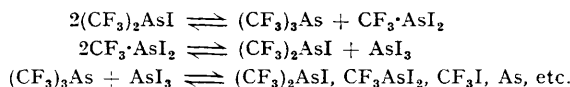**316.** *Organometallic and Organometalloidal Fluorine Compounds. Part VI.* Trifluoromethyl Arsenicals.†*

By H. J. EMELÉUS, R. N. HASZELDINE, and E. G. WALASCHEWSKI.

The compounds $(CF_3)_3As$, $(CF_3)_2AsI$, and $CF_3 \cdot AsI_2$ have been used to prepare $(CF_3)_2AsX$, $CF_3 \cdot AsX_2$, $(CF_3)_3AsX_2$ (X = Br, Cl, F, CN, SCN), and $[(CF_3)_2As]_2O$. The hydrolysis of these compounds and of the hydrides $(CF_3)_2AsH$ and CF_3AsH_2 (which are also prepared) has been studied, and an explanation is advanced to account for the unusual results.

A novel type of exchange reaction involving the replacement of trifluoromethyl by methyl groups in tristrifluoromethylarsine is described and has been used to obtain $(CF_3)_2AsMe$, independently synthesised from $(CF_3)_2AsI$. Oxidative hydrolysis of the iodo-compound yields the strong, monobasic bistrifluoromethylarsinic acid. Ultra-violet and infra-red data for a variety of trifluoromethyl arsenicals are discussed.

INTERACTION of arsenic and trifluoroiodomethane yields tristrifluoromethylarsine, iodobistrifluoromethylarsine, di-iodotrifluoromethylarsine, and arsenic tri-iodide (Part V, *loc. cit.*; Walaschewski, forthcoming publication). There is now evidence that a series of equilibria is set up in this reaction. Thus, when iodobistrifluoromethylarsine is heated alone, trifluoroiodomethane and tristrifluoromethylarsine are the main products, and small amounts of arsenic, arsenic tri-iodide, and di-iodotrifluoromethylarsine are also detected; similarly, di-iodotrifluoromethylarsine yields arsenic tri-iodide and tristrifluoromethylarsine. Under similar conditions, tristrifluoromethylarsine reacts with arsenic tri-iodide to give the iodotrifluoromethylarsines, trifluoroiodomethane, and arsenic:

$$2(CF_3)_2AsI \rightleftharpoons (CF_3)_3As + CF_3 \cdot AsI_2$$
$$2CF_3 \cdot AsI_2 \rightleftharpoons (CF_3)_2AsI + AsI_3$$
$$(CF_3)_3As + AsI_3 \rightleftharpoons (CF_3)_2AsI, CF_3AsI_2, CF_3I, As, \text{etc.}$$

At equilibrium, under optimum conditions, the yields of the iodotrifluoromethylarsines obtained by the reaction of arsenic with trifluoroiodomethane are low, but may be increased by the use of a mixture of arsenic and arsenic tri-iodide (see Experimental section).

The iodotrifluoromethylarsines have been used to synthesise the compounds $CF_3 \cdot AsCl_2$, $(CF_3)_2As \cdot O \cdot As(CF_3)_2$, $(CF_3)_2As \cdot As(CF_3)_2$, and $(CF_3)_2AsX$ (X = F, Cl, CN, SCN, OCN) by reaction with the appropriate silver or mercury salts (Part V; Walaschewski *loc. cit.*). The iodides have also been reduced to the hydrides, trifluoromethylarsine and bistrifluoromethylarsine, by use of lithium aluminium hydride or, preferably, zinc and hydrochloric acid. It is noteworthy that lithium aluminium hydride did not affect the trifluoromethyl groups and that trifluoromethylarsine was formed quantitatively by use of zinc and hydro-

* Part V, Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2582.
† Presented in abstract at XIIth International Congress, New York, 1951.

chloric acid. Thermal decomposition of bistrifluoromethylarsine (b. p. 19°), which is appreciably more stable than arsine, proceeds according to the equation :

$$3(CF_3)_2AsH \longrightarrow (CF_3)_3As + 2As + 3CF_3H$$
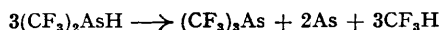
Trifluoromethylarsine similarly yielded arsenic, hydrogen, and fluoroform, but no tristri-fluoromethylarsine. In neither case was hexafluoroethane formed, and this suggests that the decomposition does not involve free trifluoromethyl radicals, and that some disproportionation of bistrifluoromethylarsine to tristrifluoromethylarsine and trifluoro-methylarsine occurs as the first step.

The hydrolysis of the trifluoromethylarsines is discussed below. Detection of the trifluoromethylarsines is best effected by their infra-red spectra. The As–H stretching vibration appears at 4·67 μ in $(CF_3)_2AsH$ and at 4·71 μ in $CF_3 \cdot AsH_2$, the intensity being appreciably greater for the latter. Robertson and Fox (*Proc. Roy. Soc.*, 1928, *A*, **120**, 161) report 4·71 μ for the As–H vibration in arsine, so replacement of two of the hydrogen atoms in arsine by trifluoromethyl groups causes a shift to shorter wave-length. The weaker bands at 4·45 μ are ascribed to overtones and combination frequencies of the strong C–F stretching absorptions at 8—9 μ.

Tristrifluoromethylarsine shows only end-absorption in the ultra-violet and, by comparison with trifluoromethylarsine, replacement of hydrogen by trifluoromethyl causes

TABLE 1.

	λ 250	240	230	220
$CF_3 \cdot AsH_2$ vapour	ε 0·21	0·88	2·07	7·75
$(CF_3)_3As$ vapour	ε 1·89	6·75	12·6	18·7

appreciable increase in absorption (Table 1). The chromophoric effect of the As–As bond is revealed by the spectrum of tetrakistrifluoromethyldiarsine ($\lambda_{max.}$ 223 mμ; ε 3000).

In Table 2 the effect of replacement of an iodine atom by a trifluoromethyl group on the ultra-violet spectrum of arsenic tri-iodide is shown. The long-wave-length maximum of the tri-iodide becomes an inflection in di-iodotrifluoromethylarsine with considerable shift to shorter wave-length, whereas the 280-mμ maximum moves to 271 mμ in the di-iodide and to 290 mμ in the monoiodide. The shifts to shorter wave-length are analogous

TABLE 2.

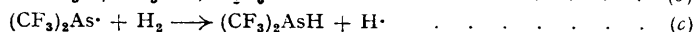|	Solvent *	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$	$\lambda_{infl.}$	$\varepsilon_{infl.}$
AsI_3	Pet.	378	1,600	350	750	—	—
		280	5,600	261	2,900	—	—
		225	12,000	—	—	—	—
CF_3AsI_2	Pet.	271	4,200	252	3,100	325	1,700
		229	6,500	219	5,600	—	—
	Ether	267	4,000	254	3,800	326	1,500
		230	5,500	220	5,000	—	—
$(CF_3)_2AsI$	Vapour	290	—	248	—	—	—
	Pet.	290	1,200	255	350	—	—
	Ether	287	1,200	256	500	—	—

* Pet. = light petroleum (b. p. 60—80°).

to those observed for methyl and trifluoromethyl sulphur compounds (Brandt, Eméleus, and Haszeldine, *J.*, 1952, 2549). The effect of solvent is negligible, ether producing only the usual slight shift relative to light petroleum or to the vapour.

Attempts were made to prepare trifluoromethyl- and bistrifluoromethyl-arsine from tristrifluoromethylarsine and hydrogen. Fluoroform and arsenic were the only products from the thermal reaction, but the conditions necessary to effect reaction were such that thermal decomposition of the hydrides would have occurred. Exposure of a mixture of tristrifluoromethylarsine and hydrogen to ultra-violet light yielded a mixture of fluoroform (mainly) and hexafluoroethane. Photochemical decomposition of tristrifluoromethyl-arsine alone yields arsenic and hexafluoroethane, but since the number of trifluoromethyl radicals present at any one instant is small, it is not surprising that when hydrogen is present reaction (*a*) occurs in preference to (*b*). The arsines $CF_3 \cdot AsH_2$ and $(CF_3)_2AsH$ were not detected by infra-red spectroscopic examination, thus indicating that a reaction

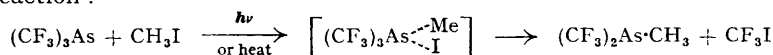of type (*c*) does not occur, or that the trifluoromethyl arsines are decomposed by light much faster than tristrifluoromethylarsine.

$$CF_3\cdot + H_2 \longrightarrow CHF_3 + H\cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$
$$CF_3\cdot + CF_3\cdot \longrightarrow C_2F_6 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$
$$(CF_3)_2As\cdot + H_2 \longrightarrow (CF_3)_2AsH + H\cdot \quad . \quad . \quad . \quad . \quad . \quad (c)$$
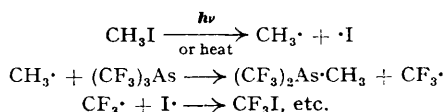
A novel type of radical-exchange reaction occurred when tristrifluoromethylarsine and methyl iodide were exposed to ultra-violet light, and products of the type $(CF_3)_n(CH_3)_{3-n}As$ were produced, as well as trifluoroiodomethane and hexafluoroethane. The main product, methylbistrifluoromethylarsine, could not be separated from tristrifluoromethylarsine by distillation, but was detected by its infra-red spectrum. Treatment of the mixture with aqueous sodium hydroxide removed the tristrifluoromethylarsine preferentially, since methylbistrifluoromethylarsine is only slowly hydrolysed by this reagent (see below). Small amounts of trimethylarsine and possibly dimethyltrifluoromethylarsine formed by the exchange reaction were removed by compound formation with mercuric chloride; methylbistrifluoromethylarsine, like tristrifluoromethylarsine, fails to react with mercuric chloride. The identity of the methylbistrifluoromethylarsine obtained by the exchange reaction was confirmed by its synthesis from iodobistrifluoromethylarsine and methyl magnesium iodide : $(CF_3)_2AsI + CH_3MgI \longrightarrow (CF_3)_2AsCH_3 + MgI_2$. The successful application of this synthesis opens up a route for the preparation of a wide variety of mixed perfluoroalkyl–alkyl- or –aryl-arsenicals. The infra-red spectrum of methylbistrifluoromethylarsine (b. p. 52°) enables it to be distinguished from tristrifluoromethylarsine (b. p. 33°) more easily than by its boiling point, which is somewhat higher than that of trimethylarsine (b. p. 49·5°), again illustrating the increase in boiling point on replacement of only a few atoms of hydrogen in a compound by fluorine. In particular the infra-red spectrum shows C–H bands at 3·40, 3·50, 7·03, and 7·25 μ due to the methyl group, and the pattern of the C–F bands at 8·5—9·0 μ shows its similarity to tetrakistrifluoromethyl-diarsine which also contains the $(CF_3)_2As$ group.

The mechanism of the photochemical reaction of tristrifluoromethylarsine with methyl iodide is not yet clear. The influence of the strongly electronegative trifluoromethyl groups in this arsine is made apparent by its failure to form compounds with mercuric chloride or sulphur. Quaternary-salt formation was not observed with tristrifluoromethyl-arsine and trifluoroiodomethane even at 200°, again illustrating the resistance of the carbon–iodine bond in trifluoroiodomethane to heterolytic fission (cf. Banus, Eméleus, and Haszeldine, *J.*, 1951, 60). Methyl iodide readily forms quaternary salts with trialkyl-arsines, but is substantially immiscible with tristrifluoromethylarsine at, or below, room temperature and fails to react even at 140°. At 235°, however, the reaction is similar to that brought about by light, and yields trifluoroiodomethane, fluoroform, methylbistri-fluoromethylarsine, and a mixture of methyltrifluoromethyl- and bistrifluoromethyl-iodoarsines. A stable quaternary salt of methyl iodide and tristrifluoromethylarsine could not be isolated, but it is probable that this is the intermediate in the exchange reaction :

$$(CF_3)_3As + CH_3I \xrightarrow[\text{or heat}]{h\nu} \left[(CF_3)_3As \begin{matrix} \cdot\cdot Me \\ \cdot I \end{matrix} \right] \longrightarrow (CF_3)_2As\cdot CH_3 + CF_3I$$

Since methyl radicals will be produced rather than trifluoromethyl radicals under the conditions used, a simple radical mechanism would be :

$$CH_3I \xrightarrow[\text{or heat}]{h\nu} CH_3\cdot + \cdot I$$
$$CH_3\cdot + (CF_3)_3As \longrightarrow (CF_3)_2As\cdot CH_3 + CF_3\cdot$$
$$CF_3\cdot + I\cdot \longrightarrow CF_3I, \text{ etc.}$$

but although this would account for the formation of hexafluoroethane (radical combination) and fluoroform (hydrogen abstraction), it might be expected that other products, *e.g.*, methane or 1 : 1 : 1-trifluoroethane, arising from the known reactions of methyl or trifluoromethyl radicals in the presence of hydrogen-containing compounds, would have been observed. The absence of tetramethylarsonium iodide shows that the

methyl iodide reacts completely in the initial stages, and is not available for combination with the trimethylarsine produced in the later stages of the reaction.

The scope and mechanism of this radical-exchange reaction, which may be of general application, are being investigated.

Tristrifluoromethylarsine is the main product from the interaction of arsenic and trifluoroiodomethane, and its conversion into other compounds of use in further syntheses has been investigated. When heated with chlorine, tristrifluoromethylarsine is converted quantitatively into chlorotrifluoromethane and arsenic trichloride. If the reaction is carried out in the liquid phase at room temperature, however, smooth conversion into the quinquevalent derivative, $(CF_3)_3AsCl_2$, occurs. This compound, b. p. 98·5°, can be distilled without decomposition, but on prolonged heating at 125° decomposes to chloro-trifluoromethane, tristrifluoromethylarsine, chlorobistrifluoromethylarsine, dichlorotri-fluoromethylarsine, and arsenic trichloride. Tristrifluoromethylarsenic dichloride is reconverted into tristrifluoromethylarsine by reaction with mercury at room temperature. Reaction of tristrifluoromethylarsine with chlorine in a small sealed tube for a long period at 15° yielded bistrifluoromethylarsenic trichloride and chlorotrifluoromethane. The

Boiling points of methyl- and trifluoromethyl-substituted arsines.

Broken lines: R = CH₃;
solid lines: R = CF₃.
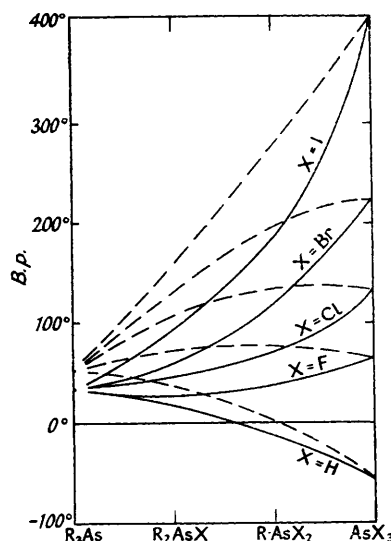
interaction of chlorine and tristrifluoromethylarsine in the vapour phase followed a different course and gave chlorotrifluoromethane, arsenic trichloride, and chlorotrifluoro-methylarsine, but not the quinquevalent arsenic compounds. Thus, by suitable adjust-ment of reaction conditions, the compounds $(CF_3)_2AsCl$, CF_3AsCl_2, $(CF_3)_3AsCl_2$, or $(CF_3)_2AsCl_3$ can readily be prepared.

No evidence was obtained for the intermediate formation of tristrifluoromethylarsenic dibromide from tristrifluoromethylarsine and bromine; at −5° arsenic tribromide was deposited and bromotrifluoromethane evolved, and distillation of the residual liquid gave bromobistrifluoromethylarsine and dibromotrifluoromethylarsine. Although a solution of iodine in tristrifluoromethylarsine was slowly decolorised at room temperature, appreciable reaction occurred only at 100°. There was no evidence for the formation of a quinquevalent compound, and the products were iodobistrifluoromethylarsine, di-iodotrifluoromethyl-arsine, trifluoroiodomethane, and arsenic tri-iodide. Quantities of the iodotrifluoro-methylarsines of value for further synthetic work may thus be prepared from tristrifluoromethylarsine.

Attempts to prepare tristrifluoromethylarsenic difluoride from tristrifluoromethyl-arsine and fluorine diluted by nitrogen, at temperatures between −100° and −20°, were unsuccessful. Carbon–arsenic bond fission occurred preferentially, as it did when tristrifluoromethylarsine was passed over cobalt trifluoride, and fluorobistrifluoromethyl-

arsine and probably difluorotrifluoromethylarsine were obtained. Tristrifluoromethyl-arsenic difluoride was successfully prepared, however, by the interaction of silver fluoride and tristrifluoromethylarsenic dichloride at room temperature; it can be distilled at atmospheric pressure; like the corresponding dichloride, it was converted by mercury into tristrifluoromethylarsine. It was apparent during the distillation of the several halogeno-trifluoromethylarsines, that the order of thermal stability is As–F > As–Cl > As–Br > As–I. There is a systematic variation in the boiling points of the derivatives CF_3AsX_2, $(CF_3)_2AsX$ (X = F, Cl, Br, I, H) relative to the parent compounds $As(CF_3)_3$ and AsX_3. This is illustrated by the Figure where comparison with the corresponding methyl analogues is also made. It will be noted that the trifluoromethyl compounds invariably boil lower than their methyl analogues. The boiling points of the following unknown or uncharacterised compounds can be estimated from the diagram: $CF_3 \cdot AsF_2$, 24°; $(CH_3)_2AsF$, 72°; $CH_3 \cdot AsBr_2$, 200°; $CH_3 \cdot AsI_2$, 275°.

The infra-red spectra of a series of compounds $CF_3 \cdot AsX_2$ and $(CF_3)_2AsX$, and of $(CF_3)_3AsCl_2$, $(CF_3)_3As$, and $[(CF_3)_2As]_2$, have proved most useful for identification and analysis of mixtures. Examination reveals that the $CF_3 \cdot AsX_2$ compounds (X = Cl, I, or H) are closely similar in the pattern of their C–F stretching vibrations in the 8—9-μ region, showing one main maximum, often broad, whose position depends on the nature of X : 8·95 μ (X = Cl), 9·14 μ (X = I), 8·80 μ (X = H). Compounds $(CF_3)_2AsX$ show two main C–F absorption bands, A and B, between 8 and 9·5 μ, A being broad with sub-maxima

TABLE 3.

X in $(CF_3)_2AsX$	Band A	Band B	X in $(CF_3)_2AsX$	Band A	Band B	X in $(CF_3)_2AsX$	Band A	Band B
Cl	8·45	9·13	H	8·44	8·97	CH₃	8·50	8·90
	8·85	—		8·58	—		8·64	9·03
I	8·5	9·20	CN	8·6	9·18	As(CF₃)₂ ...	8·54	9·04
	8·9	—		8·8	—		8·65	—
F	8·26	9·72	SCN	8·86	9·12	CF₃	8·25	9·04
	8·63	9·46					8·53	—
	8·85	—					8·70	—

(Table 3). Overtone and combination frequencies lie at 4·4—4·5 μ. The As–C and As–X vibrations usually lie at wave-lengths >15 μ.

The infra-red spectra * of all the arsenic compounds so far studied show a strong band *ca.* 13·6 μ (Table 4). This band is probably a CF_3 deformation frequency although it is
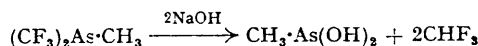
TABLE 4.

C.S. no.		μ	C.S. no.		μ	C.S. no.		μ
22	$(CF_3)_3As$	13·59		$(CF_3)_2As \cdot SCN$ ...	13·67	31	$CF_3 \cdot AsCl_2$	13·69
23	$(CF_3)_2AsI$ ...	13·70	27	$(CF_3)_2As \cdot CN$ ...	13·62	32	$CF_3 \cdot AsH_2$	13·66
24	$(CF_3)_2AsCl$ ...	13·66	28	$(CF_3)_2As \cdot CH_3$ ...	13·70	33	$(CF_3)_3AsCl_2$	13·42
25	$(CF_3)_2AsF$ ...	13·62	29	$[(CF_3)_2As]_2$	13·62	34	$(CF_3)_2AsO_2H$ ...	13·54
26	$(CF_3)_2AsH$ ...	13·65	30	$CF_3 \cdot AsI_2$	13·75			

possible that it is the C–As stretching vibration moved to shorter wave-length by the influence of the trifluoromethyl groups, as observed for other fluorine compounds (Haszeldine, *Nature*, 1951, **168**, 1028).

Hydrolysis of Trifluoromethyl Arsenicals.—When the results described in the present communication are combined with those from Part V (*loc. cit.*), it is now seen that the following compounds liberate fluoroform rapidly and quantitatively on treatment with aqueous base : $As(CF_3)_3$, $(CF_3)_2AsX$ (X = F, Cl, Br, I, CN, or SCN), CF_3AsX_2 (X = Cl, Br, or I), $(CF_3)_3AsX_2$ (X = F or Cl), and $(CF_3)_2As \cdot O \cdot As(CF_3)_2$. The electronegative tri-fluoromethyl groups doubtless make the arsenic more susceptible to nucleophilic attack, and this is illustrated by the very marked decrease in rate of reaction when a trifluoro-methyl group in tristrifluoromethylarsine is replaced by a methyl group. Thus, whereas

* Some of the spectra have been deposited with the Chemical Society (cf. *Proc.*, 1952, 164), and photocopies may be obtained from the General Secretary. Identifying C.S. numbers are listed in the Table and must be cited in requests for photocopies.

the reaction with tristrifluoromethylarsine is complete in 5—10 min., that with methyl-bistrifluoromethylarsine is incomplete with 20% sodium hydroxide solution even at 100°. Fluoroform, but no fluoride, is produced :

$$(CF_3)_2As \cdot CH_3 \xrightarrow{2NaOH} CH_3 \cdot As(OH)_2 + 2CHF_3$$

Tetrakistrifluoromethyldiarsine was shown in Part V (*loc. cit.*) to undergo hydrolysis to both fluoroform and fluoride. The mechanism of this hydrolysis, which involves destruction under mild conditions of the normally stable trifluoromethyl group, has been studied further. The proportion of the trifluoromethyl groups appearing as fluoroform varies slightly according to the reaction conditions, but by use of a standard procedure 84% of the trifluoromethyl groups in tetrakistrifluoromethyldiarsine were converted into fluoroform and 16% into fluoride (and carbonate). The suggested mechanism (Part V) involves hydrolytic fission of the As–As bond :

$$(CF_3)_2As \cdot As(CF_3)_2 \xrightarrow{H_2O} (CF_3)_2AsH + (CF_3)_2As \cdot OH$$
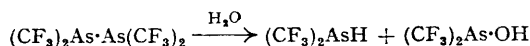
Evidence given below shows that bistrifluoromethylarsinous acid decomposes in acid, neutral, or basic solution with the liberation of its trifluoromethyl groups as fluoroform. Study of bistrifluoromethylarsine, independently prepared as described above, shows that, under the standard conditions used for tetrakistrifluoromethyldiarsine, hydrolysis to fluoroform, fluoride, and carbonate occurs, 66% of the trifluoromethyl groups appearing as fluoroform and 34% as fluoride and carbonate. Thus, by the postulated mechanism, 1 mole of the diarsenic compound would be expected to give 2 moles of fluoroform from $(CF_3)_2As \cdot OH$ and $\frac{2}{3} \times 2$ moles from $(CF_3)_2AsH$, a total of $3\frac{1}{3}$ mole, *i.e.*, a *theoretical* conversion of 83% of the trifluoromethyl groups of tetrakistrifluoromethyldiarsine into fluoroform. The excellent agreement with the 84% found experimentally thus supports the suggested mechanism.

The reason for the instability of bistrifluoromethylarsine is not yet clear. Trifluoromethylarsine under similar conditions is also decomposed to give fluoroform (12—14%), fluoride, and carbonate, but appreciably less fluoroform is obtained as the number of hydrogen atoms attached to the arsenic increases. Other evidence is available which suggests that the analogous group $CF_2 \cdot NH_2$ is unstable in basic solution. The disproportionation of trifluoromethylarsine to tristrifluoromethylarsine and arsine as an initial step of the hydrolysis can be excluded, since the absence of arsine was established by infra-red spectroscopy. As for bistrifluoromethylarsine, the ratio of fluoride to fluoroform varies slightly with the experimental conditions.
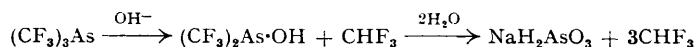
The hydrolysis of trifluoromethylarsine involves formation of *ca.* 15% of an unidentified bright yellow amorphous solid, which is also formed in small amount from bistrifluoromethylarsine, and in very small amount from tetrakistrifluoromethyldiarsine. The solid contains As^{III} and As^{V}, and is mainly arsenic, although a small percentage of a trifluoromethyl-containing compound can be detected by infra-red spectroscopic examination. After treatment with nitric acid, arsenic and fluoride can be estimated in the usual way. It is suggested that the solid is a compound, or mixture, of trifluoromethylarsine and arsenic. An analogous yellow powder formed by the decomposition of diphosphine, and as by-product involving other phosphorus hydrides, has formula P_2H according to Schenk (*Ber.*, 1903, **36**, 991, 4202), although the more recent work of Royen (*Z. anorg. Chem.*, 1936, **229**, 369) indicates that it is phosphine adsorbed on amorphous phosphorus.

The compounds $(CF_3)_2AsI$, $(CF_3)_2AsCl$, $CF_3 \cdot AsI_2$, and $CF_3 \cdot AsCl_2$ are stable to water at room temperature, and when they are compared with the corresponding methyl compounds or with arsenic trichloride or tri-iodide a decrease in the ease of hydrolysis is apparent. This is analogous to the increased stability of chloro- or iodo-trifluoromethane relative to methyl chloride or iodide. The first stage in the hydrolysis of the compounds $(CF_3)_2AsX$ (X = Cl, I, etc.) is presumably

$$OH^- + As(CF_3)_2 \!-\! I \longrightarrow (CF_3)_2As \cdot OH + I^-$$
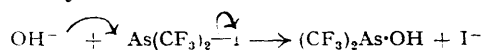
followed by further attack on the bistrifluoromethylarsinous acid. The electronegative trifluoromethyl groups facilitate nucleophilic attack on arsenic, but not the loss of iodine as an anion. Attempts to prepare bistrifluoromethylarsinous acid by stepwise hydrolysis of tristrifluoromethylarsine have been unsuccessful. This arsine is stable to water, but hydrolysis, which is fast in a buffer solution at pH 9·3, can still be detected at pH 7·2. If 85% of the sodium hydroxide theoretically required for removal of *one* trifluoromethyl group from tristrifluoromethylarsine is used, all three trifluoromethyl groups are lost. Since 15% of the tristrifluoromethylarsine remains, and since tristrifluoromethylarsine is substantially stable to hot concentrated acid, it follows (*a*) that hydroxide ion is essential to bring about hydrolysis, and that when it is used up hydrolysis ceases, and (*b*) that bistrifluoromethylarsinous acid is unstable in water :

$$(CF_3)_3As \xrightarrow{OH^-} (CF_3)_2As \cdot OH + CHF_3 \xrightarrow{2H_2O} NaH_2AsO_3 + 3CHF_3$$

and stepwise hydrolysis cannot be achieved.

Cyanobistrifluoromethylarsine is the only compound which can be hydrolysed by water, as distinct from alkali, and yields fluoroform and hydrogen cyanide. This also illustrates the instability of bistrifluoromethylarsinous acid :

$$(CF_3)_2As \cdot CN \xrightarrow{H_2O} (CF_3)_2As \cdot OH + HCN \xrightarrow{2H_2O} 2CHF_3 + HCN + H_3AsO_3$$

The silver salt of bistrifluoromethylarsinous acid was obtained by reaction of the monoiodo-compound with moist silver oxide, but, on liberation of the acid by hydrogen sulphide, potassium iodide or cyanide, etc., fluoroform was evolved. Mercuric oxide similarly gave the mercuric salt.

Reaction of iodobistrifluoromethylarsine with aqueous hydrogen peroxide liberated iodine and gave bistrifluoromethylarsinic acid (hexafluorocacodylic acid) with the formation of only traces of fluoroform :

$$(CF_3)_2AsI \xrightarrow[H_2O_2]{H_2O-} (CF_3)_2AsO_2H$$
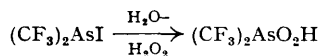
The acid, purified by recrystallisation from chloroform or by sublimation, liberated fluoroform quantitatively on treatment with an excess of base, but was stable in aqueous solution ; cold concentrated hydriodic or sulphuric acid had no effect. Hexafluorocacodylic acid forms a monosilver salt which is readily soluble in water and so prevents titration of the acid with aqueous silver nitrate. The infra-red spectra of bistrifluoromethylarsinic acid and its silver salt show C–F absorption at 8—9 μ and weak broad bands at 4·3 and 4·4 μ which can be distinguished from the C–F overtone bands. If these weak bands are ascribed to the As–OH stretching vibration, they indicate, without being decisive, that the acid exists in part as $(CF_3)_2As(OH)_3$, giving a silver salt $(CF_3)_2As(OH)_2(OAg)$ [cf. $(CF_3)_2AsO_2Ag$].

The molecular conductivity of an aqueous solution of bistrifluoromethylarsinic (hexafluorocacodylic) acid is 230 times as great as that of cacodylic acid at a dilution (l. mole^{-1}) of 32. The marked increase in acid strength so indicated is confirmed by titration with base. The hexafluoro-acid is a strong acid, comparable with hydrochloric and tri-fluoroacetic acid in aqueous solution, and is probably dibasic, since the first point of inflection on the titration curve is at pH 3·7 ; rapid titration with base at pH >7 gives some indication of a second point of inflection corresponding to $(CF_3)_2As(OH)(ONa)_2$. Cacodylic acid (K 4·2 × 10^{-7}) is an acid not much stronger than hydrogen sulphide. Hantzsch (*Ber.*, 1904, **37**, 1076) from conductivity data postulated that cacodylic acid may be dibasic in strongly alkaline solution : $(CH_3)_2AsO_2H + 2NaOH \rightleftharpoons (CH_3)_2As(OH)(ONa)_2$. Replacement of methyl by trifluoromethyl will increase the tendency to react as a dibasic or possibly even as a tribasic acid. The very large increase in acid strength of the hexafluoro-acid again illustrates the powerful inductive effect of the trifluoromethyl group.

EXPERIMENTAL

Preparation of Tristrifluoromethylarsine, Iodobistrifluoromethylarsine, and Di-iodotrifluoromethylarsine.—Arsenic powder (100 g.) was mixed with broken porcelain (to prevent sintering to a solid mass and to give maximum surface area), and heated to 220° for 18—24 hr. in a stainless-steel autoclave (100-ml. capacity) with trifluoroiodomethane (40 g.). The trifluoromethylarsenic compounds were removed by pumping and fresh trifluoroiodomethane inserted for repeat preparations, made without emptying of the autoclave. The products, containing maximum yields of the iodo-compounds. were tristrifluoromethylarsine (78%), iodobistrifluoromethylarsine (13%), di-iodotrifluoromethylarsine (4%), b. p. 100°/48 mm., 137°/190 mm., 183°/760 mm. (slight decomp.), and trifluoroiodomethane (5%).

Tristrifluoromethylarsine failed to form an addition compound with mercuric chloride in ethanol at 100° (1 hr.), nor could compound formation be detected with sulphur.

Reaction of Tristrifluoromethylarsine with Chlorine.—Tristrifluoromethylarsine (10·3 g.) and dry chlorine (2·0 g.) were set aside in a sealed Carius tube (50 ml.) at room temperature for 84 hr.; they gave unchanged tristrifluoromethylarsine (6·4 g., 62%), chlorotrifluoromethane (0·5 g., 4%), and *tristrifluoromethylarsenic dichloride* [4·4 g., 34% based on $As(CF_3)_3$ used] (Found : CF_3, 57·0; Cl, 20·1; As, 21·3%; M, 340. $C_3Cl_2F_9As$ requires CF_3, 58·6; Cl, 20·1; As, 21·3%; M, 353), b. p. 98·5°, n_D^{19} 1·386. Chlorotrifluoromethane was not liberated during the distillation. Analysis for CF_3 was effected by reaction with an excess of 20% sodium hydroxide solution and measurement of the fluoroform evolved. The low molecular weight is caused by partial decomposition of the compound on the mercury of the manometers.

The interaction of tristrifluoromethylarsine (7·6 g.) and chlorine [1·15 g., 61% of the amount for chlorination to $(CF_3)_2AsCl$], in the vapour phase in a 5-l. bulb, followed a different course. After 1·5 hr. fractionation gave chlorotrifluoromethane (1·70 g., 50% based on chlorine), arsenic trichloride (0·18 g.), a mixture (6·39 g.; M, 265) of tristrifluoromethylarsine and chlorotrifluoromethylarsines, but no tristrifluoromethylarsenic dichloride.

Tristrifluoromethylarsine (2·8 g.) and chlorine (0·70 g.) in a sealed tube during a month at room temperature gave no tristrifluoromethylarsenic dichloride, but *bistrifluoromethylarsenic trichloride* (ca. 30%) (Found : CF_3, 42·1; Cl, 33·2; As, 20·6. $C_2Cl_3F_6As$ requires CF_3, 43·2; Cl, 33·3; As, 23·5%), b. p. 93—95°/722 mm., n_D^{20} 1·423, tristrifluoromethylarsine (1·0 g., 35%), and chlorotrifluoromethane (0·7 g., 22%).

Tristrifluoromethylarsine (14·3 g.) and chlorine (12 g.) at 125° (24 hr.) gave chlorotrifluoromethane and arsenic trichloride in theoretical yield.

When tristrifluoromethylarsenic dichloride was shaken with mercury, tristrifluoromethylarsine (Found : M, 280. Calc. for C_3F_9As : M, 282) and mercuric chloride were formed. Thermal decomposition of tristrifluoromethylarsenic dichloride (2·0 g.) during 20 hr. at 125° yielded *chlorobistrifluoromethylarsine* (Found : CF_3, 55·7; Cl, 14·3; As, 30·0%; M, 249. C_2ClF_6As requires CF_3, 55·5; Cl, 14·3; As, 30·2%; M, 248), b. p. 46°, n_D^{19} 1·351, and *dichlorotrifluoromethylarsine* (combined yield ca. 38%) (Found : CF_3, 33·0; Cl, 32·2; As, 34·8%; M, 215. CCl_2F_3As requires CF_3, 32·1; Cl, 33·0; As, 34·9%; M, 215), b. p. 71°, n_D^{20} 1·431, chlorotrifluoromethane (0·2 g., 11%), tristrifluoromethylarsine (ca. 10%), and unchanged tristrifluoromethylarsenic dichloride (0·6 g., 31%), b. p. 98°. A small amount of arsenic trichloride was observed. The chlorotrifluoromethylarsines were identical with those obtained from the interaction of the corresponding iodo-compounds and silver chloride (Walaschewski, *loc. cit.*).

Reaction of Tristrifluoromethylarsine with Bromine.—In a typical experiment, tristrifluoromethylarsine (3·4 g.) and bromine [1·80 g., 93% of that required to give $(CF_3)_2AsBr$] in a sealed tube deposited arsenic tribromide (1·2 g., 33%) at −5° and liberated bromotrifluoromethane (1·73 g., 50% based on bromine) (M, 152. Calc. for $CBrF_3$: M, 149). The residual pale yellow liquid, distilled under atmospheric pressure, gave tristrifluoromethylarsine (1·24 g., 38%), *bromobistrifluoromethylarsine* (0·60 g., 17%) (Found : CF_3, 47·6; Br, 27·3; As, 25·6%; M, 280. C_2BrF_6As requires CF_3, 47·1; Br, 27·3; As, 25·6%; M, 293), b. p. 59·5°/745 mm., n_D^{20} 1·398, and *dibromotrifluoromethylarsine* (0·40 g., 12%) (Found : CF_3, 22·7; Br, 52·1; As, 24·8. CBr_2F_3As requires CF_3, 22·7; Br, 52·6; As, 24·7%), b. p. 118°/745 mm., n_D^{20} 1·528. Deposition of arsenic tribromide with evolution of bromotrifluoromethane took place even when the reactants were cooled to −22° after initiation of the reaction at −10°, and no indication was obtained of the intermediate formation of tristrifluoromethylarsenic dibromide.

In another experiment in which sufficient bromine was used to give a theoretical conversion into CF_3AsBr_2, excess of bromine was apparent after 3 days at 20°, and reacted further only on distillation of the products, which were similar to those described above.

Reaction of Tristrifluoromethylarsine with Iodine.—The arsine (2·8 g.) dissolved only a small amount of the 2·5 g. of iodine sealed with it, and assumed a reddish colour which, when the supernatant liquid was removed and set aside, slowly disappeared. After the recombined mixture had been heated at 100° for 48 hr., the products were arsenic tri-iodide, iodobistrifluoromethylarsine (*ca.* 8%), di-iodotrifluoromethylarsine (*ca.* 5%), and trifluoroiodomethane (80%). At temperatures above this optimum, increased amounts of arsenic tri-iodide and trifluoroiodomethane were formed.

Tristrifluoromethylarsine (10·5 g.) with arsenic tri-iodide (12·0 g.) at 230—240° (48 hr.) gave trifluoroiodomethane (1·9 g.), iodobistrifluoromethylarsine (3·8 g.), di-iodotrifluoromethylarsine (0·4 g.) and unchanged tristrifluoromethylarsine (6·6 g.) (see Walaschewski, *loc. cit.*).

Reaction of Tristrifluoromethylarsine with Fluorine.—A stream of pure, dry nitrogen was passed through tristrifluoromethylarsine (3·3 g.) in a trap at 10° to carry it during 3·5 hr. over a bed of cobalt trifluoride (20 g.) at 100° in a horizontal copper reaction vessel (9 cm. long, 2 cm. in diameter). The volatile products were fractionated, to give carbon tetrafluoride (1·51 g., 49%), arsenic trifluoride (0·2 g., 13%) (M, 137. Calc. for AsF_3 : M, 132), and a fraction (1·0 g.) (M, 266—275) which condensed in a trap cooled to −96°. Examination of the infra-red spectrum of this material showed it to have bands characteristic of *fluorobistrifluoromethylarsine*, independently prepared from iodobistrifluoromethylarsine and silver fluoride at 20° for 3 days (Found : CF_3, 58·9; F⁻, 8·1; As, 33·0%; M, 228. C_2F_7As requires CF_3, 59·5; F⁻, 8·2; As, 32·3%; M, 232), b. p. 25°, analysed by decomposition with 10% aqueous sodium hydroxide and measurement of the fluoroform and fluoride. Traces of difluorotrifluoromethylarsine may have been present, but no quinquevalent compounds of arsenic were isolated; *tristrifluoromethylarsenic difluoride* was prepared as a reference compound for this purpose by the interaction of tristrifluoromethyl arsenic dichloride (2·1 g.) and silver fluoride (3 g.) at 20° for 6 days (quantitative yield; 52% conversion) (Found : CF_3, 63·6; F, 11·4; As, 25·0. $C_3F_{11}As$ requires CF_3, 64·7; F, 11·9; As, 23·4%), b. p. 57—58°.

The passage of tristrifluoromethylarsine over cobalt trifluoride at 160° gave almost complete conversion into carbon tetrafluoride and arsenic trifluoride.

The reaction of liquid tristrifluoromethylarsine with elementary fluorine diluted with nitrogen was examined at various temperatures : at −100° and −85° there was little reaction, whilst at −66°, −48°, and −28° carbon tetrafluoride and arsenic trifluoride were formed in increasing amounts. Tristrifluoromethylarsenic difluoride was not isolated.

Bistrifluoromethylarsine.—Iodobistrifluoromethylarsine (2·5 g.) was distilled *in vacuo* into a flask equipped with stirrer and reflux condenser leading to traps cooled in liquid air, and to the frozen arsine was added a solution of lithium aluminium hydride (0·20 g.) in di-*n*-butyl ether (4 ml.). There was a steady gas evolution as the temperature was slowly raised to 10° and the volatile products were swept from the apparatus by a stream of nitrogen. Towards the end of the reaction the temperature was raised to 60° for 10 min. This did not complete the reaction since it was noted in subsequent experiments that a slow evolution of the arsine continued for several days. The product was freed from traces of dibutyl ether and iodobistrifluoromethyl arsine and shown to be *bistrifluoromethylarsine* (0·26 g., 16%) [Found : F, 52·2 (38·1% as CHF_3, 14·1% as F⁻); As, 34·9%; M, 215. C_2HF_6As requires F, 53·2; As, 35·0%; M, 214]. For the analysis, decomposition with 10% aqueous sodium hydroxide gave fluoroform, which was collected and measured, and fluoride and arsenite (see later). The following vapour pressures were recorded : −66·2°, 6·7 mm.; −47·7°, 28·5 mm.; −24·5°, 107·8 mm.; 0°, 349 mm., whence the extrapolated b. p. is 19°. It should be noted that mixing the reactants at room temperature causes a violent gas evolution with loss of product. There is no reaction in the absence of a solvent, which must be chosen to enable the products to be separated easily; tristrifluoromethylarsine shows no reaction with ethereal lithium aluminium hydride at 30—80°.

A better method for the preparation of bistrifluoromethylarsine is as follows : To a 100-ml. flask containing zinc (10 g.) coated with copper, water (10 ml.), and 5N-hydrochloric acid (4 ml.), iodobistrifluoromethylarsine (3·80 g.) was added during 30 min. with vigorous shaking to emulsify the iodo-compound. During 1 hr. further quantities of concentrated acid (10 ml. total) were added, and after flushing with nitrogen for 1 hr. the products which had condensed in traps attached to the reaction flask were fractionated *in vacuo*, to give bistrifluoromethylarsine (1·03 g., 43%) (Found : M, 213) and tetrakistrifluoromethyldiarsine (0·87 g., 37%) (Found : M, 412. Calc. for $C_4F_{12}As_2$: M, 426) (see Part V).

Thermal decomposition of bistrifluoromethylarsine (0·125 g.) in a sealed tube at 220—240° for 40 hr. gave arsenic (as a mirror), fluoroform [0·030 g., 37% based on $(CF_3)_2AsH$] (M, 69),

tristrifluoromethylarsine (0·043 g., 39%) (Found : *M*, 278. Calc. for C₃F₉As : *M*, 282), and a mixture of the last compound and bistrifluoromethylarsine (0·015 g.; *M*, 230).

Bistrifluoromethylarsine slowly decomposes at room temperature, and the decomposition is apparently accelerated by traces of impurities in the vacuum system (*e.g.*, mercuric iodide) which was therefore cleaned carefully before use.

Trifluoromethylarsine.—A mixture of di-iodotrifluoromethylarsine (1·52 g.) and lithium aluminium hydride (0·16 g.) in di-*n*-butyl ether (4 ml.), initially frozen in liquid air, was slowly warmed to 15° to give a steady gas evolution. Fractionation of the product *in vacuo* gave *trifluoromethylarsine* (0·24 g., 49%) (Found : F, 37·4%; *M*, 144. CH_2F_3As requires F, 39·1%; *M*, 146), b. p. −12·5°/753 mm., analysed by sodium fusion.

By the alternative procedure, di-iodotrifluoromethylarsine (3·5 g.) was added in 3 portions at 5-min. intervals to zinc (10 g.) coated with copper, water (10 ml.), and 5N-hydrochloric acid (25 ml.) with vigorous shaking. Concentrated hydrochloric acid (13 ml.) was then added portionwise during 1 hr., after which the apparatus was flushed with nitrogen for 1 hr. The volatile products were transferred to a vacuum-system and fractionated, to give trifluoromethylarsine (1·26 g., 98%) (Found : F, 39·6%; *M*, 146. Calc. for CH_2F_3As: F, 39·1%; *M*, 146), b. p. −11·6°/781 mm. The reaction of the compound with aqueous sodium hydroxide is described below.

No change was apparent when trifluoromethylarsine (0·329 g.) was heated at 220° for 12 hr., but on further heating at 330° for 40 hr. a grey mirror was produced and hydrogen was liberated. The condensable gas was fluoroform (0·154 g., 98%) (Found : *M*, 69. Calc. for CHF_3: *M*, 70).

Photochemical and Thermal Reactions of Tristrifluoromethylarsine.—(1) *Thermal hydrogenation.* Tristrifluoromethylarsine (1·15 g.), sealed in a Pyrex tube (50 ml.) with hydrogen (630 mm. pressure) and heated to 220—240° for 93 hr., gave arsenic as a grey powder, fluoroform (0·014 g., 2%) identified by its infra-red spectrum, tristrifluoromethylarsine (1·02 g., 89%) (*M*, 283), and an impure fraction of tristrifluoromethylarsine, shown by infra-red spectroscopy to contain no trifluoromethyl- or bistrifluoromethyl-arsine.

(2) *Photochemical hydrogenation.* Tristrifluoromethylarsine (0·639 g.) and hydrogen (560 mm. pressure) in a 120-ml. silica tube were irradiated for 19 hr. by a Hanovia fluorescent lamp at a distance of 4 cm., to give a mixture of fluoroform and hexafluoroethane (0·032 g.) (*M*, 100) identified by its infra-red spectrum, and tristrifluoromethylarsine (0·568 g., 85%) (*M*, 280), but no trifluoromethyl- or bistrifluoromethyl-arsine.

(3) *Photochemical decomposition.* Tristrifluoromethylarsine (0·738 g.) in a 120-ml. silica tube was exposed to ultra-violet light at a distance of 1 cm. for 16 hr. (temp. *ca.* 50°). A film of arsenic was deposited in the cooler parts of the tube, and as volatile products were isolated hexafluoroethane (0·078 g., 14%) (*M*, 139) and tristrifluoromethylarsine (0·6 g., 80%) (*M*, 283).

Preparation of Arsenic Compounds containing Methyl and Trifluoromethyl Groups.—(1) *The exchange reaction.* (*a*) Tristrifluoromethylarsine (0·65 g.) and methyl iodide (0·28 g.) in a 120-ml. silica tube were irradiated at a distance of 1 cm. for 24 hr., to give a trace of unidentified yellow solid, hexafluoroethane (0·07 g., 15%) (*M*, 136·5), trifluoroiodomethane (0·24 g., 18%) (*M*, 197), and a fraction (0·42 g.) (*M*, 237) shown by infra-red analysis to be a mixture containing tristrifluoromethylarsine. The last compound was removed from the mixture by its preferential hydrolysis with 10% aqueous sodium hydroxide at room temperature for 12 hours, and the residual gas (*M*, 217) was shown by its infra-red spectrum to be mainly methylbistrifluoromethylarsine (*ca.* 30%). A portion (0·20 g.) of the gas was sealed with mercuric chloride (1 g.) for 4 months at 20°. The infra-red spectrum of the volatile material was unchanged, but since arsenic was detected in the solid material, and a separate experiment (see below) showed that pure methylbistrifluoromethylarsine did not yield an addition compound with mercuric chloride, the presence of small amounts of dimethyltrifluoromethylarsine and possibly of trimethyl-arsine is indicated.

(*b*) Tristrifluoromethylarsine (1·77 g.) and methyl iodide (1·63 g.) form two layers at 15°, and these re-appear on cooling after 44 hr.' heating at 140°. After 24 hr. at 235° the pale yellow liquid products remained in one phase, even at −20°. Distillation gave trifluoroiodomethane (1·37 g., 64% based on methyl iodide, 37% on tristrifluoromethylarsine) (Found : *M*, 196. Calc. for CF₃I : *M*, 196) and fluoroform (0·06 g.) as volatile products; 1 : 1 : 1-trifluoroethane was not detected. The less volatile products were a mixture of methyltrifluoromethyl- and bistrifluoromethyl-iodoarsine, which attacked mercury at room temperature with the formation of mercuric iodide, and a mixture of methylbistrifluoromethylarsine and tristrifluoro-

methylarsine (1·5 g.). This mixture was shaken with 10% aqueous sodium hydroxide (30 ml.) for 3 hr., to give fluoroform and methylbistrifluoromethylarsine, identified by comparison of its infra-red spectrum with that of a known specimen (see below).

Tristrifluoromethylarsine and trifluoroiodomethane failed to yield a quaternary salt at 200° (24 hours).

(2) *Interaction of iodobistrifluoromethylarsine and methylmagnesium iodide.* Methyl-magnesium iodide (from methyl iodide, 6·0 g., and excess of magnesium in di-*n*-butyl ether, 40 ml.) was filtered and treated dropwise during 20 min. with iodobistrifluoromethylarsine (4·8 g.). No volatile products were detected at this stage, but addition of 10% sulphuric acid (25 ml.) (addition of water liberated only *ca.* 50% of the arsine), followed by slow distillation through a short column, gave a volatile fraction, b. p. 40—100°, which was dried (P_2O_5) and redistilled through a short column, to give *methylbistrifluoromethylarsine* (2·02 g., 63%) (Found : F, 49·0%; M, 218. $C_3H_3F_6As$ requires F, 50·0%; M, 228), b. p. 52°. Methylbistrifluoro-methylarsine failed to yield an addition compound when sealed with mercuric chloride for 2 days at room temperature.

Hydrolysis of Trifluoromethyl Arsenicals.—(1) The following compounds, when treated with 15—20% aqueous sodium hydroxide at room temperature for 12 hr., liberate their trifluoro-methyl groups as fluoroform quantitatively : $(CF_3)_3As$, $(CF_3)_2AsX$, X = Br, Cl, F, I, CN, or SCN; CF_3AsX_2, X = Br, Cl, I; $(CF_3)_3AsX_2$, X = Cl, F; $(CF_3)_2AsCl_3$, $(CF_3)_2As·O·As(CF_3)_2$ (b. p. 100°, n_D^{20} 1·354; prepared quantitatively from iodobistrifluoromethylarsine and mercuric oxide at room temperature).

(2) *Methylbistrifluoromethylarsine.* When this compound (0·207 g.) was shaken with 20% sodium hydroxide (5 ml.) for 3 days at room temperature, decomposition was incomplete [Found : CF_3 (as CHF_3), 41·5; As, 18·5. Calc. for $C_3H_3F_6As$: CF_3, 60·5; As, 32·9%], and unchanged methylbistrifluoromethylarsine was recovered; a test for fluoride was negative. In a second experiment, methylbistrifluoromethylarsine (0·572 g.) was heated at 100° for 72 hr. with 20% aqueous sodium hydroxide (5 ml.) but decomposition was still incomplete (Found : CF_3, 56·8; As, 30·1%), and unchanged fluoroarsine but no fluoride was detected.

(3) *Tetrakistrifluoromethyldiarsine.* The diarsine was prepared quantitatively from iodo-bistrifluoromethylarsine and mercury (Part V) and purified by distillation at atmospheric pressure (Found : M, 426. Calc. for $C_4F_{12}As_2$: M, 426), b. p. 105°/770 mm. When the diarsine (0·700 g.) was heated at 100° for 6 hours with 20% sodium hydroxide solution (5 ml.), the rate of hydrolysis was considerably slower than that of tristrifluoromethylarsine under comparable conditions [Found : F, 53·6 (44·8 as CHF_3, 8·8 as F^-); As, 33·9. Calc. for $C_4F_{12}As_2$: F, 53·3; As, 35·2%]. The ratio of fluoroform to fluoride is thus 83·5 : 16·5. The discrepancy in the arsenic figure is ascribed to the formation of a small amount of a bright yellow precipitate, unidentified, but, from the above analysis, apparently consisting entirely of arsenic (cf. the hydrolysis of the trifluoromethyl- and bistrifluoromethyl-arsine, below).

(4) *Bistrifluoromethylarsine.* The compound (0·117 g.) sealed with 15% aqueous sodium hydroxide (5 ml.) and shaken at 20° for 24 hr. gave fluoroform (0·055 g., 38%) and, by distillation of the aqueous solution, fluoride (14%). The percentage of the total fluorine appearing as fluoride was thus 73%.

In a second experiment, precautions were taken to keep disproportionation of the arsine to a minimum, and it was transferred as rapidly as possible to the hydrolysis tube. The arsine (0·279 g.) and 20% aqueous sodium hydroxide (5 ml.) were heated under the " standard conditions " (100° for 2 days) used for the hydrolysis of tetrakistrifluoromethyldiarsine, to give fluoroform (0·118 g., 34·5% of the hydride), and fluoride (0·052 g., 18·5%). The ratio of CF_3 as fluoroform to CF_3 as fluoride is thus 41·7 : 20·4, *i.e.*, approximately 2 : 1. Titration of the aqueous solution with iodine gave arsenic (0·0914 g., 33%) (Calc. for C_2HF_6As : F, 53·2; As, 35·0%). A small amount of a yellow solid formed during the hydrolysis was discarded.

(5) *Trifluoromethylarsine.* The compound (0·220 g.) was sealed with 20% sodium hydroxide solution (5 ml.) and heated at 100° for 6 hr. under the conditions used for tetrakistrifluoro-methyldiarsine. A copious, bright yellow precipitate formed was separated by centrifuging, and the fluoride and arsenic in the alkaline solution were determined (Found : F^-, 22·8; As, as $As^{III} + As^V$, 43·2; as As^{III} 14·7%). The volatile product of hydrolysis was fluoroform (equiv. to F^-, 12·5%). The yellow precipitate was slightly soluble in hot water, readily soluble in warm dilute nitric acid with production of a faint garlic odour; after its oxidation the arsenic was determined as $Mg_2As_2O_7$ (Found : additional As, 7·9%). The total arsenic figure is thus 51·1% and the total fluorine figure is 35·3% (Calc. for CH_2F_3As : F, 39·1; As, 51·8%). The

low fluorine figure is due to the small amount of fluorine (not estimated) in the yellow precipitate. Infra-red examination of the yellow solid showed only a broad band at 9·1 μ.

In a second experiment the arsine (0·257 g.) was sealed with 20% aqueous sodium hydroxide (5 ml.) and immediately inserted into a preheated furnace at 105° where it was left for 15 hr. Fluoroform (0·046 g., 14·5%) was produced (cf. 12·5% above).

(6) *Tristrifluoromethylarsine.* The arsine is stable to water at room temperature. Tristrifluoromethylarsine (0·804 g.) was shaken in a 250-ml. flask with buffer solution (100 ml.; McIlvaine's, 13·05% of 0·1M-citric acid, 86·95% of 0·2M-disodium phosphate; pH 7·2), for 48 hr. at 16—20°, and gave fluoroform (0·006 g., 1%) (M, 66) and unchanged tristrifluoromethylarsine (0·785 g., 98%). Under identical conditions the arsine (0·705 g.) and buffer solution (100 ml.; Sørensen's, 80% of a solution of 7·505 g. of glycine and 5·85 g. of sodium chloride in 1 l. of water, and 20% of 0·1M-sodium hydroxide; pH 9·3) gave fluoroform (0·076 g., 15%) (M, 70) and unchanged tristrifluoromethylarsine (0·547 g., 78%). The arsenic liberated (as arsenite) was 15%.

When tristrifluoromethylarsine (0·572 g.) was shaken at room temperature for 44 hr. with 85% of the amount of sodium hydroxide (35 ml. of 0·049N) required for removal of only one trifluoromethyl group, the volatile products were fluoroform (0·370 g., 87%) (M, 70) and tristrifluoromethylarsine (0·069 g., 12%). The aqueous solution was alkaline.

Attempts to achieve stepwise hydrolysis by use of alcoholic sodium hydroxide solutions of various concentrations and following the reaction by the pressure of fluoroform evolved, were unsuccessful.

The stability of tristrifluoromethylarsine to concentrated sulphuric acid was shown as follows : the arsine (5·50 g.) and acid (2 ml.), heated at 150° for 9 hr., gave fluoroform (0·027 g., 0·5%) (M, 68), an unidentified gas (0·074 g.) (M, 146), and tristrifluoromethylarsine (5·26 g., 96%). The recovered material was reheated with the acid to 235° for 3 hr., to give a fraction (0·160 g.) (M, 73) containing fluoroform, silicon tetrafluoride, and carbonyl fluoride, and unchanged tristrifluoromethylarsine (*ca.* 5 g.).

(7) *Cyanobistrifluoromethylarsine.* The compound (1·73 g.) and water (4 ml.), heated at 72° for 38 hours, then at 104° for 60 hr., gave white crystals of arsenic trioxide and fluoroform (0·96 g., 96%) (M, 72), separated from hydrogen cyanide (0·18 g., 92%) (M, 28) by treatment with sodium hydroxide solution. Traces of cyanogen may have been present.

(8) *Chloro- and iodo-bistrifluoromethylarsines and dichlorotrifluoromethylarsine.* Chlorobistrifluoromethylarsine and dichlorotrifluoromethylarsine failed to react with water at room temperature. Iodobistrifluoromethylarsine is similarly stable, and during 50 hr. at 100° gave less than 2% of fluoroform. After 14 hr. at 260° the iodo-compound decomposed, with attack on the reaction tube, to give silicon tetrafluoride and fluorosilicic acid. The oxidative hydrolysis of the iodo-compound is described below.

(9) *Di-iodotrifluoromethylarsine.* No volatile products were detected after the iodo-compound (0·70 g.) had been shaken vigorously with water (1·5 ml.) at room temperature for 2 weeks, and removal and analysis of the lower layer showed it to be substantially unchanged. The aqueous layer had pH 1 owing to traces of iodine present in the di-iodotrifluoromethylarsine.

Attempts to Prepare Salts of Bistrifluoromethylarsinous Acid.—Iodobistrifluoromethylarsine (1·1 g.) and silver oxide (1·16 g.; washed with dilute acetic acid) rapidly yielded silver iodide, precipitated from a neutral solution. It proved impossible to separate the silver salt, believed to be $(CF_3)_2As\cdot OAg$ from silver iodide. The salt is decomposed by alkali, nitric acid, hydrogen sulphide, or neutral potassium iodide with the evolution of fluoroform. Interaction of iodobistrifluoromethylarsine (2·1 g.) and mercuric oxide (2 g.) in water (3 ml.) gave mercuric iodide and a slow deposition of white needles which were separated by dissolution in an excess of water, filtration, and evaporation of the solution to dryness *in vacuo* at room temperature. The *mercury* salt [Found: F, 30·1 (29·0% as CHF₃, 1·1% as F⁻); As, 22·8; Hg, 29·9. $C_4F_{12}O_2As_2Hg$ requires F, 34·6; As, 22·7; Hg, 30·5%] does not melt below 310°.

Bistrifluoromethylarsinic Acid (Hexafluorocacodylic Acid).—Iodobistrifluoromethylarsine (5·04 g.) was sealed in a Pyrex tube with unstabilised hydrogen peroxide (100-vol.; 3 ml.). Warming to room temperature caused exothermic liberation of iodine which was substantially complete in 15 min. If the reaction was not interrupted at this stage, fluoroform was slowly liberated (*ca.* 8% after 3 days). The iodine was removed by filtration, and the strongly acid solution was evaporated to dryness over sulphuric acid in an evacuated desiccator (much of the arsinic acid is lost by removal of the water by continued pumping). Large translucent trigonal rhombs were obtained which, after 2 hr. in the desiccator, lost water and changed to a white powder (3·11 g., 86%). The solid was recrystallised from hot chloroform to remove

traces of arsenic oxides and gave *bistrifluoromethylarsinic acid* (Found : CF_3, 56·7; As, 30·8. $C_2HF_6O_2As$ requires CF_3, 56·1; As, 30·5%), analysed by treatment with 20% aqueous sodium hydroxide at 100° for 6 hr.; fluoride was not formed.

Bistrifluoromethylarsinic acid is readily soluble in water, less soluble in dioxan and hot chloroform. It does not melt, but sublimes with partial decomposition at $150°/10^{-3}$ mm. to give needles (Found : CF_3, 56·9; As, 31·9%) of the free acid, possibly contaminated with anhydride (Calc. for $C_4F_{12}O_3As_2$: CF_3, 58·2; As, 31·7%). The brown residue from the sublimation liberates fluoroform on treatment with aqueous alkali.

When bistrifluoromethylarsinic acid (0·077 g.) was treated with an excess of 50% sulphuric acid at 135—145°, no hydrolysis to fluoride ion was detected on titration of the distillate with thorium nitrate.

Conductivity. The conductivites at 25° of bistrifluoromethylarsinic acid and dimethyl-arsinic acid (cacodylic acid) are :

Dilution (l. mole⁻¹)	32	64	128
Molecular conductivity :			
$(CF_3)_2AsO_2H$	314	348	359
$(CH_3)_2AsO_2H$	1·37	1·96	2·76

Titration. A solution of 0·769 g. of the acid in water (100 ml.) (*i.e.*, M/32) had pH 1·67 (cf. M/32-hydrochloric acid, pH 1·50). Titration of 5 ml. against 0·1N-sodium hydroxide can be carried out accurately only below pH 7, since fluoroform is lost in alkaline solution. The solution was stirred by a fine stream of nitrogen and the pH was measured by a Cambridge Instrument Co. pH meter. The first point of inflection (pH 3·7) is at 1·60 ml. of alkali [$(CF_3)_2As\cdot ONa$ or $(CF_3)_2As(OH)_2(ONa)$ requires 1·56 ml.]. *Rapid* titration with base gives a second point of inflection at *ca.* pH 9, corresponding approximately to the equivalent for $(CF_3)_2As(OH)(ONa)_2$ (3·1 ml.). *Slow* titration of the acid with base gives completely reproducible results up to pH 7, but the decomposition of the acid at pH >7 is shown by the solution obtained from the acid (0·0217 g.) dissolved in water (10 ml.) and treated with 0·1N-sodium hydroxide (1·65 ml.); the pH after 0, 3, 6, 37, and 267 min. was 8·33, 8·23, 8·12, 7·63, and 6·98 respectively.

Silver salt. A solution of the acid in water was treated with a 50% excess of silver oxide, and the mixture was heated to 60° until pH 7 was attained (10 min.). The excess of oxide was removed by centrifuging and the aqueous solution was evaporated over sulphuric acid in an evacuated desiccator, to give glittering trigonal crystals which were recrystallised from acetone to give the *silver* salt (Found : CF_3, 38·6; As, 20·5; Ag, 29·8. $C_2F_6O_2AsAg$ requires CF_3, 39·1; As, 21·1; Ag, 30·6%). The salt is very soluble in water; in hot alcohol it becomes brown. The salt does not melt, but becomes brown at 100° and at 250° liberates arsenic trioxide. The trifluoromethyl groups were liberated quantitatively as fluoroform on treatment with aqueous sodium hydroxide.

Ultra-violet and Infra-red Spectra.—A Beckman DU spectrophotometer and a Perkin–Elmer Model 21 Double-beam instrument with rock-salt optics were used. Quartz cells of 10- or 4-cm. length, and 5- or 10-cm. cells with rock-salt end plates were used where appropriate. Nujol and hexachlorobutadiene mulls were used for solid compounds.

Cyanobistrifluoromethylarsine, b. p. 89·5°, n_D^{20} 1·359, and thiocyanatobistrifluoromethyl-arsine, b. p. 117°, n_D^{20} 1·445, were prepared from iodobistrifluoromethylarsine and the appropriate silver salt. The infra-red spectra show C⋮N absorption at 4·57 μ, and SCN absorption at 5·0 μ. No pressure was recorded for tristrifluoromethylarsenic dichloride, since the compound attacks mercury. The spectrum of silver bistrifluoromethylarsinate (C.S. no. 35*) contains weak bands at *ca.* 3 and 6·17 μ, indicating the presence of water as impurity, possibly as a hydrate.

* Cf. footnote, p. 1556.