in the last example possible $F\text{–}CH_3$ coupling was indicated by the broadness of the line. The multiplet in the spectrum of the ditin adduct is certainly due to $CH_3\text{–}CF_3$ interaction, though it

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* For a preliminary communication describing part of this work see ref. 16.

seems unlikely that the coupling occurs through the bonds, and we prefer the idea that it occurs through space[7]. The broadness of the single line in the ^{19}F NMR spectrum is probably a consequence of this weak CH_3-CF_3 coupling which is expected to be of the order of 1 cps[8].

Hexafluoro-2-butyne does not react with hexaethyldigermane or with hexamethyldisilane on ultraviolet irradiation, a result which is not unexpected in view of the expected increasing strength of the M–M bond in the compounds R_3M–MR_3 as the group is ascended[9].

Although there is a reaction between hexabutylditin and hexafluoro-2-butyne on irradiation, it is very complicated. The only product identified was dibutylbis-(1,1,1,4,4,4-hexafluoro-2-butenyl-2)tin, $(C_4H_9)_2Sn[C(CF_3){=}C(CF_3)H]_2$, b.p. 60–63° ($10^{-3}$ mm). This has the same boiling point as the diadduct formed from dibutyltin dihydride and the butyne[10], although the infrared spectrum shows some slight differences in the C=C stretching region which are probably due to a difference in isomer distribution. The ^1H NMR spectrum shows a down field quartet, $J \approx 8$ cps, typical of the group $-C(CF_3){=}C(CF_3)H$, and the absence of further splitting of this quartet indicates that the compound is predominantly the *cis,cis*-isomer[8,10]. Other fractions isolated from the reaction suggest the presence of other compounds of the type $(C_4H_9)_nSn[C(CF_3){=}C(CF_3)H]_{4-n}$. The presence of the compound with $n = 3$ could be expected since a similar compound is obtained from the thermal decomposition of the 1:1 adduct of hexamethylditin and the butyne. This reaction proceeds at 150° to give, amongst other products, tetramethyltin, hexamethylditin, and (1,1,1,4,4,4-hexafluoro-2-butenyl-2)trimethyltin.

$$(CH_3)_3SnC(CF_3){=}C(CF_3)Sn(CH_3)_3 \longrightarrow (CH_3)_4Sn + (CH_3)_3SnC(CF_3){=}C(CF_3)H + (CH_3)_3Sn{-}Sn(CH_3)_3 + ?$$

The butenyl compound probably comes from an initially formed $(CH_3)_2SnC(CF_3){=}C(CF_3)^{\bullet}$ radical. The other products also suggest the initial formation of $(CH_3)_3Sn^{\bullet}$.

The preparation and properties of these butenyl compounds is being further investigated.

The metal halide-catalysed addition of acetylene to arsenic trichloride produces Lewisite which is mainly *trans*-$ClCH{=}CHAsCl_2$[11]. Dichlorophenylarsine and acetylene also react in the presence of aluminium trichloride to give a number of products including bis(β-chlorovinyl)phenylarsine[12]. We have now found that hexafluoro-2-butyne reacts smoothly with chlorodimethylarsine on ultraviolet irradiation to give 2-chloro-3-(dimethylarsino)hexafluoro-2-butene, a colorless liquid, b.p. 79–80° (50 mm).

$$(CH_3)_2AsCl + CF_3C{\equiv}CCF_3 \longrightarrow (CH_3)_2AsC(CF_3){=}C(CF_3)Cl$$

The same compound is obtained from the thermal reaction at 140° though in this case the reaction products are more complicated, and when aluminium trichloride is used to catalyse the thermal reaction a further compound is obtained in which the β-chloro group is replaced by a fluorine yielding 2-(dimethylarsino)heptafluoro-2-butene.

$$(CH_3)_2AsCl + CF_3C{\equiv}CCF_3 \xrightarrow{AlCl_3} (CH_3)_2AsC(CF_3){=}C(CF_3)F$$

A similar replacement reaction occurs when arsenic trichloride and tetrafluoroethylene are heated in the presence of aluminium trichloride[13].

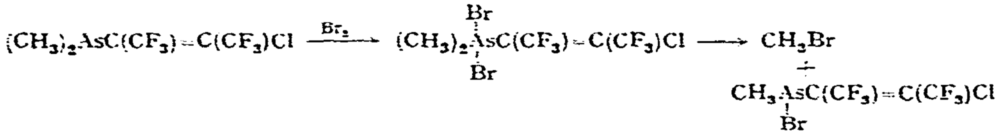
$$AsCl_3 + CF_2{=}CF_2 \longrightarrow Cl_2AsCF_2CF_3$$

The addition of the butyne to other As–Cl bonds does not readily occur (see Table) and only one other chloroarsine, chlorophenylmethylarsine, showed the possibility of reaction. The chlorides of tin and silicon do not react with acetylene[14] therefore it is not surprising to find that neither tributyltin chloride nor trimethylchlorosilane react with the butyne on irradiation.

The isomer distribution of the compound $(CH_3)_2AsC(CF_3){=}C(CF_3)Cl$ was investigated by NMR. The ^{19}F spectrum shows two main bands. Under high resolution the high field peak is split into a quartet $J = 1.4$ cps and the low field peak into a multiplet ($J \approx 1.4$ cps for 9 peaks). The appearance of the quartet suggests that it is due to CF_3–CF_3 coupling and the magnitude of the coupling indicates that the CF_3 groups are *trans* to each other[8]. The low field multiplet can best be understood in terms of the ^1H NMR spectrum, which shows the methyl peak split into a multiplet of approximately 4 peaks with $J \approx 2$ cps. Normally compounds of the type $(CH_3)_2AsR_f$ have a single unsplit methyl peak, *e.g.* $R_f = CF_3$ or C_3F_7, thus the coupling in the present example is either through space or is due to the presence of a fluorocarbon group with a double bond. The second alternative seems unlikely since the methyl group of the compound $(CH_3)_2As\overline{C{=}CFCF_2CF_2}$ is not split. On this basis the low field multiplet in the ^{19}F spectrum apparently arises from a splitting of $J \approx 1.4$ cps due to the *trans*-CF_3 groups superimposed on a weak CF_3–CH_3 coupling through space.

The ^{19}F NMR spectrum of the chlorovinyl compound also shows two weak quartets, $J = 15$ cps, outside the two main bands. Each peak of the low field quartet is broad, the middle peaks being approximate sextets with $J \approx 1.4$. The most likely explanation for these bands is that they are associated with the *cis*-isomer for which $J(CF_3$–$CF_3)$ would be expected to be greater than for the *trans* compound and to be of the order of 12 cps[8]. The further splitting of the down field peaks would then be due to coupling through space with the arsenic methyl groups. The abundance of the *cis*-isomer is, however, 5 % at the most and it is of interest to compare the formation of predominantly the *trans*-butyne-chloroarsine adduct on irradiation with the result that (*trans*-β-chlorovinyl)mercury compounds are converted into the *cis*-isomers by ultraviolet radiation[14].

The chlorovinyl compound readily reacts with 1 mole of bromine to give an unstable solid whose infrared spectrum still shows the presence of a double bond. Thus the arsine is oxidized to the pentavalent dibromide. When the dibromide is heated it decomposes quantitatively to methyl bromide and the colourless liquid, 2-chloro-3-(bromomethylarsino)hexafluoro-2-butene.



$$(CH_3)_2AsC(CF_3){=}C(CF_3)Cl \xrightarrow{Br_2} (CH_3)_2\underset{Br}{\overset{Br}{As}}C(CF_3){=}C(CF_3)Cl \longrightarrow CH_3Br + CH_3\underset{Br}{As}C(CF_3){=}C(CF_3)Cl$$

There are many known examples of this type of reaction sequence, a recent one being[15]:

$$(p\text{-}CH_3C_6H_4)CH_3AsC_6H_5 \xrightarrow[\text{(b) }-CH_3Cl]{\text{(a) }+Cl_2} (p\text{-}CH_3C_6H_4)ClAsC_6H_5,$$

and the method is valuable in that the inactive methyl is replaced by the reactive halogen.

The ^1H NMR spectrum of $Br(CH_3)AsC(CF_3){=}C(CF_3)Cl$ again showed one main band split into a multiplet of 4 with $J \approx 1.2$ cps. The ^{15}F spectrum is mainly two quartets, $J = 14$ cps, indicating that the compound is predominantly the *cis*-isomer[8]. Two other peaks of equal intensity ($< 10\%$ of the mixture) were present one of which was a quartet ($J = 1.4$ cps) and the low field one a broad multiplet; these can be assigned to the *trans*-isomer. The CF_3-CH_3 through space coupling which results in the multiplet in the ^1H spectrum is also seen in the broadening of the ^{19}F low field peaks of both the *cis*- and *trans*-isomers.

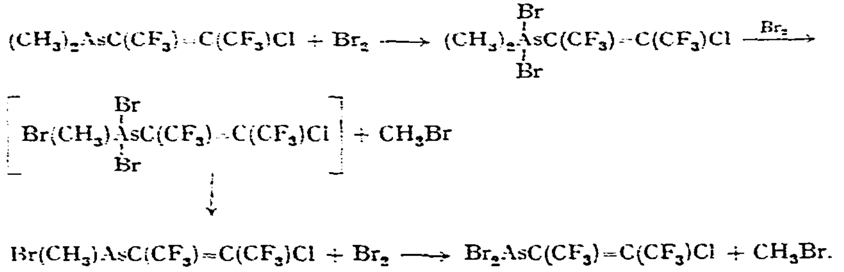
The apparent isomerisation in the process

$$(CH_3)_2AsC(CF_3){=}C(CF_3)Cl \longrightarrow Br(CH_3)AsC(CF_3){=}C(CF_3)Cl$$

is being further investigated and preliminary results indicate that a similar phenomenon occurs in the following sequence[10].

$$(CH_3)_2AsC(CF_3){=}C(CF_3)H \xrightarrow[\text{(b) heat}]{\text{(a) }Br_2} CH_3Br + Br(CH_3)AsC(CF_3){=}C(CF_3)H$$

Bromination of $(CH_3)_2AsC(CF_3){=}C(CF_3)Cl$ with two moles of bromine results in the fast uptake of part, presumably to form the dibromide, followed by a slow reaction with the rest. Methyl bromide (73% of 2 moles) is produced together with a fraction of low volatility which is probably $Br_2AsC(CF_3){=}C(CF_3)Cl$. The reaction of $Br(CH_3)AsC(CF_3){=}C(CF_3)Cl$ with one mole of bromine is slow suggesting that cleavage is occurring rather than oxidation to the dibromide. Methyl bromide (80% of 1 mole) is produced and again the involatile residue seems to be mainly $Br_2AsC(CF_3){=}C(CF_3)Cl$. These reactions are probably represented as follows



$$(CH_3)_2AsC(CF_3){=}C(CF_3)Cl + Br_2 \longrightarrow (CH_3)_2\overset{Br}{\underset{Br}{As}}C(CF_3){=}C(CF_3)Cl \xrightarrow{Br_2}$$

$$\left[Br(CH_3)\overset{Br}{\underset{Br}{As}}C(CF_3){=}C(CF_3)Cl\right] + CH_3Br$$

$$\downarrow$$

$$Br(CH_3)AsC(CF_3){=}C(CF_3)Cl + Br_2 \longrightarrow Br_2AsC(CF_3){=}C(CF_3)Cl + CH_3Br.$$

EXPERIMENTAL

Volatile reactants and products were manipulated using standard vacuum techniques. Reactions were carried out in sealed pyrex tubes, which, for ultraviolet irradiation, were placed 10 cm away from a General Electric 100 watt lamp. The tubes were shaken if the reactants were initially immiscible. Infrared spectra reported in cm^{-1} were run on a P.E.-21 instrument, those reported in microns were run on a calibrated Infracord. ^{19}F and ^{1}H NMR spectra, were obtained using Varian H.R.-60 (at 56.4 Mc/s) and A-60 spectrometers. Unless otherwise stated ^{19}F spectra are reported relative to external trifluoroacetic acid and ^{1}H spectra relative to internal tetramethylsilane references.

Microanalyses were carried out by Dr. ALFRED BERNHARDT, Mülheim, Germany (arsenic compounds) and by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N.Y., U.S.A. (tin compounds).

Reaction with tetrakis(trifluoromethyl)diarsine

The diarsine (1.4 g) and hexafluoro-2-butyne (1.7 g) were irradiated for 4 days to give 0.6 g of the 1:1 adduct 2,3-bis[bis(trifluoromethyl)arsino]hexafluoro-2-butene. (Found: C, 16.4; F, 58.0; As, 25.7. $C_8As_2F_{18}$ calcd.: C, 16.3; F, 58.2; As, 25.5%.) Infrared spectrum (liquid film): 1329 (w), 1314 (w), 1253 (vs), 1191 (s), 1173 (vs), 1154 (vs), 1132 (s), 1120 (vs), 1070 (vs), 870 (w), 808 (w), 731 (s), 711 (w), 657 (m) cm^{-1}. The boiling point was found to be 156° ± 2° by extrapolation of the vapor pressure curve. Some decomposition on the mercury surface seemed to take place. Qualitative base hydrolysis of the adduct at 100° gave only *trans*-1,1,1,4,4,4-hexafluoro-2-butene.

Reaction with hexamethylditin

Hexamethylditin (5.2 g) and hexafluoro-2-butyne (8.0 g) were immiscible at 20°. Heating at 100° (2 days) resulted in considerable reaction and 6.6 g of the acetylene were recovered. Trimethyltin fluoride of known infrared spectrum remained in the reaction tube.

When the ditin compound (6.2 g) and the acetylene (6.1 g) were irradiated for 2 days one liquid phase was produced and only 3.0 g of the butyne were recovered. The involatile colorless liquid residue in the reaction tube was identified as the expected 1:1 adduct 2,3-bis(trimethylstannyl)hexafluoro-2-butene, b.p. 53° (10^{-3} mm). (Found: C, 24.7; H, 3.8; F, 23.0; Sn, 48.4. $C_{10}H_{18}F_6Sn_2$ calcd.: C, 24.5; H, 3.7; F, 23.3; Sn, 48.5%.) Infrared spectrum (liquid films): 2960 (m), 2885 (m), 1685 (m), 1308 (w), 1261 (m), 1235 (vs), 1185 (m), 1130 (vs), 1015 (m), 847 (w), 767 (s), 692 (w), 642 (m) cm^{-1}. NMR spectra: ^{19}F spectrum has one broad peak at −1227 cps and the ^{1}H spectrum a multiplet of peaks centered at $\tau = 0.34$ ($J \approx 0.8$ cps).

Qualitative base hydrolysis of the adduct (70°, 4 days) gave only a trace of a mixture of *cis*- and *trans*-1,1,1,4,4,4-hexafluoro-2-butene. A sample of the adduct was heated at 150° (18 hours) to give tetramethyltin (mol. wt. calcd. 179, found 181) of known retention time. V.p.c. investigation of the less volatile products (Apiezon J at 120°) showed 5 components. The fifth component was identified as hexamethylditin of known infrared spectrum, the first component was a fluorocarbon, and the third component, the main product, was found to be (1,1,1,4,4,4-hexafluoro-2-butenyl-2)-

trimethyltin. (Found: C, 25.8; H, 3.0; F, 35.1; Sn, 36.0%. $C_7H_{10}F_6Sn$ calcd.: C, 25.7; H, 3.1; F, 34.9; Sn, 36.3%.) Infrared spectrum (liquid film): 3.35 (m), 3.45 (m), 5.8 (w), 7.1 (w), 7.45 (w), 7.6 (vs), 7.8 (m), 8.0 (vs), 8.3 (w), 8.35 (w), 8.8 (vs), 10.85 (w), 11.35 (m), 11.75 (m), 12.7 (m), 13.65 (w) μ.

Reaction with hexabutylditin

The ditin (11.5 g) and 15.0 g of hexafluoro-2-butyne were irradiated for 5 days. The involatile contents of the tube were distilled at 10^{-3} mm to give a small amount of material which came over at 61–63° and which was identified as dibutylbis(1,1,1,4,4,4-hexafluoro-2-butenyl-2)tin. (Found: C, 34.0; H, 3.4; F, 41.4. $C_{16}H_{20}F_{12}Sn$ calcd.: C, 34.4; H, 3.6; F, 40.8%.) The remaining involatiles distilled at 70–100°. The infrared spectra of various cuts showed a steady increase in C–H intensity and a decrease in C–F intensity with decreasing volatility.

In a second experiment after irradiation for 28 hours distillation of the involatiles (10^{-3} mm) resulted in the formation of tributyltin fluoride in the still pot. A fraction which boiled at 63–65° was analyzed by v.p.c. (Ucon Polar at 140°) and found to contain 9 components. The main component, the last peak, was collected and its ^1H NMR spectrum had a down field quartet ($J \approx 8$ cps) centered at $\tau = 3.12$. The ^1H spectrum of the earlier fractions also showed the presence of downfield protons as quartets ($J \approx 8$ cps).

Reaction with chlorodimethylarsine

(*i*) The arsine (5.0 g) and hexafluoro-2-butyne (9.5 g) were initially immiscible but after 2 days irradiation only one phase remained. Butyne (5.6 g) was recovered and the residue in the tube was distilled in a nitrogen atmosphere to give 8.7 g of 2-chloro-3(dimethylarsino)hexafluoro-2-butene, b.p. 79–80° (50 mm), 131–137° (83 mm). (Found: C, 24.0; H, 1.9; As, 24.6; Cl, 11.9; F, 37.5. $C_6H_6AsClF_6$ calcd.: C, 23.4; H, 2.0; As, 24.8; Cl, 11.7; F, 37.8%.) Infrared spectrum (liquid film): 2910 (vw), 1584 (w), 1420 (vw), 1263 (m), 1227 (vs), 1187 (s), 1156 (vs), 1130 (sh), 982 (w), 896 (vw), 875 (vw), 850 (w), 780 (w) cm^{-1}. NMR spectra: ^1H spectrum is a multiplet at $\tau = 8.7$ ($J \approx 1$ cps). ^{19}F spectrum two main peaks at $+118$ and $+285$. The down field peak is split into a multiplet of *ca.* 9 peaks ($J \approx 1.4$ cps). Two other weak quartets ($J = 15$ cps) centered at $+42$ and $+372$ cps are present. The down field quartet is split into a multiplet ($J \approx 1.4$ cps). The ^{19}F spectrum is reported relative to an internal benzotrifluoride standard.

(*ii*) When the chloroarsine and excess acetylene were heated to 140° (20 hours) one phase was again produced. Distillation of the involatile products at 760 mm did not give any well defined fractions though the bulk of the material boiled at 142°. V.p.c. examination (dinonyl phthalate at 140°) showed that 3 main components were present. The first was a fluorocarbon containing no arsenic, the third analyzed to be the 1:1 adduct described in (*a*). (Found: C, 23.8; H, 2.1; As, 24.7; Cl, 12.0; F, 38.0%.) The second component had almost the same infrared spectrum as the 1:1 adduct except for some differences in band intensity, however, the analytical results are difficult to interpret. (Found: C, 20.1; H, 3.0; Cl, 14.5; F, 31.7%.)

(*iii*) When the thermal reaction is carried out at 140° in the presence of aluminium trichloride essentially the same products were produced except that a fraction boiling in the range 148–156° was isolated which when purified by v.p.c. (dinonyl-phthalate at 110°) analysed to be 2-(dimethylarsino)heptafluoro-2-butene. (Found: C, 25.0; H, 2.0; As, 26.0; F, 46.6. $C_6H_6AsF_7$ calcd.: C, 25.2; H, 2.1; As, 26.2; F, 46.5%.)

Reaction with other chloroarsines and related compounds

The results of these experiments are summarized in the table below. Quantitative recovery of the butyne was obtained from all the experiments except the one indicated.

Wt. of $CF_3C{\equiv}CCF_3$	*Reactant*		*Conditions*[c]
9.7 g	$(CH_3)_3Si{-}Si(CH_3)_3$	(2.4 g)	UV irradiation, 2 days
7.6 g	$(C_2H_5)_3Ge{-}Ge(C_2H_5)_3$	(2.4 g)	UV irradiation, 2 days
25.0 g	$(n\text{-}C_4H_9)_3SnCl$	(6.5 g)	UV irradiation, 4 days
5.0 g	$(CH_3)_3SiCl$	(6.1 g)	UV irradiation, 1 day
17.9 g	CH_3AsCl_2	(4.8 g)	UV irradiation, 1 day
12.3 g	CH_3AsCl_2	(4.7 g)	heat 105°, 2 days[a]
10.2 g	$(C_6H_5)_2AsCl$	(4.5 g)	UV irradiation, 2 days
11.3 g	$CH_3(C_6H_5)AsCl$	(10.0 g)	UV irradiation, 3 days[b]
28.4 g	$AsCl_3$	(10.7 g)	UV irradiation, 2 days
11.2 g	$AsCl_3$	(9.4 g)	heat 135°, 2 days[a]

[a] $AlCl_3$ added. [b] Possibly some reaction as the recovery of the butyne was not quantitative.
[c] A referee has pointed out that the butyne alone can react on UV irradiation. This process probably requires light of $\lambda < 3000$ Å which would be cut off in our experiments using thick walled Pyrex tubes.

Reactions of $(CH_3)_2AsC(CF_3){=}C(CF_3)Cl$

(*i*) *Heating*. A sample of the adduct on heating to 220° (3 days) deposited a brown solid. The volatile products were mainly silicon tetrafluoride of known infrared spectrum.

(*ii*) *Bromination*. (*a*) The adduct (1.0 g) in carbon tetrachloride readily reacted with bromine (1 mole). Evaporation of the solvent left a cream crystalline solid which contained a double bond (C=C absorption at 1606 cm^{-1}). The dibromide (0.3808) was heated at 100° for 1.5 hours to give methyl bromide (0.082 g, 1 mole) identified by its molecular weight of 92.8 (calcd.: 95.0) and by its infrared spectrum. The residue in the tube was identified as 2-chloro-3(bromomethylarsino)hexafluoro-2-butene by comparison of its infrared spectrum with that of an analysed sample obtained from a larger scale preparation. The compound boils at 106–115° (70 mm). (Found: C, 16.4; H, 0.9; As, 20.4; Br, 21.6; Cl, 9.84; F, 30.9. $C_5H_3AsBrClF_6$ calcd.: C, 16.3; H, 0.8; As, 20.2; Br, 21.8; Cl, 9.66; F, 31.0%.) Infrared spectrum (liquid film): 4.4 (vw), 6.3 (m), 7.15 (m), 8.1 (vs), 8.35 (sh), 8.6 (vs), 10.05 (w), 11.4 (m), 11.7 (w), 12.05 (vw), 12.5 (vw), 14.2 (s) μ. NMR spectra: ^1H spectrum is a single multiplet (approximate quartet $J \approx 1.2$ cps) centered at $\tau = 7.92$. ^{19}F spectrum consists of two quartets ($J = 14$ cps) centered at -954 and -1400 cps the low field peak being broad and showing signs of further splitting. Another less intense pair of lines was present lying in between the other two; the high field line being a quartet ($J = 1.4$ cps) and the low field one being a broad multiplet.

(*b*) The arsine (1.4 g, 1 mole) was mixed with bromine (1.5 g, 2 mole) in carbon tetrachloride and an immediate reaction with part of the bromine took place. A colorless precipitate was produced which slowly went back into solution as the remainder of the bromine reacted. Methyl bromide (0.64 g, 73 % of 2 moles) was produced and an involatile fraction remained whose infrared spectrum suggested that it was $Br_2AsC(CF_3)=C(CF_3)Cl$.

The same compound was apparently the product of the slow reaction of $Br(CH_3)AsC(CF_3)=C(CF_3)Cl$ (1.2 g, 1 mole) and bromine (0.5 g, 1 mole) in carbon tetrachloride which also gave methyl bromide (0.24 g, 80 % of 1 mole).

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SUMMARY

Hexafluoro-2-butyne reacts with the compounds $(CH_3)_3Sn{-}Sn(CH_3)_3$, $(CF_3)_2As{-}As(CF_3)_2$, and $(CH_3)_2AsCl$ on ultraviolet irradiation yielding $(CH_3)_3SnC(CF_3)=C(CF_3)Sn(CH_3)_3$, $(CF_3)_2AsC(CF_3)=C(CF_3)As(CF_3)_2$ and $(CH_3)_2AsC(CF_3)=C(CF_3)Cl$. Evidence is presented which indicates that these compounds are predominantly the *trans*-isomers. The chloroarsine adduct reacts with bromine to give a dibromide which on heating eliminates methyl bromide yielding $Br(CH_3)AsC(CF_3)=C(CF_3)Cl$ which seems to be predominantly the *cis*-isomer. The NMR spectra of these compounds show $CH_3{-}CF_3$ interactions which are probably examples of "through space" coupling.

A number of other unsuccessful reactions of the butyne are described.

REFERENCES

1 C. G. Krespan, *J. Am. Chem. Soc.*, 83 (1961) 3432.
2 W. R. Cullen and N. K. Hota, *Can. J. Chem.*, 42 (1964) 1123.
3 W. R. Cullen and P. S. Dhaliwal, *Inorg. Chem.*, in print.
4 W. R. Cullen and G. E. Styan, unpublished work.
5 H. D. Kaesz and J. R. Holmes, *J. Am. Chem. Soc.*, 83 (1961) 3903.
6 H. C. Clark, J. T. Kwon, L. W. Reeves and E. J. Wells, *Can. J. Chem.*, 41 (1963) 3005.
7 A. H. Lewin, *J. Am. Chem. Soc.*, 86 (1964) 2304; D. R. Davis, R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, 83 (1961) 246.
8 P. M. Treichel, E. Pitcher and F. G. A. Stone, *Inorg. Chem.*, 1 (1962) 511.
9 T. L. Cottrell, *The Strengths of Chemical Bonds*, Academic Press, New York, 1958.
10 W. R. Cullen, D. S. Dawson and G. E. Styan, unpublished work.
11 C. A. McDowell, H. G. Emblem and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, (1948) 1206.
12 C. K. Banks, F. H. Kahler and C. S. Hamilton, *J. Am. Chem. Soc.*, 69 (1947) 933.
13 A. B. Bruker, T. G. Spiridonova and L. Z. Soborovskii, *J. Gen. Chem. USSR*, 28 (1958) 347.
14 H. D. Kaesz and F. G. A. Stone, in H. Zeiss, *Organometallic Chemistry*, Reinhold, New York, 1960.
15 K. Mislow, A. Zimmerman and J. T. Melillo, *J. Am. Chem. Soc.*, 85 (1963) 594.
16 W. R. Cullen, D. S. Dawson, N. K. Hota and G. E. Styan, *Chem. Ind. (London)*, (1963) 983.