Organometallic and Organometalloidal Compounds. Part VIII. Properties of Trifluoromethyl-arsenic Acids and of Other Fluorine-containing Acids.*

By H. J. Emeléus, R. N. Haszeldine, and Ram Chand Paul.

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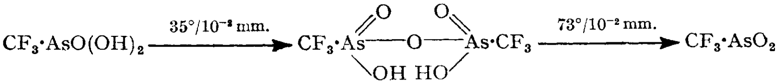
Trifluoromethylarsonic acid, readily obtained by oxidative hydrolysis of di-iodo(trifluoromethyl)arsine, is readily converted into the pyro-acid, and into the anhydride $CF_3\cdot AsO_2$. Trifluoromethylarsonic acid and bistrifluoromethylarsinic acid are almost completely ionised in aqueous solution, and are thus much stronger acids than methylarsonic acid or cacodylic acid. The order of decreasing strength of a series of acids in anhydrous acetic acid is $H_2SO_4 > HCl > (CF_3)_2AsO\cdot OH > CF_3\cdot AsO(OH)_2 \gg CF_3\cdot CO_2H$, HNO_3, $C_3F_7\cdot CO_2H$. Trifluoroacetic acid is slightly stronger than heptafluorobutyric acid.

The preparation of bistrifluoromethylarsinic acid $(CF_3)_2AsO\cdot OH$ by oxidative hydrolysis of iodobistrifluoromethylarsine was described in Part VI (Emeléus, Haszeldine, and Walaschewski, *J.*, **1953**, 1552), and this acid was shown to be much stronger than the unsubstituted cacodylic acid. In the present investigation trifluoromethylarsonic acid $CF_3\cdot AsO(OH)_2$ has been prepared, and its conductivity compared with that of bistrifluoromethylarsinic acid in water, and with mineral acids, the fluoroarsinic acid, and trifluoroacetic and heptafluorobutyric acids in acetic acid solution.

Di-iodo(trifluoromethyl)arsine is stable to water, but when treated with aqueous hydrogen peroxide undergoes exothermic oxidative hydrolysis to iodine and trifluoromethylarsonic acid :

$$CF_3I \xrightarrow{As} CF_3\cdot AsI_2 \xrightarrow[-H_2O]{H_2O_2} CF_3\cdot AsO(OH)_2$$

This is a stable white solid which resembles arsenic acid in that it undergoes progressive dehydration *in vacuo* forming first a pyro-acid and then an anhydride :



The ortho-acid is characterised by its infra-red spectrum (Table 1) which reveals the As·OH group, and by its mono- and di-silver salts. The monosilver salt, shown to contain the As·OH group by its infra-red spectrum (Table 1), is readily soluble in water; the disilver salt shows no As·OH group vibrations in the infra-red (Table 1), and has a much lower solubility.

Table 1. *Infra-red spectra* (in μμ).

Compound	C.S. No.*	As·O–H	C–F	As=O	CF_3 deformation
$CF_3\cdot AsO(OH)_2$	97	4·3	8·67	12·33	13·50
$(CF_3)_2AsO\cdot OH$	34	4·3	8·44	12·27	13·54
$CF_3\cdot AsO(OH)(OAg)$	94	4·3	8·69	12·17	13·67
$CF_3\cdot AsO(OAg)_2$	95	Absent	8·53 8·75	12·05	13·41
$(CF_3)_2AsO(OAg)$	35	Absent	8·77	12·13(?)	13·56
$[CF_3\cdot AsO(OH)]_2O$	92	4·35	8·42 8·70	12·35	13·40
$CF_3\cdot AsO_2$	96	Absent	8·83	12·25	13·64

* Spectra thus marked have been deposited with the Society. Photocopies can be obtained (price 3*s*. 0*d*. per copy per spectrum, post free) on application to the General Secretary stating the C.S. No.

The pyro-acid, which shows the As·O–H vibration in the infra-red (Table 1), reverts to the ortho-form in water, and attempts to prepare its silver salt were unsuccessful; monosilver trifluoromethylarsonate was not converted into the disilver salt of the pyro-acid when heated *in vacuo*.

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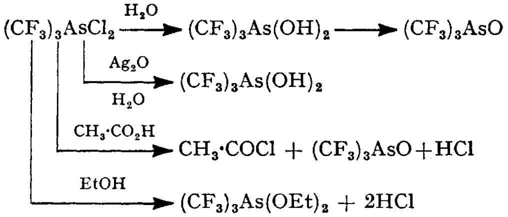
* Part VII, Bennett, Emeléus, and Haszeldine, *J.*, **1953**, 1565.

The anhydride, $CF_3·AsO_2$, shows no As·O–H absorption in the infra-red (Table 1), and is immediately converted into the ortho-acid when dissolved in water. Bistrifluoromethylarsinic acid does not form an anhydride quantitatively when heated *in vacuo*, and intramolecular dehydration clearly occurs more readily than intermolecular dehydration in these arsenic acids. Methylarsonic acid forms a pyro-acid, but further dehydration to the anhydride has not been reported.

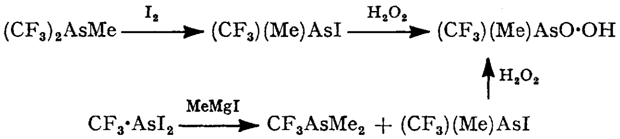
Attempts to prepare tristrifluoromethylarsine oxide, the anhydride of the hypothetical acid $(CF_3)_3As(OH)_2$, the acid itself, or its ethyl ester, by the following reactions were unsuccessful:



$$(CF_3)_3AsCl_2 \xrightarrow{H_2O} (CF_3)_3As(OH)_2 \longrightarrow (CF_3)_3AsO$$
$$(CF_3)_3AsCl_2 \xrightarrow[H_2O]{Ag_2O} (CF_3)_3As(OH)_2$$
$$(CF_3)_3AsCl_2 \xrightarrow{CH_3·CO_2H} CH_3·COCl + (CF_3)_3AsO + HCl$$
$$(CF_3)_3AsCl_2 \xrightarrow{EtOH} (CF_3)_3As(OEt)_2 + 2HCl$$

The reaction with water gave tristrifluoromethylarsine (mainly) and bistrifluoromethylarsinic acid; with silver oxide, chlorobistrifluoromethylarsine, carbon dioxide, fluoride, and bistrifluoromethylarsinic acid were obtained, *i.e.*, one trifluoromethyl group was broken down to carbonate and fluoride. Acetic acid gave mainly chlorobistrifluoromethylarsine and chlorotrifluoromethane, which are the usual thermal breakdown products of tristrifluoromethylarsenic dichloride. Ethanol converted the last compound into tristrifluoromethylarsine quantitatively.

Two reactions were studied in unsuccessful attempts to prepare methyltrifluoromethylarsinic acid, required for comparison with bistrifluoromethylarsinic acid:



$$(CF_3)_2AsMe \xrightarrow{I_2} (CF_3)(Me)AsI \xrightarrow{H_2O_2} (CF_3)(Me)AsO·OH$$
$$CF_3·AsI_2 \xrightarrow{MeMgI} CF_3AsMe_2 + (CF_3)(Me)AsI \xrightarrow{H_2O_2} (CF_3)(Me)AsO·OH$$

During the preparation of methylbistrifluoromethylarsine from tristrifluoromethylarsine by the exchange reaction with methyl iodide described in Part VI (*loc. cit.*), it was noted that the last two compounds appear to form a 1 : 1 azeotrope; this is probably a weakly-bonded molecular compound, which is the nearest approach to salt formation that has yet been observed with tristrifluoromethylarsine (see *J.*, 1952, 2552; 1953, 1552). The reaction of methylbistrifluoromethylarsine with iodine yielded only methyl iodide, trifluoroiodomethane, and complex products.

The replacement of only one iodine atom in di-iodo(trifluoromethyl)arsine by methyl could not be achieved. Dimethyltrifluoromethylarsine was isolated, however, and thus completes the series $(CF_3)_3As$ (b. p. 33°), $(CF_3)_2AsMe$ (b. p. 52°), $CF_3·AsMe_2$ (b. p. 58°), and $AsMe_3$ (b. p. 49·5°). The highest boiling point is reached when only a few fluorine atoms are present in the molecule, an effect often noted with other fluorine compounds.

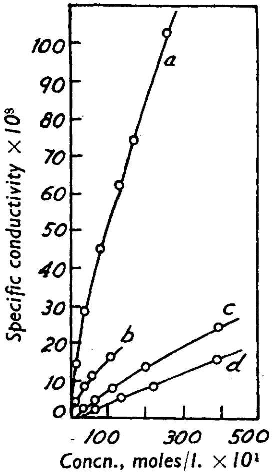
Tristrifluoromethylarsine reacts rapidly with aqueous sodium hydroxide (Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2552), methylbistrifluoromethylarsine reacts much more slowly (Part VI, *loc. cit.*), and trimethylarsine is stable. Dimethyltrifluoromethylarsine has now been found to fit into this sequence; fluoroform is produced quantitatively (*i.e.*, without liberation of fluoride), but extremely slowly, even when the arsine is heated with strong aqueous base for several days.

Trifluoromethylarsonic acid and bistrifluoromethylarsinic acid are almost completely ionised in water (Table 2), and are thus much stronger acids than methylarsonic acid ($K_1 = 2·46 \times 10^{-4}$, $K_2 = 5·69 \times 10^{-9}$; Backer and Bolt, *Rec. Trav. chim.*, 1935, **54**, 186), phenylarsonic acid ($K_1 = 3·4 \times 10^{-4}$; $K_2 = 3·3 \times 10^{-9}$; Pressman and Brown, *J. Amer. Chem. Soc.*, 1943, **65**, 540), or arsenic acid [$K_1 = 5 \times 10^{-3}$, $K_2 = 4 \times 10^{-5}$, $K_3 = 6 \times 10^{-10}$ (20°); Rosenheim and Antelmann, *Z. anorg. Chem.*, 1930, **187**, 385; **193**, 73. Washburn and

Strachan (*J. Amer. Chem. Soc.*, 1913, **35**, 681) report $4{\cdot}3 \times 10^{-3}$ for K_1 at 25°]. Cacodylic acid is amphoteric ($K_a = 7{\cdot}5 \times 10^{-7}$, $K_b = 5{\cdot}6 \times 10^{-13}$; Fraenkel, *Z. physikal. Chem.*, 1907, **60**, 202; Holmberg, *ibid.*, 1910, **70**, 153) and is not much stronger than carbonic acid ($K_1 = 3{\cdot}2 \times 10^{-7}$) or hydrogen sulphide ($K_1 = 1{\cdot}3 \times 10^{-7}$).

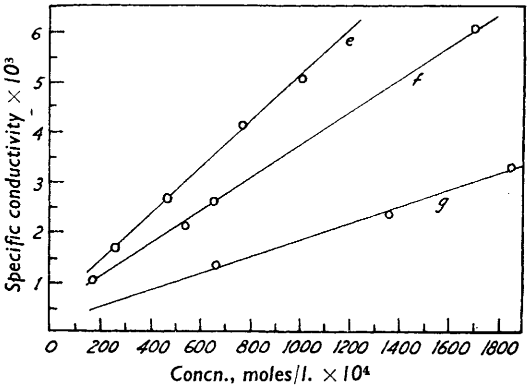
Equivalent conductivities of the acids $CF_3{\cdot}AsO(OH)_2$ and $(CF_3)_2AsO{\cdot}OH$ at infinite dilution have been extrapolated from the plot of the λ–$\sqrt{c}$ data summarised in Tables 3 and 4; the values are 398·0 and 399·5, respectively. The trifluoromethylarsonic acid behaves as a monobasic acid, since, for a dibasic acid with both hydrogen atoms ionised, a much higher value for the equivalent conductivity would be expected. At dilutions greater than 0·001M, however, the experimental points on the graph of the data in Table 3 lie above the straight line drawn through the points at higher concentrations. This fact has been repeatedly verified and probably represents a slight ionisation of the second hydrogen atom at these high dilutions. By contrast, methylarsonic acid is dibasic (see above). The degree of ionisation (α) of trifluoromethylarsonic and bistrifluoromethylarsinic acids in aqueous solution as a function of concentration is shown in Table 2.

FIG. 1. *Conductivities in acetic acid.*



(*a*) H_2SO_4. (*c*) $(CF_3)_2AsO{\cdot}OH$
(*b*) HCl (*d*) $CF_3{\cdot}AsO(OH)_2$

FIG. 2. *Conductivities in acetic acid.*



(*e*) $CF_3{\cdot}CO_2H$. (*f*) HNO_3. (*g*) $C_3F_7{\cdot}CO_2H$.

TABLE 2.

		$CF_3{\cdot}AsO(OH)_2$			$(CF_3)_2AsO{\cdot}OH$		
c	$\sqrt{c}$	λ_c	λ_x	α	λ_c	λ_x	α
0·05	0·2236	328·4	365·9	0·897	294·0	369·3	0·796
0·01	0·1000	366·8	383·2	0·957	352·8	385·0	0·916
0·002	0·0447	384·0	391·3	0·981	379·0	392·8	0·964
0·001	0·0316	388·2	393·2	0·987	384·9	394·8	0·975

(See p. 885 for meaning of *c*, λ_c, and λ_x.)

Since these trifluoromethyl acids are highly ionised, measurements in aqueous solution are not suitable for comparison of their relative strengths or for comparison with other acids which are strong in aqueous solution. Measurements on nitric, hydrochloric, hydrobromic, perchloric, and sulphuric acids in anhydrous acetic acid, made by Kolthoff and Willman (*J. Amer. Chem. Soc.*, 1934, **56**, 1007) and Hlasko and Michalski (*Roczn. Chem.*, 1938, **18**, 220), show that in this solvent the relative strengths of the acids are well differentiated and may be placed in the order $HNO_3 < HCl < H_2SO_4 < HBr < HClO_4$. The conductivities of the trifluoromethyl arsenic acids and of trifluoroacetic and heptafluorobutyric acids have now been measured in anhydrous acetic acid to enable a general comparison of acid strength to be made. The results (Table 5) are best represented graphically as in the Figures, where recorded data on sulphuric, hydrochloric, and nitric acid (Kolthoff and Willman, *loc. cit.*) are also shown. The conductivities are much lower in acetic acid (dielectric constant 6 at 25°) than in aqueous solution. It is seen that bistrifluoromethylarsinic acid is stronger than trifluoromethylarsonic acid in anhydrous acetic acid, although it is slightly less ionised in aqueous solution. The increase in acidity can be attributed to the presence of two electron-attracting trifluoromethyl groups [cf. C_3F_7·CHMe·OH, $K = 4 \times 10^{-12}$; $(C_3F_7)_2$CH·OH, $K = 30 \times 10^{-12}$; Haszeldine, *J.*, 1953, 1757].

Swarts (*Bull. Acad. roy. Belg.*, 1922, **8**, 343) showed that trifluoroacetic acid in aqueous solution was almost completely ionised, and this acid has often been loosely called as strong as hydrochloric acid. The Figures show that the fluoro-carboxylic acids are relatively weak in acetic acid, and are comparable only with nitric acid. Trifluoroacetic acid is slightly stronger than heptafluorobutyric acid, and a reason for this has been suggested (*J.*, 1953, 1758). The order of acid strength in anhydrous acetic acid is thus $H_2SO_4 > HCl > (CF_3)_2AsO{\cdot}OH > CF_3{\cdot}AsO(OH)_2 \gg CF_3{\cdot}CO_2H, HNO_3, C_3F_7{\cdot}CO_2H$. It is thus apparent that when a polyfluoroalkyl group such as trifluoromethyl is attached to carbon, as in a carboxylic acid, the acid is much weaker than when the group is attached to an element such as arsenic. It has similarly been shown that in aqueous solution trifluoromethylphosphonic acid is (apart from pyrophosphoric acid) the strongest known acid of phosphorus ($K_1 = 6{\cdot}8 \times 10^{-2}$, $K_2 = 1{\cdot}2 \times 10^{-4}$; Bennett, Emeléus, and Haszeldine, Amer. Chem. Soc. Meeting, Chicago, Sept. 1953).

EXPERIMENTAL

Trifluoromethylarsonic Acid.—Di-iodotrifluoromethylarsine (4·0 g.; Part VI, *loc. cit.*) was condensed into a previously evacuated tube which contained unstabilised hydrogen peroxide (100-vol.; 3 ml.) and water (5 ml.). An exothermic reaction occurred at room temperature, and the tube was cooled intermittently in ice. The iodine was filtered off after 20 min., and the solution was evaporated *in vacuo* over phosphoric anhydride (12 hr.). Transparent crystals corresponding to a hydrate containing 7—8 mols. of water first separated, and on further evaporation changed to a white powder (1·85 g., 96%). The solid gave no test for iodide or iodate. For analysis the *trifluoromethylarsonic acid* [Found: CF_3(as CHF_3), 37·2; As, 40·1. $CH_2O_3F_3As$ requires CF_3, 35·6; As, 38·6%] was dried for 4 hr. at 10^{-2} mm., then a sample (0·1470 g.) was heated at 80° for 24 hr. with 15% aqueous sodium hydroxide (15 ml.); the fluoroform evolved was measured, and arsenic was determined in the residual solution by precipitation of silver arsenate and volumetric estimation of the silver by Pearce's method as improved by Waddell (*Ind. Eng. Chem.*, 1919, **11**, 939). The discrepancy in the analytical data is attributed to partial pyro-acid formation (see below).

Trifluoromethylarsonic acid (0·1021 g.) was dissolved in water (55·2 ml.) to give an approx. 0·01M-solution, which had pH 2·10. Titration of this solution (10 ml.) with 0·1N-sodium hydroxide gave a first point of inflection at pH 3·77, from which the equivalent weight of the acid is 93·3 [CF_3·AsO(OH)(ONa) requires equiv., 96·95]. Rapid titration gave a second point of inflection at pH 8·2; when the solution was left at this pH, decomposition occurred, with evolution of fluoroform, and the pH decreased.

A second sample of the acid, stored in a bottle for 3 months, had an equivalent weight of 96·8, indicating conversion of pyro- into ortho-acid.

Silver Salts.—Trifluoromethylarsonic acid (2·0 g.), dissolved in water (10 ml.), was treated with alkali-free silver oxide (1·3 g., 10% excess for the mono-silver salt) at 60°. The solution was filtered and evaporated *in vacuo* over phosphoric anhydride to give a pale brown first crop of crystals (see below) followed by a white main crop of the *monosilver* salt (1·3 g., 40%) [Found: CF_3(as CHF_3), 22·6; As, 24·6; Ag, 35·7. CHO_3F_3AsAg requires CF_3, 22·9; As, 24·9; Ag, 35·9%].

The first crop of solid was combined with a further quantity of the monosilver salt (1·5 g.) obtained from the mother-liquor, and dissolved in water (20 ml.). Treatment with an excess of silver oxide (1·0 g.) at 60° for 15 min. gave, by filtration and evaporation *in vacuo*, the *disilver* salt (0·5 g., 30%) which was recrystallised from water [Found: CF_3(as CHF_3), 16·7; As, 18·5; Ag, 52·7. $CO_3F_3AsAg_2$ requires CF_3, 16·9; As, 18·4; Ag, 52·9%].

Pyrotrifluoromethylarsonic Acid.—A sample of trifluoromethylarsonic acid (1·00 g.), which had been partly converted into the pyro-acid by drying *in vacuo* over phosphoric anhydride for

4 hr., was heated at 33° for 12 hr. *in vacuo*. There was no further loss in weight after a further 4 hr.' heating under the same conditions. The loss in weight (0·011 g.) showed that the starting product contained 23% of ortho- and 77% of pyro-acid. The *trifluoromethylpyroarsonic acid* (Found: CF_3, 37·2; As, 40·9. $C_2H_2O_5F_3As_2$ requires CF_3, 37·3; As, 40·6%) was titrated potentiometrically with 0·1N-sodium hydroxide (Found: equiv., 92·75. $C_2H_2O_5F_3As_2$ requires equiv., 92·5), thus showing complete conversion of the pyro- into the ortho-acid in water.

The pyro-acid (0·4 g.) was dissolved in water (10 ml.) and heated with silver oxide (0·27 g.) for 15 min. at 50° in an attempt to prepare a silver salt of the pyro-acid. The middle crop of crystals was shown by analysis and infra-red spectroscopic examination to be the monosilver salt of trifluoromethyl(ortho)arsonic acid (Found: CF_3, 23·0; As, 24·4; Ag, 35·8. Calc. for CHO_3F_3AsAg: CF_3, 22·9; As, 24·9; Ag, 35·9%). A sample of the monosilver salt was unchanged in weight, and its infra-red spectrum was unaltered after 48 hr.' heating at 100°/10^{-2} mm.

Trifluoromethylarsonic Anhydride.—The pyro-acid (0·5100 g.), heated at 56° under 10^{-2} mm. for 12 hr., lost 0·0130 g., and there was no further loss in weight after another 6 hr. at this temperature. After the acid had been heated at 73° for 48 hr. the total loss in weight was 0·0253 g. The *trifluoromethylarsonic anhydride* (Found: CF_3, 40·2; As, 42·8. CO_2F_3As requires CF_3, 39·2; As, 42·6%) would theoretically be formed by loss in weight of 0·0250 g. Titration with carbonate-free aqueous sodium hydroxide gave equiv., 88·06 (CO_2F_3As requires equiv., 87·95).

Conductivity Measurements.—Bistrifluoromethylarsinic acid was prepared from iodobistrifluoromethylarsine (*J.*, 1953, 1522). Trifluoroacetic and heptafluorobutyric acid were freshly distilled (b. p. 72·0° and 121°, respectively). "AnalaR" acetic acid, further purified by Kolthoff and Willman's method (*loc. cit.*), had m. p. 16·5° and specific conductivity 1·5—1·8 × 10^{-8}. Haszeldine and Woolf's apparatus (*Chem. and Ind.*, 1950, 544) was used to measure conductivity, with cells with constants 13·29 (*A*), 4·359 (*B*), and 0·05338 (*C*). Auxiliary resistances were used in parallel when dilute solutions were being measured. Solutions were prepared by weight and subsequent dilutions were by weight. All measurements were at 25° ± 0·02°.

The results are given in Tables 3 and 4, where c = concentration in moles/l., κ = specific conductivity, λ_c = molecular conductivity, $\lambda_{corr.}$ = corrected molecular conductivity, calculated from the equation $\lambda_c = \lambda_{corr.} - (A + B\lambda_{corr.})\sqrt{c}$ with $A = 60{\cdot}21$, $B = 0{\cdot}2289$.

TABLE 3. $CF_3{\cdot}AsO(OH)_2$.

10^4c	$10^2\sqrt{c}$	$10^4\kappa$	λ_c	$\lambda_{corr.}$	Cell	10^4c	$10^2\sqrt{c}$	$10^4\kappa$	λ_c	$\lambda_{corr.}$	Cell
500·0	22·36	164·2	328·4	360·3	*A*	25·00	5·000	9·583	383·3	390·7	*B*
250·0	15·81	87·06	348·2	371·2	*A*	20·00	4·472	7·693	384·6	391·3	*B*
125·0	11·18	45·24	362·2	378·6	*A*	12·50	3·535	4·827	386·2	391·3	*B*
100·0	10·00	36·87	368·7	383·5	*A*, *B*	10·00	3·162	3·864	386·4	391·1	*B*, *C*
62·27	7·905	23·15	371·6	383·2	*A*, *B*	5·00	2·236	2·002	397·4	400·7 *	*B*, *C*
50·00	7·071	18·89	377·8	388·4	*B*	2·50	1·581	1·007	402·8	405·2 *	*B*, *C*

* See text.

λ_∞ (graphical) = 398·0.

TABLE 4. $(CF_3)_2AsO{\cdot}OH$.

10^4c	$10^2\sqrt{c}$	$10^4\kappa$	λ_c	$\lambda_{corr.}$	Cell	10^4c	$10^2\sqrt{c}$	$10^4\kappa$	λ_c	$\lambda_{co.r.}$	Cell
500·0	22·36	146·8	293·6	323·6	*A*	20·00	4·472	7·63	381·5	388·2	*B*
250·0	15·81	80·93	323·7	345·7	*A*	10·00	3·162	3·83	386·5	391·3	*B*
123·9	11·13	42·99	347·0	362·9	*B*	5·00	2·236	1·946	389·4	392·7	*B*
62·50	7·905	22·63	362·1	373·7	*B*	2·50	1·581	0·9747	389·9	392·2	*B*
40·00	6·324	14·94	373·5	382·8	*B*						

λ_∞ (graphical) = 399·5.

In Table 2, $\alpha (= \lambda_c/\lambda_x)$ was calculated from the equation $\lambda_x = \lambda_\infty (A + B\lambda_\infty)\sqrt{c\lambda_c/\lambda_x}$. Provisional values of λ_x were obtained for different concentrations, the quantity λ_x under the square-root sign being replaced by λ_∞. The approximate results for λ_x were then used in the $\sqrt{c\lambda_c/\lambda_x}$ term and a more accurate value of λ_x computed; this was continued until λ_x remained constant, and α was then calculated. Molecular weights were used as equivalent weights.

The accuracy of these results is not high, since the resistances measured were low, particularly for the carboxylic acids.

Attempted Preparation of Tristrifluoromethylarsine Oxide.—Tristrifluoromethylarsenic dichloride (1·75 g.) (*J.*, 1953, 1552), sealed with water (5 ml.) and left overnight at room temperature, gave tristrifluoromethylarsine (1·15 g., 85%) (Found: *M*, 281. Calc. for C_3F_9As:

M, 282). The solution was freeze-dried to give bistrifluoromethylarsinic acid (0·15 g.) [Found : CF_3(as CHF_3), 59·2; As, 29·3. Calc. for $C_2HO_2F_6As$: CF_3, 55·3; As, 30·5%] containing at most only a trace of tristrifluoromethylarsine oxide (Calc. for C_3OF_9As : CF_3, 69·6; As, 25·1%).

Tristrifluoromethylarsenic dichloride (2·88 g.), sealed with ethanol (5 ml.) at room temperature for 48 hr., gave tristrifluoromethylarsine (2·25 g., 98%) (Found : *M*, 281), identified by means of its infra-red spectrum.

TABLE 5. *Conductivities in acetic acid.*

(Cell *C* with resistances in parallel.)

10^4c	$10^2\sqrt{c}$	$10^8\kappa$	$10^2\lambda_c$	10^4c	$10^2\sqrt{c}$	$10^8\kappa$	$10^2\lambda_c$
$CF_3\cdot AsO(OH)_2$				$(CF_3)_2AsO\cdot OH$			
386·6	19·66	15·35	0·397	389·6	19·73	23·87	0·613
214·8	14·66	7·97	0·409	203·5	14·27	13·13	0·657
133·4	11·55	6·06	0·457	107·5	10·37	7·34	0·683
52·1	7·22	2·80	0·537	64·5	8·03	4·52	0·701
				38·8	6·23	2·61	0·721
$CF_3\cdot CO_2H$				$C_3F_7\cdot CO_2H$			
1000	31·62	5·12	0·051	1849	42·99	3·30	0·018
762·6	27·62	4·08	0·054	1361	36·89	2·27	0·016
465·2	21·57	2·70	0·058	652·0	25·54	1·33	0·020
256·0	16·00	1·70	0·066				

Tristrifluoromethylarsenic dichloride (1·3 g.) and glacial acetic acid (0·5 ml.), kept at 20° for 72 hr., gave chlorobistrifluoromethylarsine (0·9 g., 98%) (Found : *M*, 243. Calc. for C_2ClF_6As : *M*, 248) and chlorotrifluoromethane (0·3 g., 80%) (Found : *M*, 105. Calc. for $CClF_3$: *M*, 104·5).

Tristrifluoromethylarsenic dichloride (2·3 g.), shaken with silver oxide (1·5 g.) and water (5 ml.) for 24 hr. at 20°, gave carbon dioxide (0·205 g.) (Found : *M*, 45. Calc. for CO_2 : *M*, 44), identified tensimetrically, and chlorobistrifluoromethylarsine (0·21 g., 31%) (Found : *M*, 248). The aqueous solution was filtered and freeze-dried to give bistrifluoromethylarsinic acid (1·25 g., 78%) [Found : CF_3(as CF_3H), 55·3; As, 30·25. Calc. for $C_2HO_2F_6As$: CF_3, 55·3; As, 30·5%]. Fluoride (*ca.* 0·05 g.) was detected in the aqueous phase.

Reaction of Di-iodotrifluoromethylarsine with Methylmagnesium Iodide.—The Grignard reagent, prepared from methyl iodide (2·0 g.), ether (20 ml.), and magnesium (0·90 g.), was filtered and added dropwise (30 min.) with stirring and cooling to di-iodotrifluoromethylarsine (5·3 g.) in ether (10 ml.). Benzene (20 ml.) was added and the ether was removed by use of a water-bath at 60°. The benzene solution was shaken three times with 5N-hydrochloric acid (20 ml.) and then added to hydrogen peroxide (5 ml., 30%) and water (20 ml.). Examination of the aqueous layer failed to reveal methyl(trifluoromethyl)arsinic acid. The ethereal solution obtained as above was treated with mercuric chloride. The precipitate was washed with water, dried between filter-papers, and heated *in vacuo* to give *dimethyltrifluoromethylarsine* (0·067 g.), b. p. 58° (isoteniscope) (Found : CF_3, 39·0%; *M*, 172. $C_3H_6F_3As$ requires CF_3, 39·7%; *M*, 174), shown to be free from trimethylarsine, methylbistrifluoromethylarsine, and tristrifluoromethylarsine by its infra-red spectrum (C.S. No. 93). The compound was analysed as follows : 0·0623 g., sealed with 15% aqueous sodium hydroxide (20 ml.) and kept at 80° for 5 days, gave unchanged dimethyltrifluoromethylarsine (0·024 g., 38·1%). The fluoroform evolved was weighed (0·149 g.).

Reaction of Tristrifluoromethylarsine with Methyl Iodide.—This reaction (*J.*, 1952, 1552), carried out on a 0·2 molar scale, gave methylbistrifluoromethylarsine, b. p. 53°, in 50% yield. Attempts to prepare methyliodotrifluoromethylarsine by reaction of iodine with methylbistrifluoromethylarsine were unsuccessful.

Tristrifluoromethylarsine appears to form an equimolar azeotrope with methyl iodide, b. p. *ca.* 25° [Found : *M*, 206, 219. Calc. for $(CF_3)_3As,CH_3I$: *M*, 212]. It separates into two layers when cooled.

Infra-red Spectra.—These were recorded by a Perkin-Elmer Model 21 Spectrophotometer with rock salt optics.

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UNIVERSITY CHEMICAL LABORATORY
CAMBRIDGE.

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