Organometallic Compounds containing Fluorocarbon Radicals.

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THE rapid advance during the last twenty years in our knowledge of the chemistry of fluorocarbons has resulted in a situation which parallels that of classical organic chemistry towards the close of the last century. Fluorocarbon analogues of large numbers of aliphatic and alicyclic hydrocarbons have been prepared, together with many derivatives containing the familiar functional groups of organic chemistry. The comparative study of the two classes of compound has served to reveal similarities in physical properties and differences, which are often very great, in chemical behaviour. There was, however, until very recently, an outstanding gap in this rapidly developing subject. Practically nothing was known of the fluorocarbon analogues of organometallic and organometalloidal compounds. The field was attractive to us since it offered a possible route to the study of free fluorocarbon radicals. Moreover it was expected that, if compounds of this new type could be prepared, they would find applications in the synthesis of fluorocarbon derivatives. That an investigation of this sort should have been undertaken in a laboratory of inorganic chemistry can be justified by the fact that, as the subject has developed, the vacuum-techniques which are used for the quantitative manipulation of small amounts of volatile substances have proved singularly valuable. Indeed, many of the problems encountered could hardly have been approached in any other way. Before describing this work in detail I would like to express my indebtedness and thanks to all those who have collaborated in it, and to Dr. R. N. Haszeldine, who, in addition to participating in the experimental programme, has shared in its direction.

The obvious starting material for the preparation of organometallic compounds containing fluorocarbon radicals was trifluoroiodomethane, CF_3I, the analogue of methyl iodide. This was first prepared as a result of the study of the reactions of the halogen fluorides with the halogenomethanes, during which it was found that iodine pentafluoride reacted with carbon tetraiodide to form the desired compound. It also reacted with tetraiodoethylene to give pentafluoroiodoethane (Banks, Emeléus, Haszeldine, and Kerrigan, *J.*, 1948, 2188; Emeléus and Haszeldine, *J.*, 1949, 2948).

$$CI_4 \xrightarrow{IF_5} CF_3I \text{ (b. p. } -22{\cdot}5^\circ)$$

$$C_2I_4 \xrightarrow{IF_5} C_2F_5I \text{ (b. p. } 13^\circ) \xleftarrow{IF_5} C_2F_4I_2 \longleftarrow C_2F_4$$

Neither of these preparative methods was particularly convenient, however, and subsequent investigations have been greatly facilitated by the discovery of a general method for the preparation of fluoroalkyl iodides, depending on the reaction which occurs when the silver salt of a fully fluorinated aliphatic acid is heated with iodine (Haszeldine, *J.*, 1951, 584; 1952, 4259). The reaction shown below, for example, occurs at 150° and gives trifluoroiodomethane in high yield :

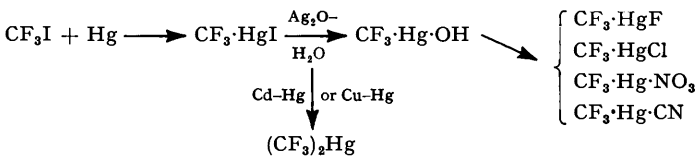
$$CF_3{\cdot}CO_2Ag + I_2 = CF_3I + CO_2 + AgI$$

Both trifluoroiodomethane and pentafluoroiodoethane are stable compounds which boil at $-22{\cdot}5^\circ$ and 13°, respectively, and are therefore very readily manipulated by the standard vacuum-technique, which was developed originally by Stock for the study of the hydrides of boron and silicon. The two compounds differ considerably from their alkyl analogues. Thus, it is impossible to replace the iodine atom by groups such as NO_2, NH_2 or CN by reactions which are applicable to the alkyl iodides. Moreover trifluoroiodomethane is readily hydrolysed by ethanolic alkali to give fluoroform ($CF_3I + KOH = CHF_3 + KOI$), a clear indication that it behaves as a positive iodine compound. Reaction with organic solvents also occurs under comparatively mild conditions favouring free-radical formation, and gives fluoroform. The behaviour of pentafluoroiodoethane is similar.

In one important respect there is a close analogy between methyl iodide and trifluoroiodomethane. Both show strong absorption of light in the region 2500—2700 Å and, on irradiation, undergo photochemical decomposition. The quantum yield is low in each case. That the

trifluoromethyl radical is produced in the photolysis is inherently probable, and this view is supported by the nature of the products obtained when the irradiation is done in presence of oxygen, chlorine, or cyanogen. Moreover, both ethylene and tetrafluoroethylene are polymerised when irradiated with trifluoroiodomethane (Banus, Emeléus, and Haszeldine, *J.*, 1950, 3041; 1951, 60; Haszeldine, *J.*, 1949, 2856; 1953, 3761). Similar polymerisations may be induced by heating the unsaturated compound to 200—300° with trifluoroiodomethane, and it is likely, therefore, that homolytic fission of the C–I bond also occurs under the action of heat.

These experiments provided a basis for attempting to prepare organometallic compounds containing trifluoromethyl radicals by a direct route and it was found that when trifluoroiodomethane was heated or irradiated with mercury a white crystalline compound, which proved to be trifluoromethylmercuric iodide, was formed. This, like the methyl analogue, reacted with an aqueous suspension of silver oxide to yield the base, $CF_3{\cdot}Hg{\cdot}OH$. The latter was readily



converted into the usual salts, but the preparation of bistrifluoromethylmercury proved to be impossible by the reactions which are applicable to the methyl analogue. It was necessary to use copper-, silver-, or cadmium-amalgam (Emeléus and Haszeldine, *J.*, 1949, 2948, 2953).

Bistrifluoromethylmercury was very different from dimethylmercury. It was a white crystalline solid which could be sublimed and dissolved, without decomposition, in both water and organic solvents. These properties suggest an analogy with mercuric chloride rather than with the typically covalent dimethyl compound. The aqueous solution had a small but definite electrical conductivity. That this was not due to formation of the base, $CF_3{\cdot}Hg{\cdot}OH$, is shown by the fact that no fluoroform was evolved from the aqueous solution. No experimental work has so far been done to determine the nature of the ions in aqueous solution, but it is unlikely that CF_3^- is present and more probable that a complex anion such as $[Hg(CF_3)_4]^{2-}$ is formed.

The direct reaction of trifluoroiodomethane with other metals has not yet been studied in detail. There were indications that the most electropositive elements (*e.g.*, sodium) abstracted fluorine from the trifluoromethyl radical when heated to a temperature sufficiently high to initiate reaction. Some evidence of the formation of volatile products, which may be organometallic derivatives, has been obtained in preliminary experiments on the reaction of trifluoroiodomethane with elements such as indium and germanium, and in addition work has been done on Grignard and Grignard-type compounds obtained from magnesium, lithium, and zinc, as is described below.

The reaction of trifluoroiodomethane with non-metals has been examined in much greater detail and has yielded a number of new products of outstanding interest. The experimental approach in this case was essentially the same as that used with mercury. Trifluoroiodomethane was heated with an excess of the element (phosphorus, arsenic, antimony, sulphur, or selenium), in either a sealed tube or a stainless-steel autoclave. The temperature at which reaction occurred was roughly the same as that at which the polymerisation of ethylene and tetrafluoroethylene was induced (200—250°). One may therefore assume that homolytic fission of the C–I bond occurred and that some of the iodine set free reacted with excess of the element used. The products obtained in this way are shown in Table 1.

These products were separated either by fractionation in the vacuum-apparatus or by normal distillation techniques. It is convenient first to consider the phosphorus and arsenic derivatives together, since they show many points of similarity. The yields of the types $(CF_3)_3M$, $(CF_3)_2MI$, and $CF_3{\cdot}MI_2$ are in each case approximately in the ratio 7 : 2 : 1, and there is evidence that an equilibrium is set up between these substances and the tri-iodide, MI_3, which is also formed in the reaction. All six of the compounds are decomposed when heated with an excess of aqueous alkali, and the fluorine is liberated quantitatively as fluoroform. Direct measurement of the gaseous fluoroform produced has greatly facilitated analysis. Both trimethylphosphine and trimethylarsine are stable under these conditions. The electronegative trifluoromethyl groups exert a strong influence on the phosphorus and arsenic atoms in the tristrifluoromethyl derivatives and attempts to prepare co-ordination compounds analogous to those formed by trimethyl-phosphine and -arsine have so far been unsuccessful. The effect of negative groups is

also seen in other cases. Thus, triarylphosphines do not form compounds with carbon disulphide, though they do so with sulphur.

Both tristrifluoromethylphosphine and tristrifluoromethylarsine are readily oxidised by air. They also combine with chlorine and give the quinquevalent derivatives $(CF_3)_3PCl_2$ and

TABLE 1. *Products of the reaction of trifluoroiodomethane with non-metals.*

Element (& ref.)	Product	B. p.	Element (& ref.)	Product	B. p.
P (1)	$(CF_3)_3P$	17·5°	Sb (3)	$(CF_3)_3Sb$	72°
	$(CF_3)_2PI$	73		$(CF_3)_2SbI$	—
	$CF_3{\cdot}PI_2$	69°/29 mm.	S (4)	$(CF_3)_2S_2$	35
As (2)	$(CF_3)_3As$	33·3		$(CF_3)_2S_3$	86·5
	$(CF_3)_2AsI$	92		$(CF_3)_2S_4$	135
	$CF_3{\cdot}AsI_2$	154	Se	$(CF_3)_2Se$	−1
				$(CF_3)_2Se_2$	70

(1) Bennett, Emeléus, and Haszeldine, *J.*, 1953, 1565; 1954, in the press. (2) Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2552; Emeléus, Haszeldine, and Walaschewski, *J.*, 1953, 1552; Walaschewski, *Chem. Ber.*, 1953, **86**, 272. (3) Dale, Emeléus, and Haszeldine, Abstr. Amer. Chem. Soc. Meeting, Atlantic City, Sept. 1952, p. 14K; Robison, unpublished results. (4) Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2198, 2549; Haszeldine and Kidd, *J.*, 1953, 3219.

$(CF_3)_3AsCl_2$, which are unstable above their boiling points. The compound $(CF_3)_3AsCl_2$ is converted by silver fluoride into $(CF_3)AsF_2$. By using an excess of chlorine it has proved possible to convert chlorobistrifluoromethylphosphine into bistrifluoromethylphosphorus trichloride, but this also loses chlorotrifluoromethane. The compound $(CF_3)_2AsCl_3$ may be prepared similarly.

$$(CF_3)_3P + Cl_2 \longrightarrow (CF_3)_3PCl_2 \longrightarrow (CF_3)_2PCl + CF_3{\cdot}Cl \xrightarrow{Cl_2} (CF_3)_2PCl_3$$

No definite addition compounds with bromine or iodine have been obtained, though there is some evidence that addition of bromine occurs at low temperatures. At higher temperatures products such as $(CF_3)_2AsBr$ and $CF_3{\cdot}AsBr_2$ are formed, together with bromotrifluoromethane. Tristrifluoromethyl-phosphine and -arsine react with iodine only when heated, and give the mono- and di-iodo-compounds.

The iodine atoms in the mono- and di-iodides are readily replaced by other groups; for example, by reaction with the appropriate silver salt. Table 2 shows a number of typical derivatives which have been obtained by this and other reactions.

TABLE 2. *Derivatives of fluoroalkyl-phosphines and -arsines.*[a]

Product	Method	B. p.	Product	Method	B. p.
$(CF_3)_2PCN$	$(CF_3)_2PI + AgCN$	48°	$(CF_3)_2AsCN$ ...	$(CF_3)_2AsI + AgCN$	89·5
$(CF_3)_2PCl$	$(CF_3)_2PI + AgCl$	21	$(CF_3)_2AsCl$	$(CF_3)_2AsI + AgCl$	46
$CF_3{\cdot}PCl_2$	$CF_3{\cdot}PI_2 + AgCl$	37	$CF_3{\cdot}AsCl_2$	$CF_3{\cdot}AsI_2 + AgCl$	71
			$(CF_3)_2AsBr$	$(CF_3)_3As + Br_2$	59·5
$(CF_3)_2PH$	$(CF_3)_2PI + H_2$	1	$(CF_3)_2AsF$	$(CF_3)_2AsI + AgF$	25
$CF_3{\cdot}PH_2$	$CF_3{\cdot}PI_2 + LiAlH_4$	−26·5	$(CF_3)_2AsH$	$(CF_3)_2AsI + LiAlH_4$	19
$(CF_3)_4P_2$	$(CF_3)_2PI + Hg$	83—84	$CF_3{\cdot}AsH_2$	$CF_3{\cdot}AsI_2 + LiAlH_4$	−20
			$(CF_3)_4As_2$	$(CF_3)_2AsI + Hg$	106—107
			$(CF_3)_4As_2O$	$(CF_3)_2AsI + HgO$	97—100

[a] See references in Table 1.

The derivatives in which one or two atoms of iodine are replaced by other atoms or groups by interaction with a silver salt call for little comment. The substituted phosphines and arsines are of greater interest. Bistrifluoromethylphosphine is best prepared by reducing iodobistrifluoromethylphosphine with hydrogen in the presence of Raney nickel. The most convenient method for the preparation of trifluoromethylphosphine, $CF_3{\cdot}PH_2$, is the hydrolysis of di-iodotrifluoromethylphosphine in concentrated aqueous solution, followed by freeze-drying of the solution. During the latter process the phosphonous acid undergoes partial decomposition:

$$CF_3{\cdot}PI_2 \xrightarrow{H_2O} CF_3{\cdot}P(OH)_2 \longrightarrow CF_3{\cdot}PH_2$$

Both of the substituted phosphines are spontaneously inflammable. Unlike dimethylphosphine, bistrifluoromethylphosphine forms no addition compounds with methyl iodide, carbon disulphide, silver iodide, or chloroplatinic acid. The two substituted arsines are readily prepared by reducing the iodo-compounds with lithium aluminium hydride in di-*n*-butyl ether. They, too, do not form addition compounds as do the methylarsines.

The reactions leading to formation of the diphosphine and diarsine occur readily at room

temperature and are of special interest. No methyl analogue of tetrakistrifluoromethyldiphosphine is known : the arsenic compound, $(CF_3)_4As_2$, corresponds to cacodyl. Both of the fluorinated substances are comparatively stable, though they are oxidised in air. They differ from other trifluoromethyl derivatives of phosphorus in that, on hydrolysis by aqueous alkali, both fluoride ion and fluoroform are produced. It seems probable that the initial step in the hydrolysis will involve cleavage of the bond between the two metalloidal atoms, as shown below for the diarsine, and that the nature of the hydrolysis products can be explained in terms of the behaviour of the intermediates postulated :

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

Evidence on the hydrolysis of the hypothetical acid, $(CF_3)_2As{\cdot}OH$, is furnished by the reaction of iodobistrifluoromethylarsine with aqueous sodium hydroxide, all of the fluorine being evolved as fluoroform (2 mols.). Bistrifluoromethylarsine, on hydrolysis under conditions identical with those used in the experiments with tetrakistrifluoromethyldiarsine, gives 66% of the trifluoromethyl groups as fluoroform and 34% as fluoride and carbonate. By the mechanism postulated, 1 mole of the diarsine should give 2 moles of fluoroform by alkaline hydrolysis of the acid $(CF_3)_2As{\cdot}OH$ and ($\frac{2}{3} \times 2$) moles from $(CF_3)_2AsH$, *i.e.*, a conversion of 83% of the fluorine into fluoroform, and the balance into fluoride. This agrees well with the experimentally determined value of 84% conversion into fluoroform. These experiments provide good evidence for the mechanism of hydrolysis of the diarsine, though they do not explain the breakdown of some of the trifluoromethyl groups to fluoride. Trifluoromethylarsine, $CF_3{\cdot}AsH_2$, also hydrolyses under similar conditions to fluoride, fluoroform, carbonate, and arsenite, but the proportion of fluoroform is only 12—14% and an amorphous yellow solid, which may be a polymerised unsaturated arsenic hydride, is also produced.

The behaviour of tetrakistrifluoromethyldiphosphine on hydrolysis with aqueous alkali is similar to that of the diarsine in that three of the four trifluoromethyl groups appear as fluoroform. The residual fluorine is, however, present partly as fluoride (9%) and partly (13%) as the salt of a relatively stable trifluoromethyl acid of phosphorus, which has not been identified with certainty. If the hydrolytic fission of the P–P bond is postulated as the initial step, one may again attempt to correlate the observed distribution of fluorine among the hydrolytic products with that predicted from the products of the initial reaction :

$$(CF_3)_2P{\cdot}P(CF_3)_2 \xrightarrow{H_2O} (CF_3)_2PH + (CF_3)_2P{\cdot}OH$$

The alkaline hydrolysis of iodobistrifluoromethylphosphine yields all of the fluorine as fluoroform. Hydrolysis under identical conditions of the substituted phosphine $(CF_3)_2PH$, prepared by the method already described, shows that half of the fluorine is liberated as fluoroform, 18% as fluoride and 28% as the salt of a trifluoromethyl acid of phosphorus, the infra-red spectrum of which is identical with that of the salt obtained in the hydrolysis of the diphosphine. The mechanism postulated would thus predict the formation of 75% of fluoroform (*i.e.*, 3 mols.), 9% of fluoride and 14% of the trifluoromethyl acid, in good agreement with the experimental figures.

Interesting support for this mechanism is given by experiments on the reaction of tetrakisdimethyldiphosphine with water or dilute acid at 100°. Half of the fluorine appears as fluoroform and, in addition, both trifluoromethylphosphine, $CF_3{\cdot}PH_2$, and bistrifluoromethylphosphine, $(CF_3)_2PH$, may be isolated. The former was identified by its infra-red spectrum, and it is known to be one of the products of reaction of bistrifluoromethylphosphine with water at

$$(CF_3)_2P{\cdot}P(CF_3)_2 \xrightarrow{H_2O} (CF_3)_2PH + (CF_3)_2P{\cdot}OH \xrightarrow{H_2O} CF_3{\cdot}PHO{\cdot}OH \xrightarrow[100^\circ]{H_2O} CHF_3$$

$$(CF_3)_2PH \xrightarrow{H_2O\ (100^\circ)} CF_3{\cdot}PH_2 + F^- + CO_3^{2-}$$

$$CF_3{\cdot}PHO{\cdot}OH \rightarrow + CHF_3$$

120°. The phosphinic acid $CF_3{\cdot}PHO{\cdot}OH$, shown in the reaction scheme, has been synthesised (see below) and is found to be decomposed by water at 100°. Thus the general picture of the hydrolysis mechanism is established, though, for both the diphosphine and the diarsine, it is desirable to extend the work by studying products of hydrolysis under more diverse conditions.

Experiments on the hydrolysis and oxidative hydrolysis of iodotrifluoromethyl-phosphines and -arsines has yielded several new acids with interesting properties associated with the

presence of the strongly negative trifluoromethyl group. The formulæ of the acids of phosphorus are shown in Table 3, together with values of the dissociation constants and those of their methyl analogues. Trifluoromethylphosphinic acid, $CF_3{\cdot}PHO{\cdot}OH$, is formed in the slow hydrolysis

TABLE 3. *Trifluoromethyl and methyl acids of phosphorus.*

$CF_3{\cdot}PHO{\cdot}OH$	$K = 10 \times 10^{-3}$	$CH_3{\cdot}PHO{\cdot}OH$	$K = -$
$CF_3{\cdot}PO(OH)_2$	$K_1 = 6{\cdot}8 \times 10^{-2}$	$CH_3{\cdot}PO(OH)_2$	$K_1 = 3{\cdot}3 \times 10^{-3}$
	$K_2 = 1{\cdot}2 \times 10^{-4}$		$K_2 = 1{\cdot}2 \times 10^{-8}$
$(CF_3)_2PO{\cdot}OH$	$K = \infty$	$(CH_3)_2PO{\cdot}OH$	$K = 8{\cdot}3 \times 10^{-4}$

by cold water of either di-iodotrifluoromethylphosphine or iodobistrifluoromethylphosphine. The bistrifluoromethylphosphinic acid, formed initially from iodobistrifluoromethylphosphine, is unstable and, by loss of one CF_3 group as fluoroform, yields $CF_3{\cdot}PHO{\cdot}OH$ which is a moderately strong monobasic acid with weak reducing properties. It is, for example, oxidised by per-

$$(CF_3)_2PI + 2H_2O = CF_3{\cdot}PHO{\cdot}OH + CHF_3 + HI$$
$$CF_3{\cdot}PI_2 + 2H_2O = CF_3{\cdot}PHO{\cdot}OH + 2HI$$

manganate, though not by iodine solution. It has not been isolated in the pure state, since it is volatile in water vapour at reduced pressure. Above pH 11, or when the aqueous solution is heated to 100°, fluoroform is lost quantitatively. The infra-red spectrum of the monosodium salt shows bands which may be attributed to P–H and P=O vibrations, in keeping with the formula shown in Table 3, in which the phosphorus atom is four-co-ordinated.

The acids $CF_3{\cdot}PO(OH)_2$ and $(CF_3)_2PO{\cdot}OH$ have both been isolated in the pure state and shown to be di- and mono-basic, respectively. The first is a white crystalline solid and is prepared by hydrolysing compounds of the type $CF_3{\cdot}PX_2$ or $(CF_3)_2PX$ (X = Cl or I), or by controlled hydrolysis of $(CF_3)_3P$, followed by oxidation. The second acid is a liquid (b. p. 182°) and is most conveniently prepared by the following method (Paul, unpublished observations) :

$$(CF_3)_2PI \xrightarrow{AgCl} (CF_3)_2PCl \xrightarrow{Cl_2} (CF_3)_2PCl_3 \xrightarrow{H_2O} (CF_3)_2PO{\cdot}OH$$

It is completely dissociated in aqueous solution, in marked contrast to the methyl analogue.

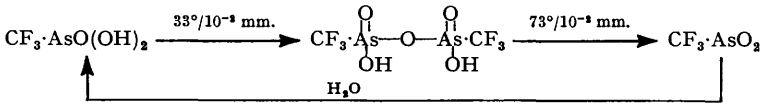
The two iodoarsines, $(CF_3)_2AsI$ and $CF_3{\cdot}AsI_2$, differ from their phosphorus analogues in that both are stable to water, although readily decomposed by alkali. Attempts to prepare the free acids $(CF_3)_2As{\cdot}OH$ and $CF_3{\cdot}As(OH)_2$ have so far been inconclusive. Oxidative hydrolysis of the mono- and di-iodo-compounds has, however, yielded two substituted arsonic acids, the dissociation constants of which are compared in Table 4 with those of their methyl analogues.

TABLE 4. *Trifluoromethyl and methyl acids of arsenic.*

$(CF_3)_2AsO{\cdot}OH$	$K = 4 \times 10^{-2}$	$(CH_3)_2AsO{\cdot}OH$	$K = 7{\cdot}5 \times 10^{-7}$
$CF_3{\cdot}AsO(OH)_2$	$K_1 = 7{\cdot}7 \times 10^{-2}$	$CH_3{\cdot}AsO(OH)_2$	$K_1 = 2{\cdot}5 \times 10^{-4}$
	$K_2 = 5 \times 10^{-6}$		$K_2 = 5{\cdot}7 \times 10^{-9}$

The trifluoromethylarsonic acids are highly ionised in aqueous solution and much stronger than the corresponding methyl acids. Since water is unsuitable as a solvent for differentiating between strong acids, conductivity measurements have been made in anhydrous acetic acid, in which the acid strengths are found to be in the order: $H_2SO_4 > HCl$, $CF_3{\cdot}PO(OH)_2 > (CF_3)_2AsO{\cdot}OH > CF_3{\cdot}AsO(OH)_2 \gg CF_3{\cdot}CO_2H$, HNO_3, $C_3F_7{\cdot}CO_2H$.

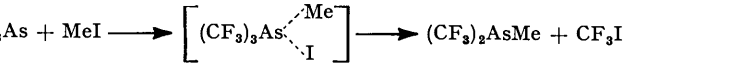
Trifluoromethylarsonic acid undergoes dehydration *in vacuo*, first to a pyro-acid and then to an anhydride, both of which revert to the ortho-form in water :



Methylarsonic acid also forms a pyro-acid on dehydration, though its anhydride has not been reported. No conclusive evidence of pyro-acid or anhydride formation was obtained for the second of the two new acids of arsenic.

Mixed arsines may be prepared by two methods. In the first the Grignard reaction is applied to iodotrifluoromethyl arsines. Thus, $CF_3{\cdot}AsI_2$ and methylmagnesium iodide gave $CF_3{\cdot}AsMe_2$, and a similar reaction could certainly be used with the fluoroalkyl iodides of other elements. In the second, it has been found that, when tristrifluoromethylarsine is heated to

about 230° with methyl iodide, an exchange reaction occurs, and mixed alkyl-fluoroalkylarsines may be isolated from the product. The reaction mechanism probably involves the formation of an unstable quaternary compound, thus :



Similar exchange reactions have been observed with tristrifluoromethylphosphine and there are indications that the reactions may be even more general.

The trifluoromethylantimony compounds are less stable than the arsenicals. Thus, tristrifluoromethylstibine decomposes thermally at about 200°, whereas the arsenic analogue is stable up to about 350° (Ayscough, unpublished observations). Iodobistrifluoromethylstibine also disproportionates readily and has not yet been fully characterised. It resembles the monoiodoarsenic compound in that it reacts readily with mercury and forms the distibine, $(CF_3)_4Sb_2$. Tristrifluoromethylstibine also adds on chlorine to form $(CF_3)_3SbCl_2$ which, with water, gives a dihydrate, $(CF_3)_3SbCl_2,2H_2O$. The latter is decomposed by warm water to a strong monobasic acid, which has been characterised as the silver salt $Ag[Sb(CF_3)_3(OH)_3]$. The free acid has not yet been isolated, but the pyridine salt is crystalline and may be recrystallised from organic solvents (Moss, unpublished results). When it is treated with hydrochloric or hydrobromic acid the following transformations occur :

$$PyrH[Sb(CF_3)_3Br_3] \xleftarrow{HBr} PyrH[Sb(CF_3)_3(OH)_3] \xrightarrow{HCl} PyrH[Sb(CF_3)_3Cl_3]$$

Pyr = Pyridine

This behaviour is in accord with the general chemistry of other antimonic acids and, when the field has been more fully explored, it is likely that the fluoroalkyl-acids will be found to be much stronger and better defined than other antimonic acids.

The reaction of trifluoroiodomethane with sulphur and selenium gives, from sulphur, the polysulphides $(CF_3)_2S_2$, $(CF_3)_2S_3$, and $(CF_3)_2S_4$ and, from selenium, $(CF_3)_2Se$ and $(CF_3)_2Se_2$. In the reaction with sulphur the main product is the disulphide $(CF_3)_2S_2$. Both the di- and the tri-sulphide are formed in an interesting reaction between carbon disulphide and iodine pentafluoride in a steel autoclave at 100° (Haszeldine and Kidd, *J.*, 1953, 3219).

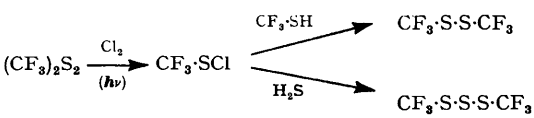
The structure of the disulphide follows from the reactions :

$$Hg(S{\cdot}CF_3)_2 \xleftarrow[\text{light}]{Hg} C_2S_2F_6 \xrightarrow[300°]{Cl_2} 2CF_3Cl + S_2Cl_2$$

Chlorine gives a yield of chlorotrifluoromethane in excess of 90%, and thus shows the presence of two CF_3 groups. The reaction with mercury occurs in ultra-violet light and shows the presence of the $S{\cdot}CF_3$ group in the disulphide. The mercurial is a white crystalline solid which may be sublimed, and is a salt of the thiol, $CF_3{\cdot}SH$, which may be prepared in the pure state by decomposing bistrifluoromethylthiomercury with dry hydrogen chloride, $Hg(S{\cdot}CF_3)_2 + 2HCl = HgCl_2 + 2CF_3{\cdot}SH$. The thiol is a gas (b. p. −37°) which is decomposed by water with the formation of carbonyl sulphide, $CF_3{\cdot}SH \xrightarrow{-HF} CSF_2 \xrightarrow{H_2O} COS + 2HF$.

The monosulphide, $(CF_3)_2S$, is not a product of the reaction of trifluoroiodomethane with sulphur, but is produced together with sulphur when the disulphide is irradiated with ultra-violet light. The thiol is much more stable than the disulphide and resists hydrolysis by aqueous alkali, whereas the di-, tri-, and tetra-sulphides are completely decomposed, all of the fluorine being converted into fluoride. This stability parallels that of bistrifluoromethyl ether, $(CF_3)_2O$, and of the amine, $(CF_3)_3N$.

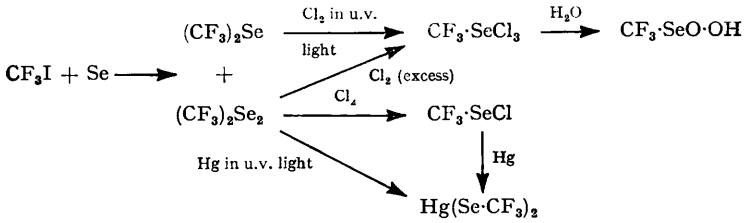
Bistrifluoromethyl disulphide, when mixed with chlorine and irradiated in ultra-violet light, gives trifluoromethylsulphenyl chloride, $CF_3{\cdot}SCl$ (b. p. 0°). The latter, on treatment with trifluoromethanethiol gives bistrifluoromethyl disulphide, while, with hydrogen sulphide, the



trisulphide is produced. These reactions serve to establish the interrelationship of the compounds. Electron-diffraction studies have shown that the di- and the tri-sulphide contain a

bent chain of sulphur atoms. Trifluoromethanesulphonic acid is obtained by oxidising the sulphur compounds with hydrogen peroxide. It may be isolated as the barium or the sodium salt, from which the free acid is liberated by concentrated sulphuric acid. Trifluoromethanesulphonic acid resembles sulphuric acid in many respects : it is a fuming oily liquid and is one of the strongest known sulphur acids. Reaction with phosphorus pentachloride gives trifluoromethanesulphonyl chloride, b. p. 32° (Kidd, unpublished results).

Reaction of trifluoroiodomethane with selenium yields the monoselenide and diselenide in a ratio of about 2 : 1. The former is much more readily hydrolysed than the monosulphide. The reactions of the latter which have so far been studied are shown below (Dale, Emeléus, and Haszeldine, Abstr. Amer. Chem. Soc. Meeting, Atlantic City, Sept. 1952, p. 14K) :



There is a general resemblance to the sulphur compounds and such differences as exist appear to follow the general trends of Group VI. Thus, the compound $CF_3{\cdot}SeCl_3$ is much more stable than $CF_3{\cdot}SCl_3$. Some evidence of the formation of the latter compound has been obtained, though its dissociation pressure at room temperature is high. The mercurial resembles its sulphur analogue in general characteristics, though the corresponding selenol, $CF_3{\cdot}SeH$, has not yet been prepared. A few experiments on the reaction between trifluoroiodomethane and tellurium have failed to yield either a mono- or a di-telluride. It is possible, however, that these compounds can be prepared by this route under modified conditions, though their thermal stability may be low.

An alternative method for the preparation of fluoroalkyl organometallic and organometalloidal compounds is by use of Grignard-type reagents. They are less readily prepared, and less stable, than Grignard reagents containing an alkyl or aryl group. Nevertheless, by using pure magnesium, and with suitable initiation of the reaction, trifluoromethylmagnesium iodide has been obtained in solution in ethyl or butyl ether. The solutions are relatively stable at −30° to −10° and have been shown to exhibit normal reactions, such as the formation of fluoroform with water, of fluorinated acids with carbon dioxide, and of ketones with acyl chlorides (Haszeldine, *Nature*, 1951, **167**, 139; **168**, 1028; *J.*, 1954, 1273). Pentafluoroiodoethane and heptafluoroiodopropane also yield magnesium derivatives, and the latter has given an 80% yield in solution at low temperatures (Haszeldine, *J.*, 1952, 3423; 1953, 1748). Heptafluoro-*n*-propylzinc iodide has also been prepared by the reaction of heptafluoroiodopropane with zinc in a solvent such as dioxan or dibutyl ether, and from dioxan solution the solvated compound $C_3F_7{\cdot}ZnI,C_4H_8O_2$ was isolated. This, when heated in vacuum, lost dioxan and gave heptafluoro-*n*-propylzinc iodide (Haszeldine and Walaschewski, *J.*, 1953, 3607).

An alternative route for the preparation of perfluoroalkyl Grignard compounds is by radical exchange (Haszeldine, unpublished observations). Thus phenylmagnesium iodide reacts with heptafluoroiodopropane and an equilibrium is set up ($PhMgI + C_3F_7I \rightleftharpoons C_3F_7{\cdot}MgI + PhI$). Another exchange reaction which is potentially of great importance is that between lithium alkyls and perfluoroalkyl iodides. Here the exchange is almost complete :

$$MeLi + C_3F_7I = C_3F_7Li + MeI$$

The extremely reactive perfluoroalkyl-lithium must, like the Grignard compound, be manipulated at below −10°. Heptafluoropropyl-lithium can thus be prepared in solution in over 80% yield and trifluoromethyl-lithium in about 20% yield. The lithium compounds undergo a variety of reactions of the normal types with organic functional groups. Of particular interest, however, is their reaction with silicon tetrachloride. Solutions of trifluoromethylmagnesium iodide react with silicon tetrachloride and give $(CF_3)_2SiCl_2$ in low yield. Preliminary experiments have shown that the perfluoroalkylsilicon compounds are obtained in much better yields from solutions of the perfluoroalkyl-lithiums. These experiments offer a clear route for the preparation of perfluoroalkylsilicones, and it may well prove possible to use these reagents to

obtain other perfluoroalkyl derivatives, which are not accessible by the direct method depending on the reaction of the element with a fluoroalkyl iodide.

A different approach to the same problem is by the electrochemical fluorination of organometallic compounds with the object of fluorinating alkyl groups directly. The process of electrochemical fluorination has been widely applied to the preparation of fully fluorinated organic compounds (Brice, Dresdner, Francis, Harland, Hogg, Pearlson, Simons, and Wilson, *Trans. Electrochem. Soc.*, 1949, **95**, 47). It depends on the electrolysis of a solution of the substance to be fluorinated in anhydrous hydrogen fluoride, with a nickel anode, and at a voltage lower than that at which free fluorine is evolved. When applied to the electrochemical fluorination of dimethyl sulphide the compounds $CF_3{\cdot}SF_5$ and $(CF_3)_2SF_4$ were obtained, the latter in small yield (Clifford, El-Shamy, Emeléus, and Haszeldine, *J.*, 1953, 2372). These experiments demonstrate the possibility of converting a methyl group directly into trifluoromethyl, though not without considerable loss arising from the breakdown of the molecule to give both sulphur hexafluoride and carbon tetrafluoride. In other cases solvolysis of organometallic compounds with the liberation of hydrocarbon is likely to occur, but in spite of this the method clearly warrants closer study as it offers the advantages of simplicity and ready accessibility of raw materials.

When the progress made so far in this new field is reviewed one is struck by the great differences which exist between organometallic compounds containing fluoroalkyl and alkyl groups. Structurally the two types are similar and there is also a general similarity in physical properties, but the chemical properties have little in common. This can be explained qualitatively in terms of the high negativity of the fluoroalkyl groups, but much remains to be done before any quantitative discussion of the problem can be attempted. The results obtained thus support the view that, in general, fluorocarbon chemistry is quite distinct from hydrocarbon chemistry, and that progress may well be hindered by too great a dependence on analogy in considering future developments.

The work described serves to open up the chemistry of fluoroalkyl organometalloidal compounds, though even in the field so far explored many gaps remain. Much progress has been made with a simple preparative method based on the direct reaction of fluoroalkyl iodides with non-metals. Even allowing for the possibility that derivatives of some other elements may be produced in the same way under more closely controlled conditions, it is unlikely that many more will yield to this approach. Of the two other synthetic methods described, the Grignard reagent holds a promise of fairly general applicability. Electrochemical fluorination on the other hand may well prove to be very limited in its scope. There remains, therefore, a need for yet other methods of synthesis with which to prepare fluoroalkyl derivatives of the more electropositive elements, and of elements such as lead and tin, the alkyl derivatives of which are well known. It is in the search for these compounds, which are unknown at present, that some of the new non-metallic fluoroalkyl derivatives may be useful.

Physicochemical problems associated with the new organometallic compounds are many and, for the most part, are untouched. Indeed, with a few exceptions, this is true of the whole field, and one may hope that the greater availability of fluorocarbons and their derivatives will lead to a more intensive study of kinetic problems in particular. Major experimental difficulties are likely to be encountered in studying free fluorocarbon radicals as their reactivity is so much greater than that of hydrocarbon radicals. This, indeed, has been our own experience in studying the kinetics of the pyrolysis of tristrifluoromethylarsine. Such difficulties are, however, a challenge which I hope some of my audience will accept.