Trifluoromethyliodine(v) Tetrafluoride and Related Compounds †

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Trifluoromethyl iodide is oxidised by chlorine trifluoride in C_6F_{14} at −78 °C to give trifluoromethyliodine(v) tetrafluoride. Evidence for the formation of trifluoromethyliodine(III) difluoride has also been obtained. CF_3IF_4 Decomposes readily at 20 °C but is more stable in this respect than CF_3IF_2. Other R_FIF_4 [$R_F = C_2F_5$, $(CF_3)_2CF$, or n-C_4F_9] compounds are more stable with respect to decomposition than had been supposed. CF_3IF_4 Reacts with methylmethoxosilanes at 20 °C to give $CF_3IF_{4-n}(OMe)_n$ (n = 1—4).

ALTHOUGH there have been several reports describing the preparation of iodine(III) and iodine(V) compounds of the types RIF_2 ($R = CF_3$ [1] and other C_nF_{2n+1} groups,[2,3] C_6F_5,[3,4] or Ph and substituted Ph groups [3]) and RIF_4 ($R = C_nF_{2n+1}$ where $n \geqslant 2$,[2] Ph, or $C_6H_4{\cdot}CH_3$ [5]), little is known of their properties. Perfluoroalkyliodine(V) tetrafluorides are of interest to us in connection with a study of substituted derivatives of high oxidation state fluorides,[6] as in principle the R_F group may be used as an n.m.r. probe to follow the replacement of fluorine bound to iodine(V) by other ligands. Trifluoromethyliodine(V) tetrafluoride is the preferred compound for this purpose, but it has not been reported previously.

In this paper we report the preparation and some properties of CF_3IF_4, and an n.m.r. study of the replacement of fluoro- by methoxo-ligands. A reinvestigation of other members of the series R_FIF_4 has shown that they are more stable with respect to decomposition than had

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† No reprints available.

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[2] (*a*) C. S. Rondestvedt, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 3054; (*b*) U.S.P. 3,377/390/1968; Fr.P. 1,521,775/1968.

[3] V. V. Lyalin, V. V. Orda, L. A. Alekseeva, and L. M. Yagulpol'skii, *Zhur. Org. Khim.*, 1970, **6**, 329.

[4] M. Schmeisser, K. Dahmen, and P. Sartori, *Chem. Ber.*, 1970, **103**, 307.

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[6] (*a*) A. M. Noble and J. M. Winfield, *J. Chem. Soc.* (*A*), 1970, 501, 2574; (*b*) D. W. Walker and J. M. Winfield, *J. Fluorine Chem.*, 1971, **1**, 376; (*c*) G. Oates and J. M. Winfield, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 1093.

been supposed.[2a] A preliminary account of some of this work has been given.[7]

RESULTS AND DISCUSSION

Oxidation of Perfluoroalkyliodides by Chlorine Trifluoride.—Perfluoroalkyliodine(V) tetrafluorides R_FIF_4 [$R_F = CF_3$, C_2F_5, $(CF_3)_2CF$, or n-C_4F_9] are formed from R_FI and ClF_3 in perfluoro-n-hexane at −78 °C according to equation (1). Their characterisation is described

$$3R_FI + 4ClF_3 \longrightarrow 3R_FIF_4 + 2Cl_2 \tag{1}$$

below. The method used is a modification of that previously described,[2a] the main difference being that the addition of ClF_3 to the R_FI–C_6F_{14} mixture is far more rigorously controlled. Fast addition or too little solvent lead to violent reactions, particularly with CF_3I, resulting in extensive C–I bond cleavage and the apparent formation of ClF.

TABLE 1

^{19}F N.m.r. spectra of perfluoroalkyliodine(V) tetrafluorides

		Chemical shifts/p.p.m.[a]			Coupling constants/Hz		
Compound	Spin system	$\delta(IF_4)$ [b]	$\delta(CF_2)$ or $\delta(CF)$	$\delta(CF_3)$	$^3J(FICF)$	$^4J(FICCF)$	Others [c]
CF_3IF_4 [d,e]	A_3X_4	−32·4		−56·1	18		
$C_2F_5IF_4$ [d,e,f]	$A_3M_2X_4$	−30·2	−85·3	−77·8	14	8	$^3J(F_1F_2)$ 1
$(CF_3)_2CFIF_4$ [d]	A_6MX_4	−17·3	−143·6	−69·3	11	11	$^3J(F_1F_2)$ 6
n-$C_4F_9IF_4$ [f,g]	$A_3M_2N_2P_2X_4$	−29·2	−81·1(F_1) [c] −129·3 F_2 −124·0 F_3	−82·2	16	16	$^4J(F_2F_4)$ 11 $^3J(F_3F_4)$ <1

[a] From CCl_3F internal. All values to high field. [b] *Cf.* IF_5 $\delta(F_{ax})$ 59·7, $\delta(F_{eq})$ 10·9 p.p.m. [c] ^{19}F Nuclei in C_nF_{2n+1} numbered from the α position. [d] In CCl_3F solution. [e] Spectrum invariant down to −90 °C. [f] Chemical shifts reported previously (ref. 2*a*). [g] Neat liquid.

Oxidation of CF_3I by less ClF_3 than is required by equation (1) gives a mixture of CF_3IF_4 and a species identified as trifluoromethyliodine(III) difluoride from its n.m.r spectrum (first order A_3X_2) $\delta(F_A)$ −28·8, $\delta(F_X)$ −172·7 p.p.m., $^3J_{F_AF_X}$ 8 Hz. The value of $\delta(F_X)$ is very similar to $\delta(IF_2)$ values in other R_FIF_2 compounds.[2a] CF_3IF_2 Decomposes rapidly in $CClF_3$ at 20 °C to give a mixture of CF_4, CF_3I, I_2, and IF_5, as has been noted elsewhere,[1] and its isolation was not attempted.

Characterisation of Perfluoroalkyliodine(V) *Tetrafluorides*.—(a) *Trifluoromethyliodine*(V) *tetrafluoride*. This compound is a white, moisture-sensitive solid, which is volatile at 20 °C and freely soluble in CCl_3F, IF_5, dioxan, MeCN, or pyridine. Decomposition of the pure solid, giving a mixture of CF_4, CF_3I, IF_5, and I_2, is apparent after 4 h at 20 °C. Impure samples decompose more quickly. In CCl_3F solution there is no detectable decomposition for up to 12 h at 20 °C. The compound is characterised by its n.m.r. spectrum (Table 1). Its mass (Table 2) and vibrational spectra provide strong supporting evidence.

The n.m.r. spectroscopic equivalence of the ^{19}F nuclei in the IF_4 group and the observation of FCIF coupling indicate that CF_3IF_4 has a square pyramidal structure like that of IF_5,[8,9] with the CF_3 group axial, or that a fast intramolecular exchange process occurs. We believe the former to be more likely. The IF_4 resonance is to high field of both axial and equatorial ^{19}F nuclei in IF_5, which is also the case for IF_4OMe.[6c]

IF_5 Forms weak complexes with organic donor molecules,[10] and CF_3IF_4 shows similar behaviour. Its n.m.r. spectrum in pyridine shows no FCIF coupling and in MeCN both signals are considerably broadened. There is no n.m.r. evidence for interaction in dioxan solution but a white solid which appears to be a molecular complex, is isolated from solution.

The Raman spectrum of solid CF_3IF_4 and its gas phase i.r. spectrum suggest, but do not prove, that the molecule has C_{4v} symmetry. Some band assignments can be made by comparison with the spectra of CF_3I,[11] IF_5,[12] and CF_3SF_5 [13] as follows: **1260** (i.r.) CF_3 antisym. stretch, **1068** (i.r.) **1054** (R) CF_3 sym. stretch, **756** (i.r.) **754** (R) CF_3 sym. deformation, **599** (i.r.) IF_4 antisym. stretch, and **264** (R) cm^{-1} C–I stretch. Other Raman bands are four in the region 300—100 cm^{-1}, which may be due to an out-of-plane bending, and to deformation modes of IF_4 and a CF_3 rocking mode, and a broad envelope *ca.* 560

TABLE 2

Mass spectrum of CF_3IF_4 [a]

m/e	Relative abundance	Assignment	*m/e*	Relative abundance	Assignment
215	1	CF_3IF^+ [b]	165	70	IF_2^+
203	16	IF_4^+	146	21	IF^+
196	34	CF_3I^+ [c]	127	47	I^+
184	13	IF_3^+	69	100	CF_3^+ [c]

[a] Independent of source temperature in the range 130—210 °C. [b] Assuming bond energies to be C–F > I–F. [c] Other C–F fragments not given.

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[13] J. E. Griffiths, *Spectrochim. Acta*, 1967, **23A**, 2145.

cm^{-1} containing at least three strong bands. Three IF_4 stretching modes and a CF_3 deformation are expected in this region. There is also the possibility of an additional band as observed in liquid IF_5, which some workers have attributed to weak association between IF_5 molecules.[12c,d] A complete analysis must await a gas-phase Raman spectrum.

(b) *Other R_FIF_4 compounds.* $C_2F_5IF_4$ and n-$C_4F_9IF_4$ have been reported previously,[2a] and $(CF_3)_2CFIF_4$ has been mentioned in the patent literature.[2b] Properties that have been described already are not discussed here. The compounds are more stable with respect to decomposition than had been supposed. A solution of $C_2F_5IF_4$ in CCl_3F may be kept for at least 24 h at 20 °C without observable decomposition, and solutions of $(CF_3)_2CFIF_4$ or n-$C_4F_9IF_4$ are stable for several weeks.

^{19}F–^{19}F Spin–spin coupling between the IF_4 groups and both α and β C–F groups is observed in their n.m.r spectra (Table 1). The relatively large values of the rotationally averaged ^4J(FICCF) may mean that there is a contribution from ' though space ' coupling as has been suggested for some ^4J(FF) coupling constant in highly fluorinated propane fragments and in some fluoroethylsulphur(VI) pentafluorides.[14] Vicinal FCCF coupling constants are small, and it has been shown that in acyclic perfluoroalkanes this is due to the rotational averaging of larger coupling constants of opposite signs.[15]

TABLE 3

Mass spectra of R_FIF_4 compounds

m/e	Relative abundance	Assignment	*m/e*	Relative abundance	Assignment
		$C_2F_5IF_4$			
265	1	$C_2F_5IF^+$ [a]	146	14	IF^+
246	43	$C_2F_5I^+$	127	46	I^+
203	14	IF_4^+	119	67	$C_2F_5^+$
184	6	IF_3^+	69	100	CF_3^+ [b]
165	19	IF_2			
		$(CF_3)_2CFIF_4$			
334	<1	$C_3F_7IF_2^+$ [a]	165	1	IF_2^+
315	<1	$C_3F_7IF^+$	169	12	$C_3F_7^+$
296	41	$C_3F_7I^+$	146	1	IF^+
203	<1	IF_4^+	127	26	I^+
184	<1	IF_3^+	69	100	CF_3^+ [b]
		n-$C_4F_9IF_4$			
346	19	$C_4F_9I^+$	165	1	IF_2^+
219	35	$C_4F_9^+$	146	1	IF^+
203	2	IF_4^+	127	48	I^+
184	1	IF_3^+	69	100	CF_3^+ [b]

[a] Assuming bond energies to be C–F > I–F. [b] Peaks assigned to other C–F ions not given.

The R_F chemical shifts are as expected by comparison with the parent iodides.[16] In the straight chain compounds substitution of an iodine atom by an IF_4 group results in increased shielding of the α ^{19}F nuclei, but the reverse is the case for the $(CF_3)_2CF-$ compounds.

The mass spectra (Table 3) of these compounds are very similar to that of CF_3IF_4, and extensive fragmentation is observed.

Decomposition of CF_3IF_4.—This is rationalised by the following scheme. The formation of CF_4 and IF_3 can be

$$\begin{tikzcd} CF_3IF_4 \arrow[r] \arrow[dd, "I_2/IF_5 \text{ or } IF"'] & IF_3 + CF_4 \arrow[d] \\ & IF + IF_5 \arrow[d] \\ CF_3I + IF_5 & I_2 + IF_5 \end{tikzcd}$$

most simply explained by a fluorine transfer process. Evidence for the association of IF_5 molecules in the liquid state *via* weak fluorine bridges has been mentioned above and is indicated also by heat capacity measurements.[17] If similar interactions are present in solid CF_3IF_4 intermolecular fluorine transfer can be readily visualised. IF_3 is known to disproportionate below 20 °C to give I_2 and IF_5, IF being a possible intermediate,[18] and a single broad peak, δ −165 p.p.m., in the n.m.r. spectrum of partially decomposed CF_3IF_4, which disappears with time, is tentatively assigned to IF_3. In the presence of AsF_5, CF_3IF_4 decomposes at −78 °C to give CF_4 and a thermally unstable solid which may be $IF_3{\cdot}AsF_5$.

The presence of CF_3I as a decomposition product can be accounted for either by a series of F transfers from CF_3IF_4 to other species, or by C–I bond cleavage with ' IF '. The latter route is considered more likely for the following reasons. It explains the catalytic effect of I_2 and IF_5 on the decomposition. It is analogous to the reaction of CF_3IF_4 with hexafluoropropene at 20 °C which gives $(CF_3)_2CFI$. This product is also formed from the reaction of $CF_3{\cdot}CF{:}CF_2$ with an I_2–IF_5 mixture or IF.[19] A series of I–F bond cleavage reactions involving CF_3IF_4 would produce CF_3IF_2 as an intermediate which was not observed.

The increasing stability of R_FIF_4 to decomposition as the size of R_F increases is consistent with the proposed scheme and the decomposition of CF_3IF_2 is similarly envisaged with CF_4 and IF as the initial products. In contrast to the conclusions drawn previously[2a] about the relative stabilities of R_FIF_2 and R_FIF_4 compounds, CF_3IF_2 decomposes more readily than does CF_3IF_4.

Reactions of CF_3IF_4 *with Methyl(methoxo)silanes.*—In

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common with many other high oxidation state fluorides[6,20] CF_3IF_4 reacts with trimethylmethoxo- or dimethyldimethoxo-silane in CCl_3F at 20 °C with the replacement of I–F by I–OMe groups and the formation of Me_3SiF or Me_2SiF_2. Reactions designed to produce individual members of the series $CF_3IF_{4-n}(OMe)_n$ give colourless involatile liquids for which decomposition is apparent within 0·5 h at 20 °C giving HF as one product. They are stable in solution for longer periods. The species present are identified by their n.m.r. spectra (Table 4) and their mass spectra (Table 5) provide additional support.

Assignment of the ^{19}F n.m.r. spectra is straightforward except for the signals in product (1) due to $CF_3IF_3(OMe)$ which are temperature dependent. At −80 °C a complete A_3M_2X spectrum is observed. At 20 °C neither the F_X signal nor F_A–F_X coupling in the F_A signal are observed. Usually F_A–F_M coupling is not observed in the F_M signal at 20 °C, but it is always observed in the F_A signal. The spectral changes are completely reversible. Thus the unique F atom of the $-IF_3$ group undergoes intermolecular exchange more readily than the other two, and is possibly subject to more efficient quadrupolar relaxation by ^{127}I.

TABLE 4

N.m.r. spectra of involatile liquids from reactions of CF_3IF_4 with methyl(methoxo)silanes

	Reactants/mmol		Compounds identified	^{19}F Spin system [b]	Chemical shifts (p.p.m.) [c]		Coupling constants/Hz
No.	$[CF_3IF_4]$	[OMe] [a]			$\delta(^{19}F)$	$\delta(^1H)$	
1	3·0	3·1	CF_3IF_4	A_3X_4	$-33{\cdot}4(F_X)$		$^3J(AX)$ 18
					$-57{\cdot}6(F_A)$		
			$CF_3IF_3(OMe)$	A_3M_2X	$-7{\cdot}0(F_X)$	3·91	$^3J(AM)$ 17
					$-46{\cdot}5(F_M)$		$^3J(AX)$ 25
					$-56{\cdot}6(F_A)$		$^2J(MX)$ 113
			$CF_3IF_2(OMe)_2$	A_3X_2	$-23{\cdot}3(F_X)$		$^3J(AX)$ 24
					$-59{\cdot}1(F_A)$		
2	1·7	3·4	$CF_3IF_2(OMe)_2$	A_3X_2	$-21{\cdot}9(F_X)$	4·34	$^3J(AX)$ 24
					$-58{\cdot}3(F_A)$		
3	1·8	5·4	$CF_3IF_2(OMe)_2$ [d]	A_3X_2	$-21{\cdot}0(F_X)$	4·20	
					$-58{\cdot}2(F_A)$		
			$CF_3IF(OMe)_3$	A_3X	$-33{\cdot}3(F_X)$		$^3J(AX)$ 22
					$-56{\cdot}8(F_A)$		
4	1·25	5·0	$CF_3IF(OMe)_3$	A_3X	$-35{\cdot}7(F_X)$	4·15	$^3J(AX)$ 22
					$-57{\cdot}5(F_A)$		
			$CF_3I(OMe)_4$	A_3	$-55{\cdot}8$		

[a] $[Me_3SiOMe]$ or $2[Me_2Si(OMe)_2]$. [b] Neglecting ^1H–^{19}F coupling. [c] From CCl_3 internal or Me_4Si external. [d] Product ratio *ca.* 1 : 2.

Separate ^1H signals due to the chemically different –OMe groups in products (1), (3), and (4) were not observed, either due to rapid exchange between species, or because of very small chemical shift differences. However a ^1H-{^{19}F} double resonance experiment on product (4) indicates the presence of a very small ^1H–^{19}F coupling in $CF_3I(OMe)_4$.

The products' mass spectra (Table 5) show qualitative differences with increasing substitution, for example the base peak in products (1) and (2) is *m/e* 69 assigned to CF_3^+, and in products (3) and (4) is *m/e* 29 assigned to CHO^+. Parent ions were not observed but peaks attributable to $P - 69$, $P - 31$, or $P - 19$ are present. In product (2) *m/e* 277 (1) and 265 (1) are assigned to $CF_3IF(OMe)_2^+$ and $CF_3IF_2(OMe)^+$ respectively, in product (3) *m/e* 289 (<1) and 239 (3) are assigned to $CF_3I(OMe)_3^+$ and $IF(OMe)_3^+$ respectively, and in product (4) *m/e* 251 (<1) is assigned to $I(OMe)_4^+$. Some assignments are ambiguous due to the identical mass numbers of OMe and CF, but they are reasonable in view of the likely order of bond energies and the mass spectrum of CF_3IF_4.

Assuming that $CF_3IF_{4-n}(OMe)_n$ have square pyramidal structures with axial CF_3 groups and F and OMe ligands in equatorial positions, the unique F atom in $CF_3IF_3(OMe)$ must be *trans* to the OMe group. Two structures having *cis* or *trans* OMe groups are possible for $CF_3IF_2(OMe)_2$. The $\delta(IF_2)$ value is more consistent with the former which also would be favoured on statistical grounds. It is noteworthy that $TeF_4(OMe)_2$ has a *cis*-configuration.[21] However a *trans*-configuration might be expected because of the faster exchange observed for the unique F in $CF_3IF_3(OMe)$. An unambiguous decision between the two is not possible, but we tentatively suggest that $CF_3IF_2(OMe)_2$ has a *cis*-configuration, the *trans*-isomer being a possible intermediate in its formation.

The rates of the individual OMe for F substitutions are very different, for example the 1 : 1 reaction [reaction (1) in Table 4] is complete after 0·5 h at 20 °C but quantitative formation of $CF_3I(OMe)_4$ is not achieved even after 9 h. The presence of $CF_3IF_2(OMe)_2$ and CF_3IF_4 in addition to $CF_3IF_3(OMe)$ from reaction (1) is substantiated by the distribution of products observed at different times in reaction (3) (1 : 3 mole ratio). $CF_3IF_3(OMe)$ and $CF_3IF_2(OMe)_2$ are both detected at the same time. Both increase at the expense of CF_3IF_4, the maximum concentrations of $CF_3IF_3(OMe)$ being observed *ca.* 1·5 h after it is first detected. Thereafter $CF_3IF_2(OMe)_2$ in-

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[21] A. Clouston, R. D. Peacock, and G. W. Fraser, *Chem. Comm.*, 1970, 1197.

TABLE 5

Mass spectra of involatile liquids from the reactions of CF_3IF_4 with methyl(methoxo)silanes [a]

m/e	Relative abundance	Assignment [b]	*m/e*	Relative abundance	Assignment [b]
Mole ratio CF_3IF_4 : [OMe] = 1 : 1					
265	1	$CF_3IF_2OMe^+$	165	10	IF_2^+
227	3	CF_3IOMe^+	158	7	$IOMe^+$ CFI^+
215	2	CF_3IF^+ IF_3OMe^+	146	10	IF^+
196	39	CF_3I^+ IF_2OMe^+	127	56	I^+
189	2	$I(OMe)_2^+$	69	100	CF_3^+
184	1	IF_3^+	31	35	OMe^+
177	23	$IFOMe^+$ CF_2I^+	29	56	OCH^+
Mole ratio CF_3IF_4 : [OMe] = 1 : 2					
277	1	$CF_3IF(OMe)_2^+$	177	51	$IFOMe^+$ CF_2I^+
265	1	$CF_3IF_2OMe^+$	165	17	IF_2^+
227	23	CF_3IOMe^+	158	9	$IOMe^+$ CFI^+
215	3	CF_3IF^+ IF_3OMe^+			
196	94	CF_3I^+ IF_2OMe^+	157	3	$IOCH_2$
195	6	$IF_2OCH_2^+$	146	17	IF^+
189	6	$I(OMe)_2^+$	127	71	I^+
			69	100	CF_3^+
184	1	IF_3^+	31	65	OMe^+ CF^+
			29	77	OCH^+
Mole ratio CF_3IF_4 : [OMe] = 1 : 3					
289	<1	$CF_3I(OMe)_3^+$	177	28	$IFOMe^+$ CF_2I^+
277	3	$CF_3IF(OMe)_2^+$	165	5	IF_2^+
239	3	$IF(OMe)_3^+$	158	20	$IOMe^+$ CFI^+
265	11	CF_3IOMe^+ $IF_2(OMe)_2^+$	157	6	$IOCH_2^+$
215	1	CF_3IF^+ IF_3OMe^+	146	8	IF^+
			127	69	I^+
196	37	CF_3I^+ IF_2OMe^+	69	79	CF_3^+
195	2	$IF_2OCH_2^+$	31	63	OMe^+ CF^+
189	14	$I(OMe)_2^+$			
			29	100	OCH^+
Mole ratio CF_3IF_4 : [OMe] = 1 : 4					
289	<1	$CF_3I(OMe)_3^+$	177	13	$IFOMe^+$ CF_2I^+
277	<1	$CF_3IF(OMe)_2^+$			
			165	<1	IF_2^+
251	<1	$I(OMe)_4^+$			
			158	19	$IOMe^+$ CFI^+
239	1	$IF(OMe)_3^+$			
			157	7	$IOCH_2^+$
227	4	$IF_2(OMe)_2^+$ $CF_3IF(OMe)_2^+$	146	2	IF^+
			127	41	I^+
196	25	CF_3I^+ IF_2OMe^+	69	31	CF_3^+
189	3	$I(OMe)_2^+$	31	100	OMe^+ CF^+
			29	100	OCH^+

[a] Source temperatures (1) 147; (2) 75; (3) 127; (4) 110 °C. [b] In some cases are ambiguous due to the identical mass numbers of CF and OCH_3. Assignments made are those which appear to be most reasonable.

creases at the expense of both CF_3IF_4 and $CF_3IF_3(OMe)$ and after a further 1 h is the only species observed. Additional substitution occurs very slowly and after a further 3·5 h the ratio $CF_3IF(OMe)_3 : CF_3IF_2(OMe)_2$ is *ca.* 2 : 1. These observations strongly imply that $CF_3IF_3(OMe)$ undergoes a redistribution reaction according to equation (2) which is consistent with the lability of the unique F atom.

$$2CF_3IF_3(OMe) \longrightarrow CF_3IF_2(OMe)_2 + CF_3IF_4 \quad (2)$$

EXPERIMENTAL

Volatile compounds were manipulated in a Pyrex vacuum line equipped with PTFE–glass stop-cocks (Rotaflow or West–Glass) or in a Monel-metal vacuum line constructed from standard couplings and valves (Autoclave Engineers) and a Monel Bourdon Gauge (Helicoid). Reactions involving ClF_3 were carried out in Kel-F traps (Argonne National Laboratory) attached to the line *via* Hoke diaphragm valves. The line was calibrated with CO_2 and both line and traps were well seasoned with ClF_3 before use. Other reactions were performed in Pyrex vessels fitted with PTFE–glass stop-cocks. Involatile compounds were handled in a Lintott inert atmosphere box in which the concentrations of H_2O and O_2 were $\leqslant$10 p.p.m.

N.m.r. spectra were recorded using Perkin-Elmer R10 and Jeol C60-HL instruments at 60 MHz (^1H referred to Me_4Si) and 56·4 MHz (^{19}F referred to CCl_3F). Chemical shifts are reported as δ values which are positive to low field of the reference. Mass spectra were obtained using a G.E.C./A.E.I. MS 12 instrument at 70 V, samples being introduced directly or *via* the gas inlet as appropriate. I.r. and laser Raman spectra were obtained using Perkin-Elmer 457 and Spex Ramalog instruments.

Chlorine trifluoride (Matheson), perfluoroalkyl iodides (Peninsular Chem Research or Fluorochem), and perfluoro-n-hexane were used as received. Methylmethoxosilanes (Pierce) and organic solvents were degassed, dried over molecular sieves (4A), and stored *in vacuo*. Microanalyses were by A. Bernhardt, W. Germany.

Preparation of Perfluoroalkyliodine(V) *Tetrafluorides*.—**Caution!** Care must be exercised in these reactions. On some occasions the mixture ignited and small explosions occurred. A mixture of CF_3I (4·6 mmol) and n-C_6F_{14} (16·5 mmol) in a Kel-F trap attached to the Monel line was held at −78 °C. Gaseous ClF_3 (9·1 mmol) was added in small portions the time for the total addition being 0·5 h. Reaction was rapid to give a white solid and a greenish yellow solution. The mixture was allowed to warm to −40 °C over 14 h and the bulk of the liquid removed by distillation. The trap was transferred to a Pyrex line and the contents distilled onto NaF. Fractional distillation of the mixture gave a white solid, identified as *trifluoromethyliodine*(V) *tetrafluoride*, as the least volatile component.

Similarly prepared were $C_2F_5IF_4$, $(CF_3)_2CFIF_4$ m.p. 48 °C (Found: C, 9·6; F, 56·4; I, 34·0. $C_3F_{11}I$ requires C, 9·7; F, 56·2; I, 34·1%), and n-$C_4F_9IF_4$ which is liquid at 20 °C.

The vibrational spectrum of CF_3IF_4 was as follows: Raman (solid) $\nu_{max.}$ 1054(5), 754(10), 584(15), 553(50), 548(27), 298(7), 264(33), 220(3), 163(8), 105(2) cm^{-1}. I.r. (gas 2000—400 cm^{-1}) $\nu_{max.}$ 1260vs, 1237m, 1187m, 1068vs, 1028wsh, 845m, 756s, 736sh, 646m, 599vs, 488w cm^{-1}. The i.r. spectra of other R–IF_4 compounds contained bands characteristic of the R_F group,[22] and a strong band *ca.* 600 cm^{-1} which appeared to be characteristic of the IF_4 group.

Decomposition of R_FIF_4.—Decomposition of CF_3IF_4 at 20 °C was followed in the gas phase by i.r. spectroscopy, in the solid state by monitoring the i.r. spectrum of the volatile products, and in CCl_3F solution by n.m.r. spectroscopy. Decomposition of impure samples was detectable within 0·5 h, but that of pure samples was much slower. $C_2F_5IF_4$ Behaved similarly, the products being C_2F_5I, C_2F_6, IF_5, and I_2.

Reactions of CF_3IF_4.—(a) *Hydrolysis*. In ethanolic KOH the products were CHF_3 and a sparingly soluble white solid containing positive I and C–F groups. Similar solids were obtained from other R_FIF_4 hydrolyses and have been formulated previously [2a] as impure $(R_F)_2I^+$ compounds.

(b) *With hexafluoropropene*. CF_3IF_4 Reacted slowly with C_3F_6 over 2 days at 20 °C to give $(CF_3)_2CFI$, identified by its mass spectrum *m/e* 296 (17) assigned to $C_3F_7I^+$ and i.r. spectrum which distinguishes it from $CF_3CF_2CF_2I$.[19a,b] Decomposition products of CF_3IF_4 were also formed. U.v. irradiation had no effect on the reaction rate or products. $C_2F_5IF_4$ Reacted similarly but more slowly.

(c) *With arsenic pentafluoride*. A vigorous reaction occurred at −78 °C to give CF_4 as the sole volatile product and a red-brown solid, soluble in IF_5 giving a green solution, which contained As, F, and I. It appeared to be similar to the previously reported $IF_3{\cdot}AsF_5$.[18a]

(d) *With trimethylmethoxo- or dimethyldimethoxo-silane*. The reaction stoicheiometries and identities of the iodine-containing products are given in Table 4. Reaction times were as follows: reaction (1) 0·5 h, reaction (2) 0·75 h, reaction (3) 6·5 h, and reaction (4) 9 h. Quantitative formation of fluoromethylsilane was observed only in reaction (1). The course of reaction (3) was followed by transferring a sample to an n.m.r. tube *in vacuo* and recording its ^{19}F spectrum after various times.

The i.r. spectra of the liquid products were all very similar and showed the presence of CF_3, I–F, and OMe groups. That of $CF_3IF_2(OMe)_2$ [reaction (2)] was as follows: $\nu_{max.}$ (4000—400 cm^{-1}) 2985sh, 2945s, 2812s, 2292m, 1452sh, 1440s, 1217vs, 1044w, 1062vs, 972vs, 837s, 746vs, 500vs,br cm^{-1}.

We thank Mr. J. Pirie for help in constructing the metal line and the S.R.C. for a grant towards the purchase of n.m.r. and Raman equipment, and for a maintenance award (to G. O.).

[3/1532 *Received*, 23*rd July*, 1973]

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