484. *Organometallic and Organometalloidal Fluorine Compounds. Part V.* Trifluoromethyl Compounds of Arsenic.*

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Interaction of arsenic and trifluoroiodomethane at 220—240° yields tristrifluoromethylarsine, $As(CF_3)_3$, and iodobistrifluoromethylarsine, $As(CF_3)_2I$. Both arsines are rapidly and quantitatively hydrolysed to fluoroform by aqueous alkali, but are stable to water and to acid at moderate temperatures. The monoiodo-compound reacts with mercury at room temperature to give tetrakistrifluoromethyldiarsine $(CF_3)_2As{\cdot}As(CF_3)_2$, the hydrolysis of which yields fluoroform, fluoride, and carbonate; a reaction mechanism is proposed.

Arsenic reacts with fluoroiodoalkanes to yield perfluoroalkyl arsenicals, and the present communication deals specifically with trifluoromethyl arsenicals. High yields of trifluoromethylarsines are obtained when finely divided arsenic is heated with trifluoroiodomethane at temperatures above 200°. Trifluoromethyl radicals can be produced by the use of ultraviolet light at room temperature (Part I, *J.*, 1949, 2948), but their reaction with arsenic under these conditions is slow. Although the perfluoroalkyl Grignard reagents described recently (Haszeldine, *Nature*, 1951, **167**, 139; 1951, **168**, 1028) should prove to be of use for

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* Part IV, preceding paper.

the preparation of perfluoroalkyl arsenicals, the other normal methods for the preparation of arsenic compounds from organic iodides (*e.g.*, by reaction with sodium arsenide) are, in general, not applicable to the fluoro-compounds.

The reaction of trifluoroiodomethane with arsenic at the optimum temperature of 220—240° yields tristrifluoromethylarsine as the main product, together with iodobistrifluoromethylarsine, di-iodotrifluoromethylarsine, and arsenic tri-iodide. If the iodo-compounds are heated, the equilibrium is again set up :

$$2CF_3{\cdot}AsI_2 \rightleftharpoons (CF_3)_2AsI + AsI_3$$
$$2(CF_3)_2AsI \rightleftharpoons (CF_3)_3As + CF_3{\cdot}AsI_2 \qquad \text{etc.}$$

Similarly, tristrifluoromethylarsine reacts with iodine to yield mono- and di-iodotrifluoromethylarsines, arsenic tri-iodide, and trifluoroiodomethane :

$$(CF_3)_3As \overset{I_2}{\underset{As}{\rightleftharpoons}} (CF_3)_2AsI + CF_3{\cdot}AsI_2 + AsI_3 + CF_3I$$

These equilibria are being studied further, since it appears that the high percentage of tristrifluoromethylarsine formed when arsenic is heated with trifluoroiodomethane is due to disproportionation reactions. Disproportionation of other substituted arsines, particularly those involving negative substituents, has been reported. Thus, 2-furyldichloroarsine and di-2-furylchloroarsine yield tri-2-furylarsine and arsenic trichloride at 150° (Morgan, Cragoe, Elpern, and Hamilton, *J. Amer. Chem Soc.*, 1947, **69**, 932), and true equilibria have been found for the system $AsPh_3$, $AsPh_2Cl$, $AsPhCl_2$, $AsCl_3$ (Evans and Warhurst, *Trans. Faraday Soc.*, 1948, **44**, 189).

The boiling point of tristrifluoromethylarsine is 16° below that of trimethylarsine and the increase in volatility on replacement of hydrogen by fluorine is again apparent. Unlike trimethylarsine, the fluoro-derivative does not form quaternary compounds. Thus, whereas methyl iodide reacts with arsenic at 100° to yield tetramethylarsonium iodide as well as methyliodoarsines (Cahours, *Annalen*, 1862, **122**, 198; Auger, *Compt. rend.*, 1907, **145**, 809), trifluoroiodomethane and arsenic yield tristrifluoromethylarsine and not tetrakistrifluoromethylarsonium iodide.

A major difference between methyl- and trifluoromethyl-arsines lies in their behaviour on hydrolysis; the methyl group is stable to dilute alkali at room temperature, whereas the trifluoromethyl group is liberated quantitatively as fluoroform. This formation of fluoroform is characteristic of compounds of the type $M(CF_3)_n$ and $M(CF_3)_yX_{(n-y)}$, where M = As, P, Sb, Hg, and X = halogen or pseudo-halogen, and affords a convenient method for analysis.

It is apparent that the more negative the group attached to the arsenic the more easily does alkaline or aqueous hydrolysis occur, and the more resistant is the compound to oxidation. Thus, trimethylarsine and other alkylarsines are stable to alkali but are easily oxidised, and triphenylarsine is stable to air and to cold alkali but yields triphenylarsine oxide with hot potassium hydroxide. Tris-2-chloroethoxyarsine, $(CH_2Cl{\cdot}CH_2{\cdot}O)_3As$, is readily hydrolysed by water or alcohol to ethylene chlorohydrin and arsenic oxide; similarly, di-(2-chloroethoxy)phenylarsine loses the negative chloroethoxy-groups on treatment with water and yields phenylarsine oxide. Tristrifluoromethylarsine is not readily oxidised and is insoluble in, and stable to, water or dilute acid at room temperature, although fluoroform is liberated when it is heated with water at 200°. The trifluoromethyl group is thus less labile than the halogenoalkoxy-group.

Iodobistrifluoromethylarsine is appreciably more volatile than the corresponding methyl compound, and has been used for the preparation of many bistrifluoromethylarsines of the type $(CF_3)_2AsX$ (E. G. Walaschewski, unpublished work). The labile iodine atom can be removed by mercury at room temperature to yield tetrakistrifluoromethyldiarsine (perfluorocacodyl) :

$$2(CF_3)_2AsI + Hg \longrightarrow (CF_3)_2As{\cdot}As(CF_3)_2 + HgI_2$$

The fluoro-diarsine is more volatile than the alkyl analogue, and in its hydrolysis differs sharply from the trifluoromethylarsines described above. The diarsenic compound is stable to water, but with sodium hydroxide at room temperature gives *ca.* 75% of the theoretical amount of fluoroform, and *ca.* 25% of the trifluoromethyl groups are converted into fluoride and carbonate. The mechanism of this hydrolysis, which involves destruction under mild conditions of the normally stable trifluoromethyl group, is being studied further. Tetrakistrifluoromethyldiphosphine (F. W. Bennett, unpublished results) and bistrifluoromethyl disulphide (Part III, *loc. cit.*) are hydrolysed partly or completely to fluoride and carbonate, and it is apparent that the effect is associated with the system $(CF_3)_nM{\cdot}M(CF_3)_n$. It is considered that hydrolytic fission of the M–M bond first occurs, *e.g.*:

$$(CF_3)_2As{\cdot}As(CF_3)_2 \xrightarrow{H_2O} (CF_3)_2AsH + (CF_3)_2As{\cdot}OH$$

The acid, which is also the intermediate in the hydrolysis of iodobistrifluoromethylarsine

$$(CF_3)_2AsI \xrightarrow{H_2O} (CF_3)_2As{\cdot}OH \longrightarrow 2CF_3H$$

is completely converted into fluoroform, whereas the hydride yields fluoroform, fluoride, and carbonate:

$$(CF_3)_2AsH \xrightarrow{H_2O} CF_3H + F^- + CO_3^=$$

The synthesis and reactions of bistrifluoromethylarsine supporting this mechanism will be reported later.

EXPERIMENTAL

Reaction of Trifluoroiodomethane with Arsenic.—(a) *In glass vessels.* Finely ground arsenic (10 g.) and trifluoroiodomethane (3 g.) were heated in a Carius tube of *ca.* 50 ml. capacity for 48 hours at 220° The products of b.p. <40° were taken into a vacuum system and separated by fractional condensation into (1) small amounts of silicon tetrafluoride and carbon dioxide, (2) unchanged trifluoroiodomethane (*ca.* 5%), and (3) *tristrifluoromethylarsine* (70%) [Found: C, 12·4; As, 25·9; CF_3 (as CF_3H), 71·5%; *M*, 282. C_3F_9As requires C, 12·8; As, 26·6; CF_3. 73·4%; *M*, 282].

For analysis, 0·2—0·3 g. of tristrifluoromethylarsine was weighed and transferred quantitatively *in vacuo* to a Carius tube containing 5 ml. of 15% sodium hydroxide. The tube was sealed and allowed to warm to room temperature, whereupon a vigorous reaction was apparent. After 24 hours' heating at 50°, the volatile product of reaction was shown to be fluoroform (Found: *M*, 70. Calc. for CHF_3: *M*, 70), b. p. −80°, and its weight was used to calculate the CF_3 content in the fluoroarsine. Arsenic(III) in the residual solution was determined iodometrically, and carbon by combustion.

Examination of products of b. p. >40° is described below.

(b) *In an autoclave.* Larger-scale preparations have been made in a steel autoclave of 100-ml. capacity, a 4—5-fold excess of powdered arsenic being used. Silicon tetrafluoride and carbon dioxide formation are thus prevented.

Properties of Tristrifluoromethylarsine.—The arsine is a colourless liquid with a pungent odour, and is stable to glass or mercury. It does not ignite in air, but decomposes when heated in an open flame. Its vapour pressure measured from −23° to +28° is given by the equation $\log p$ (mm.) = 7·866 − 1528·0/*T*, whence the b. p. is calculated as 33·3°, the latent heat of vaporisation as 6990 cal./mole, and Trouton's constant as 22·8.

Iodobistrifluoromethylarsine.—The products with b. p. >40° from the interaction of arsenic and trifluoroiodomethane in glass or metal vessels were arsenic tri-iodide, *iodobistrifluoromethylarsine* (20%) (Found: C, 7·5; I, 36·6; As, 22·2; CF_3, 40·6%; *M*, 338. C_2F_6IAs requires C, 7·1; I, 37·3; As, 22·1; CF_3, 40·6%; *M*, 340), b. p. 92°, n_D^{25} 1·425, and a higher-boiling oil (10%) later shown to be di-iodotrifluoromethylarsine (E. G. Walaschewski, unpublished). The last two compounds were distilled in an atmosphere of nitrogen.

Numerous preparations of the trifluoromethylarsenic compounds have been made, and optimum conditions are: 220—240° for 48 hours with an excess of finely ground arsenic. Yields of *ca.* 90% of the mixed arsines are thereby obtained in a ratio of 6 : 2 : 1 by weight.

Reactions of Tristrifluoromethylarsine and Iodobistrifluoromethylarsine.—Iodobistrifluoromethylarsine is a yellow non-inflammable oil which does not attack glass. Like tristrifluoromethylarsine, it is soluble in ether but insoluble in water or 3N-hydrochloric acid. Rapid, quantitative decomposition of both arsenicals to fluoroform and the sodium salt of arsenious acid is brought about at 50° by 15% sodium hydroxide solutions. Tristrifluoromethylarsine gave an 87% yield of fluoroform after being heated with water to 300° for 48 hours.

Tristrifluoromethylarsine (4·65 g.), heated with iodine (12 g.) at 100—105° for 3 days, yielded iodobistrifluoromethylarsine (1·27 g., 22%), trifluoroiodomethane (0·86 g., 28%), di-iodotrifluoromethylarsine, and unchanged starting material. The interconversion of the trifluoromethylarsines will be described later.

Preparation of Tetrakistrifluoromethyldiarsine.—Iodobistrifluoromethylarsine (1·34 g.) was shaken gently in a sealed Carius tube with mercury (2 ml.). Immediate reaction was apparent and after 2 days at room temperature the product was pumped from the mercuric iodide into the vacuum system and fractionated, to give *tetrakistrifluoromethyldiarsine* (0·80 g., 91%) (Found: F, 53·3; As, 34·7%; *M*, 422. $C_4F_{12}As_2$ requires F, 53·3; As, 35·2%; *M*, 426), b. p. 106—107° (distilled in nitrogen atmosphere), n_D^{19} 1·372. The compound was analysed for arsenic and fluorine after sodium fusion.

Hydrolysis of Tetrakistrifluoromethyldiarsine.—A sample (0·343 g.) was treated with 15% sodium hydroxide solution (5 ml.) at room temperature. Vigorous evolution of gas occurred, and after 24 hours 76·0% of the theoretical amount of fluoroform had been evolved. A second determination gave 75·2%. Fluoride ion was also formed by the hydrolysis and distillation as fluorosilicic acid and titration with thorium nitrate accounted for the missing 25% of fluoroform. Arsenic was determined iodometrically.

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