PERFLUOROALKYL ARSENICALS

PART IX. SOME REACTIONS OF COMPOUNDS CONTAINING As–As BONDS[1]

W. R. CULLEN AND N. K. HOTA
Department of Chemistry, University of British Columbia, Vancouver, British Columbia

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ABSTRACT

Arsenobenzene reacts with CF_3I to give $C_6H_5As(CF_3)_2$, $C_6H_5As(CF_3)I$, and $C_6H_5AsI_2$. $C_6H_5As(CF_3)I$ and AgCl yield $C_6H_5As(CF_3)Cl$. The compounds $CF_2{=}CFX$ react with $(CH_3)_2As{-}As(CH_3)_2$ under mild conditions to give 1:1 adducts $(CH_3)_2As{-}CF_2CFX{-}As(CH_3)_2$ ($X = CF_3$, Br). Some $(CH_3)_2As{-}CF{=}CF_2$ is produced when X = Br and is the major product when X = I. When X = F a 1:4 adduct $(CH_3)_2As{-}(CF_2CF_2)_4{-}As(CH_3)_2$ is probably formed on ultraviolet irradiation. $(CH_3)_2As{-}As(CH_3)_2$ reacts with $CF_3C{\equiv}CCF_3$ to give *cis* and *trans* $(CH_3)_2AsC(CF_3){=}C(CF_3)As(CH_3)_2$ and with $\overline{CF{=}CFCF_2CF_2}$ to give $(CH_3)_2AsF$ and $(CH_3)_2As{-}\overline{CF{=}CFCF_2CF_2}$.

DISCUSSION AND RESULTS

Compounds containing weak bonds such as As–As (1), P–P (1, 2, 3), and Sn–Sn (4, 5) are readily cleaved when treated with perfluoroalkyl iodides, for example,

$$(CH_3)_2As{-}As(CH_3)_2 + CF_3I \rightarrow (CH_3)_2AsCF_3 + IAs(CH_3)_2.$$

We have now found that the As–As bonds in arsenobenzene, better named hexaphenylcyclohexaarsine (6), undergo a similar reaction when heated with an excess of trifluoroiodomethane at 115°, or at lower temperatures when the reactants are exposed to ultraviolet radiation. The products are phenylbis(trifluoromethyl)arsine, iodophenyltrifluoromethylarsine, and diiodophenylarsine.

$$(C_6H_5As)_6 + CF_3I \rightarrow C_6H_5As(CF_3)_2 + C_6H_5As(CF_3)I + C_6H_5AsI_2$$

Similar products have been isolated from the thermal and photochemical reaction of tetraphenylcyclotetraphosphine with trifluoroiodomethane (2). In an attempt to extend this type of reaction to the preparation of more complex aryltrifluoromethylarsines, *p*-nitroarsenobenzene was heated to 100° with trifluoroiodomethane. After a few hours the reaction tube exploded. This result was reproducible.

Iodophenyltrifluoromethylarsine, a new compound, b.p. 136–137° (35 mm), 158° (65 mm), reacts with silver chloride to give the more volatile chloroarsine, b.p. 118° (65 mm). The iodoarsine does not react with methyl iodide in the presence of mercury to give the expected methylphenyltrifluoromethylarsine (7). However, coupling of the iodoarsine appears to take place to give a white solid diarsine which decomposes in air to benzenearsonic acid.

$$2\ C_6H_5(CF_3)AsI + Hg \rightarrow C_6H_5(CF_3)As{-}As(CF_3)C_6H_5 + HgI_2$$

Chlorophenyltrifluoromethylarsine reacts with bis(trifluoromethyl)arsine at 100° to give hydrogen chloride, tris(trifluoromethyl)arsine, tetrakis(trifluoromethyl)diarsine, and possibly chlorobis(trifluoromethyl)arsine. A white solid is also produced which decomposes to benzenearsonic acid on exposure to air. The formation of hydrogen chloride and an unstable solid suggests that the main reaction is a coupling one to produce a diarsine.

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[1] *For a preliminary publication see W. R. Cullen, D. S. Dawson, N. K. Hota, and G. E. Styan. Chem. Ind. London, 983 (1963).*

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However, analysis of the solid product indicates that it is mainly the symmetrical diarsine $(C_6H_5(CF_3)As)_2$ (Anal. Found: C, 36.6, H, 2.3%. Calc.: C, 37.9, H, 2.3%) rather than the unsymmetrical one $C_6H_5(CF_3)As—As(CF_3)_2$. Either diarsine could decompose to give benzenearsonic acid. The symmetrical diarsine could arise from reactions of the following sort (8).

$$C_6H_5(CF_3)AsCl + HAs(CF_3)_2 \rightarrow C_6H_5(CF_3)As—As(CF_3)_2 + HCl$$

$$-\ HCl \uparrow \downarrow +\ HCl$$

$$C_6H_5(CF_3)AsH + ClAs(CF_3)_2$$

$$(CF_3)_2AsH + ClAs(CF_3)_2 \rightleftarrows (CF_3)_2As—As(CF_3)_2 + HCl$$

$$C_6H_5(CF_3)AsH + ClAs(CF_3)C_6H_5 \rightleftarrows C_6H_5(CF_3)As—As(CF_3)C_6H_5 + HCl$$

Such a scheme would also explain the formation of tetrakis(trifluoromethyl)diarsine and chlorobis(trifluoromethyl)arsine. It does not, however, account for the presence of tris(trifluoromethyl)arsine in the reaction products.

There are a few examples known of the addition of olefins and acetylenes to compounds containing M–M bonds (M = P (9, 10), B (11), Sn (12), S (13)), for example

$$(CH_3)_2P—P(CH_3)_2 + C_2F_4 \rightarrow (CH_3)_2P—CF_2CF_2—P(CH_3)_2.$$

Cacodyl (tetramethyldiarsine) has now been found to react similarly with fluorine containing olefins and acetylenes. Thus when the diarsine is treated with excess hexafluoropropene under mild conditions, a 1:1 adduct, 1,2-bis(dimethylarsino)hexafluoropropane, is formed.

$$(CH_3)_2As—As(CH_3)_2 + CF_3CF{=}CF_2 \rightarrow (CH_3)_2As—CF(CF_3)CF_2—As(CH_3)_2$$

The adduct distills at 116–117° (50 mm) and is hydrolyzed by hot alkali to give 1,2,3,3,3,-pentafluoroprop-1-ene. The olefin is probably produced by HF elimination from the initially formed propane, which would contain two adjacent CHF groups (14).

$$(CH_3)_2As—C(CF_3)F—CF_2—As(CH_3)_2 \xrightarrow{NaOH} (CH_3)_2AsONa + CF_3CFH—CF_2H$$

$$CF_3CFH—CF_2H \longrightarrow CF_3CF{=}CFH + HF$$

Cacodyl also reacts easily with hexafluorobut-2-yne to give a 1:1 adduct 2,3-bis(dimethylarsino)hexafluorobut-2-ene, b.p. 42° (10^{-3} mm), 99° (17 mm).

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

The F^{19} nuclear magnetic resonance spectrum shows only two peaks of approximately equal intensity such as would be shown by an approximately equimolar mixture of the *cis* and *trans* forms of the adduct. The infrared spectrum of the adduct shows only a weak double-bond absorption at 1570 cm^{-1}. Hydrolysis gives a small amount of *trans*-1,1,1,4,4,4,-hexafluorobut-2-ene. The adduct reacts with mercuric chloride to give a complex of indefinite constitution. A similar adduct is obtained from hexamethylditin and hexafluorobut-2-yne on ultraviolet irradiation, although in this case the F^{19} n.m.r. spectrum has only one peak, indicating that only one isomer is formed (15). Grant (2) has found that the iodine catalyzed reaction of tetrakis(trifluoromethyl)diphosphine with acetylene gives a *trans* adduct.

$$(CF_3)_2P—P(CF_3)_2 + HC{\equiv}CH \rightarrow (CF_3)_2P—CH{=}CH—P(CF_3)_2$$

In the present investigation we have found that tetrakis(trifluoromethyl)-diphosphine and -diarsine do not react with hexafluorobut-2-yne at 100°. The nature and variety of these addition reactions and their products makes it difficult to suggest a reaction mechanism without a much more detailed study; however, the *trans* orientation of one product and the 1:1 distribution of isomers in another seems to rule out a general four-center mechanism.

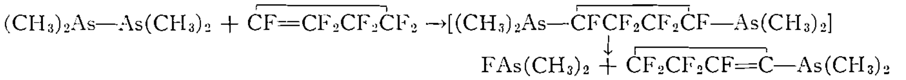
Cacodyl does not react immediately with tetrafluoroethylene at 20°, but, when the two are irradiated with ultraviolet light, reaction does occur. Trimethylarsine is produced in small amounts, but the main reaction product is an involatile, air-stable liquid which analysis indicates to be mainly the 1:4 adduct $(CH_3)_2As—(C_2F_4)_4—As(CH_3)_2$. The F^{19} n.m.r. spectrum supports this result. It shows three broad lines with chemical shifts of the magnitude expected for CF_2 groups in a chain (16). The relative areas of the peaks are 58:30:27, but because of overlap the ratio of the smaller peaks, 30:27, is not very accurate. However, their total relative area of 57 is reliable. These figures strongly indicate that the relative areas are in fact 2:1:1 or 4:2:2, the ratios which would be expected from the compound

$$(CH_3)_2As\cdot\overset{\text{i}}{CF_2}\cdot\overset{\text{ii}}{CF_2}\cdot\overset{\text{iii}}{(C_2F_4)_2}\cdot\overset{\text{ii}}{CF_2}\cdot\overset{\text{i}}{CF_2}\cdot As(CH_3)_2$$

where the fluorines on carbon atoms i, ii, and iii would have different chemical shifts (16). Similar products have been obtained from the iodine-catalyzed reaction of tetrafluoroethylene with dimethyl disulphide (13).

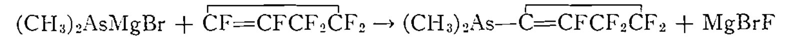
$$(CH_3)_2S_2 + C_2F_4 \rightarrow CH_3S(C_2F_4)_nSCH_3$$

The reaction of cacodyl with hexafluorocyclobutene at 20° yields fluorodimethylarsine and the novel compound 1-dimethylarsinopentafluorocyclobutene, b.p. 125°, in good yield. The n.m.r. spectrum of this compound, which will be reported in detail later, is complex but contains three general regions of fluorine absorption as expected. The infrared spectrum shows a strong double-bond absorption at 1659 cm^{-1}. The method of preparation of the compound and the results described above suggest that the first product of the reaction is a 1:1 adduct which eliminates fluorodimethylarsine to give the cyclobutene derivative.



$$(CH_3)_2As—As(CH_3)_2 + \overline{CF{=}CF_2CF_2CF_2} \rightarrow [(CH_3)_2As—\overline{CFCF_2CF_2CF}—As(CH_3)_2]$$
$$\downarrow$$
$$FAs(CH_3)_2 + \overline{CF_2CF_2CF{=}C}—As(CH_3)_2$$

A similar reaction sequence has been suggested (17) to account for the formation of 1-alkyl-pentafluorocyclobutenes from the reaction of hexafluorocyclobutene with alkylmagnesium halides. The same cyclobutene derivative can be made by reacting hexafluorocyclobutene with the "Grignard reagent" made from dimethylarsine (18).



$$(CH_3)_2AsMgBr + \overline{CF{=}CFCF_2CF_2} \rightarrow (CH_3)_2As—\overline{C{=}CFCF_2CF_2} + MgBrF$$

A 1:1 adduct is probably formed when the diarsine reacts with bromotrifluoroethylene under mild conditions, although in this case analysis of the product 1-bromo-1,2-bis(dimethylarsino)trifluoroethane, b.p. 65° (10^{-3} mm), indicated it to be impure. The adduct slowly decomposes at 20° to give dimethyltrifluorovinylarsine and presumably bromodimethylarsine.

$$(CH_3)_2As—As(CH_3)_2 + CF_2{=}CFBr \rightarrow (CH_3)_2As—CF_2CFBr—As(CH_3)_2 \rightarrow$$
$$(CH_3)_2AsCF{=}CF_2 + (CH_3)_2AsBr$$

Both these decomposition products as well as fluorodimethylarsine, the dimer of bromotrifluoroethylene, and other unidentified fractions are also formed in the initial reaction to produce the adduct. Addition followed by elimination is probably the source of the dimethylperfluorovinylarsine and the bromodimethylarsine. In a similar way the reaction of bromotrifluoroethylene with tetrakis(trifluoromethyl)-diarsine and -diphosphine at 100° probably gives bis(trifluoromethyl)trifluorovinyl-arsine and -phosphine (19). Dimethyltrifluorovinylarsine is also produced when cacodyl and trifluoroiodoethylene interact at 20°. Iododimethylarsine and an unidentified volatile yellow solid are the other products. A stable adduct $(CH_3)_2As—(CF_2CFI)_n—As(CH_3)_2$ does not seem to be formed in this last reaction; the least volatile reaction products are air sensitive and the analytical data fit cacodyl better than any adduct of cacodyl with the olefin.

Dimethyltrifluoromethylarsine is produced when trifluoroiodomethane reacts with trimethylarsine (20) and with iododimethylarsine in the presence of mercury (1). It has now been found that trimethylarsine slowly interacts with trifluorovinyl bromide and iodide but does not give the expected dimethyltrifluorovinylarsine. This compound can, however, be prepared in low yield from the reaction of trifluorovinyl iodide with iododimethylarsine in the presence of mercury.

$$CF_2{=}CFI + Hg + IAs(CH_3)_2 \rightarrow CF_2{=}CFAs(CH_3)_2 + HgI_2$$

Trifluorovinyl bromide does not react with either iododimethylarsine or diiodomethylarsine in the presence of mercury. Since the vinyl bromide readily reacts with cacodyl yet does not react with iododimethylarsine and mercury, it seems that cacodyl itself is not a reactive intermediate in these coupling reactions. This conclusion is substantiated by the failure of hexafluorobut-2-yne to react with iododimethylarsine in the presence of mercury.

Dimethyltrifluorovinylarsine, b.p. 71°, is a colorless liquid slightly less volatile than trimethylarsine, b.p. 51°, and dimethyltrifluoromethylarsine, b.p. 58°. It is slowly hydrolyzed by hot alkali to trifluoroethylene, a result analogous to the slow hydrolysis of dimethyltrifluoromethylarsine to fluoroform (21). There appears to be a considerable difference in the hydrolytic stability of the easily hydrolyzed tris(trifluoromethyl)arsine and the stable tris(trifluorovinyl)arsine (22).

EXPERIMENTAL

Apparatus and Techniques

Most of the methods used in the present investigation have been described in earlier papers in this series. The F^{19} n.m.r. spectra were obtained using a Varian spectrometer operating at 56.4 Mc/sec. The spectra are reported relative to a trifluoroacetic acid external standard. A dinonylphthalate on firebrick column (12 ft) in an Aerograph instrument was used for vapor phase chromatographic separations. Helium was used as the carrier gas and the temperature of the column is indicated in the text. Starting materials were prepared by methods described in the literature.

Reaction of Arsenobenzene with Trifluoroiodomethane

(*a*) Arsenobenzene (10.0 g) and trifluoroiodomethane (18 g) did not react at 20° (3 days). However, reaction occurred at 115° (1 day) giving a dark-brown liquid product. Trifluoroiodomethane (5.4 g) was recovered, and the remaining contents of the reaction tube were distilled in a nitrogen atmosphere (65 mm) to give phenylbis(trifluoromethyl)arsine (8 g, 42% yield, b.p. 88°) of known infrared spectrum and a pale-yellow liquid shown by analysis to be *iodophenyltrifluoromethylarsine* (6.2 g, 27% yield, b.p. 158°). Anal. Found: C, 23.9; H, 1.54%. Calc. for $C_7H_5AsF_3I$: C, 24.2; H, 1.44%. The residue in the still pot (5.3 g) was largely diiodophenylarsine. The infrared spectrum of iodophenyltrifluoromethylarsine showed the following absorption bands (liquid film): 3055(w), 2230(vw), 1575(vw), 1482(m), 1435(m), 1330(m), 1302(w), 1252(m), 1185(s), 1110(broad vs), 1072(s), 1020(m), 997(m), 735(s), 725(m), 687(s) cm^{-1}.

(*b*) A similar reaction took place when arsenobenzene and trifluoroiodomethane were irradiated with ultraviolet light.

Reactions of Iodophenyltrifluoromethylarsine

(*a*) *With silver chloride.*—The arsine (3.4 g) and an excess of freshly prepared, dry silver chloride were shaken at 20° for 2 days. A colorless liquid, *chlorophenyltrifluoromethylarsine*, which was sufficiently volatile to be taken into the vacuum system, was quantitatively produced. It distilled at 118° (65 mm) in a nitrogen atmosphere. Anal. Found: C, 33.0; H, 1.76; As, 28.9; Cl, 13.6%. Calc. for $C_7H_5AsClF_3$: C, 32.7; H, 1.93; As, 29.2; Cl, 13.8%. The infrared spectrum was almost identical with that of the iodoarsine.

(b) With iodomethane in the presence of mercury.—The arsine (6.2 g), iodomethane (13.4 g), and mercury (40 g) were shaken for 3 weeks at 20°. Iodomethane (13.3 g) was quantitatively recovered. A white solid in the reaction tube was extracted with benzene to give a solution which slowly deposited crystals of benzenearsonic acid. The acid was identified by means of its X-ray powder photograph.

Reaction of Chlorophenyltrifluoromethylarsine with Bis(trifluoromethyl)arsine

The chloroarsine (0.7 g) and bis(trifluoromethyl)arsine (0.812 g) were left at 100° for 7 days. Trap-to-trap distillation gave hydrogen chloride (0.043 g; mol. wt. 36.6), bis(trifluoromethyl)arsine (0.466 g), chlorophenyltrifluoromethylarsine (0.14 g), and a middle fraction which contained tris(trifluoromethyl)arsine, tetrakis(trifluoromethyl)diarsine, and possibly a trace of chlorobis(trifluoromethyl)arsine, all of known infrared spectra. A cream solid which was left in the reaction tube was highly unstable to air. Anal. Found: C, 36.5; H, 2.33%. The end product of the decomposition was benzenearsonic acid.

Reaction of Cacodyl with Hexafluoropropene

The diarsine (5.3 g) and the propene (16.0 g) were left at 20° for 13 days. A small amount (1.9 g) of a liquid, b.p. 36–38° (10^{-3}) mm, which fumed slightly in air was isolated. The infrared spectrum of this fraction showed the presence of C–F and As–CH_3 groups. All reactants and products were combined and heated to 50° (7 days). Distillation of the less volatile material in a nitrogen atmosphere at 50 mm gave 1.1 g of cacodyl, b.p. 78°; a middle fraction, b.p. 78–114°; and 1.6 g (18% yield) of *1,2-bis(dimethylarsino)-1,1,2,3,3,3-hexafluoropropane*, b.p. 114–116°. The last fraction still fumed in air, so air was bubbled through it until the fuming had ceased. An analytical sample, b.p. 116–117° (50 mm) was obtained from another distillation. Anal. Found: C, 23.2; H, 3.29; As, 41.6; F, 31.8%. Calc. for $C_7H_{12}As_2F_6$: C, 23.3; H, 3.33; As, 41.6; F, 31.7%. The infrared spectrum (liquid film) showed the following bands; 3005(w), 2915(w), 1670(w), 1418(m), 1277(s), 1265(s), 1195(broad, vs), 1142(s), 1158(broad, m), 999(w), 912(broad, m), 850(m), 798(w), 720(w) cm^{-1}. When the adduct (0.291 g) was heated (100°, 24 hours) with 8 ml of 10% aqueous sodium hydroxide, 0.034 g of 1,2,3,3,3-pentafluoroprop-1-ene, of known infrared spectrum (23), was produced.

Reaction of Cacodyl with Hexafluorocyclobutene

Cacodyl (5.0 g) and the butene (17.8 g) were left for 12 days at 20°. Apart from some white deposit on the glass all the contents of the tube were volatile. Trap-to-trap distillation isolated 1.149 g of fluorodimethylarsine, which attacked glass and which stopped in a trap cooled to −64°. Anal. Found: C, 18.2; H, 4.7%; mol. wt. 127; b.p. 66–68° (by distillation in a nitrogen atmosphere at 760 mm). Calc. for C_2H_6AsF: C, 19.4; H, 4.8%; mol. wt. 124; b.p. 75° (24). The most volatile fraction was perfluorocyclobutene (14.6 g), which contained some fluorodimethylarsine. The least volatile fraction (7.0 g) was distilled in a nitrogen atmosphere to give 0.52 g of fluorodimethylarsine, b.p. 70–75°, and 4.9 g (83% yield) of *1-dimethylarsino-pentafluorocyclobutene*, b.p. 122–125°. An analytical sample, b.p. 125°, was obtained by redistillation. Anal. Found: C, 29.0; H, 2.41; As, 30.0; F, 38.0%. Calc. for $C_6H_6AsF_5$: C, 29.0; H, 2.42; As, 30.1; F, 38.4%. The infrared spectrum showed the following bands (liquid film): 3010(w), 2920(w), 2360(w), 2349(sh,w), 1695(s), 1424(w), 1397(s), 1374(m), 1275(vs), 1206(m), 1117(vs), 1104(s), 950(vs), 900(w), 865(m), 812(m) cm^{-1}.

Reaction of Cacodyl with Bromotrifluoroethylene

The diarsine (4.0 g) and bromotrifluoroethylene (16.5 g) were left for 7 days at 20°. Qualitative investigation showed that although some reaction had occurred considerable amounts of the diarsine were still present. The reactants were then heated to 50° (5 days). The volatile material was taken into the vacuum system leaving 4.3 g of a pale-yellow liquid in the reaction tube. Trap-to-trap distillation gave 13.5 g of bromotrifluoroethylene, 0.4 g of 1,2-dibromohexafluorocyclobutane (25), and 1.7 g of a mixture which was separated by vapor phase chromatography (v.p.c.) at 135° into fluorodimethylarsine (0.2 g; mol. wt. 121; calc. mol. wt. 124) of known infrared spectrum, bromodimethylarsine (0.4 g) of known retention time and infrared spectrum, and one other volatile fraction. This last fraction was a mixture of dimethyltrifluorovinylarsine and one other unidentified unsaturated compound.

The involatile reaction product distilled at 65° (10^{-3} mm) and analysis of the pale-yellow distillate suggested that it was an impure sample of 2-bromo-1,2-bis(dimethylarsino)-1,1,2-trifluoroethane. Anal. Found: C, 21.0; H, 3.47; As, 40.3; Br, 18.7; F, 16.9%. Calc. for $C_6H_{12}As_2BrF_3$: C, 19.4; H, 3.24; As, 40.4; Br, 21.6; F, 15.4%. The infrared spectrum showed the following bands (liquid film): 2985(m), 2905(m), 2800(w), 2330(w), 1723(m), 1705(m), 1420(m), 1290(m), 1265(m), 1152(m), 1110(m), 1067(s), 1015(m), 985(m), 904(m), 850(s), 825(m), 792(m), 682(m) cm^{-1}. An ethanolic solution of the adduct reacted with an ethanolic solution of mercuric chloride to give a white precipitate which was insoluble in boiling ethanol. An infrared spectrum of the solid showed the presence of C–H and the absence of C–F groups. The adduct slowly decomposed on standing at 20°, since some months after its preparation it was found to be volatile enough to be taken into the vacuum system where trap-to-trap distillation isolated slightly impure dimethyltrifluorovinylarsine.

Reaction of Cacodyl with Iodotrifluoroethylene

Cacodyl (1.7 g) and the ethylene (10.0 g) were left for 7 days at 20°. Trap-to-trap distillation gave iodotrifluoroethylene (8.9 g), a volatile unidentified yellow solid, iododimethylarsine, and dimethyltrifluorovinylarsine. These fractions could not be separated quantitatively. The trifluorovinylarsine was purified by v.p.c. (90°) to give 0.1 g of product. An involatile air-sensitive material which contained As–CH_3 and some C–F remained in the reaction tube. Anal. Found: C, 24.8; H, 4.9%.

Reaction of Cacodyl with Tetrafluoroethylene

When cacodyl (1.5 g) was exposed to the olefin at a pressure of 30 cm (20°) there was no drop in pressure. The diarsine (1.5 g) and the olefin (2.9 g) were irradiated in a sealed tube with ultraviolet light (24 hours), to give tetrafluoroethylene (0.4 g) and trimethylarsine (0.053 g) of known infrared spectra. The air-stable colorless involatile product (4.3 g) distilled at 10^{-3} mm in the range 110–125°. Elemental analysis of a middle cut, b.p. 120°, showed it to be probably a 1:4 addition product of the diarsine and the olefin, $(CH_3)_2As(CF_2CF_2)_4As(CH_3)_2$. Anal. Found: C, 23.2; H, 1.8; As, 22.7; F, 51.7%. Calc. for $C_{12}H_{12}As_2F_{16}$: C, 23.6; H, 1.97; As, 24.6; F, 49.9%. Two other cuts were taken and these analyzed as follows: C, 23.5; H, 2.4% (110–120°); C, 22.5; H, 1.6% (120–125°). The infrared spectra of the three fractions were very similar. The F^{19} n.m.r. spectrum of the third cut showed peaks at +2450, +2290, and +2240 c/s of relative area 58:30:27.

Reaction of Cacodyl with Hexafluorobut-2-yne

The acetylene (7.5 g) and the diarsine (5.0 g) reacted on warming to 20° to give a reddish-brown solution. The tube was left at 20° for 14 days. Hexafluorobut-2-yne (4.3 g) was the only volatile substance present in the tube. The involatile, air-stable reaction product distilled at 42° (10^{-3} mm) and at 99° (17 mm) and was identified as *2,3-bis(dimethylarsino)-1,1,1,3,3,3-hexafluorobut-2-ene*. Anal. Found: C, 26.0; H, 3.4; As, 40.2; F, 30.9%, mol. wt. 350. Calc. for $C_8H_{12}As_2F_6$: C, 25.8; H, 3.22; As, 40.3; F, 30.6%, mol. wt. 372. The infrared spectrum showed the following bands (liquid film): 2990(w), 2915(w), 1570(w), 1425(m), 1300(w), 1230(vs), 1175(sh,s), 1152(vs), 1135(vs), 897(w), 867(w), 852(w), 652(m) cm^{-1}. The F^{19} n.m.r. spectrum consisted of two peaks of nearly equal intensity at −1368 and −1483 c/s. The adduct (0.283 g) was hydrolyzed with 15% aqueous sodium hydroxide (5 days, 110°) to give a small amount (0.019 g) of *trans*-1,1,1,3,3,3-hexafluorobut-2-ene, of known infrared spectrum. The adduct had partially decomposed to a black solid and unidentified volatile products after 3 days at 150°. When ethanolic solutions of the adduct and mercuric chloride were mixed, a cream precipitate was obtained which was recrystallized from ethanol. Anal. Found: C, 11.5; H, 1.29; As, 12.7; Cl, 14.4; F, 10.7; Hg, 38.1%.

Reaction of Hexafluorobut-2-yne with Tetrakis(trifluoromethyl)-diarsine and -diphosphine

The arsine (1.53 g) and the acetylene (4.9 g) did not react after 7 days at 100° or, in a separate experiment, after 10 days at 150°. The acetylene (4.9 g) and the diarsine (1.50 g) were recovered. Similarly, the acetylene and the diphosphine did not react when heated to 100° for 2 days.

Reaction of Bromotrifluoroethylene with Iodoarsines in the Presence of Mercury

(*a*) Iododimethylarsine (25.7 g), mercury (250 g), and bromotrifluoroethylene (49.0 g) were shaken at 20° for 11 days. The only volatile substance present in the reaction tube was bromotrifluoroethylene (48.7 g).

(*b*) Diiodomethylarsine (18.9 g), mercury (200 g), and bromotrifluoroethylene (49.6 g) did not produce any trifluorovinylarsine after being shaken for 18 days at 20°. The weight of the ethylene recovered was 49.0 g.

Reaction of Iodotrifluoroethylene with Iododimethylarsine in the Presence of Mercury

Iododimethylarsine (24.2 g), mercury (240 g), and iodotrifluoroethylene (66 g) were shaken for 10 days at 20°. Iodotrifluoroethylene (64.4 g) was recovered and *dimethyltrifluorovinylarsine* (1.0 g) was produced. The arsine was identified by its molecular weight of 181 (calc. mol. wt. 186). An analytical sample was obtained by v.p.c. at 55°. Found: C, 26.0; H, 3.31; As, 40.3; F, 30.4%. Calc. for $C_4H_6AsF_3$: C, 25.8; H, 3.26; As, 40.4; F, 30.6%. Infrared spectrum (vapor): 3010(m), 2920(m), 1780(w), 1730(s), 1428(m), 1298(s), 1140(s), 1020(s), 897(m), 852(m), 715(m) cm^{-1}. The boiling point was found to be 71°, the latent heat of vaporization 8180 cal/mole, and Trouton's constant 23.8. When the arsine (0.086 g) was hydrolyzed by 15% aqueous sodium hydroxide (100°, 24 hours) trifluoroethylene (0.0094 g) was produced. Unreacted arsine was also isolated.

Reaction of Iododimethylarsine with Hexafluorobut-2-yne in the Presence of Mercury

Iododimethylarsine (21.0 g) and hexafluorobut-2-yne (30.0 g) did not react on being shaken for 7 days at 20° in the presence of 217 g of mercury. The butyne was recovered quantitatively.

Reaction of Trimethylarsine with Bromotrifluoroethylene and Iodotrifluoroethylene

Trimethylarsine (0.60 g) and bromotrifluoroethylene (6.5 g) were kept at 20° for 1 year. Trap-to-trap distillation of the volatile material recovered 6.4 g of bromotrifluoroethylene and 0.54 g of trimethylarsine. A small amount of unidentified brown solid remained in the reaction tube. The recovered arsine was left with 6.0 g of iodotrifluoroethylene for 14 days. Examination of the volatile contents of the reaction tube showed only the presence of starting materials. A small amount of dark solid remained in the reaction tube.

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