699. *Radical Exchange in Organometallic Compounds. Part I.* The Replacement of Methyl by Trifluoromethyl.*†

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Trifluoroiodomethane reacts with trimethyl-phosphine, -arsine, or -stibine at room temperature to give the quaternary tetramethyl iodide and dimethyltrifluoromethyl-phosphine, -arsine, or -stibine. By contrast, trimethylamine and trifluoroiodomethane give mainly fluoroform. Possible reaction schemes are considered.

Tristrifluoromethyl-phosphine, -arsine, and -stibine, prepared by direct reaction of trifluoroiodomethane with phosphorus, arsenic, or antimony, show properties markedly different from their trimethyl analogues. In particular they do not form addition compounds of the usual type and are readily hydrolysed by aqueous base to fluoroform.[1, 2] The compounds $CF_3{\cdot}M(CH_3)_2$ and $(CF_3)_2M{\cdot}CH_3$ ($M = P$, As, or Sb) have now been synthesised in order to study the properties of compounds intermediate between the two extremes $(CF_3)_3M$ and $(CH_3)_3M$.

A convenient route to the compounds $CF_3{\cdot}M(CH_3)_2$ has been found in the reaction of trifluoroiodomethane with trimethyl-phosphine, -arsine, or -stibine. Reaction occurs in the liquid phase at room temperature in absence of a solvent and is accelerated by heat. The products are $CF_3{\cdot}M(CH_3)_2$ (*ca.* 50%), $[(CH_3)_4M]^+I^-$ (*ca.* 50%), and a small amount of fluoroform (1—2% based on trifluoroiodomethane):

$$2(CH_3)_3M + CF_3I \longrightarrow CF_3{\cdot}M(CH_3)_2 + [(CH_3)_4M]^+I^-$$

The course of the reaction is readily followed because of precipitation of the quaternary iodide. An equilibrium exists at room temperature, and removal of the solid periodically is necessary to cause further deposition of solid and ultimately completion of reaction. There is no indication of replacement of more than one methyl group by trifluoromethyl at room temperature.

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* For earlier related work see Haszeldine, " Fluorocarbon Derivatives," R.I.C. Monograph 1956, No. 1.

† For a preliminary publication see *Angew. Chem.*, 1954, **66**, 696.

[1] Bennett, Emeléus, and Haszeldine, *J.*, 1954, 3896 *et seq.*

[2] Emeléus, Haszeldine, and Walaschewski, *J.*, 1953, 1552 *et seq.*; Dale, Moss, Emeléus, and Haszeldine, unpublished results.

The reaction of trifluoroiodomethane with trimethylamine at room temperature is markedly different. Fluoroform is produced in >70% yield, together with tetramethylammonium iodide and an unidentified solid, possibly $[NMe_3I]^+CF_3^-$; dimethyltrifluoromethylamine cannot be detected. This reaction in its early stages gives mainly tetramethylammonium iodide and a larger amount of the unknown solid without the formation of fluoroform, and the volatile products at this stage are only trifluoroiodomethane and trimethylamine.

The most plausible intermediate in these reactions is the quaternary compound of the type $[P(CH_3)_3\cdot CF_3]^+I^-$. This was synthesised by the direct combination of dimethyltrifluoromethylphosphine and methyl iodide (see below), and is stable at room temperature, which together with the fact that this iodide is not a product from the reaction of trimethylphosphine and trifluoroiodomethane, requires that the further step or steps in any reaction scheme postulated shall be such that the quaternary iodide is removed completely.

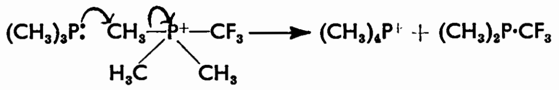
Several qualitative observations are relevant: (*a*) The compound $[P(CH_3)_3\cdot CF_3]^+I^-$ is obtained admixed with tetramethylphosphonium iodide when trifluoroiodomethane and trimethylphosphine react in carbon tetrachloride solution. This shows that the quaternary salt can be prepared by a reaction involving a solvent; that it does not react further is due to its insolubility in carbon tetrachloride. (*b*) The compound $[P(CH_3)_3\cdot CF_3]^+I^-$ is readily soluble in liquid trifluoroiodomethane at room temperature, and is recovered unchanged on evaporation of the solvent; in particular, neither tetramethylphosphonium iodide nor dimethyltrifluoromethylphosphine is produced. There is thus no direct reaction between the quaternary compound and trifluoroiodomethane. (*c*) Tetramethylphosphonium iodide is also partially soluble in liquid trifluoroiodomethane, but is recovered unchanged on evaporation. (*d*) The compound $[P(CH_3)_3\cdot CF_3]^+I^-$ is almost insoluble in trimethylphosphine and not even traces of tetramethylphosphonium iodide are formed even after prolonged contact, but in ethanol some tetramethylphosphonium iodide is formed.

It thus appears that a solvent effect plays an important part in the reaction; since both $[P(CH_3)_4]^+I^-$ and $[P(CH_3)_3\cdot CF_3]^+I^-$ are readily soluble in trifluoroiodomethane but only sparingly soluble in trimethylphosphine, trifluoroiodomethane is regarded as the " solvent " for the reaction. The ready solubility of the quaternary compounds explains why the exchange reaction goes to completion in trifluoroiodomethane but not in carbon tetrachloride. The formation of the compound $[P(CH_3)_3\cdot CF_3]^+I^-$ could thus be followed by one of two closely related reactions:

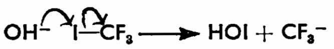
(1) Dissociation of the quaternary compound in trifluoroiodomethane to dimethyltrifluoromethylphosphine and methyl iodide, the latter then reacting with trimethylphosphine to give tetramethylphosphonium iodide:

$$[P(CH_3)_3\cdot CF_3]^+I^- \longrightarrow CF_3\cdot P(CH_3)_2 + CH_3I \xrightarrow{P(CH_3)_3} [(CH_3)_4P]^+I^-$$

(2) Nucleophilic attack of trimethylphosphine on a methyl group of the quaternary compound:



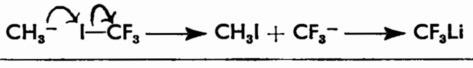
It was suggested earlier [3] that nucleophilic attack of hydroxide ion on trifluoroiodomethane to give fluoroform involves the relatively positive iodine atom rather than carbon:



$$OH^- \; I{-}CF_3 \longrightarrow HOI + CF_3^-$$

$$\text{Solvent} + CF_3^- \longrightarrow CHF_3$$

The formation of trifluoromethyl-lithium by reaction of methyl-lithium with trifluoroiodomethane [3] is similarly interpreted:



$$CH_3^- \; I{-}CF_3 \longrightarrow CH_3I + CF_3^- \longrightarrow CF_3Li$$

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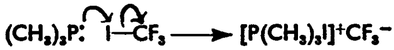
[3] Haszeldine, *J.*, 1952, 4259, and unpublished results.

The formation of the quaternary compound $[P(CH_3)_3{\cdot}CF_3]^+I^-$ can be visualised by a similar nucleophilic attack on iodine :



$$(CH_3)_3P{:}\ I{-}CF_3 \longrightarrow [P(CH_3)_3I]^+CF_3^-$$

followed by transformation of the product *via* a transient quinquecovalent state into $[P(CH_3)_3{\cdot}CF_3]^+I^-$. The small amount of fluoroform which is always isolated during the exchange reactions involving trimethyl-phosphine, -arsine, or -stibine, can thus be attributed to a side-reaction in which the trifluoromethyl anion derived from $[P(CH_3)_3I]^+CF_3^-$ attacks a neighbouring molecule RH to abstract hydrogen :

$$CF_3^- + R{-}H \longrightarrow CHF_3 + R^-$$

The low yield of fluoroform suggests that the change of $[P(CH_3)_3I]^+CF_3^-$ into $[P(CH_3)_3{\cdot}CF_3]^+I^-$ *via* the quinquecovalent state is rapid. Phosphorus, arsenic, and antimony can accommodate a fifth covalency and this permits the above change.

The situation is different for nitrogen, which cannot form more than four covalent bonds. It is suggested that the initial step in the reaction of trifluoroiodomethane with trimethylamine yields $[N(CH_3)_3I]^+CF_3^-$ by nucleophilic attack on iodine, but that this compound cannot rearrange to $[N(CH_3)_3{\cdot}CF_3]^+I^-$ *via* a quinquecovalent compound. The fluoroalkyl anion is thus able to abstract hydrogen from neighbouring molecules; fluoroform is therefore the major reaction product, and the exchange reaction to give dimethyltrifluoromethylamine does not occur.

Phosphine reacts with trifluoroiodomethane to yield trifluoromethylphosphine so a P–C bond is not essential for reaction; fluoroform is a major product, however, at the elevated temperatures necessary and is probably produced by attack of trifluoromethyl radicals on phosphine.

Dimethyltrifluoromethylphosphine has less co-ordinating power than trimethylphosphine. It does not react with carbon disulphide to form a red compound of the type given by trimethylphosphine and other phosphines,[4] and one trifluoromethyl group thus exerts a marked effect. Dimethyltrifluoromethylphosphine yields a white crystalline compound when shaken with a solution of silver iodide in aqueous potassium iodide at *ca.* 0°, but the solid dissociates so readily that it could not be obtained in a form suitable for analysis. It is probably $[AgI,CF_3{\cdot}P(CH_3)_2]_4$ by analogy with complexes [5] of the general type $[AgI{\leftarrow}PR_3]_4$. The corresponding trimethylphosphine–silver iodide complex is much more stable at room temperature, and the decrease in stability on replacement of a methyl by a trifluoromethyl group is attributed to the inductive effect of the CF_3 group which makes the unshared electron pair of the phosphorus atom less available for co-ordination. Studies on the relative co-ordinating powers of the compounds $P(CH_3)_3$, $CF_3{\cdot}P(CH_3)_2$, $(CF_3)_2P{\cdot}CH_3$, and $P(CF_3)_3$ with platinum chloride would be interesting, since there may be a gradual change in co-ordination from a single σ-bond in the trimethylphosphine complexes to complexes involving double bonds between ligand and metal as has been postulated [6] for the complexes of platinum with strongly electronegative ligands such as phosphorus trifluoride.

Tristrifluoromethylphosphine is hydrolysed instantly by aqueous base at room temperature, whereas hydrolysis of dimethyltrifluoromethylphosphine to fluoroform requires, for completion, prolonged contact with concentrated base at 100°.

Dimethyltrifluoromethylarsine failed to yield a silver iodide complex under any conditions tried. It gave fluoroform only slowly when treated with concentrated aqueous base at room temperature, whereas tristrifluoromethylarsine is hydrolysed quantitatively in a few minutes under comparable conditions. Dimethyltrifluoromethylstibine evolves the theoretical amount of fluoroform with cold aqueous base, though less rapidly than does tristrifluoromethylstibine. The ease of hydrolysis is $CF_3{\cdot}P(CH_3)_2 < CF_3{\cdot}As(CH_3)_2 < CF_3{\cdot}Sb(CH_3)_2$, the converse, as expected, of the ease of complex formation with silver iodide.

[4] Brown and Harris, *J. Amer. Chem. Soc.*, 1949, **71**, 2751; Davies and Walters, *J.*, 1935, 1786.

[5] Mann, Purdie, and Wells, *J.*, 1937, 1828.

[6] Chatt *et al.*, *Nature*, 1950, **165**, 637; *J.*, 1955, 4456.

The difficulty of separation by distillation of compounds of the $CF_3{\cdot}M(CH_3)_2$ type from trifluoroiodomethane is much greater than would be expected from the boiling-point differences, and this suggests the formation of weak molecular complexes of the type $[CF_3{\cdot}(CH_3)_2M^+-(ICF_3)^-]$ with the donated electron derived from the lone pair of electrons in M. Such complex formation has been shown to occur [7] between a polyfluoroiodoalkane and a neutral-molecule Lewis base such as an ether or an alcohol, and is of the donor–acceptor type with formation of a weak covalent bond.

Quaternary compounds $[CF_3{\cdot}M(CH_3)_3]^+I^-$ have been prepared by reaction of the compounds $CF_3{\cdot}M(CH_3)_2$ (M = P or As) with methyl iodide at room temperature in absence of a solvent. The ease of quaternary formation is, qualitatively, $(CH_3)_3P > CF_3{\cdot}P(CH_3)_2 > CF_3{\cdot}As(CH_3)_2$. The trifluoromethyl quaternary compounds are white crystalline solids which are readily soluble in water and sparingly soluble in ethanol. Both aqueous and ethanolic solutions precipitate silver iodide immediately on treatment with aqueous silver nitrate. The readiness with which the above quaternary compounds are formed can be attributed to the ease of heterolysis of the carbon–iodine bond in methyl iodide. As pointed out earlier, quaternary salt formation involving trifluoroiodomethane probably involves heterolysis of the carbon–iodine bond in a sense opposite to that in methyl iodide, and the quaternary compound reacts further in trifluoroiodomethane solution.

The preparation and properties of the compounds $(CF_3)_2M{\cdot}CH_3$ will be described in Part II of this series.

EXPERIMENTAL

Reactions were carried out in sealed Pyrex tubes with complete exclusion of moisture and air. Volatile products were manipulated in a vacuum-apparatus. Trifluoroiodomethane was prepared from silver trifluoroacetate. [8]

Fluorine was determined by titration of fluorosilicic acid with thorium nitrate, with sodium alizarinsulphonate as indicator. Arsenic, phosphorus, or antimony did not interfere if their salts present after sodium fusion of the compound and treatment with water were oxidised by hydrogen peroxide; fluorosilicic acid was then separated by steam-distillation.

Reaction of Trifluoroiodomethane with Trimethylphosphine.—In a typical small-scale experiment trimethylphosphine (1·00 g., 13 mmoles) was sealed in a 40-ml. Pyrex tube with trifluoroiodomethane (4·88 g., 25 mmoles). A white crystalline solid was rapidly formed below the surface of the liquid as soon as the temperature approached that of the room, and reaction was substantially complete within 30 min. The volatile products were removed after 17 hr. and fractionated *in vacuo*, to give dimethyltrifluoromethylphosphine (0·85 g., 50%; purified as described below), fluoroform (0·032 g., 2% based on trifluoroiodomethane), and trifluoroiodomethane (3·46 g., 71%). The residual solid was identified as tetramethylphosphonium iodide (1·46 g., 50%) by comparison of its infrared spectrum with that of a sample prepared from trimethylphosphine and methyl iodide; it also gave the mercuric iodide complex [9] $[(CH_3)_4P]I,2HgI_2$ as yellow prisms, m. p. 172° (from ethanol).

Trifluoroiodomethane reacts only slowly with trimethylphosphine in the vapour phase.

Purification and Properties of Dimethyltrifluoromethylphosphine.—Some difficulty was experienced in removing the last traces (2—3%) of trifluoroiodomethane from dimethyltrifluoromethylphosphine by distillation *in vacuo*, and the purity of the last compound is thus best assessed by means of its infrared spectrum. The following procedure was adopted to obtain a sample of analytical purity. Trifluoroiodomethane was allowed to react with an excess of trimethylphosphine (mole ratio 1 : 3), and the dimethyltrifluoromethylphosphine obtained by preliminary fractionation was condensed *in vacuo* on to a large excess of finely powdered silver iodide (10 g. per g. of phosphine). The volatile material which did not react with the silver iodide at room temperature was then removed and condensed on to a fresh portion of silver iodide. Successive treatments with silver iodide in this way separated most of the dimethyltrifluoromethylphosphine from the trifluoroiodomethane. The dimethyltrifluoromethylphosphine was recovered when its silver iodide complex was heated *in vacuo*. Traces of trimethylphosphine were removed from the dimethyltrifluoromethylphosphine by utilising the fact that the dissociation pressure of the dimethyltrifluoromethylphosphine silver iodide

[7] Haszeldine, *J.*, 1953, 2622.
[8] Haszeldine, *J.*, 1951, 584.
[9] Cahours and Hofmann, *Annalen*, 1857, **104**, 31.

complex is considerably greater at 20° (approx. 25 mm.) than that of the corresponding trimethylphosphine complex (approx. 2 mm.); the fluoroalkylphosphine can thus be removed preferentially from silver iodide.

Pure *dimethyltrifluoromethylphosphine* (Found: F, 43·5%; *M*, 130·5. $C_3H_6F_3P$ requires F, 43·8%; *M*, 130·0) is a colourless liquid whose vapour pressure over the range 18—47° is represented by the equation $\log_{10} p$ (mm.) $= 7{\cdot}630 - 1519/T$, whence the b. p. is 46·8°, the latent heat of vaporisation is 6950 cal./mole, and Trouton's constant is 21·7. The phosphine reacts with air to give a solid, presumably the oxide, but can be heated in absence of air up to 240° for 48 hr. without decomposition or disproportionation. It was decomposed by fusion with sodium for analysis.

Dimethyltrifluoromethylphosphine fails to react with carbon disulphide at room temperature (48 hr.) or at 100° (1 hr.), or when their ethanolic solutions are mixed at room temperature.

There was no visible reaction at room temperature when dimethyltrifluoromethylphosphine (0·18 g.) in anhydrous ether (3 ml.) was shaken in a sealed tube with a 20% solution of silver iodide in aqueous potassium iodide (3 ml.). White needles were formed at the interface of the liquid when the mixture was shaken and cooled to 0—5°, and redissolved on warming.

The solid was separated by filtration at low temperature, but decomposed rapidly during filtration and attempts to purify it failed. The reaction of liquid dimethyltrifluoromethylphosphine with solid silver iodide at room temperature or just below caused the silver iodide to become white in places. Vapour-pressure measurements carried out on a sample of this material prepared in a glass bulb attached to a spoon gauge gave a value of 25 mm. for the vapour pressure of the complex at 20°. It dissociated too rapidly to enable it to be manipulated for analysis.

Reaction of Trifluoroiodomethane with Trimethylarsine.—Into each of three Carius tubes (185 ml. capacity) were condensed trifluoroiodomethane (9·00 g., 46 mmoles) and trimethylarsine (4·33 g., 36 mmoles). The sealed tubes were kept at room temperature (24 hr.). White needles had been formed in the liquid phase after 1 hr., but the rate of formation of the solid was much less than that from the corresponding reaction with trimethylphosphine. The volatile products were combined and transferred to a 200 ml. stainless-steel autoclave and heated at 50—55° (78 hr.). Fractionation then gave trifluoroiodomethane (20·8 g., 106 mmoles), fluoroform (0·061 g., 0·6%), and crude dimethyltrifluoromethylarsine (7·8 g., 41%) contaminated by trifluoroiodomethane (2%). Further distillation through a packed column, followed by repeated distillation *in vacuo*, gave *dimethyltrifluoromethylarsine* (4·9 g., 26%) (Found: F, 32·1%; *M*, 173. $C_3H_6F_3As$ requires F, 32·7%; *M*, 174), shown by infrared spectroscopic examination to be free from trifluoroiodomethane. The vapour pressure of dimethyltrifluoromethylarsine is given by the equation $\log_{10} p$(mm.) $= 7{\cdot}3737 - 1487/T$, whence the b. p. is calculated as 58·0°, the latent heat of vaporisation is 6800 cal./mole, and Trouton's constant is 20·6. The solid formed during the reaction was shown to be tetramethylarsonium iodide (11·8 g., 42%) by comparison of its infrared spectrum with that of a specimen prepared by the direct reaction of trimethylarsine with methyl iodide.

Dimethyltrifluoromethylarsine failed to react with a solution of silver iodide in aqueous potassium iodide at 20° or at 0°. The trimethylarsine–silver iodide complex has a higher dissociation pressure at 20° (approx. 15 mm.) than the trimethylphosphine complex (approx. 2 mm.), and the arsenic complexes are clearly less stable than their phosphorus analogues.

Reaction of Trifluoroiodomethane with Trimethylstibine.—Trifluoroiodomethane (6·0 g., 31 mmoles) and trimethylstibine (5·0 g., 30 mmoles), sealed in a 300-ml. Pyrex tube, began to deposit needles after 1 hr. The rate of reaction was roughly comparable with that with trimethylarsine. The volatile products were removed after 40 days and fractionated *in vacuo*, to give trifluoroiodomethane (2·8 g.), fluoroform (0·02 g., 1%), and crude dimethyltrifluoromethylstibine (50%). The last fraction was redistilled through a packed column in nitrogen, to give *dimethyltrifluoromethylstibine* (1·36 g., 21%) (Found: F, 26·0%; *M*, 219. $C_3H_6F_3Sb$ requires F, 25·8%; *M*, 221) as a colourless liquid, spectroscopically free from trifluoroiodomethane. The solid (4·6 g., 50%) was identified spectroscopically as tetramethylstibonium iodide.

The vapour pressure of dimethyltrifluoromethylstibine at 16—86° is given by the equation $\log_{10} p$(mm.) $= 7{\cdot}4403 - 1636/T$, whence the b. p. is calculated as 85·8°, the latent heat of vaporisation is 7490 cal./mole, and Trouton's constant is 20·9.

Reaction of Trifluoroiodomethane with Trimethylamine.—Trifluoroiodomethane (6·62 g., 34 mmoles) and trimethylamine (3·96 g., 67 mmoles), sealed in a 400 ml. Pyrex tube, began to deposit a white solid as soon as the temperature reached that of the room. Distillation of the volatile products after 33 days gave trimethylamine (0·89 g., 23%), trifluoroiodomethane (0·97 g., 15%), and fluoroform (1·82 g., 77% based on trifluoroiodomethane). Spectroscopic examination of the volatile products failed to reveal dimethyltrifluoromethylamine. Infrared spectroscopic examination of the solid (6·9 g.) revealed the presence of tetramethylammonium iodide and an unidentified material containing carbon–fluorine bonds. Almost 80% of the trimethylamine and all the iodine originally present in the trifluoroiodomethane later converted into fluoroform had thus been converted into solid by the end of the reaction.

In a second experiment with trimethylamine (0·79 g.) and trifluoroiodomethane (1·70 g.) the solid (0·13 g.) which had been formed after 5 hr. contained tetramethylammonium iodide and a considerable amount of material shown by spectroscopic examination to contain C–F bonds. Less than 2% of fluoroform had been produced.

Reaction of Trifluoroiodomethane with Phosphine.—Phosphine was prepared in 97% yield by heating phosphorous acid under 40—50 cm. pressure of nitrogen in a flask connected to a trap cooled to −196°.

Trifluoroiodomethane (1·08 g., 5·5 mmoles) and phosphine (0·186 g., 5·5 mmoles), heated at 240° in a 40 ml. Pyrex tube for 4 hr., gave trifluoromethylphosphine (0·072 g., 13%), trifluoroiodomethane (0·284 g., 27%), fluoroform (0·303 g., 79%), hydrogen iodide (0·008 g.), phosphonium iodide (0·11 g.), and phosphorus tri-iodide.

Hydrolysis of Dimethyltrifluoromethyl-phosphine, -arsine, or -stibine.—The stabilities against hydrolysis were examined by shaking these compounds with 20% aqueous sodium hydroxide (5 ml.) in a 40 ml. Pyrex tube. The volatile products were then fractionated *in vacuo* to separate the unchanged phosphine, arsine, or stibine from the fluoroform produced. Fluoride was not liberated. The results are summarised in the annexed Table.

	Wt. (g.)	Temp.	Time (days)	$CF_3{\cdot}M(CH_3)_2$ unchanged (%)	CHF_3 (%)
$CF_3{\cdot}P(CH_3)_2$ …………………	0·292	20°	3	93·5	6·5
	0·254	100	6	9	91
$CF_3{\cdot}As(CH_3)_2$ …………………	0·220	20	3	91	9
$CF_3{\cdot}Sb(CH_3)_2$ …………………	0·160	20	3	0	100

Trimethyltrifluoromethylphosphonium Iodide.—(i) Methyl iodide (0·683 g., 4·8 mmoles) and dimethyltrifluoromethylphosphine (0·995 g., 7·6 mmoles) in a sealed tube began to deposit white needles after 30 min. After 24 days the volatile products were fractionated, giving methyl iodide (0·333 g., 48%), fluoroform (0·004 g., 0·7%), and dimethyltrifluoromethylphosphine (0·670 g., 67%). The solid was *trimethyltrifluoromethylphosphonium iodide* (0·68 g., 52% based on methyl iodide) (Found: C, 17·6; H, 3·3; I, 46·5. $C_4H_9F_3IP$ requires C, 17·6; H, 3·2; I, 46·7%). The solid does not melt below 300° in a sealed evacuated capillary tube. It is very soluble in water, soluble in ethanol and in trifluoroiodomethane, but insoluble in benzene, carbon tetrachloride, ether, dioxan, or chloroform.

(ii) In a second experiment, trifluoroiodomethane (0·25 g.) and trimethylphosphine (0·09 g.) were dissolved in anhydrous carbon tetrachloride (5 ml.). Reaction began as soon as the tube reached room temperature and a pasty mass was produced within 5 min. The solid produced (0·17 g.) was found spectroscopically to contain trimethyltrifluoromethylphosphonium iodide (32% yield) and tetramethylphosphonium iodide (26% yield).

(iii) Tetramethylphosphonium iodide was not produced and no reaction was detected when trimethyltrifluoromethylphosphonium iodide (0·06 g.) was dissolved in trifluoroiodomethane (2·33 g.) and kept at room temperature (14 days).

(iv) Trimethyltrifluoromethylphosphonium iodide (0·120 g., 0·4 mmole), trimethylphosphine (0·051 g., 0·7 mmole), and anhydrous ethanol (5 ml.), kept in a sealed tube at 20° (30 days), yielded a solid containing tetramethylphosphonium iodide (76% yield) and trimethyltrifluoromethylphosphonium iodide (34% yield).

(v) Trimethyltrifluoromethylphosphonium iodide (0·130 g., 0·6 mmole) did not dissolve appreciably in trimethylphosphine (0·184 g., 2·4 mmoles), or react with it during 3 days at 20°. Spectroscopic examination gave no evidence of tetramethylphosphonium iodide.

Trimethyltrifluoromethylarsonium Iodide.—Dimethyltrifluoromethylarsine (0·45 g., 2·6 mmoles) and methyl iodide (0·36 g., 2·5 mmoles) deposited a small amount of a white crystalline solid after 30 min. After 12 hr. at room temperature the amount of solid had only slightly increased. The tube was therefore heated at 85° (14 hr.) and the amount of solid appreciably increased. Infrared spectroscopy of the *trimethyltrifluoromethylarsonium iodide* (0·03 g., 4%) (Found: C, 15·5; H, 2·6. $C_4H_9F_3IAs$ requires C, 15·1; H, 2·9%) showed it to be free from tetramethylarsonium iodide. The solid is soluble in water and in ethanol but insoluble in ether and benzene.

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