PERFLUOROALKYL DERIVATIVES OF METALS AND NON-METALS

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SINCE the conclusion of World War II, perfluoroalkyl† derivatives of many elements have been prepared and characterised. This Review deals with the chemistry and properties of the known perfluoroalkyl derivatives of the elements other than carbon, oxygen, nitrogen, and the halogens.

Many of the physical and chemical properties of trifluoromethyl derivatives of the elements can be correlated with the dual nature of this group. As an organic radical it gives compounds formally related to normal alkyl compound, and many of the reactions of perfluoroalkyl derivatives are analogous to those of the corresponding covalently bonded alkyl compounds. Replacement of the hydrogen atoms in an alkyl group by fluorine atoms produces a group with a substantial inductive character, *i.e.*, a highly electronegative group, and a number of observations suggest that the effective electronegativity of a trifluoromethyl group lies between that of fluorine and of chlorine.

Effective Electronegativity of Perfluoroalkyl Groups.—Values for the electronegativity‡ of an atom have been principally obtained from (*a*) thermochemical data, (*b*) ionization potentials and electron affinities, and (*c*) stretching force constants; considerations of other molecular properties have also been used. Methods (*a*) and (*c*) have been extended to the determination of the electronegativity of organic radicals, but method (*b*) does not appear practicable at present since so little is known of the electron affinity of organic groups. Qualitative electronegativity scales for organic radicals are usually based on a comparison of the relative reactivities of various molecules containing the radical under observation or on the relative reactivities of molecules possessing a particular structure with varying substituents. The results of such studies are often conflicting, and it has been concluded that other factors besides the electronegativity of the radical are operative.[2] An attempt is made here to establish the effective electronegativity of the trifluoromethyl group by using methods (*a*) and (*c*).

The empirical observation has been made, that the energy of a bond A–B [D(A–B)] is generally larger than the additive mean of the energies of the bonds A–A [D(A–A)] and B–B [D(B–B)] and the difference, Δ

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† In this Review the terms fluoroalkyl and perfluoroalkyl denote partially fluorinated and fully fluorinated alkyl groups, respectively.

‡ Electronegativity values are those given by Pauling[1], unless otherwise stated.

[1] Pauling, "The Nature of the Chemical Bond", 2nd edn., Cornell University Press, Ithaca, New York, 1948.

[2] Pritchard and Skinner, *Chem. Rev.*, 1955, **55**, 745.

(defined by equation 1), was found to be proportional to the difference between the electronegativities of the atoms (equation 2):[1]

$$\Delta = [D(\text{A–B})] - \tfrac{1}{2}[D(\text{A–A}) + D(\text{B–B})] \quad \ldots \quad (1)$$

$$|\chi_{\text{A}} - \chi_{\text{B}}| = 0{\cdot}208\Delta^{\frac{1}{2}} \quad \ldots\ldots\ldots \quad (2)$$

Bond dissociation energies of a number of simple trifluoromethyl compounds of the type CF_3X have been reported, and the calculated values of Δ and the electronegativity differences for these compounds appear in Table 1. The values for Δ parallel the trends observed in the hydrogen halides, but, unlike those of the alkyl halides, the values for the electronegativity of the trifluoromethyl group apparently do not require a correction term.[2] There is fair agreement between the values calculated for the electronegativity of the trifluoromethyl group from the data for CF_3Cl, CF_3Br, CF_3I, and CF_3H, and it is significant that all are equal to, or greater than, the electronegativity of chlorine.

TABLE 1. *The electronegativity of the* CF_3 *group estimated from bond dissociation energies.*

X	$D(CF_3–X)$	Δ[a]	$\lvert\chi_{CF_3}-\chi_X\rvert$[b]	χ_{CF_3}[c]
Cl	79·5[d]	17·5	0·88	3·9
Br	64·5[e]	9·0	0·62	3·4
I	57·0[f]	6·6	0·53	3·3
H	102·0[g]	18·0	0·88	3·0

[a] Calculated from equation (1) by using the following values of $D(X–X)$: $(CF_3)_2$ 65 (ref. 118); H_2 104; Cl_2 58·0; Br_2 46·1; I_2 36·1 (ref. 1) (all in kcal./mole).

[b] Calculated from equation (2).

[c] Calculated by assuming the "best values" of the electronegativity of X as given in ref. 1, *viz.*, H 2·1, Cl 3·0, Br 2·8, I 2·5.

[d] Rabinovitch and Reed, *J. Chem. Phys.*, 1954, **22**, 2092.

[e] Sehon and Szwarc, *Proc. Roy. Soc.*, 1951, *A*, **209**, 110.

[f] Farmer, Henderson, Lossing, and Marsden, *J. Chem. Phys.*, 1956, **24**, 348.

[g] Pritchard, Pritchard, Schiff, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1956, **52**, 849.

The shift which occurs in the characteristic infrared absorption frequency of a bond with changes in the nature of a substituent originates in the altered electron distribution in the bond brought about by the overall electron-withdrawing ability (which is the sum of the inductive and mesomeric effects) of the substituent. It is often difficult to separate these effects in systems where the bonds in question are coplanar. Non-planar structures should be comparatively free from mesomeric effects, and the substituent's effect on the group frequency should be almost wholly due to an inductive effect operating along the bonds, independent of the molecular geometry, and dependent on the electronegativity of the substituent. A tabulation of effective group electronegativities has been made by observing the change in the position of the P–O frequency in a series of phosphoryl compounds.[3] The P–O bond can be described as the sum of the structures $\geqslant$P=O and $\geqslant$P$^{+}\rightarrow$O^{-}. The former structure will be more important when strongly electronegative substituents are attached to the phosphorus atom, and, hence, the frequency of the P–O absorption band should increase with respect to that for similar compounds carrying less electronegative substituents. A similar study has been made by using the C=O frequency of a series of carbonyl compounds with varying substituents, and the effective electronegativity of the trifluoromethyl group has been calculated to be 3·20 on the Gordy scale of electronegativity.[4] The planar structure of the carbonyl group permits a greater degree of mesomerism than is possible in the tetrahedral phosphoryl group, and it would be expected that the effective electronegativity of a substituent as determined by its influence on the position of the C=O vibration in a carbonyl compound will be less than that determined from the shift in P–O vibration frequency.

The position of the characteristic group frequencies in several other systems has been shown to be dependent on the electronegativity of the substituents,[5] and the approach used to determine the effective electronegativity of the trifluoromethyl group is similar to that used in references 3 and 4, but with some modifications. The dependence of the phosphoryl, carbonyl, and HX vibrations on the sum of the Pauling electronegativities of the substituents is shown in Fig. 1. Substituents were chosen whose

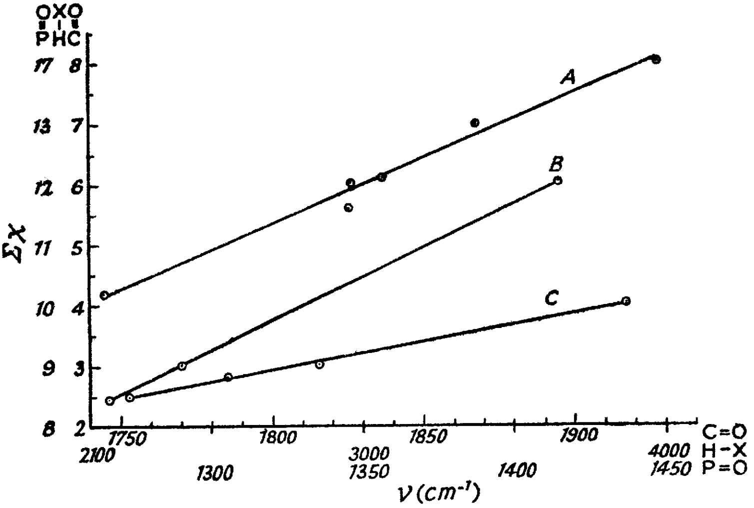

FIG. 1 *The* PO, CO, *and* HX *stretching frequency as the sum of the electronegativities of substituents in*: *A*, X_2CO; *B*, X_3PO; *and C*, HX, *respectively*.

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[3] Bell, Heisler, Tannenbaum, and Goldenson, *J. Amer. Chem. Soc.*, 1954, **76**, 5185.
[4] Kagarise, *J. Amer. Chem. Soc.*, 1955, **77**, 1377.
[5] Daasch, *Spectrochim. Acta*, 1958, **13**, 257.

electronegativities had been determined by other methods, *i.e.*, hydrogen and the halogens (Tables 2, 3, 4). By using the carbonyl or phosphoryl absorbing frequencies for compounds containing the trifluoromethyl group, the effective electronegativity of this group was estimated graphically. The P–O frequency in tristrifluoromethylphosphine oxide occurs[6] at 1327 cm.$^{-1}$, which corresponds to an effective electronegativity of 3·3. The results of a similar treatment of trifluoroacetyl halides appear in Table 5. The values obtained for the acid chlorides being excluded, the effective electronegativity of a trifluoromethyl group lies between those of chlorine and fluorine.

TABLE 2. *Phosphoryl absorption frequencies for* X_3PO *compounds.*

X in X_3PO	F	Cl	Br	CF_3
$\Sigma\chi_X$	12·0	9·0	8·4	9·9[b]
ν_{PO}(cm.$^{-1}$)	1415[a]	1290[a]	1266[a]	1327[c]

[a] Data taken from ref. 3. [b] Determined graphically. [c] Data taken from ref. 6.

TABLE 3. *Carbonyl absorption frequencies for* X_2CO *compounds.*

X_2CO	COF_2	$COCl_2$	$COBr_2$	COHF	COClF	COH_2
$\Sigma\chi_X$	8·0	6·0	5·6	6·1	7·0	4·2
ν_{CO}(cm.$^{-1}$)	1928[a]	1827[a]	1826[b]	1834[a]	1868[a]	1745[a]

[a] Data taken from ref. 4. [b] Bellamy and Williams, *J.*, 1957, 4294.

TABLE 4. *The electronegativity of the* CF_3 *group estimated from the position of the carbonyl absorption band for compounds of the type* $CF_3{\cdot}COX$.

X in $CF_3{\cdot}COX$	F	Cl	Cl	Br	I	CF_3
ν_{CO}(cm.$^{-1}$)	1901[c]	1810[c]	1820[d]	1838[c]	1812[c]	1825[c]
$\chi_{(X+CF_3)}$[a]	7·5	5·6	5·8	6·2	5·7	5·9
χ_{CF_3}	3·5	2·6	2·8	3·4	3·2	3·0[b]

[a] Estimated from Fig. 1. [b] Estimated as $\frac{1}{2}\chi_{(X+CF_3)}$. [c] Bellamy and Williams, *J.*, 1957, 4294. [d] See ref. 9.

TABLE 5. *Absorption frequency of the* HX *vibration.*

X in HX	F	Cl	Br	I	CF_3
χ	4·0	3·0	2·8	2·5	3·2[b]
ν_{HX}(cm.$^{-1}$)[a]	3875	2856	2553	2230	3021

[a] See ref. 8. [b] Determined graphically.

The HX stretching frequency of the hydrogen halides, corrected for mass effects, has been shown to be a linear function of the electronegativity

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[6] Emeléus, Haszeldine, and Paul, *J.*, 1955, 563.

TABLE 6. *Absorption frequency of the* SO *vibration in compounds of the type* SO_2X_2.

Compound		ν_{SO_2}(cm.$^{-1}$)	
		Sym.	Asym.
SO_2F_2[a]	8·0	1269	1502
SO_2Cl_2[b]	6·0	1205	1434
SO_2CF_3Cl[c]	6·2[e]	1240	1439
SO_2CF_3F[d]	7·3[e]	1240	1478

[a] Perkins and Wilson, *J. Chem. Phys.*, 1952, **20**, 1791. [b] Martz and Lagemann, *J. Chem. Phys.*, 1954, **22**, 1193. [c] See ref. 148. [d] See ref. 137. [e] Estimated by the method outlined in the text.

of X.[7] The mass-corrected hydrogen stretching frequency in trifluoromethane has been calculated to be 3021 cm.$^{-1}$;[8] by using this value and the data for HX (Fig. 1) the effective electronegativity of the trifluoromethyl group can be estimated as 3·3.

Substituted sulphuryl compounds, SO_2XH_2 and SO_2XX', should be essentially free from mesomeric effects on structural grounds, and the variation of the S–O stretching frequency with the substituent should be primarily due to inductive, *i.e.*, electronegativity, effects of the substituents. Although the necessary infrared values are known for only two sulphuryl halides (Table 6), it is apparent that both the symmetric and the asymmetric stretching frequencies increase with increasing electronegativity of the substituents. If the trifluoromethyl group has an effective electronegativity of 3·0 or greater, the corresponding frequencies for trifluoromethanesulphonyl chloride or fluoride should be between that of SO_2Cl_2 and SO_2F_2, and this is observed experimentally. The symmetrical stretching frequencies have been reported to be the same for both $CF_3{\cdot}SO_2Cl$ and $CF_3{\cdot}SO_2F$, but there is a difference in the asymmetrical frequencies. Assuming that there is a linear relation between the sum of the electronegativities of the substituents and the $:SO_2$ asymmetrical frequencies, the slope of which can be obtained from the experimentally determined frequencies of sulphuryl chloride and fluoride, we can estimate the sum of the effective electronegativities of the substituents in trifluoromethanesulphonyl chloride and fluoride as 6·2 and 7·3, respectively; it follows that the estimates for the effective electronegativity of the trifluoromethyl group are 3·2 and 3·3, respectively.

The methods used to determine the effective electronegativity of a trifluoromethyl group give consistent results in that all of the estimated values lie between that of fluorine and of chlorine; the "best value" is apparently 3·3. The effective electronegativities of other perfluoroalkyl

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[7] Bellamy, "The Infra-red Spectra of Complex Molecules", Methuen and Co. Ltd., London, 1958, pp. 377–409.

[8] Bellamy and Williams, *J.*, 1956, 2753.

groups might be expected to be similar to that of the trifluoromethyl group. If the position of the C=O frequency is taken as a measure of the overall electron-withdrawing ability of the substituents, then the position of this band for compounds of the type R·CO·X (R_f=perfluoroalkyl, X=halogen) should be essentially constant and independent of R_f for a given halogen. This effect is observed in the perfluoroacyl fluorides and chlorides (R_f = CF_3, C_2F_5, C_3F_7, C_5F_{11}) where the C=O frequency is 1900—1891 and 1809—1815 cm.$^{-1}$, respectively.[9]

Preparative Methods.—Four general methods have been employed for the preparation of perfluoroalkyl derivatives of the elements: (*a*) reactions involving the interaction of perfluoroalkyl halides with metalloids or metals, (*b*) exchange reactions, (*c*) the use of reactive perfluoroalkyl intermediates, and (*d*) direct fluorination of alkyl compounds. Method *d* has been very successfully applied to the preparation of perfluoroalkyl derivatives of carbon, nitrogen, and oxygen, but reactive intermediates such as R_fLi and R_fMgI (method *c*) have been used relatively little, undoubtedly because of the difficulties involved in their preparation. High-temperature exchange reactions and exchange reactions in solutions between perfluoroalkyl iodides and alkyl derivatives have been employed in only a few instances. Method *a* has been the most successful for the preparation of organometallic compounds containing perfluoroalkyl groups. Perfluoroalkyl iodides react directly with metalloids and some metals at high temperatures to form perfluoroalkyl derivatives, but the formation of the more reactive perfluoroalkyl derivatives (with respect to alkylation) requires the use of a solvent, which aids in the stabilisation of the perfluoroalkyl compound (see p. 239).

Group I.—Lithium is the only element in Group I which has been shown to form relatively stable and reactive perfluoroalkyl derivatives. Although perfluoroalkyl iodides do not react directly with lithium,[10] perfluoroalkyl-lithium compounds can be prepared by a halogen–metal interchange with an alkyl-lithium (eqn. 3); trifluoroiodomethane, however, does not undergo this conversion.[11] Trifluoromethyl-lithium has been reported, but no experimental details were given.[12,13]

$$RLi + C_3F_7I \rightarrow C_3F_7Li + RI \quad \ldots\ldots\ldots\ldots \quad (3)$$

Syntheses involving perfluoroalkyl-lithium compounds are best conducted by adding the alkyl-lithium and the other reactant simultaneously to an ether solution of the perfluoroalkyl iodide at −40° to −50°. Perfluoroalkyl-lithium reagents undergo the displacement and the addition reactions common to Grignard reagents and lithium alkyls, and

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[9] Weiblen, in Simons, "Fluorine Chemistry", Vol. II, Academic Press Inc., New York, 1954, p. 449.

[10] Emeléus and Haszeldine, *J.*, 1949, 2948.

[11] Pierce, McBee, and Judd, *J. Amer. Chem. Soc.*, 1954, **76**, 474.

[12] Haszeldine, *Nature*, 1951, **168**, 1028.

[13] Haszeldine, *Angew. Chem.*, 1954, **66**, 693.

are unstable with respect to hexafluoropropene and lithium fluoride; in some instances the perfluoroalkyl-lithium reagent causes reduction of ketones to occur.[14] Although the perfluoroalkyl-lithium compounds have not been investigated extensively as a synthetic route for preparation of perfluoroalkyl derivatives of elements other than carbon, heptafluoro-n-propyl-lithium reacts with diethylsilicon dichloride to yield diethylbisheptafluoro-n-propylsilane and chlorodiethylheptafluoro-n-propylsilane.[11]

Group II.—Perfluoroalkyl derivatives of magnesium, zinc, and mercury have been prepared by the action of a perfluoroalkyl iodide on the element. The mercury derivatives are most satisfactorily prepared without a solvent, but a basic solvent is necessary for the formation of the magnesium and zinc compounds. The nature of the solvent used is important, and no reaction occurs in solvents with little or no basicicity. It has been suggested that basic solvents form molecular addition compounds with perfluoroalkyl iodides in which the nature of the C–I bond approaches that in the alkyl iodides because of a partial transfer of charge from the base to the initially positive iodine atom.[15,16] Under these conditions perfluoroalkyl iodides should undergo heterolysis more readily than in the absence of a basic solvent. A perfluoroalkylcadmium compound has been reported,[12] but no details were given concerning its preparation.

Although the alkyl derivatives of the Group II elements have been classically used as alkylating agents for the preparation of other organometallic compounds, perfluoroalkyl-zinc or -mercury compounds have not yet proved useful for this purpose. Perfluoroalkylmagnesium derivatives have been suggested as a route to perfluoroalkyl compounds of elements other than carbon, but no detailed investigations have appeared.[12,13,17]

Magnesium. Perfluoroalkyl Grignard reagents can be prepared from perfluoroalkyl iodides and magnesium in basic solvents in the usual manner. Although heptafluoro-n-propylmagnesium iodide has been the most widely investigated because of its stability,[15,18–22] there are indications that the less stable trifluoromethylmagnesium iodide can be prepared by using special precautions.[17,23,24] The nature of the solvent, the reaction temperature, the dilution of the perfluoroalkyl iodide, and the purity of

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[14] McBee, Roberts, and Curtis, *J. Amer. Chem. Soc.*, 1955, **77**, 6387.

[15] Haszeldine, *J.*, 1952, 3423.

[16] Haszeldine, *J.*, 1953, 2622.

[17] Haszeldine, Abstracts of Papers, 120th Meeting of the American Chemical Society, 1951, p. 6K.

[18] Henne and Francis, *J. Amer. Chem. Soc.*, 1951, **73**, 3518.

[19] Haszeldine, *J.*, 1953, 1748.

[20] Henne and Francis, *J. Amer. Chem. Soc.*, 1953, **75**, 992.

[21] Pierce and Levine, *J. Amer. Chem. Soc.*, 1953, **75**,. 1254.

[22] Brice, Pearlson, and Simons, *J. Amer. Chem. Soc.*, 1946, **68**, 968.

[23] Haszeldine, *J.*, 1954, 1273.

[24] Haszeldine, Abstracts of Papers, 122nd Meeting of the American Chemical Society, 1952, p. 13K.

the magnesium used in the reaction have all been investigated as variables in the preparation of perfluoroalkyl Grignard reagents. Tetrahydropyran, tetrahydrofuran, tertiary amines, ethyl ether, and n-butyl ether have all been used as solvents, but the aliphatic ethers are less effective for the stabilisation of the Grignard reagent than of the other compounds. The stability of perfluoroalkyl Grignard reagents increases, but the rate of their formation and the ease of initiation of the reaction decreases, with decreasing temperature. As a practical compromise between these temperature effects the reaction is initiated at room temperature or above, and then the reaction temperature is lowered. Grignard reagent formation and reaction has been observed down to —80°; the optimum temperature appears to be about —20°.[15] The purity of the magnesium employed in the reaction has been cited as a critical factor in the formation of perfluoroalkyl Grignard reagents,[15] but there appears to be no general agreement on this point. Although heptafluoro-n-propylmagnesium iodide reacts with aldehydes, acid chlorides, and esters to form the expected secondary alcohols, ketones, and tertiary alcohols,[19,20] there are no recorded attempts to extend these reactions to the preparation of other perfluoroalkylmetallic compounds. Trifluoromethylmagnesium iodide undergoes similar reactions, but the conditions for its formation are difficult to reproduce precisely.[23] Better overall yields are obtained in reactions employing perfluoroalkyl Grignard reagents if the Grignard reagent is formed in the presence of the substance with which it is to react.

An exchange reaction between perfluoroalkyl iodides and phenylmagnesium bromide (eqn. 4; $R_f = C_2F_5, C_3F_7$) occurs at normal temperatures in ether solution and may prove to be more practicable from a manipulative standpoint:[25–27]

$$R_fI + C_6H_5MgBr \rightarrow R_fMgI + C_6H_5Br \quad . \; . \; . \; . \; . \; . \; . \; . \; (4)$$

Zinc. Although trifluoromethylzinc derivatives have not been reported, higher perfluoroalkylzinc halides are known.[28] Heptafluoro-n-propylzinc iodide and bisheptafluoro-n-propylzinc have been isolated from dioxan or 1,2-dimethoxyethane solution as stable solvates;[28,29] the removal of solvent molecules was reported to occur during high-vacuum sublimation,[30] but this has not been confirmed.[29] The ether solvate molecules are readily displaced by stronger bases, and the 1:1 pyridine addition compounds of heptafluoro-n-propylzinc iodide and bisheptafluoro-n-propylzinc are formed from the 1,2-dimethoxyethane solvates of these substances in this

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[25] Pierce, Meiner, and McBee, *J. Amer. Chem. Soc.*, 1953, **75**, 2516.

[26] McBee, Meiner, and Roberts, *Proc. Indiana Acad. Sci.*, 1954, **64**, 112; *Chem. Abs.*, 1956, **50**, 5546*h*.

[27] McBee, Roberts, and Meiner, *J. Amer. Chem. Soc.*, 1957, **79**, 335.

[28] Miller, Bergman, and Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 4159.

[29] Miller and Bergman, Abstracts of Papers, 126th Meeting of the American Chemical Society, 1954, p. 35M.

[30] Haszeldine and Walachewski, *J.*, 1953, 3607.

manner. Zinc alkyls form complexes of the type $MZnR_3$ ($M = Na, Li; R = C_2H_5$), but no complexes have been described with amines or ethers. On the other hand, zinc halides form complexes with these donors.[31] Thus, the zinc atom in perfluoroalkylzinc compounds acquires some of the properties of that atom in zinc halides because of the presence of the perfluoroalkyl groups. Attempts to convert perfluoroalkylzinc iodide into bisperfluoroalkylzinc by heat led to decomposition. The major product is hexafluoropropene which presumably arises from the reaction:

$$C_3F_7ZnI \rightarrow ZnIF + C_3F_6$$

small amounts of bisheptafluoro-n-propylzinc are also formed.[30,32] There is no indication that the equilibrium

$$2C_3F_7ZnI \rightleftharpoons (C_3F_7)_2Zn + ZnI_2$$

exists in dioxan solution. The yield of heptafluoro-n-propylzinc iodide is reported to be temperature-sensitive,[30] but other investigations have shown that dioxan solutions of this compound are stable at reflux temperatures for long periods.[28]

The chemical reactivity of heptafluoro-n-propylzinc iodide apparently lies between that of the very reactive perfluoroalkylmagnesium halides and the relatively unreactive perfluoroalkylmercury compounds. Neither heptafluoro-n-propylzinc iodide in dioxan solution nor its dioxan adduct reacts with carbonyl compounds, but aldehydes, ketones, and acid anhydrides containing enolisable hydrogen atoms liberate heptafluoro-n-propane with the formation of condensation products.[28] Acid chlorides and perfluoro-acid chlorides yield the expected ketone.[29,30] Attempts to carry out typical organometallic syntheses in dioxan solution were unsuccessful.[28,29] Oxygen had little effect on heptafluoro-n-propylzinc iodide over prolonged periods, and water decomposed it only slowly.

Mercury. Perfluoroalkylmercuric iodides can be prepared by the action of perfluoroalkyl iodides on mercury under the influence of ultraviolet radiation,[33-35] and the bisperfluoroalkylmercury compounds are best prepared by the reaction of perfluoroalkyl iodides with cadmium amalgam.[33,34] Bisheptafluoro-n-propylmercury could not be prepared by this method;[36] only an oil, consisting of a mixture of fluorocarbons and a substance with a mercurial odour, was obtained (cf. p. 247). Fluoro-olefins, either partially or fully fluorinated, react with mercuric fluoride to form fluoroalkyl- or perfluoroalkyl-mercury derivatives; bispentafluoroethylmercury can be prepared in good yields from tetrafluoroethylene in this

[31] Gmelin's, "Handbuch der Anorganischer Chemie: Zinc", Verlag Chemie, G.m.b.H., Weinheim, 1952, pp. 875, 877.

[32] Miller, Fainberg, and Bergman, Abstracts of Papers, 122nd Meeting of the American Chemical Society, 1952, p. 14K.

[33] Banus, Emeléus, and Haszeldine, *J.*, 1950, 3041.

[34] Emeléus and Haszeldine, *J.*, 1949, 2953.

[35] Emeléus and Lagowski, *J.*, 1959, 1497.

[36] Lagowski, Ph.D. Diss., Cambridge, 1949.

manner.[37] Conversion of perfluoroalkylmercuric iodides into other perfluoroalkylmercuric salts can be effected by treatment with moist silver oxide and subsequent neutralisation of the resulting perfluoroalkylmercuric hydroxide with an appropriate acid.

Bisperfluoroalkylmercury derivatives and perfluoroalkylmercuric halides react with excess of halogen to give quantitative yields of perfluoroalkyl halides and, presumably, mercuric halides; these reactions are similar to those of dialkylmercury compounds. There is no indication that a reaction occurs between bispentafluoroethylmercury and cyanogen under the influence of ultraviolet radiation except that the latter is polymerised to paracyanogen.[38] This is to be contrasted with the formation of phenylmercuric thiocyanate from diphenylmercury and thiocyanogen in ether solution.[39] Bistrifluoromethylmercury reacts with mercuric halides to yield trifluoromethylmercuric halides; the reaction occurs readily at the melting point of the mercurial, but in the presence of a solvent, *e.g.*, acetone, trifluoromethane is liberated.

The reaction of bisperfluoroalkylmercury derivatives with metal or metalloid halides does not yield the perfluoroalkyl derivatives expected by analogy with the corresponding alkylmercury compounds. Only decomposition products arising from the mercurial, *i.e.*, mercury, silicon tetrafluoride, and carbon dioxide (the last two presumably arise from the decomposition of trifluoromethyl radicals on the walls of the reaction vessel), were obtained on reaction of trifluoromethylmercury derivatives with zinc, magnesium, amalgams of either of these metals,[34] aluminium halides,[40] or the halides of arsenic and antimony.[36] The principal reaction of trifluoromethylmercury derivatives at high temperatures appears to be their decomposition, but no fluorocarbons are formed.[34] In contrast to these results, hydrocarbons are formed when dialkylmercury compounds are pyrolysed or irradiated. The photochemical or pyrolytic decomposition products of bistrifluoromethylmercury have been reported to initiate the polymerisation of ethylene, tetrafluoroethylene, and other unsaturated compounds, but no details were given.[41] The higher perfluoroalkylmercurials, however, appear to undergo the expected radical reactions. Bispentafluoroethylmercury, when irradiated in a silica tube, decomposes to give free mercury and perfluoro-n-butane.[33,38] Small amounts of carbon dioxide, silicon tetrafluoride, and hexafluoroethane were formed also; the last two compounds were formed in equivalent amounts as would be expected from the disproportionation of pentafluoroethyl radicals.

Possibly the most intriguing property of bistrifluoromethylmercury is its solubility in water (437 g./l., *i.e.*, 1·3M);[36] aqueous solutions give no

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[37] Krespan, U.S. P. 2,844,614.

[38] Banus, Ph.D. Diss., Cambridge, 1949.

[39] Söderbach, *Annalen*, 1919, **419**, 266.

[40] Pugh, unpublished results, University of Cambridge.

[41] Haszeldine. *J.*, 1949, 2856.

indication of the presence of mercuric ions, and the mercurial can be recovered unchanged. On the other hand, dimethylmercury is insoluble in water, as would be expected for a covalent compound.The solubility of trifluoromethylmercuric iodide (61·4 g./l., *i.e.*, 0·16M), although lower than that of bistrifluoromethylmercury, is greater than that of methylmercuric iodide (1×10^{-3}M).[42] Aqueous solutions of trifluoromethylmercuric salts conduct a current, but the slight conductivity of aqueous solutions of bistrifluoromethylmercury is wholly unexpected.[34] If the relative electronegativity of a trifluoromethyl group is 3·3, the electronic environment of the mercury atom in bistrifluoromethylmercury is similar to that in mercuric chloride, and the properties of these two compounds should be similar. Ionic mercuric salts are extensively hydrolysed in aqueous solution, but the more covalent compounds, *e.g.*, mercuric halides, undergo hydrolysis to a smaller extent. The evidence available indicates that the conductivity of bistrifluoromethylmercury can be attributed to hydrolysis without the displacement of a trifluoromethyl group:[36]

$$Hg(CF_3)_2 + H_2O \rightleftharpoons Hg(CF_3)_2OH_2 \rightleftharpoons Hg(CF_3)_2OH^- + H^+$$

In analogy with the mercuric halides, trifluoromethylmercurials can form addition compounds with halide ions.[35,43] Conductometric titrations of aqueous solutions of bistrifluoromethylmercury, trifluoromethylmercuric iodide, or heptafluoro-n-propylmercuric iodide with potassium halides indicate the existence of ionic species of the types $Hg(CF_3)_2X^-$, $Hg(CF_3)_2X_2^{2-}$, $Hg(R_f)IX^-$, and $Hg(R_f)IX_2^{2-}$ ($X = Cl, Br, I$; $R_f = CF_3, C_3F_7$). The complex ions become less stable in passing from the iodo- to the chloro-type. Anionic complexes of mercury-containing organic radicals other than cyanide have not been reported, although compounds of the type $LiM(C_6H_5)_3$ have been characterised for the other elements of Group II.B The relative stabilities decrease with increasing atomic weight of the central atom; no compound is formed with diphenylmercury.[44] The complex anions containing two moles of iodide per mole of perfluoroalkylmercury derivative, $Hg(CF_3)I_3^{2-}$, $Hg(CF_3)_2I_2^{2-}$, and $Hg(C_3F_7)I_3^{2-}$, were isolated by precipitation from aqueous solution with salts of ethylenediamine–transition metal complexes, *e.g.*, $Cu(en)_2^{2+}$, $Ni(en)_3^{2+}$, $Cd(en)_2^{2+}$, $Zn(en)_3^{2+}$ (en = ethylenediamine).[35]

Group III.—Attempts to prepare perfluoroalkyl derivatives of this group of elements have been unsuccessful, and there are indications that these compounds may be unstable. Only indirect evidence has been obtained for their existence.

Boron. The synthetic methods used to prepare boron alkyls have not been successfully extended to the preparation of the analogous perfluoroalkyl compounds. Bisperfluoroalkylmercury reacts readily with either

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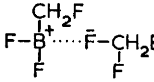
[42] Waugh, Walton, and Laswick, *J. Phys. Chem.*, 1955, **59**, 395.
[43] Emeléus and Lagowski, *Proc. Chem. Soc.*, 1958, 231.
[44] Wittig and Hornberger, *Annalen*, 1952, **557**, 11.

boron halides or alkylboron halides to yield boron *trifluoride* or its derivatives as the major volatile products; under certain conditions a very small amount of a substance which has the properties expected of a compound containing a B–R_f bond is formed.[45] The low-temperature reaction of heptafluoro-n-propyl-lithium with boron chloride or bromide leads to extensive decomposition with the formation of tetrafluoroborate ions.[45] In contrast, the reactions of dialkylmercury compounds or reactive metallic alkyls with boron halides give good yields of the corresponding trialkylboron.[46,47]

Although diborane reacts with non-fluorinated olefins to form a trialkylboron,[48] yet with tetrafluoroethylene, trifluoroethylene, 1,1-difluoroethylene, and vinyl fluoride it yields boron trifluoride, substituted boron fluorides, and triethylboron.[49] The distribution of products is in the order $BF_3 > C_2H_5{\cdot}BF_2 \gg (C_2H_5)_2BF > (C_2H_5)_3B$ with tetrafluoroethylene, but the order changes as the fluorine content of the olefin decreases becoming $C_2H_5{\cdot}BF_2 > (C_2H_5)_2BF \gg BF_3 \sim (C_2H_5)_3B$ in the case of vinyl fluoride.

Only one fluoroalkylboron compound, $F_2B{\cdot}CH_2F$, has been described,[50] and its physical and chemical properties are of interest since they would be those, with suitable modifications, of compounds containing a B–CF_3 bond. Fluoromethylboron difluoride is a liquid between −47° and +7°, has a value of 30·5 for Trouton's constant, and has an observed molecular weight 3·5% higher than that calculated, suggesting that association occurs in the vapour and the liquid phase. Spectral data support this conclusion and indicate that association occurs through the fluorine atom substituted on the alkyl group (structure I). The fact that neither methylboron



$$\mathrm{F{-}\underset{F}{\overset{CH_2F}{\overset{+}{B}}}\cdots\overset{-}{F}{-}\underset{F}{C}H_2B{-}F}$$

(I)

difluoride nor trimethylboron is associated also supports this suggestion. Liquid fluoromethylboron difluoride attacks glass, forming silicon tetrafluoride and boron trifluoride; the formation of the latter can be easily visualised from structure (I). By analogy, the isolation of boron trifluoride or its derivatives from the reaction of boron halides with bisperfluoroalkylmercury suggests that an unstable perfluoroalkylboron compound is formed as an intermediate. Recent data indicate that stable compounds containing B–R_f bonds can be prepared by using reactive perfluoroalykl-metal compounds if the acceptor properties of boron are eliminated or

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[45] Emeléus and Lagowski, unpublished results.
[46] Michaelis, *Annalen*, 1901, **315**, 19.
[47] Krause and Nitsche, *Ber.*, 1921, **54**, 2784.
[48] Hurd, *J. Amer. Chem. Soc.*, 1948, **70**, 2053.
[49] Bastocha, Graham, and Stone, *J. Inorg. Nuclear Chem.*, 1958, **6**, 119.
[50] Goubeau and Rohwedder, *Annalen*, 1957, **604**, 168.

substantially reduced, *e.g.*, by employing stable boron halide addition compounds or *B*-halogenoborazole derivatives.[51]

Aluminium. Perfluoroalkylaluminium derivatives have not been isolated, but the existence of a perfluoroalkylaluminium complex in ether is indicated by studies of the reaction of lithium aluminium hydride with perfluoroalkyl iodides.[52] The products, stoicheiometry, and hydrolytic behaviour of ether solutions observed in the stepwise reaction can be interpreted by assuming the formation of complexes of the type shown in equations (5)—(7) ($R_f = C_3F_7$):

$$R_fI + LiAlH_4 \rightarrow LiAlR_fH_2I + H_2 \quad \ldots \quad (5)$$

$$R_fI + LiAlR_fH_2I \rightarrow LiAlR_fHI_2 + R_fH \quad \ldots \quad (6)$$

$$R_fI + LiAlR_fHI_2 \rightarrow LiAl(R_f)_2I_2 + HI \quad \ldots \quad (7)$$

Equation (5) represents the stoicheiometry observed for trifluoroiodomethane, but solutions containing the complex $LiAl(CF_3)H_2I$ decomposed to a mixture of trifluoromethane and methane on the addition of water. In contrast, solutions of $LiAl(C_3F_7)HI_2$ yielded heptafluoropropane quantitatively under the same conditions. Attempts to isolate the complex $LiAl(C_3F_7)H_2I$ led to extensive decomposition forming aluminium, lithium iodide, hydrogen, and probably heptafluoropropane.

Group IV.—With the exception of carbon, more is known about the fluoroalkyl derivatives of silicon than of any other element in this group. Attempts to prepare trifluoromethyl derivatives of germanium by reaction of sodium germanyl derivatives with trifluoroiodomethane were unsuccessful; trifluoromethane was the only volatile product obtained.[53] Trimethyl(trifluoromethyl)tin has recently been obtained by reaction of trifluoroiodomethane and hexamethylditin.[54]

Silanes substituted with fluoroalkyl groups can be prepared by the interaction of (*a*) a reactive fluoroalkyl-metal compound (*e.g.*, LiR_f, R_fMgI) and silicon tetrahalides, (*b*) a fluoroalkyl halide and elemental silicon, (*c*) silanes and unsaturated compounds containing fluorine, or (*d*) fluoroalkyl iodides or bromides and an alkene-silicon compound.[55] It should be noted that fully fluorinated alkylsilanes cannot be prepared by methods *c* and *d* and that all four methods can be used in preparing partially fluorinated silanes. The use of a perfluoroalkyl Grignard or lithium reagent for the preparation of perfluoroalkyl derivatives of silicon has been described in only one instance,[11] although its use has been reported without experimental details.[13,17] Partially fluorinated alkylsilanes have also been prepared by this method.[56,57] Perfluoroalkyl halides when passed

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[51] Lagowski and Thompson, *Proc. Chem Soc.*, 1959, 301.

[52] Haupschein, Suggeomo, and Stokes, *J. Amer. Chem. Soc.*, 1956, **78**, 680.

[53] Cullen, Ph.D. Diss., Cambridge, 1958.

[54] Clark and Cullen, personal communication.

[55] Geyer, Haszeldine, Leedham, and Marklow, *J.*, 1957, 4472.

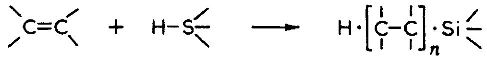
[56] Pierce, McBee, and Cline, *J. Amer. Chem. Soc.*, 1953, **75**, 5618.

[57] McBee, Roberts, Judd, and Chao, *J. Amer. Chem. Soc.*, 1955, **77**, 1292.

over a heated mixture of silicon and copper metal yield bisperfluoroalkylsilicon dihalides (eqn. 8; X = Cl, Br, I; $R_f = CF_3$, C_2F_5, C_3F_7);[58] by altering the conditions trifluoro(trifluoromethyl)silane and bromodifluoro(trifluoromethyl)silane were obtained.[59]

$$2R_fX + Si \rightarrow (R_f)_2SiX_2 \quad \ldots\ldots\ldots\ldots \quad (8)$$

Method *c* has been the most fruitful for the preparation of partially fluorinated alkylsilanes. The reaction of a silane with a fluoro-olefin under the influence of ultraviolet radiation or in the presence of organic peroxides yields partially fluorinated alkylsilanes (eqn. 9). Partially or fully fluorinated olefins as well as halogeno- and alkyl-silanes have been employed in this reaction.[55,60–67] In the reactions of tetrafluoroethylene with silanes, the length of the partially fluorinated alkyl chains attached to the silicon atom is determined by the ratio of the reactants. If the silane contains two hydrogen atoms, the products of the reaction with tetrafluoroethylene include substances which can be represented as $H\cdot[CF_2\cdot CF_2]_x\cdot SiR_2\cdot[CF_2\cdot CF_2\cdot]_y\cdot H$ arising from secondary reactions.[60]


. . . . . (9)

The Si–H bond in silanes containing highly fluorinated alkyl groups (*e.g.*, $R_2SiH\cdot[CF_2\cdot CF_2]_n\cdot H$) is not attacked by water, but these compounds are immediately cleaved by bases with the formation of hydrogen and the partially fluorinated alkanes, $H\cdot[CF_2\cdot CF_2]_n\cdot H$.[60] This behaviour parallels that of silanes substituted with highly electronegative groups.[68] Fluoroalkylsilicon trihalides hydrolyse to yield polysiloxanes of the type $(R_fSiO_{1\cdot5})_n$; the rate of hydrolysis decreases as the length of the fluoroalkyl chain increases.[61] Alkyl(fluoroalkyl)silicon dihalides, exemplified by $CHF_2\cdot CF_2\cdot Si(CH_3)Cl_2$, undergo hydrolysis to form fluorine-containing silicones, $[-Si\cdot(CH_3)\cdot(CF_2\cdot CF_2H)\cdot O-]_n$, which are high-boiling oils, stable to water but hydrolysed by base yielding fluorocarbons of the type $HCF_2\cdot CF_2H$.

Group V.—The reaction of a Group V element (M = P, As, Sb) with CF_3I under pressure produces a mixture containing $(CF_3)_3M$,

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[58] Passino and Rubin, U.S. P. 2,686,194; *Chem. Abs.*, 1955, **49**, 1363*h*.
[59] Simons and Dunlap, U.S. P. 2,651,651; *Chem. Abs.*, 1954, **48**, 10056*a*.
[60] Geyer and Haszeldine, *J.*, 1957, 1038.
[61] Haszeldine and Marklow, *J.*, 1956, 962.
[62] Hazeldine and Marklow, *Nature*, 1956, **178**, 808.
[63] McBee, Roberts, and Puerckhauere, *J. Amer. Chem. Soc.*, 1957, **79**, 2329.
[64] Geyer and Haszeldine, *J.*, 1957, 3925.
[65] Frost, U.S. P. 2,596,967; *Chem. Abs.*, 1953, **47**, 4365*h*.
[66] Wagner, U.S. P. 2,637,738; *Chem. Abs.*, 1954, **48**, 8254*b*.
[67] Tarrant, Dyckes, Dunmire, and Butler, *J. Amer. Chem. Soc.*, 1957, **79**, 6536.
[68] Hurd, "Chemistry of the Hydrides", John Wiley and Sons, New York, 1953, p. 58.

$(CF_3)_2MI$, $CF_3{\cdot}MI_2$, and iodides of the element.[69–72] Reaction occurs in the same temperature range, 200—220°, for phosphorus and arsenic, but antimony reacts at a substantially lower temperature, 165—175°. The lower limit in the optimum range gives a larger percentage of the iodo-compound, and the addition of metal tri-iodides also increases the proportion of these compounds. There are indications that a series of equilibria (10—12) is established during the reaction:

$$2(CF_3)_2MI \rightleftharpoons (CF_3)_3M + CF_3{\cdot}MI_2 \qquad (10)$$

$$2(CF_3)MI_2 \rightleftharpoons (CF_3)_2MI + MI_3 \qquad (11)$$

$$(CF_3)_3M + MI_3 \rightleftharpoons (CF_3)_2MI,\ CF_3{\cdot}MI_2,\ CF_3I,\ \text{etc.} \qquad (12)$$

If the temperature of the reaction is allowed to rise above the optimum, decomposition occurs, producing fluorocarbons as well as the Group V metal fluorides. Some anomalies have been observed in the preparation of higher perfluoroalkyl-phosphorus and -arsenic compounds, although the preparation of $(C_2F_5)_3As$ by this method appears to have been successful.[73] The interaction of C_3F_7I and phosphorus produced only two iodoheptafluoro-n-propylphosphorus compounds, and an attempt to prepare heptafluoro-n-propylarsenic compounds gave only fluorocarbons.[74]

The molecular structures of compounds of the type $(CF_3)_3M$ (M = P, As, Sb) have been determined by electron-diffraction methods,[75] and the data indicate that the CMC angles are normal but that C–M bonds are systematically longer for the trifluoromethyl compounds than for the corresponding methyl derivatives.

Phosphorus. The equilibrium mixture of tristrifluoromethylphosphine, di-iodotrifluoromethylphosphine, and iodobistrifluoromethylphosphine obtained by reaction of trifluoroiodomethane with phosphorus is the starting point for all other trifluoromethylphosphorus compounds which have been prepared. Iodoperfluoroalkylphosphorus compounds can be converted into the corresponding cyano- or chloro- (and presumably bromo-) derivatives by using the appropriate silver salt (eqns. 13, 14; $R_f = CF_3$,[69] C_3F_7[74]); fluorobistrifluoromethylphosphine has been prepared by the action of antimony trifluoride on the corresponding iodo-compound.[76]

$$(R_f)_2PI + AgX \rightarrow (R_f)_2PX + AgI \qquad (13)$$

$$R_fPI_2 + 2AgX \rightarrow R_fPX_2 + 2AgI \qquad (14)$$

Phosphorus acids containing perfluoroalkyl groups can be prepared by the hydrolysis of various halogenoperfluoroalkylphosphorus compounds

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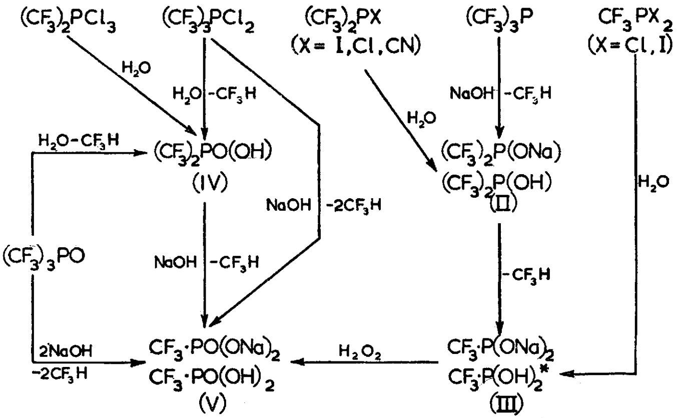
[69] Bennett, Emeléus, and Haszeldine, *J.*, 1953, 1565.
[70] Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2552.
[71] Dale, Emeléus, Haszeldine, and Moss, *J.*, 1957, 3708.
[72] Burg, Mahler, Bilbo, Haber, and Herring, *J. Amer. Chem. Soc.*, 1957, **79**, 247.
[73] Ayscough and Emeléus, *J.*, 1954, 3381.
[74] Emeléus and Smith, *J.*, 1959, 375.
[75] Bowen, *Trans. Faraday Soc.*, 1954, **50**, 463.
[76] Burg and Brendel, *J. Amer. Chem. Soc.*, 1958, **80**, 3198.



*Corresponding C_3F_7 acids known.[74]

FIG. 2 *Hydrolysis of perfluoroalkylphosphorus compounds to form phosphorus acids containing perfluoroalkyl groups.*[6,77,78]

(Fig. 2). The fact that these acids are all stronger than their alkyl counterparts can be attributed to the strong inductive effect of the perfluoroalkyl groups present (Table 7). As would be expected, trifluoromethylphosphonic acid is a stronger acid than trichloromethylphosphonic acid.

TABLE 7. *Dissociation constants of substituted phosphorus acids.*

Acid	pK_1	pK_2	Ref.	Acid	pK_1	pK_2	Ref.
$CF_3{\cdot}PO(OH)_2$	1·16	3·95	77	$Cl_3C{\cdot}PO(OH)_2$	1·63	4·81	[b]
$(CF_3)_2PO(OH)$	1·0	—	6	$Me_2PO(OH)$	3·08	—	[a]
$(C_3F_7)PO(OH)_2$	0·9	3·96	74	H_3PO_3	1·41	6·7	[c]
$CF_3{\cdot}P(OH)_2$	1·01	—	6	H_3PO_4	1·97	6·82	[d]
$Me{\cdot}PO(OH)_2$	2·38	7·74	[a]				

[a] Crofts and Kosolapoff, *J. Amer. Chem. Soc.*, 1953, **75**, 3379. [b] Crofts and Kosolapoff, *J. Amer. Chem. Soc.*, 1953, **75**, 5738. [c] Yost and Russell, "Systematic Inorganic Chemistry", Prentice-Hall, New York, 1944, p. 228. [d] Kumler and Eiler, *J. Amer. Chem. Soc.*, 1943, **65**, 2355.

The loss of one equivalent of trifluoromethane during the neutral aqueous hydrolysis of halogenobistrifluoromethylphosphines indicates the instability of bistrifluoromethylphosphinous acid (II), and the latter has not been well characterised.[77,78] This behaviour is in agreement with the relative instability of the dialkylphosphinous acids (eqn. 15); however they usually yield the corresponding phosphine on hydrolysis.

$$2R_2P{\cdot}OH \rightarrow R_2PH + R_2PO{\cdot}OH \quad \ldots\ldots\ldots \quad (15)$$

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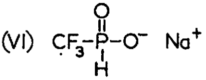
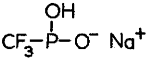
[77] Bennett, Emeléus, and Haszeldine, *J.*, 1954, 3598.
[78] Bennett, Emeléus, and Haszeldine, *J.*, 1954, 3986.

Trifluoromethylphosphonous acid (III) has not been isolated as the free acid since it is volatile in steam at reduced pressure;[77] it behaves as a monobasic acid ($pK = 1{\cdot}01$), liberating trifluoromethane at $pH > 11$. Infrared studies of the mono-potassium and -sodium salts of (III) suggest that the structure is best represented as the keto-form (VI) rather than

(VI)

$$CF_3-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-O^-\ Na^+$$


$$CF_3-\overset{\overset{OH}{|}}{P}-O^-\ Na^+$$
(VII)

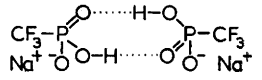
as the enol form (VII). Aqueous solutions of the free acid are most conveniently prepared by distillation of the alkali-metal salts with dilute sulphuric acid. Potassium iodate, dichromate, and permanganate and mercuric chloride (at 60°) are slowly reduced by aqueous solutions of (III), but molecular iodine resists reduction.[6] Aqueous solutions evolve trifluoromethane and form phosphorous acid at 140°; a side reaction (8% of the total reaction), which is dependent on the acid concentration, produces trifluoromethylphosphonic acid (V) and trifluoromethylphosphine. This reaction is similar to the decomposition of alkylphosphonous acids (eqn. 16), and even phosphorous acid is known to undergo a similar disproportionation (eqn. 17).

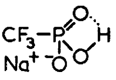
$$3RP(OH)_2 \rightarrow RPH_2 + 2RPO{\cdot}(OH)_2 \quad . \ . \ . \ . \quad (16)$$

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3 \quad . \ . \ . \ . \ . \ . \ . \ . \quad (17)$$

Bistrifluoromethylphosphinic acid (IV) is also steam-volatile and aqueous solutions of it have been prepared in a manner analogous to that used for the preparation of trifluoromethylphosphonous acid.[6] The pure acid can be distilled from the silver salt by heating the latter with concentrated sulphuric acid. It is a strong monobasic acid, in contrast to the very weak dimethylphosphinic acid, and liberates trifluoromethane at $pH > 8{\cdot}7$.

Trifluoromethylphosphonic acid (V), the most stable of the trifluoromethylphosphorus acids which have been studied, is dibasic and gives a sparingly soluble barium salt.[77] Infrared absorption studies on the mono-sodium and -potassium salts indicate the presence of strong hydrogen bonds which could be either inter- (VIII) or intra-molecular (IX) in nature.

(VIII)




(IX)

Heptafluoro-n-propylphosphonic acid has been prepared by a similar method and, according to the value of its first ionisation constant, it appears to be slightly stronger than trifluoromethylphosphonic acid;[74] however, the reverse effect is observed in the acidity of primary and secondary perfluoroalkyl alcohols and has been attributed to the replacement of a fluorine atom with a less electronegative perfluoroalkyl group.[79]

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[79] Haszeldine, *J.*, 1953, 1257.

The precision with which ionisation constants of acids can be determined decreases as the acid strengths increase, and this could account for the apparent anomaly in the values observed for the first ionisation constant. On the other hand, the values of pK_2 (given to a higher degree of precision) for trifluoromethyl- and heptafluoro-n-propyl-phosphonic acids indicate that the latter is slightly weaker than the former, which is in agreement with the data for the ionisation of primary and secondary alcohols.

Bistrifluoromethylphosphinic acid has been shown to be stronger than trifluoromethylphosphonic acid by conductivity measurements in anhydrous acetic acid.[6] This is the order which would be expected from a consideration of the inductive effect of a second trifluoromethyl group. The slight increase in acid strength in going from trifluoromethylphosphonic acid to trifluoromethylphosphonous acid parallels the increased acid strength of phosphorous acid compared with phosphoric acid.

Bistrifluoromethylphosphine[78,80] and trifluoromethylphosphine[78] can be prepared by the reduction of the corresponding iodo-compounds with zinc and hydrochloric acid, by hydrogenation in the presence of Raney nickel, by lithium aluminium hydride, or by mercury and anhydrous hydrogen chloride. Trifluoromethylphosphine has also been obtained by the decomposition of concentrated aqueous solutions of trifluoromethylphosphonous acid;[78] bistrifluoromethylphosphine is prepared by acid hydrolysis of tetrakistrifluoromethyldiphosphine.[78,80] The trifluoromethylpolyphosphines $(CF_3{\cdot}PH)_2$ and $H_2(P{\cdot}CF_3)_3$ have been obtained on hydrolysis of tetrakistrifluoromethyltetraphosphine and pentakistrifluoromethylpentaphosphine, respectively.[81] Although no study of the co-ordinating ability of the trifluoromethylmonophosphines has been reported, there are indications that they do interact with transition metals. Reduction of di-iodotrifluoromethylphosphine with hydrogen in the presence of Raney nickel failed to yield the expected phosphine (or, indeed, any unchanged starting material), although this method has been used to prepare bistrifluoromethylphosphine.[78] The suggestion has been made that compound formation with the nickel could explain the failure of the reduction; the difficulty of removing bistrifluoromethylphosphine from the reduction catalyst has also been attributed to compound formation.[78] This behaviour is consistent with the observation that a trifluoromethyl group has an electronegativity greater than that of chlorine, but less than that of fluorine. The trifluoromethylphosphines should behave in a manner analogous to phosphorus trichloride or trifluoride; both of these phosphorus halides form addition compounds with transition elements, *i.e.*, palladium,[82] platinum,[83,84] and nickel[85,86] (see p. 254).

[80] Burg and Mahler, *J. Amer. Chem. Soc.*, 1957, **79**, 4242.
[81] Mahler and Burg, *J. Amer. Chem. Soc.*, 1958, **80**, 6161.
[82] Fink, *Compt. rend.*, 1892, **115**, 176.
[83] Schützenberger, *Compt. rend.*, 1870, **70**, 1287, 1414.
[84] Chatt and Williams, *J.*, 1951, 3061.
[85] Irvine and Wilkinson, *Science*, 1951, **113**, 742.
[86] Wilkinson, *J. Amer. Chem. Soc.*, 1951, **73**, 559.

The reaction of iodotrifluoromethylphosphine or iodobistrifluoromethylphosphine with mercury gives rise to a series of compounds containing P–P bonds (eqns. 18, 19).[69,81,87] Higher polymers are formed in

$$(CF_3)_2PI \rightarrow (CF_3)_2P{-}P(CF_3)_2 \quad \ldots \quad (18)$$

$$(CF_3)PI_2 \rightarrow (CF_3P)_4 + (CF_3P)_5 \quad \ldots \quad (19)$$

$$(CF_3)_2P{-}P(CF_3)_2 \rightarrow (CF_3P)_4 + (CF_3P)_5 + (CF_3P)_x \quad \ldots \quad (20)$$

addition to the cyclic polymers $(CF_3P)_4$ and $(CF_3P)_5$ when either tetrakistrifluoromethyldiphosphine or bistrifluoromethylphosphine is pyrolysed (eqn. 20).[81,87] Pentakistrifluoromethylpentaphosphine, which is thermally less stable than the corresponding tetramer, decomposes into the tetramer in addition to tetrakistrifluoromethyldiphosphine and tristrifluoromethylphosphine on heating, which suggests that reaction (20) is reversible to some extent. The ultraviolet spectra of the cyclic polymers indicate that the phosphorus lone-pair electrons are delocalised and are supplementing the normal σ-bonding.

Basic hydrolysis of most trifluoromethylphosphorus compounds yields trifluoromethane quantitatively,[78] but those containing P–P bonds give a mixture of trifluoromethane and fluoride ions.[78,81] The formation of fluoride ions in the hydrolysis of trifluoromethylpolyphosphines, exemplified by tetrakistrifluoromethylphosphines,[78] can be explained if the initial step is cleavage of a P–P bond followed by decomposition of the products (eqn. 21). It was shown independently that bistrifluoromethylphosphinous

$$\left.\begin{array}{l} (CF_3)_2P{-}P(CF_3)_2 + H_2O \rightarrow (CF_3)_2PH + (CF_3)_2P{\cdot}OH \\ (CF_3)_2PH + H_2O \rightarrow CF_3H + F^- + CO_2 \\ (CF_3)_2P{\cdot}OH + H_2O \rightarrow 2CF_3H \end{array}\right\} \quad \ldots \quad (21)$$

acid gives only trifluoromethylphosphine, and that bistrifluoromethylphosphine yields a mixture of trifluoromethane and fluoride ion on hydrolysis under similar conditions.[78] Basic hydrolysis of the trifluoromethylphosphorus cyclic polymers can be visualised as an initial opening of the phosphorus ring followed by equal and quantitative conversion of trifluoromethyl groups into trifluoromethylphosphine and trifluoromethylphosphinous acid, which then decompose to fluoride ions and trifluoromethane, respectively.[81] Basic hydrolysis of trifluoromethylpolyphosphine chains appears to occur in such a manner that the second group, either H or OH, substituted on a phosphorus atom is identical with the previously substituted group.

Solutions of the tetramer in fluorocarbon solvents absorb gaseous oxygen in two distinct steps, each corresponding to the addition of one oxygen atom per atom of phosphorus, to yield a substance with the empirical formula $(CF_3{\cdot}PO_2)_x$. The observed induction period suggests a chain reaction, the first step of which is probably the formation of a peroxy-phosphorus compound. The oxidation product, which appears to be

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[87] Mahler and Burg, *J. Amer. Chem. Soc.*, 1957, **79**, 251.

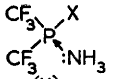
a mixture of polymeric anhydrides of trifluoromethylphosphonic acid, is slowly converted into this acid on reaction with water; titration curves of incompletely hydrolysed aqueous solutions of the polymeric oxide suggest the presence of the strong acid $CF_3\cdot P(O)(OH)\cdot P(O)(OH)\cdot CF_3$.[81]

Polymers containing B–P bonds and trifluoromethyl groups have been prepared by the reaction of diborane with either fluorobistrifluoromethylphosphine or bistrifluoromethylphosphine.[76] The major product is the air-stable trimer $[(CF_3)_2PBH_2]_3$, but traces of the tetramer $[(CF_3)_2PBH_2]_4$ were also formed in the reaction with bistrifluoromethylphosphine. Dimethyl ether not only catalyses the reaction of the latter compound with diborane, but it also attacks the phosphine to yield methylbistrifluoromethylphosphine. There was no evidence for the existence of the borine adducts $(CF_3)_3P,BH_3$ or $(CF_3)_2PH,BH_3$, but there were indications that a very unstable $(CF_3)_2PF,BH_3$ adduct was formed. The phosphorus atom in $(CF_3)_2PF,BH_3$ has an electronic environment similar to that in the unstable adduct BH_3,PF_3[88] if the electronegativity of a trifluoromethyl group is taken as 3·3. It may be significant that, although phosphorus halides (the donor properties of the phosphorus atoms have been essentially removed) do not form adducts with boron halides (which should be better acceptors than borine), yet unstable addition compounds of borine are formed with both phosphorus trifluoride and fluorobistrifluoromethylphosphine. It has been suggested that the inertness of the hydrogen atoms in the polymer $[(CH_3)_2P\cdot BH_2]_2$ towards protonic reagents may be due to weak multiple π-bonding in which the B–H electrons enter the phosphorus *d* levels, thus lowering the electronic density about the hydrogen atoms.[89,90] Electronic drift of this type should occur less easily when both boron and phosphorus carry highly electronegative groups.

Halogenobisperfluorophosphines react with ammonia and primary or secondary amines to yield aminotrifluoromethylphosphines and hydrogen halides (eqn. 22).[74,91,92] Only one hydrogen atom in ammonia could be

$$(R_f)_2PX + 2R_2NH \rightarrow (R_f)_2P\cdot NR_2 + R_2NH,HX \quad . \; . \; . \; . \; . \quad (22)$$

replaced by a $\cdot P(CF_3)_2$ group, which is consistent with the suggestion that reaction occurs *via* the intermediate (X) with subsequent elimination of



(X)

hydrogen halide.[92] The electron-withdrawing effect of the trifluoromethyl groups, which facilitates the formation of (X), decreases the availability

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[88] Parry and Bissot, *J. Amer. Chem. Soc.*, 1956, **78**, 1524.
[89] Burg and Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 3872.
[90] Graham and Stone, *J. Inorg. Nuclear Chem.*, 1956, **3**, 164.
[91] Harris, *J.*, 1958, 512.
[92] Harris, *Proc. Chem. Soc.*, 1957, 118.

of the lone-pair electrons on the nitrogen atom in $(CF_3)_2P{\cdot}NH_2$ for donation to another molecule of $(CF_3)_2PX$. These factors should also make the hydrogen atoms in aminobistrifluoromethylphosphine more acidic than those in the methyl analogue. The loss of basic nitrogen properties is exemplified by the fact that aminobistrifluoromethylphosphine does not form a quaternary salt with methyl iodide; attempts to prepare the silver and sodium salts were unsuccessful, although pyridine solutions of aminobistrifluoromethylphosphine do conduct a current more readily than the pure solvent. The high values of Trouton's constants for aminobistrifluoromethylphosphine and methylaminobistrifluoromethylphosphine suggest that association occurs in the liquid phase, possibly as hydrogen bonds: $-F \cdots H-N-$.[92] The aminoperfluoroalkylphosphines are unstable to hydrolytic agents as well as to hydrogen chloride and chlorine; fission of the P–N bond occurs in each case.

Tristrifluoromethylphosphine is an inflammable liquid which is stable to water and aqueous hydrochloric acid, but it reacts with aqueous alkali yielding trifluoromethane by a series of reactions involving bistrifluoromethylphosphinous acid (II) and trifluoromethylphosphonous acid (III) as intermediates (see Fig. 2).[78] A mixture of iodotrifluoromethylphosphines, phosphorus iodides, and trifluoroiodomethane is formed when tristrifluoromethylphosphine reacts with iodine, but tristrifluoromethylphosphine readily adds chlorine to form dichlorotristrifluoromethylphosphorane, which in turn yields trifluoromethylphosphonic acids on hydrolysis. Tristrifluoromethylphosphine oxide was not obtained by atmospheric oxidation of the phosphine but was successfully prepared by using anhydrous oxalic acid.[93] In contrast to the alkyl- or aryl-phosphine oxides, which form stable hydrates, tristrifluoromethylphosphine oxide and dichlorotristrifluoromethylphosphorane react with water to form bistrifluoromethylphosphinic acid and trifluoromethane.[6]

The electrolytic behaviour of dichlorotristrifluoromethylphosphorane in acetonitrile is similar to that of phosphorus pentachloride. Acetonitrile solutions of dichlorotristrifluoromethylphosphorane exhibit a greater molar conductance at infinite dilution than solutions of either phosphorus trichloride or tribromide.[94] It has been suggested that this conductance behaviour is due to an equilibrium (23) which is analogous to that found

$$2P(CF_3)_3Cl_2 \rightleftharpoons P(CF_3)_3Cl^+ + P(CF_3)_3Cl_3^- \quad \ldots\ldots\ldots \quad (23)$$

in similar solutions of other phosphorus pentahalides.[95,96] Trichlorobistrifluoromethylphosphorane is a non-conductor under these conditions, and infrared data suggest that this compound is a trigonal bipyramid with trifluoromethyl groups at the apices. If the mechanism of ionization involves the apical bond, trichlorobistrifluoromethylphosphorane would

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[93] Paul, *J.*, 1955, 574.
[94] Emeléus and Harris, *J.*, 1959, 1494.
[95] Payne, *J.*, 1953, 1052.
[96] Harris and Payne, *J.*, 1956, 4617.

not be expected to conduct, since the trifluoromethide ion has not been observed in any system.

Mixed methyltrifluoromethylphosphines can be prepared by the action of methyl iodide on tristrifluoromethylphosphine at 240°; dimethyltrifluoromethylphosphine reacts rapidly with additional methyl iodide to form the quaternary phosphonium iodide.[97] The reaction is reversible to some extent, since trimethylphosphine reacts with trifluoroiodomethane to form dimethyltrifluoromethylphosphine, but neither the latter compound nor methylbistrifluoromethylphosphine reacts further with trifluoroiodomethane. The reaction with trifluoroiodomethane has been considered to involve the formation of an unstable phosphonium salt of a trifluoromethide ion, which then rapidly rearranges to a more stable phosphonium salt:

$$(CH_3)_3P + ICF_3 \longrightarrow (CH_3)_3P\!:\!\overset{\delta+}{I}-\overset{\delta-}{C}F_3 \longrightarrow [(CH_3)_3PI]^+CF_3^- \longrightarrow (CH_3)_3PCF_3^+\,I^- \qquad (24)$$

The mixed methyltrifluoromethylphosphines yield trifluoromethane quantitatively on basic hydrolysis, and the rate of hydrolysis increases as the number of trifluoromethyl groups attached to the phosphorus atom increases. This is consistent with the hypothesis that the hydrolysis proceeds *via* a nucleophilic attack on the phosphorus atom, since the basicity of the phosphine should decrease with an increase in the number of trifluoromethyl groups present. Apparently the introduction of two or more trifluoromethyl groups into the phosphine is sufficient to prevent quaternary salt formation. No reaction was observed between methyl iodide and either tristrifluoromethylphosphine or methylbistrifluoromethylphosphine, but dimethyltrifluoromethylphosphine reacted to form trimethyltrifluoromethylphosphonium iodide.

The tervalent phosphorus compounds PX_3 (X is any group) can form co-ordination compounds with electron-acceptor molecules which have filled, or partially filled, *d* orbitals. If the *d* orbitals of the acceptor are filled, the stability of the compound is governed mainly by the basicity of the tervalent phosphorus compound. When the phosphorus atom carries strongly electronegative groups, as, for example, in phosphorus trifluoride or trichloride, either no or very unstable addition compounds are formed with strong electron-acceptors like boron trifluoride.[84, 98–100] If quaternary salt formation is taken as a rough guide to the basicity of the phosphorus atoms in different trifluoromethyl compounds, only dimethyltrifluoromethylphosphine will form complexes with electron acceptors which have no electrons in their *d* orbitals. This suggestion is supported by the isolation of the boron trifluoride addition compound of dimethyltrifluoromethyl-

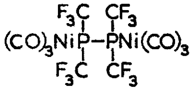
[97] Haszeldine and West, *J.*, 1956, 3631.
[98] Chatt, *Nature*, 1950, **165**, 637.
[99] Chatt, *J.*, 1949, 3340.
[100] Baumgarten and Brune, *Ber.*, 1947, **80**, 517.

phosphine (m.p. −9°) and the failure to isolate similar compounds of methylbistrifluoromethylphosphine or tristrifluoromethylphosphine.[101]

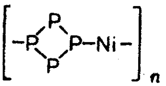
If the acceptor has available *d* electrons, the bond formed has two components, the normal σ bond formed by donation of the lone-pair electrons and the so-called π component formed by back-donation of the acceptor's *d* electrons to vacant *d* orbitals of the phosphorus atom.[98] As the electronegativity of the groups attached to phosphorus increases, the availability of the phosphorus lone pair of electrons for σ-bond formation will decrease, but this will be partially compensated by a strengthening of the π component. The stability of complexes of tervalent phosphorus compounds is not greatly affected by the electronegativity of the substituents on the phosphorus atom, and phosphorus halides as well as alkylphosphines form stable addition compounds with transition metals. Thus, tristrifluoromethylphosphine reacts with nickel carbonyl to form $(CF_3)_3P{\cdot}Ni(CO)_3$ and $[(CF_3)_3P]_2Ni(CO)_2$[102,103] in a manner analogous to the replacement of carbon monoxide from nickel carbonyl by phosphorus trihalides.[85,104] Direct reaction with phosphorus trifluoride or tristrifluoromethylphosphine does not replace all of the carbon monoxide from nickel carbonyl; with tristrifluoromethylphosphine only two carbon monoxide molecules could be replaced.

Trifluoromethylpolyphosphines also react with nickel carbonyl.[102] The compound obtained from the reaction of tetrakistrifluoromethyldiphosphine with nickel carbonyl has been formulated as (XI). The reaction with tetrakistrifluoromethyltetracyclophosphine yields a mixture containing compounds of the type $(CF_3)_4[Ni(CO)_3]_n$ ($n = 1, 2, 3$) and

(XI)



$$(CO)_3Ni\overset{F_3C}{\underset{F_3C}{P}}-\overset{CF_3}{\underset{CF_3}{P}}Ni(CO)_3$$



(XII)

chains of the type (XII) with terminal $Ni(CO)_3$ groups and $Ni(CO)_2$ units cross-linking the chains through phosphorus.

The formation of platinous chloride co-ordination compounds with dimethyltrifluoromethylphosphine and methylbistrifluoromethylphosphine[101] is consistent with the formation of similar compounds with phosphorus trichloride[83] and alkylphosphines.[105,106] The mixed methyltrifluoromethylphosphines can thus be treated as mixed halogenomethylphosphines with respect to the electronic environment on the phosphorus atom. It is surprising that tristrifluoromethylphosphine did not form co-ordination compounds with platinous chloride under the same conditions

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[101] Begg and Clark, Abstracts of the International Conference on Co-ordination Chemistry, London, 1959, Abstract No. 62.

[102] Burg and Mahler, *J. Amer. Chem. Soc.*, 1958, **80**, 2334.

[103] Emeléus and Smith, *J.*, 1958, 527.

[104] Wilkinson, *J. Amer. Chem. Soc.*, 1951, **73**, 5501.

[105] Cahours and Gal, *Compt. rend.*, 1870, **70**, 1380; **71**, 208.

[106] Klason and Wanselin, *J. prakt. Chem.*, 1903, **67**, 41.

since both phosphorus trichloride and trifluoride[84] form stable compounds and since the electronegativity effect in tristrifluoromethylphosphine should be intermediate between those of phosphorus trifluoride and trichloride.

Arsenic. The reactions and chemical properties of trifluoromethylarsenic compounds very closely parallel those of the corresponding phosphorus compounds. Halogenotrifluoromethylarsines can be prepared by the action of an appropriate silver salt on the iodotrifluoromethylarsines or by the reaction of tristrifluoromethylarsine with halogens.[107] In the latter reaction only chlorine gave a quinquevalent arsenic compound, $(CF_3)_3AsCl_2$, but by altering the reaction conditions bistrifluoromethylarsenic trichloride was also formed and could be thermally decomposed into chlorobistrifluoromethylarsine and dichlorotrifluoromethylarsine. Only fluorobistrifluoromethylarsine was obtained from the reaction of elemental fluorine with tristrifluoromethylarsine.

Methylbistrifluoromethylarsine and trifluoromethylarsine can be prepared from the corresponding iodoarsines by the action of either lithium aluminium hydride or zinc and hydrochloric acid;[108] the latter reagents gave better yields in each case. Tetrakistrifluoromethyldiarsine was obtained admixed with bistrifluoromethylarsine by using a modification of the lithium aluminium hydride procedure described for the corresponding diphosphine.

Mixed methyltrifluoromethylarsines can be prepared by the action of methylmagnesium iodide on the appropriate iodotrifluoromethylarsine,[108] by the interaction of tristrifluoromethylarsine and methyl iodide,[97,109,110] or by the reaction of trifluoroiodomethane with trimethylarsine.[97,109] Trifluoroiodomethane will replace two methyl groups stepwise from trimethylarsine to yield first dimethyltrifluoromethylarsine and then methylbistrifluoromethylarsine; in contrast, the analogous reaction with trimethylphosphine yields only dimethyltrifluoromethylphosphine. The co-ordinating ability of the mixed methyltrifluoromethylarsines is markedly influenced by the presence of trifluoromethyl groups. Dimethyltrifluoromethylarsine does not form addition compounds with mercuric halides,[111–113] and no reaction occurs between tristrifluoromethylarsine and nickel carbonyl.[114] These results are in accord with the facts that addition compounds of arsenic trihalides with transition metals apparently are not formed and that arsenic trichloride does not displace carbon monoxide from nickel carbonyl.[104] From the data available, it appears that the stability of the complexes formed by transition metals and

[107] Walachewski, *Chem. Ber.*, 1953, **86**, 272.
[108] Emeléus, Haszeldine, and Walachewski, *J.*, 1953, 1552.
[109] Haszeldine and West, *J.*, 1957, 3880.
[110] Emeléus, Haszeldine, and Paul, *J.*, 1954, 881.
[111] Challenger, Higgenbottom, and Ellis, *J.*, 1933, 35.
[112] Challenger and Ellis, *J.*, 1935, 398.
[113] Challenger and Rawlings, *J.*, 1936, 264.
[114] Smith, Ph.D. Diss., Cambridge, 1958.

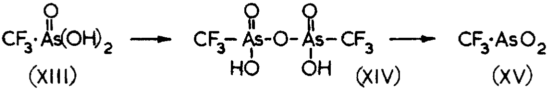
tervalent arsenic compounds, unlike those formed with tervalent phosphorus and antimony compounds, is dependent on the relative electronegativity of the substituents on arsenic.

Dimethyltrifluoromethylarsine forms a quaternary salt with methyl iodide, indicating that the donor properties of the arsenic lone-pair electrons are not completely lost by the introduction of a trifluoromethyl group. This quaternary compound appears to be less stable than the corresponding phosphonium iodide.[97] Bistrifluoromethylarsine or tristrifluoromethylarsine shows no tendency towards complex formation with mercuric chloride[108] or towards quaternary-salt formation with either trifluoroiodomethane or methyl iodide, although methyl iodide apparently forms a 1:1 azeotrope with tristrifluoromethylarsine.[110]

All halogenotrifluoromethylarsines yield trifluoromethane, or a mixture of trifluoromethane and fluoride ions, on alkaline hydrolysis. The latter products are formed in the hydrolysis of bistrifluoromethylarsine, trifluoromethylarsine, and tetrakistrifluoromethyldiarsine, and this behaviour parallels that found in the coresponding phosphorus compounds. Cyanobistrifluoromethylarsine is the only arsine which is hydrolysed by water alone; the products are trifluoromethane and hydrogen cyanide. The instability of the resulting bistrifluoromethylarsinous acid, $(CF_3)_2As{\cdot}OH$, which this behaviour implies, parallels the instability of bistrifluoromethylphosphinous acid, although the latter appears to be more stable than the former. The silver salt of bistrifluoromethylarsinous acid can be isolated, but attempts to liberate the acid in aqueous solution lead to decomposition with the formation of trifluoromethane.[108]

Bistrifluoromethylarsinic acid can be prepared by the oxidation of iodobistrifluoromethylarsine with aqueous hydrogen peroxide.[110] The solid acid has an empirical formula corresponding to $(CF_3)_2AsO{\cdot}OH$, but in aqueous solution it behaves as a dibasic acid; two points of inflection occur in the titration curve corresponding to $(CF_3)_2As(OH)_2{\cdot}ONa$ and $(CF_3)_2As(OH)(ONa)_2$. The acid decomposes rapidly in solutions of pH > 7, liberating trifluoromethane. When heated *in vacuo*, bistrifluoromethylarsenic acid does not form an anhydride quantitatively but undergoes intramolecular dehydration.

Trifluoromethylarsonic acid (XIII) can be prepared from di-iodotrifluoromethylarsine by an extension of the techniques used to prepare the corresponding phosphorus acid.[110] The acid undergoes stepwise dehydration to give the pyro-form (XIV) and the anhydride (XV). The ortho-form (XIII) is a dibasic acid, and one hydrogen atom is almost completely ionised in aqueous solutions ($\alpha = 0{\cdot}96$ at $0{\cdot}01$M). Conductivity measurements in anhydrous acetic acid indicate that bistrifluoromethylarsonic



$$CF_3{\cdot}\overset{\overset{O}{\|}}{As}(OH)_2 \longrightarrow CF_3-\underset{\underset{HO}{|}}{\overset{\overset{O}{\|}}{As}}-O-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{As}}-CF_3 \longrightarrow CF_3{\cdot}AsO_2$$

(XIII) (XIV) (XV)

acid is stronger than trifluoromethylarsonic acid, which is to be expected from the inductive effect of the trifluoromethyl group; both are stronger than their methyl analogues. Attempts to prepare tristrifluoromethyl arsine oxide, the anhydride of the hypothetical acid $(CF_3)_3As(OH)_2$, the acid itself, or its ethyl ester were unsuccessful.

The interactions of halogenobistrifluoromethylarsines with liquid ammonia follow essentially the same course as the corresponding phosphines.[115] Whereas only one $(CF_3)_2P\cdot$ group can be substituted on the nitrogen atom in ammonia, it is possible to replace two hydrogen atoms with $(CF_3)_2As\cdot$ groups. Chlorobistrifluoromethylarsine reacts with gaseous ammonia to give $(CF_3)_2As{\cdot}NH_2$ and $[(CF_3)_2As]_2NH$, but reaction in liquid ammonia yields only the latter. The corresponding compound in the water system, $[(CF_3)_2As]_2O$, was prepared by the reaction of iodobistrifluoromethylarsine with mercuric oxide.[107] The reaction of chlorobistrifluoromethylarsine with primary or secondary amines produces products containing only one $(CF_3)_2As\cdot$ group attached to a nitrogen atom. There are no indications that tristrifluoromethylarsine forms addition compounds with amines, although arsenic trichloride is known to form addition compounds with organic nitrogen bases.[116,117]

Kinetic data on the pyrolysis of trisperfluoroalkylarsines indicate that the primary reaction is the formation of perfluoroalkyl radicals which then combine to form fluorocarbons.[73] Tristrifluoromethylarsine gives hexafluoroethane in 60—90% yield in the temperature range 350—410°; in addition, up to 10% of perfluoropropane and perfluorobutane are formed, but no unsaturated fluorocarbons were detected. The remainder of the volatile products, 20—30%, consists of silicon tetrafluoride and carbon dioxide. If the pyrolyses are conducted in a platinum vessel, the reaction is still of the first order, but the rate constant increases by about 50%, and the composition of the products is greatly changed. A larger proportion of higher fluorocarbons is detected and, although silicon tetrafluoride and carbon dioxide are not formed, the trifluoromethyl radicals appear to decompose to give fluorinated products, as indicated by the formation of appreciable amounts of arsenic trifluoride. Increasing the surface area of the silica reaction tube, by adding powdered silica, not only increases the rate constant for the decomposition of tristrifluoromethylarsine by 25% but also increases the ratio of carbon dioxide plus silicon tetrafluoride to fluorocarbons tenfold. Although the mechanism for the formation of silicon tetrafluoride and carbon dioxide is uncertain, these products probably arise from the attack of trifluoromethyl radicals on silica; such attack is indeed known to occur at lower temperatures than those used for the pyrolysis of tristrifluoromethylarsine. Trispentafluoroethylarsine decomposes to a mixture containing 92% of fluoro-

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[115] Cullen and Emeléus, *J.*, 1959, 372.
[116] Grossman, *Z. phys. Chem.*, 1906, **57**, 545.
[117] Dafert and Melinski, *Ber.*, 1926, **59**, 789.

carbons and only 8% of silicon tetrafluoride and carbon dioxide. It thus appears that pentafluoroethyl radicals are more stable in the presence of silica than trifluoromethyl radicals.

The first-order decomposition of tristrifluoromethylarsine has an activation energy of 57·5 kcal./mole,[73] and, if this is assumed to be the dissociation energy of the C–As bond, it appears that replacement of a hydrogen atom by a fluorine atom has little effect on the bond energy; the decomposition of trimethylarsine has an activation energy of 54·6 kcal./mole. A similar effect has been noted in a comparison of the dissociation energies of the C–H bond in methane and trifluoromethane;[118] both bond energies were determined to be 102 kcal./mole. Trispentaethylarsine decomposes with an activation energy of 48·0 kcal./mole.[73]

Antimony. The halogenotrifluoromethylstibines, although they do undergo many of the reactions of the corresponding phosphines and arsines, are difficult to handle in the laboratory since they readily disproportionate to yield tristrifluoromethylstibine and antimony trihalides as the major products.[71] As is the case with most of the trifluoromethyl compounds of the Group V elements, the trifluoromethylstibines are quantitatively hydrolysed with aqueous base to yield trifluoromethane. In contrast with the hydrolysis of the corresponding arsenic and phosphorus compounds, tetrakistrifluoromethyldistibine gives almost quantitative yields of trifluoromethane and only about 1—2% of fluoride ion. If the reactions postulated for the basic hydrolysis of tetrakistrifluoromethyldi-phosphine and -arsine are correct, the results for the distibine suggest that bistrifluoromethylstibine should yield all of its fluorine as trifluoromethane. Of the halogens, only chlorine gives stable quinquevalent compounds with tristrifluoromethyl-phosphine and -arsine, but both chlorine and bromine react with tristrifluoromethylstibine to form compounds of the type $(CF_3)_3SbX_2$. Only one mixed alkylperfluoroalkylstibine, $Sb(CH_3)_2{\cdot}CF_3$, has been prepared.[97]

The properties of tristrifluoromethylstibine appear to be more similar to those of the antimony trihalides than the alkylstibines. When similarities occur between the alkyl- and perfluoroalkyl-stibines, the same properties can also be observed for antimony trihalides. This is consistent with the value calculated for the electronegativity of the trifluoromethyl group. Antimony trichloride and trifluoride have very slight donor properties, but they can act as acceptors, as exemplified by the formation of the 1:1 adduct of these trihalides with ammonia and organic nitrogen bases.[119,120,121] Tristrifluoromethylstibine forms a 1:1 pyridine adduct,[122,123] whereas the trialkylstibines behave only as weak donors, as is

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[118] Pritchard, Pritchard, Schiff, and Trotman-Dickenson, *Chem. and Ind.*, 1956, 896.
[119] Ruff, *Ber.*, 1906, **39**, 4310.
[120] Ephraim and Weinberg, *Ber.*, 1909, **42**, 4447.
[121] Biltz and Rahlfs, *Z. anorg. Chem.*, 1927, **166**, 351.
[122] Rose, *Compt. rend.*, 1901, **132**, 204.
[123] Vincent, *Z. analyt. Chem.*, 1880, **19**, 479.

illustrated by the formation of quaternary stibonium compounds. Trialkylstibines add sulphur quantitatively to form compounds of the type R_3SbS,[124] but neither tristrifluoromethylstibine nor antimony trihalides does so. Both antimony trichloride[104] and trialkylstibines[125,126] form complexes with transition metals, which presumably are stabilised through $d\pi$–$d\pi$ bonding in a manner similar to that which occurs in the phosphorus–transition metal complexes (cf. p. 254). In view of this, it is surprising that a reaction does not occur between tristrifluoromethylstibine and mercuric chloride or palladium chloride.[71]

Trifluoromethyl compounds of quinquevalent antimony are also more nearly comparable to antimony pentachloride or pentafluoride than to the corresponding alkyl compounds. Both antimony pentachloride[127,128] and tristrifluoromethylantimony dichloride[71] form 1:1 complexes with water and pyridine. A second stable hydrate of tristrifluoromethylantimony dichloride, $Sb(CF_3)_3Cl_2,2H_2O$, can be isolated and has been formulated as $[Sb(CF_3)_3Cl_2OH]^- H_3O^+$ in analogy to the dihydrate of antimony pentafluoride.[129]

Quinquevalent antimony halides can also accept halide ions to form compounds containing ions of the type SbX_6^-. Tristrifluoromethylantimony dichloride reacts with nitrosyl chloride, yielding a compound which has been formulated as $NO^+[(CF_3)_3SbCl_3]^-$, in analogy to the compound formed between antimony pentachloride and nitrosyl chloride.[130] Pyridinium tristrifluoromethylantimonate is readily converted into the corresponding pyridinium trihalogenotristrifluoromethylantimonate:

$$C_5H_5NH^+[(CF_3)_3Sb(OH)_3]^- + 3HX \rightarrow C_5H_5NH^+[(CF_3)_3SbX_3]^- + 3H_2O \quad . \quad (25)$$

In contrast to the weakly acidic properties of alkylantimonic acids, an aqueous solution of $[Sb(CF_3)_3(OH)_3]^-H_3O^+$ [prepared by the action of silver oxide on solutions of tristrifluoromethylantimony dichloride] is a strong acid ($pK = 1{\cdot}85$). The silver salt has been characterised as the benzene addition compound, $Ag(CF_3)_3Sb(OH)_3,C_6H_6$, and salts of larger cations as well as of organic nitrogen bases can be readily isolated. The salts of the heavy metals and of most simple inorganic cations appear to be soluble.

Group VI.—Perfluoroalkyl derivatives of sulphur[131,132] and selenium[133] have been prepared by the direct action of trifluoroiodomethane on the

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[124] Landolt, *Annalen*, 1852, **84**, 44.
[125] Morgan and Yarsley, *J.*, 1925, **127**, 184.
[126] Jensen, *Z. anorg. Chem.*, 1936, **229**, 225.
[127] Anschutz and Evens, *Annalen*, 1887, **239**, 291.
[128] Williams, *J.*, 1876, **30**, 463.
[129] Emeléus and Moss, *Z. anorg. Chem.*, 1955, **282**, 24.
[130] Gall and Mengdehl, *Ber.*, 1927, **60**, 86.
[131] Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2198.
[132] Hauptschein and Grosse, *J. Amer. Chem. Soc.*, 1951, **73**, 5461.
[133] Dale, Emeleus, and Haszeldine, *J.*, 1958, 2939.

free element at high temperatures. The reaction with sulphur yields mainly bistrifluoromethyl disulphide together with small amounts of bistrifluoromethyl tri- and tetra-sulphides, but no monosulphides are formed. In contrast, the reaction with selenium gives bistrifluoromethyl monoselenide and diselenide only. A more convenient method for the preparation of bistrifluoromethyl disulphide is the fluorination of carbon disulphide with iodine pentafluoride;[134] sulphur tetrafluoride as well as small quantities of bistrifluoromethyl trisulphide are also formed in this reaction. The polysulphides have been shown, by a combination of chemical and physical methods,[131,134–136] to contain linear S–S bonds.

The electrolytic fluorination of alkyl sulphur compounds in anhydrous hydrogen fluoride solution has been used to prepare perfluoroalkyl derivatives of sulphur. Complete decomposition with fluorination of the fragments is often observed, and the sulphur-containing fragments generally appear as sulphur hexafluoride or its derivatives.[137] Thus, the electrolytic fluorination of dimethyl sulphide or carbon disulphide yields the extremely inert compounds $CF_3{\cdot}SF_5$, $(CF_3)_2SF_4$, $CF_2(SF_5)_2$, and $CF_2(SF_3)_2$.[138] Trifluoromethylsulphur pentafluoride is the major reaction product; it is also formed in the fluorination (with cobalt trifluoride) of carbon disulphide, methanethiol, and carbonyl sulphide.[139,140] Attempted electrolysis of solutions of dimethyl selenide or carbon diselenide in anhydrous hydrogen fluoride leads to extensive decomposition and deposition of elemental selenium. The electrolytic fluorination of alkanesulphonyl halides yields perfluoroalkanesulphonyl fluorides, which give rise to a series of perfluoroalkanesulphonic acids on hydrolysis.[141,142] The properties and some of the reactions of these perfluoroalkanesulphonic acids have been described.[143]

Sulphur. Of the bistrifluoromethyl polysulphides which have been prepared, the disulphide is the most valuable from a synthetic viewpoint. The chemical inter-relation of bistrifluoromethyl disulphide, bistrifluoromethylthiomercury, trifluoromethanethiol, and trifluoromethylsulphenyl chloride are shown in Fig. 3. Heptafluoro-n-propyl derivatives undergo similar reactions.[144] Bistrifluoromethylthiomercury can also be prepared by the high-temperature reaction of carbon disulphide with mercuric fluoride.[145]

Trifluoromethanesulphenyl chloride reacts with a number of hydrogen-

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[134] Haszeldine and Kidd, *J.*, 1953, 3219.
[135] Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2549.
[136] Bowen, *Trans. Faraday Soc.*, 1954, **50**, 452.
[137] Gramstad and Haszeldine, *J.*, 1956, 173.
[138] Clifford, El-Shamy, Emeléus, and Haszeldine, *J.*, 1953, 2372.
[139] Silvey and Cady, *J. Amer. Chem. Soc.*, 1950, **72**, 3624.
[140] Silvey and Cady, *J. Amer. Chem. Soc.*, 1952, **74**, 5792.
[141] Gramstad and Haszeldine, *J.*, 1957, 2640.
[142] Brice and Trott, U.S. P. 2,732,398; *Chem. Abs.*, 1956, **50**, 13982*h*.
[143] Gramstad and Haszeldine, *J.*, 1957, 4069.
[144] Haszeldine and Kidd, *J.*, 1955, 3871.
[145] Muetterties, U.S. P. 2,729,663; *Chem. Abs.*, 1956, **50**, 11362*c*.

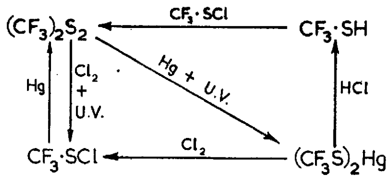

FIG. 3 *Interconversion of trifluoromethyl sulphur compounds.*
U.V. = Ultraviolet irradiation.

containing compounds with the elimination of hydrogen chloride (reactions 26);[134,146] it can be oxidised with chlorine water to trifluoromethanesulphonyl chloride,[147] which is very slowly hydrolyzed by water at room

$$\left.\begin{array}{ll} H_2S + 2CF_3{\cdot}SCl & \rightarrow CF_3{\cdot}S{\cdot}S{\cdot}S{\cdot}CF_3 + 2HCl \\ CF_3{\cdot}SH + CF_3{\cdot}SCl & \rightarrow CF_3{\cdot}S{\cdot}S{\cdot}CF_3 + HCl \\ MH + CF_3{\cdot}SCl & \rightarrow M{\cdot}SCF_3 + HCl\ (M{=}N,\ P,\ As)^{146} \end{array}\right\} \quad . \quad (26)$$

temperature, and more rapidly at higher temperatures, to trifluoromethanesulphonic acid, $CF_3{\cdot}SO_3H$. This acid can also be prepared by the action of aqueous hydrogen peroxide on bistrifluoromethylthiomercury, but attempts to oxidise bistrifluoromethyl disulphide directly led to extensive decomposition.[147] As would be expected, trifluoromethanesulphonic acid is a strong acid in aqueous solution and has many of the properties of the mineral acids; a monohydrate, $H_3O^+CF_3{\cdot}SO_3^-$, has been isolated.[141] The free acid boils considerably lower (162°) than its methyl analogue (165°/8 mm.), thus paralleling the decrease in the boiling point of the trifluoromethyl derivatives with respect to their methyl analogues noted for other compounds. The resistance of trifluoromethanesulphonic acid to alkaline hydrolysis is similar to that of the trifluoromethyl-phosphonic and -arsonic acid. Thus, trifluoromethyl-oxy-acids appear to be most resistant to hydrolysis when the central element exhibits its maximum valency.

Trifluoromethanesulphinic acid, $CF_3{\cdot}SO_2H$, has not been isolated, but its sodium salt, $CF_3{\cdot}SO_2Na,H_2O$, has been prepared by the action of zinc dust on trifluoromethanesulphonyl chloride in air-free water.[148] Basic hydrolysis of trifluoromethanesulphinic acid yields trifluoromethane quantitatively; this is the only trifluoromethyl sulphur derivative which does so, since the other sulphur compounds are either stable to hydrolysis or decompose completely to yield fluoride, sulphide, and carbonate ions. Neither trifluoromethanesulphenic acid nor any of its salts has been isolated,[148] but its formation has been assumed in the initial step of the hydrolysis of its acid chloride, $CF_3{\cdot}SCl$.[131,148]

Trifluoromethanethiol, the sulphur analogue of the unknown trifluoromethanol, is a stable gas at room temperature. It is decomposed slowly by

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[146] Nabi, unpublished results.
[147] Haszeldine and Kidd, *J.*, 1954, 4228.
[148] Haszeldine and Kidd, *J.*, 1953, 2901.

water and rapidly by aqueous base, yielding fluoride, sulphide, and carbonate ions quantitatively. There is some evidence that the decomposition occurs through the formation of thiocarbonyl fluoride and hydrogen fluoride (eqn. 27).[144] This reaction is favoured in ionising solvents and in those which can act as acceptors of hydrogen fluoride, suggesting that the

$$CF_3{\cdot}SH + H_2O \rightarrow H_3O^+ + CF_3{\cdot}S^- \rightarrow CF_2S + F^- \quad . \; . \; . \; . \; . \quad (27)$$

trifluoromethyl sulphide ion is unstable. Alkanethiols are more acidic than their oxygen analogues, and on the basis of electronegativity considerations trifluoromethanethiol should exhibit marked acidic properties in aqueous solution. Thus, trifluoromethanethiol follows the decomposition pattern of compounds containing the $CF_3{\cdot}MH$ portion.

Bistrifluoromethylthiomercury is substantially different from its methyl analogue; it is a low-melting solid (m.p. 37·5°) which is soluble in water and in most organic solvents, and it can be used to introduce trifluoromethanethio groups into molecules containing an acidic halogen (reactions 28—31; M = As, P).[40,144,149] There are indications that this may be a general reaction. Preliminary results[150] indicate that bis(trifluoromethylthio)mercury can form 1:1 addition compounds with halide ions

$$\left.\begin{array}{ll} MX_3 + Hg(S{\cdot}CF_3)_2 & \rightarrow Hg(S{\cdot}CF_3)X + MX_2S{\cdot}CF_3 \\ MX_3 + 2Hg(S{\cdot}CF_3)_2 & \rightarrow 2Hg(S{\cdot}CF_3)X + MX(S{\cdot}CF_3)_2 \\ MX_3 + 3Hg(S{\cdot}CF_3)_2 & \rightarrow 3Hg(S{\cdot}CF_3)X + M(S{\cdot}CF_3)_3 \end{array}\right\} \quad . \quad (28)$$

$$Cl_2C{:}S + 2Hg(S{\cdot}CF_3)_2 \rightarrow (CF_3{\cdot}S)_2C{:}S + 2CF_3{\cdot}S{\cdot}HgCl \quad . \; . \; . \; . \; . \quad (29$$

$$CF_3{\cdot}S{\cdot}C({:}S){\cdot}F + Hg(S{\cdot}CF_3)_2 \rightarrow (CF_3{\cdot}S)_2C{:}S + CF_3{\cdot}S{\cdot}HgF \quad . \; . \; . \; . \; . \; . \quad (30)$$

$$R{\cdot}CO{\cdot}Cl + Hg(S{\cdot}CF_3)_2 \rightarrow R{\cdot}C({:}O){\cdot}S{\cdot}CF_3 + Hg(S{\cdot}CF_3)Cl \quad . \; . \; . \; . \quad (31)$$

in a manner analogous to bisperfluoroalkylmercury compounds; attempts to prepare higher addition compounds gave decomposition products.* Other metallic derivatives containing the trifluoromethylthio-group have been prepared. Bistrifluoromethylthiomercury precipitates trifluoromethylthiosilver from aqueous solutions of silver nitrate, and trifluoromethylthiocopper(I) can be obtained by interaction of bistrifluoromethylthiomercury and copper powder at 100°.[145]

Selenium.[133] Bistrifluoromethyl diselenide, trifluoromethylselenium chloride, trifluoromethaneselenol, and bistrifluoromethylselenomercury undergo reactions analogous to those of the corresponding sulphur compounds (cf. Fig. 3). Their physical and chemical properties show a general resemblance to those of the sulphur compounds, and the differences

[149] Downs, unpublished results.

[150] Jellinek and Lagowski, *J.*, in the press.

* Recent work[150a] indicates that bistrifluoromethylthiomercury is associated in benzene as well as in the pure state. In addition, this compound dissolves with evolution of heat in solvents which exhibit donor properties, and the relative stabilities of the solvate appear to be $PR_3 > NR_3 > SR_2 > OR_2$, in agreement with the suggestion[150] that bistrifluoromethylthiomercury can act as an acceptor towards halide ions aqueous solution.

[150a] Man, Coffman, and Mueterties, *J. Amer. Chem. Soc.*, 1959, **81**, 3575.

which appear follow the trends noted in Group VI. Trifluoromethy derivatives of selenium are more reactive than the corresponding sulphur compounds, and this is attributed to the weaker C–Se and Se–Se bonds.

The presence of the very electronegative trifluoromethyl groups in bistrifluoromethyl selenide makes the unshared electrons on the selenium atom unavailable for donation to form a selenonium compound; compound formation did not occur with either methyl iodide or mercuric chloride. Similar results were obtained with bistrifluoromethyl diselenide. Alkyl selenides readily form addition compounds with both of these reagents,[151–153] but the donor ability of selenium dihalides has not been investigated. Bistrifluoromethyl selenide reacts with chlorine to give selenium tetrachloride, chlorotrifluoromethane, and trifluoromethylselenium trichloride. The last compound presumably arises from the addition of chlorine to trifluoromethylselenium chloride. Although alkylselenium compounds readily form dihalides (R_2SeX_2), there has been no indication that bistrifluoromethylselenium dichloride can be prepared.

Bistrifluoromethyl diselenide reacts with excess of chlorine to form trifluoromethylselenium trichloride, or with a limited amount of chlorine to form trifluoromethylselenium chloride. Reaction with bromine yields only trifluoromethylselenium bromide, while only trifluoroiodomethane was formed with iodine. Trifluoromethylseleninic acid, $CF_3{\cdot}SeO{\cdot}OH$, was obtained from both the oxidation of bistrifluoromethyl diselenide with concentrated nitric acid and the action of water on trifluoromethylselenium trichloride. The increased acid strength relative to that of the methyl analogue parallels the effect noted with other acids containing the trifluoromethyl group. Attempts to oxidise trifluoromethylselenic acid to the selenonic acid were unsuccessful, although trifluoromethylsulphonic acid can be prepared in this manner.

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[151] Morgan and Burstall, *J.*, 1929, 1096; 1930, 1497; 1931, 173.

[152] Carr and Pearson, *J.*, 1938, 282.

[153] Jackson, *Annalen*, 1875, **179**, 1.