

249. The Difluoroarsines.

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Methyl- and *ethyl-difluoroarsine* have been completely identified and their more important physical and chemical properties described. They are liquids boiling at 76.5° and 94.3° respectively. The solid *phenyl-difluoroarsine* and the liquid 2-chlorovinyl difluoroarsine have also been characterised. The method employed for the preparation of difluoroarsines was to treat the corresponding dichloroarsines with anhydrous ammonium fluoride at 80–100°. This fluoride will also fluorinate dimethylchloroarsine, and is recommended as a very convenient agent for the general preparation of fluorine-substituted arsines from the chloro-compounds. The fluorination is normally smooth and the yields are almost quantitative.

APART from dimethylfluoroarsine, AsMe_2F , described by Bunsen (*Annalen*, 1841, **37**, 38) there are no data concerning any of the alkylfluoroarsines. For the preparation of the alkyl difluoroarsines four lines of attack are possible, namely: (i) from the corresponding chlorides, bromides, or iodides; (ii) replacement of halogen by fluorine in, e.g., AsMe_2Cl_3 , the required substance being obtained by thermal decomposition of the primary product, $\text{AsMe}_2\text{F}_3 \rightarrow \text{AsMe}_2\text{F}_2 + \text{MeF}$, by analogy with the chlorine compound; (iii) the action of hydrogen fluoride on the corresponding alkylarsenine oxide, $\text{AsRO} + 2\text{HF} \rightarrow \text{AsRF}_2 + \text{H}_2\text{O}$; (iv) addition of a suitable alkylmagnesium halide to excess of arsenic trifluoride, $\text{AsF}_3 + \text{MgRI} \rightarrow \text{AsRF}_2 + \text{MgIF}$. Method (i) was adopted as being the most suited to laboratory preparation. The starting materials were methyl- and ethyl-dichloroarsine, prepared as outlined below.

EXPERIMENTAL.

Preparation of the Alkyl dichloroarsines.—(i) *Methyldichloroarsine.* The method employed was essentially the same as the industrial method described by Uhlinger and Cook (*J. Ind. Eng. Chem.*, 1919, **11**, 105) but modified somewhat in the later stages to avoid an awkward steam-distillation and provide a more satisfactory yield on the scale usually carried out in the laboratory. After the production of sodium methylarsinate in the reaction $\text{Na}_3\text{AsO}_3 + \text{Me}_2\text{SO}_4 \rightarrow \text{AsMeO}(\text{ONa})_2 + \text{NaMeSO}_4$, methyl alcohol formed by hydrolysis is distilled off at 100°. A small quantity of potassium iodide is added and the solution neutralised with sulphuric acid. The cold solution is mixed with an equal volume of fuming hydrochloric acid, rapidly filtered, and reduced with a stream of sulphur dioxide until no more oil separates: $\text{AsMeO}(\text{OH})_2 + 2\text{HCl} + \text{SO}_2 \rightarrow \text{AsMeCl}_2 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$. The methyldichloroarsine is run off, dried, and fractionated under atmospheric pressure (b. p. 132–133°; yield 30–50%, depending chiefly on the success of the initial methylation).

(ii) *Ethyldichloroarsine.* This preparation was carried out in a similar manner, except that the alkylating agent employed was ethyl iodide. The latter compound is refluxed with sodium arsenite solution under continuous stirring until no more ethyl iodide is absorbed: $\text{Na}_3\text{AsO}_3 + \text{EtI} \rightarrow \text{AsEtO}(\text{ONa})_2 + \text{NaI}$. Before acidification and reduction as in the previous preparation, the bulk of the sodium iodide is removed by adding methyl sulphate and distilling off the methyl iodide formed. The final fractionation of the ethyldichloroarsine is conducted under reduced pressure (for vapour-pressure data, see Gibson and Johnson, *J.*, 1931, 2520); yield 60–65%.

Preparation of Alkyl difluoroarsines.—The substance found to be most suitable for the replacement of the chlorine in dichloroarsines was anhydrous ammonium fluoride, which effects the conversion at 80° in almost quantitative yield, whereas antimony trifluoride, with or without a catalyst, and zinc fluoride are without action at 100°. A fair excess of ammonium salt is to be recommended, as otherwise the reaction tends to become very slow as it approaches completion. The difluoroarsine may be removed as it is formed by continuous fractionation. The following is a description of the procedure finally adopted for the conversion of methyl- and ethyl-dichloroarsines.

Crystalline ammonium fluoride (3 mols.), dried thoroughly in a vacuum desiccator, and pure methyldichloroarsine (1 mol.) are placed in a "Pyrex" Kon fractionating flask, the system being protected from atmospheric moisture by a calcium chloride guard-tube. The flask is heated in a water-bath to 70° and then more slowly to 90°. Reaction sets in a little below 80° as is seen by the loss of crystalline appearance of the ammonium fluoride. When the temperature of the bath reaches about 90° distillation commences, the temperature at the head of the column registering 76–77°. The distillation is complete in 2–3 hours. The temperature at the head of the column must not exceed 78° or the product becomes contaminated with chloro-compound. The product is refractionated and distils constantly at 76.5°.

With slight modification the same procedure can be adopted with ethyldichloroarsine. Since ethyldifluoroarsine boils at 94° the reaction is best carried out under a somewhat reduced pressure, e.g., 400 mm., at which the b. p. is 74°. Alternatively an oil-bath at 110–120° may be employed, but the former method is to be preferred since chemical attack on the flask increases with temperature. "Pyrex" flasks are only slightly etched below 100° in either preparation.

90–95% Yields of *methyl-* and *ethyl-difluoroarsines* can be obtained in this manner without difficulty. It is not advisable to crush the ammonium fluoride finely beforehand as this causes the reaction to set in somewhat vigorously and the product is contaminated with unchanged dichloroarsine. Since there is a slow but definite attack on glass, the difluoroarsines cannot be kept in glass bottles, but should be stored in platinum, copper, or lead. Both compounds are solid at –80°, and at this temperature there is no noticeable action on glass.

Characterisation of the Alkyl difluoroarsines.—The methyl and the ethyl compound on hydrolysis yield the corresponding oxides, which possess very characteristic unpleasant odours resembling that of asafetida. The hydrolysis products of the difluoroarsines possess these typical smells, indistinguishable from those produced by hydrolysing the corresponding dichloroarsines. The methyl oxide (AsMeO) produced by hydrolysis of methyldifluoroarsine was identified by oxidation

with sodium peroxide to sodium methylarsonate, $\text{AsMeO}(\text{ONa})_2$. This substance is known to evolve methane when heated with sodium hydroxide (Auger, *Compt. rend.*, 1908, **146**, 1280). The salt was obtained by evaporation and fused in an evacuated tube connected with a Töpler pump. The gas evolved was passed at low pressure through a U-tube cooled in liquid nitrogen and collected in the reservoir of the Töpler pump; it was odourless, and when ignited, burnt with a faintly luminous flame. The mass left after fusion was shown by qualitative tests to contain sodium arsenate: $\text{AsMeO}(\text{ONa})_2 + \text{NaOH} \rightarrow \text{Na}_3\text{AsO}_4 + \text{CH}_4$.

The quantitative analysis of methyl difluoroarsine was carried out by two independent methods, one gravimetric and one volumetric. The first involved hydrolysis of a known amount, conversion of the combined arsenic present into arsenate, and estimation of this as silver salt (Sarudi, *Z. anal. Chem.*, 1938, **113**, 248). After removal of excess silver as oxide, the fluorine present was estimated as calcium fluoride (Hillebrand and Lundell, "Applied Inorganic Analysis," 1929, p. 802). The procedure was carried out in platinum apparatus except for the weighing of the difluoroarsine which was done in small "Pyrex" ampoules. A small error was hereby introduced owing to the formation of a trace of silicon fluoride (Found: As, 57.15, 57.51, 57.45; F, 30.64, 28.95, 30.21. CH_3AsF_2 requires As, 58.55; F, 29.70%).

An attempt was made to estimate the percentage of methyl radical by measuring the volume of methane formed in the conversion of methylarsonate into arsenate: Auger (*loc. cit.*) states that the production of methane at 250° is quantitative. This proved to be difficult, since the presence of relatively large amounts of sodium fluoride and carbonate, formed by absorption of atmospheric carbon dioxide during evaporation, prevented complete fusion, and even when the temperature was raised somewhat, several hours elapsed before the evolution of methane was completed. The value for methyl in methyl difluoroarsine was estimated as 11.67% (Calc.: 11.75%). Against this, however, a rather high "blank" determination carried out on the sodium peroxide and hydroxide used must be considered, which reduces the experimental figure to about 11.4%.

The second method for the estimation of arsenic and fluorine, used by Uhlinger and Cook (*loc. cit.*, p. 108), involved hydrolysing a known amount of substance and titrating the solution formed, first with alkali to determine the hydrogen fluoride, and secondly with iodine to determine the trivalent arsenic. The following results were obtained: For AsMeF_2 : Found: As, 58.21, 58.50, 58.46; F, 29.56, 29.74, 29.76 (CH_3AsF_2 requires As, 58.55; F, 29.70%). For AsEtF_2 : Found: As, 52.70, 52.75, 52.62; F, 26.93, 26.81, 26.87 ($\text{C}_2\text{H}_5\text{AsF}_2$ requires As, 52.77; F, 26.77%).

Physical Properties of the Alkyl difluoroarsines.—Methyl- and ethyl-difluoroarsines are colourless, mobile liquids. The vapours possess powerful, irritating smells, and resemble those of the alkyl dichloroarsines in their aggressiveness. There is a tendency to fume in moist air, a property not shared by the dichloroarsines.

Vapour pressure. The compound was distilled into a small bulb connected with a mercury manometer. The bulb was surrounded by a large acetone-carbon dioxide bath kept well stirred, and the pressures recorded for a series of temperatures. To avoid error due to the formation of traces of silicon fluoride, a tap connecting the bulb to an evacuating pump was momentarily opened immediately before the taking of a reading, and the pressure noted as soon as equilibrium was re-established. The temperature was measured by a sulphur dioxide vapour-pressure thermometer over the range below -10°, and by a standardised mercury thermometer at higher temperatures.

Above room temperature it was impossible to determine the vapour pressure accurately in a closed Stock vapour-pressure bulb owing to formation of silicon tetrafluoride, which becomes more rapid as the temperature increases. Resort had therefore to be made to distillation under reduced pressure. The usual temperature corrections for the mercury manometer and exposed thermometer stem were applied throughout. The experimental data are tabulated below. In neither case is the relation between the logarithm of the pressure and the reciprocal of the absolute temperature truly linear. A second term involving T has therefore been introduced into the derived equations.

Experimental data for methyl difluoroarsine.

Temp.	-29.0°	-21.3°	-15.1°	-10.1°	-4.6°	+0.1°	4.5°	9.0°	13.7°
p (mm.)	3.0	5.5	8.0	11.5	16.5	22.0	29.0	37.5	48.5
Temp.	18.0°	23.3°	28.4°	36.1°	45.2°	54.2°	63.3°	71.2°	77.0°
p (mm.)	61.5	80.0	103.5	143	225	330	475	632	772

These data are represented by the equation $\log p_{\text{mm.}} = 7.5315 - 1399/T - 79,400/T^2$. The vapour pressure reaches 760 mm. at 76.5°.

Experimental data for ethyl difluoroarsine.

Temp.	-25.5°	-17.0°	-10.3°	-4.3°	+0.8°	5.6°	10.3°	15.3°	20.3°	24.9°
p (mm.)	2.0	3.5	5.5	8.5	11.5	15.0	20.0	26.5	34.5	44.0
Temp.	31.9°	39.5°	46.8°	53.3°	60.1°	67.2°	75.4°	83.2°	91.0°	94.6°
p (mm.)	63	94	130	178	236	305	412	546	678	767

The following vapour-pressure equation has been deduced: $\log p_{\text{mm.}} = 6.0960 - 590/T - 217,100/T^2$. The vapour pressure reaches 760 mm. at 94.3°.

Melting point. The melting point of the ethyl compound was very sharp, the values obtained being -38.7°, -38.9°, -38.7°, -38.6°, -38.6° (mean -38.7°). The methyl compound, however, even after repeated fractionations in vacuum apparatus, melted over a range of 1.0-1.5°, and the temperature of initial melting was recorded. The following experimental values were obtained: -29.8°, -29.6°, -29.7°, -29.7°, -29.8° (mean -29.7°).

Liquid density. For the determination of liquid density, use was made of a capillary tube of even bore with a suitable-sized bulb blown at one end. This was calibrated with pure benzene and with water. The difluoroarsines were distilled in a vacuum into the bulbs, which were attached to vacuum apparatus by means of ground glass joints. The bulbs were subsequently sealed off. The measurements were made in a large Dewar flask with an unsilvered strip down one side to enable the necessary cathetometer observations to be made. The temperature of the bath was accurately measured by a vapour-pressure thermometer or a standardised mercury thermometer. Measurements were made between -30° and +35°. Above the latter temperature there was a noticeable etching of the inside of the glass bulb. For the methyl compound the density at $t^\circ \text{C.}$ is given by the expression: $d_t = 1.972 - 0.00267t$. A check determination on a fresh sample furnished a value of 1.924 at 18.4°. The mean coefficient of expansion is 0.00138. For the ethyl compound the density relation calculated from experimental figures (-28.7° to 33.3°) is $d_t = 1.743 - 0.00217t$. A separate determination gave a value of 1.708 at 17.0°. The mean coefficient of expansion is 0.00128.

A point of interest is that the liquid densities of the difluoroarsines are considerably higher than those of the corresponding dichloroarsines, a fact which possibly indicates association in the liquid phase. It will be shown later that other considerations point to the same conclusion.

Vapour density. This was the most difficult physical property to determine. The measurements obviously could not be conducted in glass. The method adopted involved the use of an all-platinum vessel of nearly 300 ml. capacity,

which had been employed for the determination of the vapour density of hydrogen fluoride (Thorpe, *J.*, 1889, **55**, 163). A suitable quantity of substance was distilled into the evacuated bulb and the increase in weight noted. One of the platinum cocks was connected by a short piece of thick rubber tubing to a U-tube constructed of 1-mm. capillary tubing containing a quantity of mercury. The limb of the U-tube connected to the vapour-density bulb was about 10 cm. long. The other limb was much longer and was connected to an evacuating pump. The short limb was provided with a small bulb near the base to act as a mercury reservoir. The small space above the mercury in the short limb could be separately evacuated. The platinum bulb and the base of the U-tube, including the whole of the short limb, were immersed in a large water-bath which was kept at boiling temperature. Both sides of the U-tube having been evacuated, the platinum cock connecting it to the bulb was opened. By the admission of a regulated quantity of air into the tubing sealed on to the long limb, the pressures on each side of the U-tube were approximately equalised. In less than 2 minutes equilibrium was established. The pressure in the bulb was determined immediately by measuring the pressure the other side of the U-tube on a manometer and correcting for the small difference in mercury levels in the two limbs of the U-tube, determined by the help of a glass scale fixed to the back of the U-tube. To minimise error due to difference in surface tension in the two limbs of the capillary U-tube, both sides of the tube were re-evacuated, and any difference in the levels of the mercury noted. The volume of the bulb and that of the short length of capillary tubing included in the system were accurately known. The vapour density at the boiling point of water could therefore be calculated, and from this the molecular weight (Calc. for CH_3AsF_2 : 127.94; for $\text{C}_2\text{H}_5\text{AsF}_2$: 141.97).

	Experimental data for methyl difluoroarsine.			Experimental data for ethyl difluoroarsine.		
Temp.	100.5°	100.3°	100.3°	99.5°	99.7°	99.6°
Pressure, mm.	420	369	308	428	320	253
Mol. wt.	175	172	167	170	162	159

These experimental data show that there is a certain amount of association in the vapour phase at 100°, especially with the methyl compound.

Latent heat of vaporisation. The latent heat of vaporisation ($L_{b,p.}$) has been calculated for each compound from the vapour pressure equation. For the methyl compound, $L = 8480$ cal./g.-mol. or 66.3 cal./g., and for the ethyl compound, 8110 cal./g.-mol. or 57.1 cal./g. The fact that L per g.-mol. is greater in the case of the methyl compound may be explained by a higher degree of association in the liquid phase. From these values for L , the values of Trouton's constant have been calculated as 24.3 and 22.1, respectively. The value for the ethyl compound is only slightly above the mean figure for unassociated compounds, but that for the methyl compound is well above and gives strong indication of association.

Chemical Properties of the Alkyl difluoroarsines.—In most of their reactions the difluoro- resemble the dichloro-arsines. For instance, with water or aqueous alkali the corresponding alkylarsine oxide is formed. The difluoroarsines are readily oxidised. Concentrated nitric acid reacts vigorously in the cold with evolution of oxides of nitrogen. Oxidation also occurs, but less violently, with bleaching powder, bromine water, and hydrogen peroxide. Oxidation will take place with iodine solution in the presence of alkali. The primary product of oxidation is the corresponding alkylarsonic acid, $\text{AsRO}(\text{OH})_2$, or one of its salts.

One point of difference between the difluoro- and the dichloro-arsines is their behaviour towards concentrated aqueous solutions of the respective hydrogen halides. The dichloroarsines are not appreciably hydrolysed by hydrochloric acid solutions of moderate concentration: in fact, if either of these arsines is hydrolysed by the minimum quantity of water, the original dichloroarsine can be reprecipitated from solution by addition of the concentrated acid. But the difluoroarsines, once hydrolysed, cannot be reprecipitated by the addition of 40% hydrofluoric acid, although the resulting solution smells strongly of the difluoroarsine. This may be due partly to the associated difluoroarsines having a higher solubility in water, and partly to the fact that hydrofluoric is a much weaker acid than hydrochloric. Thus the difluoroarsines cannot be prepared by the action of hydrofluoric acid on the alkylarsine oxides, in accordance with the method employed for the production of the dichloroarsines; they can, however, be prepared by distilling anhydrous AsMeO or AsEtO with a mixture of concentrated sulphuric acid and calcium fluoride.

The difluoroarsines etch glass, producing silicon tetrafluoride. When the compounds are pure and dry the attack is very slow. Pyrex is less affected than soda glass. They do not react with such metals as copper and lead in the cold.

Phenyl difluoroarsine.—Pure phenyldichloroarsine was heated in a distilling flask with a large excess of anhydrous ammonium fluoride for 2 hours at 100° with exclusion of moisture. Subsequently the pressure was reduced to about 12 mm., and the product distilled off through a short air condenser and twice refractionated. At 48 mm. pressure it distilled constantly at 110°. The final product was a white crystalline solid with a waxy appearance (m. p. 42°). It fumed in moist air, possessed an irritating smell resembling that of the initial chlorine compound, and was very deliquescent. It etched glass slightly.

A little of the solid was hydrolysed with water, and the hydrolysis products shown to contain fluoride but no chloride ions. One of the products was a white solid insoluble in water, but soluble in sodium hydroxide solution and reprecipitated by dilute acids; it was identified as phenylarsine oxide by a mixed m. p. determination with authentic oxide produced by hydrolysis of the dichloroarsine. This confirms that the new compound is the anticipated phenyl difluoroarsine, AsPhF_2 . As a quantitative check, some of the solid was crushed and transferred to a weighing bottle as quickly as possible. Small quantities were accurately weighed out and treated with a large volume of water. A known volume of standardised sodium hydroxide solution was added to each portion. As soon as hydrolysis was completed, the amount of hydrogen fluoride liberated was determined by titrating the excess of alkali with hydrochloric acid. The trivalent arsenic was subsequently titrated with iodine as in the analysis of the alkyl difluoroarsines. In this case, the presence of a small amount of benzene was necessary to bring the water-insoluble arsine into solution. The end-point, in consequence, was rather more difficult to ascertain with accuracy (Found: As, 38.79, 39.02; F, 19.94, 19.68. $\text{C}_6\text{H}_5\text{AsF}_2$ requires As, 39.43; F, 20.00%).

2-Chlorovinyl difluoroarsine.—2-Chlorovinyl dichloroarsine similarly reacted with anhydrous ammonium fluoride below 80°, but it was best to heat the reagents in a Kon fractionating flask at 100° under rigid exclusion of moisture for about 1½ hours, using excess of the fluoride. The product could be subsequently distilled off in good yield from a water-bath at a pressure of 75 mm. or lower. If, instead of reducing the pressure, the temperature was raised, decomposition set in just above 140° with production of dense white fumes. The product, on refractionation at a pressure of 14.5 mm., boiled steadily at 43.5°. It was a colourless liquid considerably more volatile than the original arsine. It does not possess the geranium-like odour of the chlorovinyl dichloroarsine, but has a highly irritating smell resembling that of the alkyl difluoroarsines. The products of hydrolysis, however, smell persistently of geraniums. The behaviour towards glass is similar to that of the alkyl difluoroarsines.

The solution formed by hydrolysis of some of the substance was neutralised with dilute sodium hydroxide and rendered very faintly acid with acetic acid. On addition of calcium chloride solution, calcium fluoride was precipitated.

No precipitate was formed when the dichloroarsine was similarly treated. Again, on hydrolysing the new compound with dilute nitric acid and adding silver nitrate solution, no trace of silver chloride was precipitated, in contrast to the results of applying this test to the dichloroarsine. This indicated that both of the original hydrolysable chlorine atoms attached to the arsenic atom had been replaced by fluorine atoms. When 2-chlorovinyl-dichloroarsine is treated with aqueous alkali of sufficient concentration, acetylene is quantitatively evolved. A similar evolution took place when the fluorinated compound was shaken with potassium hydroxide solution, thus confirming the existence of the $\cdot\text{CH}:\text{CH}\cdot$ grouping. After acidification of the resulting solution with nitric acid, the production of a copious precipitate with silver nitrate solution demonstrated the presence of chloride ions liberated by the action of the alkali on the chlorovinyl group. The existence of the chlorovinyl group was thus established. This new substance is therefore 2-chlorovinyl-difluoroarsine.

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[Received, February 28th, 1946.]
