Substitution Reactions of Iodine Pentafluoride: Preparation and Properties of Methoxoiodine(v) Fluorides †

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Methoxoiodine(v) fluorides, $IF_{5-n}(OMe)_n$ (n = 1—4), and fluoro(methyl)silanes are formed from reactions of iodine pentafluoride with methoxomethylsilanes at 20 °C. The IF_5 derivatives are labile and readily decompose with reduction of iodine(v). Although Me_3SiF is formed from reactions of IF_5 with other Me_3SiX [X = Cl, SMe, OC(O)R, or Me] compounds, substituted derivatives of IF_5 are not isolated because reduction occurs.

THE Lewis acid-base properties of iodine pentafluoride and its fluorinating ability towards organic compounds are well documented,[1] but study of its substituted derivatives has been relatively neglected. Known derivatives, for example $IF_3(SO_3F)_2$ [2] and R_FIF_4 compounds,[3] are prepared by oxidation of I_2 and R_FI respectively. Attempts to prepare fluoro(methoxo)iodate(v) compounds from $R_4N^+IF_6^-$ and $As(OMe)_5$ were unsuccessful, and although $R_4N^+[IF_4(O_2CCF_3)_2]^-$ has been reported to be the product of reaction of $R_4N^+IF_6^-$ with $(CF_3CO)_2O$ it is not well characterised.[4a] A yellow solid, formulated as $IClF_4$, has been reported to be an intermediate in formation of $M^+IF_6^-$ and $M^+ICl_2F_4^-$ salts from IF_5 and MCl,[4b] but a subsequent study of the reaction of CsCl with IF_5, reported while the present work was in progress, indicated that Cl_2 and $CsF_3,3IF_5$ were the only products.[5]

An attractive route from IF_5 to the compounds $IF_{5-n}X_n$ is *via* silicon–element (X) bond-scission reactions, as this method has been widely used to prepare substituted derivatives of other covalent fluorides, for example those of phosphorus [6] and sulphur.[7] Therefore, we have studied reactions of IF_5 with the organosilicon compounds Me_3SiX and Me_2SiX_2 [X = OR, Cl, SMe, OC(O)R, or Me]. The compounds $IF_{5-n}(OMe)_n$ (n = 1—4) have been isolated, enabling comparisons to be made with analogous derivatives of W^{VI} (ref. 8) and Te^{VI} (ref. 9) which are monomeric in solution. A preliminary account of the preparation of methoxoiodine(v) tetrafluoride has been given previously.[10]

RESULTS AND DISCUSSION

Preparation and Properties of Alkoxoiodine(v) *Fluorides*.—Stoicheiometric reactions between the compounds IF_5 and $Me_3Si(OMe)$ or $Me_2Si(OMe)_2$ at 20 °C yield $IF_4(OMe)$ and the corresponding fluoro(methyl)silane (Table 1). The reagent $Me_2Si(OMe)_2$ is preferred as IF_5 reacts slowly with Me_3SiF. The compound $IF_4(OMe)$ is a white solid, m.p. 35—37 °C, volatile at room temperature. It is rapidly hydrolysed in moist air, but is soluble in IF_5, C_6F_6, or MeCN without decomposition. The compound decomposes slowly in Pyrex at 20 °C to give SiF_4, H_2CO, I_2, and an unidentified solid, IF_xO_y. Its

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† No reprints available.

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thermal stability is therefore intermediate between that of $PF_4(OMe)$, which has been identified only at low temperature,[11] and $TeF_5(OMe)$.[9]

The compound $IF_4(OEt)$, a colourless liquid, less stable thermally than $IF_4(OMe)$, was prepared in a similar manner, but IF_5 does not undergo significant reaction with $Me_3Si[OCH(CF_3)_2]$ or with $Me_3Si(OC_6F_5)$ at 20 °C. That a weak interaction exists between IF_5 and $Me_3Si[OCH(CF_3)_2]$ in solution was indicated by the non-observation of $^2J_{FIF}$ in the ^{19}F n.m.r. spectrum of the mixture. If reactions of IF_5 with silyl ethers proceed *via* Lewis acid–base intermediates,[12] the lack of significant reaction with the less-basic ethers is understandable. Ring fluorination occurs when IF_5 reacts with the compound $Me_3Si(OPh)$, and $IF_4(OMe)$ reacts similarly with C_6H_6.

Like WF_6,[8a] the compound IF_5 undergoes an MeO-for-F ligand-substitution reaction with dimethyl sulphite. The products are $(MeO)S(O)F$ and $IF_4(OMe)$ which is complexed by any excess of $(MeO)_2SO$ present (Table 1). Unlike WF_6,[8a] a similar reaction does not occur between IF_5 and trimethyl phosphite. Apparently oxidative fluorination of $(MeO)_3P$ occurs as the products include MeF, MeI, PF_6^-, and $(MeO)_2P(O)F$. The latter compound could arise from decomposition of $(MeO)_3PF_2$, a compound which is not well characterised.[13]

Increasing the mole ratio $Me_2Si(OMe)_2 : IF_5$ leads to more highly substituted members of the series $IF_{5-n}(OMe)_n$ (Table 1), and analogous ethoxo-compounds may be prepared similarly. Although mixtures of compounds were often obtained from these reactions, the products' mass * and n.m.r. spectra (Table 2) enabled the components to be identified, except in the case of $I(OMe)_5$ whose identification is only tentative. The compounds $IF_{5-n}(OMe)_n$ ($n = 2$—4) are liquids at 20 °C whose stabilities with respect to decomposition are similar to that of $IF_4(OMe)$. Their decomposition products are H_2CO, Me_2O, SiF_4, and I_2.

^1H and ^{19}F N.m.r. spectra of the compound $IF_4(OMe)$ at 20 °C both consisted of single peaks, δ_H 4·33 and δ_F −9·0 p.p.m. (in MeCN). The chemical shift of the ^{19}F signal was slightly solvent dependent (<4 p.p.m.). At 33 °C its width at half height was 12 Hz, on cooling the signal sharpened, and, at −50 °C, $^4J_{HF}$ 2 Hz was observed. The spectra are consistent either with a square-pyramidal structure in which the MeO group is apical, or with the presence of a fast exchange process. No fine structure was observed in the n.m.r. spectra of the other members of the series even at low temperatures, and signals due to chemically different MeO groups were not observed. These compounds are evidently more labile than $WF_{6-n}(OMe)_n$ ($n = 1$—4) and $TeF_{6-n}(OMe)_n$ ($n = 1$ or 2) where fine structure occurs at room temperature. An internally consistent set of assignments (Table 2) can be made by comparison with n.m.r. spectra of $(CF_3)IF_{4-n}(OMe)_n$ compounds,[3] assuming that $IF_4(OMe)$ has a square-pyramidal structure with the MeO group apical and that further substitution occurs in the equatorial plane.

Reactions designed to produce the compound $IF_3(OMe)_2$ resulted in a mixture of $IF_3(OMe)_2$ and $IF_4(OMe)$,

TABLE 1

Preparation of methoxoiodine(V) fluorides

Reaction no.	Reactants (mmol)	Conditions Temp./°C (t/h)	Identified products	Analysis (%): Found (Calc.)				
				C	H	F	I	
(1)	IF_5 (10·8) + $Me_2Si(OMe)_2$ (5·4)	20 (0·5)	$IF_4(OMe)$ [a] Me_2SiF_2 (5·3)	5·4 (5·2)	1·2 (1·3)			$2IF_4(OMe), (MeO)_2SO$,[b] and $(MeO)S(O)F$ isolated from IF_5 (5·1) + $(MeO)_2SO$ (6·9)
(2)	$IF_4(OMe)$ (9·8) + $Me_3Si(OMe)$ (9·8)	20(1) in MeCN	$IF_3(OMe)_2$ } $IF_4(OMe)$ } Me_3SiF	9·1 (10·0)	2·4 (2·5)	21·0 (23·2)	52·4 (52·9) [c]	Spectroscopically identical products obtained from IF_5 (5·7) + $Me_2Si(OMe)_2$ (5·6) and IF_5(8·0) + $Me_3Si(OMe)$ (15·7)
(3)	IF_5 (8·4) + $Me_2Si(OMe)_2$ (12·5)	20 (2·5)	$IF_2(OMe)_3$ Me_2SiF_2	13·2 (14·0)	3·5 (3·5)	14·3 (14·7)	48·6 (49·2)	
(4)	IF_5 (10·9) + $Me_2Si(OMe)_2$ (21·8)	20 (2)	$IF(OMe)_4$ Me_2SiF_2	16·3 (17·8)	4·3 (4·4)	8·2 (7·0)	49·2 (47·0)	
(5)	IF_5 (6·5) + $Me_2Si(OMe)_2$ (16·4)	20 (2)	$I(OMe)_5$ (?) $IF(OMe)_4$ (trace) Me_2SiF_2					

[a] A 1 : 1 adduct was isolated from py solution (Found: C, 22·8; H, 2·6; F, 24·1; N, 4·3. Calc. for $C_6H_8F_4INO$: C, 23·0; H, 2·6; F, 24·3; N, 4·5%). [b] Found: C, 8·1; H, 2·0; F, 26·7; I, 44·2; S, 5·4. Calc. for $C_4H_{12}F_8I_2O_5S$: C, 8·1; H, 2·1; F, 26·3; I, 43·9; S, 5·5%. [c] Those required for the compound $IF_3(OMe)_2$.

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* Complete mass spectra of these compounds are contained in Supplementary Publication No. SUP 10991 (5 pp.). For details see Notice to Authors, No. 7, in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full-size copies).

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and ^{19}F n.m.r. spectra of products from reactions designed to prepare $IF_3(OMe)(OEt)$ contained signals attributable to $IF_4(OMe)$ and $IF_4(OEt)$. It is possible that $IF_3(OR)_2$ compounds undergo reorganisation reactions similar to that proposed for $(CF_3)IF_3(OMe)$.[3]

TABLE 2

Spectroscopic properties of the compounds $IF_{5-n}(OMe)_n$ (n = 2—4)

Compound[a]	N.m.r. chemical shifts (p.p.m.)[b]		Characteristic mass-spectral peaks m/e (relative intensity[c]), and their assignment
	δF		
$IF_3(OMe)_2$ +	−5·6, −14·2[d]	4·19	246 (<0·5) $IF_3(OMe)_2^+$, 245 (<0·5) $IF_3(O_2C_2H_5)^+$,
$IF_4(OMe)$	−8·4		233 (4) $IF_4(OCH_2)^+$, 227 (4) $IF_2(OMe)_2^+$, 215 (17) $IF_3(OMe)^+$,[e] 203 (7) IF_4^+
$IF_2(OMe)_3$	−11·6	4·04	257 (0·2) $IF_2(O_3C_3H_8)^+$, 239 (0·2) $IF(OMe)_3^+$, 233(1) $IF_4(OCH_2)^+$, 215(14) $IF_3(OMe)^+$,[e] 203(2) IF_4^+, 184 (1) IF_3^+
$IF(OMe)_4$	−20·3	3·80	251 (0·5) $I(OMe)_4^+$, 239(3) $IF(OMe)_3^+$, 227(4) $IF_2(OMe)_2^+$, 215(0·4) $IF_3(OMe)^+$, 195(0·5) $IF_2(OCH_2)^+$, 181(0·3) IF_2O^+, 165(1) IF_2^+

[a] Corresponding to products from reactions (2)—(4) in Table 1. The spectra of the products from reaction (5) are similar to those from (4). [b] Solutions in CD_3CN except for $IF_2(OMe)_3$ (pure liquid). [c] m/e 31 or 29 assigned to OMe^+ or OCH^+ = 100%. [d] Relative intensities *ca.* 1 : 2 : 1. [e] A metastable ion was observed corresponding to loss of MeF from this fragment (Found: 152·3. Calc.: 152·3).

TABLE 3

Mass spectrum of the compound $IF_4(OMe)$

m/e	Relative intensity	Assignment	m/e	Relative intensity	Assignment
254	7	I_2^+	165	18	IF_2^+
234	1	$IF_4(OMe)^+$	146	9	IF^+
233	15	$IF_4(OCH_2)^+$[a]	142	5	IMe^+
215	17	$IF_3(OMe)^+$[a]	128	21	HI^+
203	21	IF_4^+	127	20	I^+
184	9	IF_3^+	31	100	OMe^+
181	28	IF_2O^+	29	76	OCH^+

[a] Confirmed by mass measurement (Found: 232·910 and 214·919. Calc.: 232·909 and 214·918).

The mass spectrum of the compound $IF_4(OMe)$ (Table 3) contained prominent peaks assigned to $IF_4(OCH_2)^+$, $IF_3(OMe)^+$, and IF_4^+, suggesting that C–H, I–F, and I–O bond scissions are all major fragmentation paths. These features were apparent in spectra of $IF_{5-n}(OMe)_n$ (n = 2—4) (Table 2), $IF_3(OEt)_2$, and $IF_3(OMe)(OEt)$, but these compounds also exhibited peaks assigned to fragment ions containing more F atoms than expected. For the products from reactions (3) and (4) in Table 1 this is inconsistent with their ^{19}F n.m.r. spectra. While it is possible that small quantities of other members of the series were present, which were not detected by n.m.r. spectroscopy, it is also possible that the observed fragment ions arise from F-atom-transfer reactions which occur in the mass spectrometer. There was no evidence for loss of H_2CO in fragmentation processes, although it is a decomposition product and its loss is important in mass-spectral fragmentation of the compounds $B(OMe)_3$ and $Ti(OMe)_4$.[14]

Decomposition of $MF_n(OR)$ compounds to give $M(:O)F_{n-1}$ and RF should be a favourable process. It has been observed for the compound $WF_5(OMe)$,[8a] and the thermal instability of many alkoxo-derivatives of fluorophosphoranes,[13,15] SF_4,[16] and MoF_6[17] has been rationalised on this basis. The different behaviour observed for the compound $IF_4(OMe)$ may be accounted for if the difference between $I^V{-}O$ and $I^V{=}O$ bond energies is relatively small. Decomposition of $IF_4(OMe)$ can be visualised as elimination of HF followed by H_2CO to leave IF_3. The latter compound will disproportionate to give I_2 and IF_5;[18] IF_5 was not observed, presumably due to its hydrolysis. HF Elimination could be an intramolecular process, as close $H \cdots F$ contact is quite possible assuming reasonable molecular parameters,* but elimination would be facilitated by the presence of intermolecular $I{-}F \cdots I$ interactions similar to the situation suggested for $(CF_3)IF_4$.[3]

We suggest that properties of the compounds $IF_{5-n}(OMe)_n$ are best explained in terms of structures comprising molecular pyramidal units between which there are weak interactions (secondary bonds[19a]) *via* F or MeO bridges. *X*-Ray work shows the presence of similar interactions in I_2O_5[19b] and possibly in IF_3O.[19c] Additionally there is evidence of similar behaviour in liquid IF_5 and XeF_4O.[20]

Reactions of IF_5 *with Other* Me_3SiX *Compounds*.—The products from these reactions (Table 4) indicate that IF_5 is behaving as a fluorinating agent. The compounds IF_4X [X = Cl, SMe, OC(O)R, or Me] may be formed initially but they either decompose or undergo further reaction. In every case reduction of iodine(V) occurs. There was no evidence for formation of compounds containing $I^{III}{-}X$ bonds, with the possible exception of ICl_3, although $I[OC(O)CF_3]_3$ is well known[21] and $MeIF_2$ has been reported very recently.[22] We suggest that IF_3

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* We thank a referee for drawing our attention to this point.

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is the initial reduction product and that disproportionation occurs subsequently.

The decomposition products of the yellow solid isolated at low temperature from the reaction of IF_5 with Me_3SiCl are consistent with its being $IClF_4$. This yellow solid reacts with pyridine to give a mixture of pyridine–interhalogen adducts. Our observations indicate that compounds containing I^V–Cl bonds are unstable with respect to reduction of I^V, in agreement with some previous work[5] and with the inability of Cl_2 to oxidise ICl_3.[23]

TABLE 4

Reactions of the compound IF_5 with other methylsilanes

Silane	Mole ratio IF_5 : silane	Reaction conditions Temp./°C (time)	Products[a]
Me_3SiCl	1 : 1	−45 (0·5 h)	Me_3SiF, yellow solid which decomposes at 20 °C to give IF_5, I_2, Cl_2, and ICl (?)
$Me_3Si(SMe)$	1 : 1	−50 to 20 (overnight)	Me_3SiF, SiF_4, SOF_2, I_2, IF_3 (?)[b]
$Me_3Si[OC(O)CF_3]$	2 : 1	20 (10 min)	Me_3SiF, Me_2SiF_2, $CF_3C(O)F$, $CF_3C(O)OMe$, I_2
$Me_3Si[OC(O)Me]$	1 : 1	10 (10 min)	Me_3SiF, Me_2SiF_2, MeC(O)F, MeC(O)OMe, I_2, IF_3 (?)[b]
Me_4Si or Me_3SiF	1 : 1	20 (up to 7 days)	Me_3SiF, Me_2SiF_2, SiF_4, I_2, IF_3 (?)[b]

[a] Except for IF_3, identified by n.m.r., mass, and i.r. spectroscopy. [b] Single peak in the ^{19}F n.m.r. spectrum of the product mixture δ_F −164 to −168 p.p.m., assigned to IF_3 by analogy with $\delta(IF_2)$ in $(CF_3)IF_2$.[3]

C–Si Bond scission occurs when the compound IF_5 reacts with $Me_3Si[OC(O)R]$ (R = Me or CF_3). A number of reaction schemes can be devised to account for the products but one possibility is that the compounds $IF_4[OC(O)R]$ and Me_3SiF are formed initially and then react to give MeOC(O)R, Me_2SiF_2, and IF_3. Me_3SiF Reacts with IF_5 but very slowly, for example the ^{19}F n.m.r. spectrum of a mixture of the two compounds recorded 7 days after mixing showed that 75% Me_3SiF is unchanged. As expected, the compounds IF_5 and Me_4Si react more quickly, significant quantities of Me_3SiF being detectable after 36 h. Similar behaviour has been reported for the compound AsF_5 which is reduced to AsF_3 in the process.[12c] Attempts to isolate IF_4Me from reaction of the compound IF_5 with Me_4Si were unsuccessful although the n.m.r. spectrum of the mixture contained single peaks, δ_H 4·32 and δ_F −4·9 p.p.m., which could be due to this species.

This work has shown that although a wide range of silicon–element bonds are cleaved by IF_5, its derivative chemistry is limited by the ease with which reduction of iodine(V) occurs. There is some evidence that IF_3 is the primary reduction product.

EXPERIMENTAL

Materials were handled in a Pyrex vacuum line or Lintott dry-box (H_2O and O_2 concentrations ⩽10 p.p.m.). Reactions were carried out in Pyrex flasks fitted with poly(tetrafluoroethylene) glass stopcocks (Rotaflow or West-Glass). N.m.r. spectra were recorded using Perkin-Elmer R.10 and Jeol C60-HL instruments at 60·0 (^1H) and 56·4 MHz (^{19}F). Samples were internally referenced (to Me_4Si and CCl_3F), except for ^1H spectra of samples containing IF_5 which were externally referenced, and chemical shifts are reported as δ values (positive to low field). Mass spectra were recorded using A.E.I. MS12 and MS902 instruments, samples being introduced directly or *via* the gas inlet as appropriate. Spectra were normally recorded at 70 eV; lower values did not materially affect the spectra. I.r. spectra were recorded using a Perkin-Elmer 457 instrument. Microanalyses were by the Microanalytical laboratory, University of Strathclyde, or by A. Bernhardt.

Iodine pentafluoride (Matheson) was shaken with Hg *in vacuo* to remove I_2, vacuum distilled over NaF several times, and stored over NaF. The compounds Me_3SiX [X = OEt, OPh, SMe, OC_6F_5, $OCH(CF_3)_2$, and OC(O)R] were prepared by literature methods.[24] No impurities were detected in their spectra except for $Me_3Si[OC(CF_3)_2OCH(CF_3)_2]$ which was present in the compound $Me_3Si[OCH(CF_3)_2]$. Other reagents and solvents were commercial products (Pierce, Aldrich, or B.D.H.). All reagents were degassed and dried over 4A molecular sieves before use.

Reactions of Iodine Pentafluoride.—Careful temperature control is necessary in the initial stages of these reactions as many of them are very exothermic. Reactions were carried out by allowing stoicheiometric mixtures to warm to the required temperature over several hours. **CAUTION**. Investigation of the IF_5–$Me_3Si(NEt_2)$ system was abandoned when a mixture detonated at *ca.* −80 °C.

Preparation of alkoxoiodine(V) *fluorides*. The preparation and characterisation of the compounds $IF_{5-n}(OMe)_n$ (n = 1—4) is summarised in Tables 1—3. The compounds Me_3SiF and Me_2SiF_2 were identified by comparison of their n.m.r., mass, and i.r. spectra with those of authentic samples. The product formulated as $I(OMe)_5$ decomposed too quickly for analyses to be obtained, and its mass spectrum * was very similar to that of $IF(OMe)_4$. Its ^{19}F n.m.r. spectrum consisted of a very weak peak, δ_F −20·3 p.p.m., and its ^1H spectrum of a strong peak at 3·86 p.p.m. It was not obtained pure and is not completely characterised.

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* Footnote as on page 1381.

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The i.r. spectra of the compounds $IF_{5-n}(OMe)_n$ were all very similar. That of $IF_4(OMe)$ was as follows: $\nu_{max.}$ (mull, 4 000—400 cm^{-1}) at 2 970w; 2 915sh; 1 443w; 962s; 880m; 725w; 610sh; and 560sbr cm^{-1}. Decomposition of the compound $IF_4(OMe)$ at 20 °C was followed by monitoring i.r. spectra of the volatile products. After 4 h SiF_4 and H_2CO [25] were detected in the mixture. The product remaining after decomposition was complete contained I_2 and a white solid whose i.r. spectrum ($\nu_{max.}$ at 1 073w, 1 043w, 828s, 809s, 712s, 630s, 605sh, and 493 cm^{-1}) indicated the presence of I–O and I–F groups. Other $IF_{5-n}(OMe)_n$ compounds behaved similarly.

Similarly prepared was the compound $IF_4(OEt)$ whose mass * [*m/e* 247(2) $IF_4(OC_2H_4)^+$ and 229(3) $IF_3(OEt)^+$] and n.m.r. (δ_F −3·9 and δ_H 1·43, 4·90 p.p.m.; $^3J_{HH}$ 7 Hz) spectra were similar to those of $IF_4(OMe)$. Reactions designed to prepare $IF_3(OEt)_2$ and $IF_3(OMe)(OEt)$ gave liquids whose mass spectra * [*m/e* 273(0·1) $IF_3(O_2C_4H_9)^+$, 255(0·3) $IF_2(O_2C_4H_{10})^+$, and 233(4) $IF_4(OCH_2)^+$; *m/e* 260(0·3) $IF_3(O_2C_3H_8)^+$, 247(5) $IF_4(OC_2H_4)^+$, and 241(2) $IF_2(O_2C_3H_8)^+$] were similar to those of $IF_3(OMe)_2$. Their n.m.r. spectra were as follows: $IF_3(OEt)_2$ δ_F 1·21 and 5·00 p.p.m., $^3J_{HH}$ 7 Hz, δ_F −13·0 p.p.m. (width at half height 200 Hz); $IF_3(OMe)(OEt)$ δ_H 1·34 and 4·52 p.p.m., $^3J_{HH}$ 7 Hz (OEt), 4·12 p.p.m. (OMe) δ_F −6·2, −8·7 [single peaks assigned to $IF_4(OEt)$ and $IF_4(OMe)$ respectively], −3·2 (broad), and −14·9 p.p.m. (apparent broad triplet). Low-temperature spectra were similar.

Reactions of IF_5 *with* $(MeO)_2SO$ *and* $P(OMe)_3$. The compound IF_5 reacted smoothly with $(MeO)_2SO$ at 20 °C (Table 1), (MeO)S(O)F being identified by its i.r., n.m.r., and mass spectra.[8a] The reaction was not complete even after several hours but the products could be separated by fractional distillation. The compounds IF_5 (1·9 mmol) and $P(OMe)_3$ (7·5 mmol) reacted vigorously at −78 °C to give a mixture of products. Fractionation yielded successively MeF, MeI, and a liquid mixture of phosphorus fluorides which included PF_6^- and $(MeO)_2P(O)F$ [*m/e* 128 assigned to $(C_2H_6O_3)PF^+$ δ_F −85·3 p.p.m., $^1J_{PF}$ 981 Hz; *cf.* $(EtO)_2P(O)F$ δ_F −81·5 p.p.m., $^1J_{PF}$ 970 Hz [26]].

Reaction of the compounds $IF_4(OMe)$ with $P(OMe)_3$ was less vigorous and after several hours at 20 °C substantial quantities of reactants were still present.

Reaction of IF_5 *with* Me_3SiCl. A mixture of the compounds IF_5 (8·4 mmol) and Me_3SiCl (8·3 mmol) reacted smoothly at −45 °C to give Me_3SiF and a yellow solid which decomposed rapidly at 20 °C. The mass spectrum of the latter was as follows: *m/e* (relative intensity) 254(100) I_2^+; 222(3) IF_5^+; 203(27) IF_4^+; 184(9) IF_3^+; 165(2) IF_2^+; 164(3) $^{37}ClI^+$; 162(10) $^{35}ClI^+$; 146(3) IF^+; 127(50) I^+; 74(3) $^{37}Cl_2^+$; 72(12) $^{37}Cl^{35}Cl^+$; 70(16) $^{35}Cl_2^+$; 37(5) $^{37}Cl^+$; and 35(12) $^{35}Cl^+$. The solid was soluble in pyridine below 0 °C and a second yellow solid isolated from solution was stable at 20 °C. Its i.r. spectrum showed the presence of co-ordinated py (Found: C, 25·1; H, 2·4; Cl, 7·2; F, 19·7; I, 39·8; N, 5·7%. Ratio C : H : Cl : F : I : N = 7·0 : 8·0 : 0·7 : 3·3 : 1·0 : 1·3). The ^{19}F n.m.r. spectrum of the solid in py and IF_5 consisted respectively of a single peak δ_F 7·1 p.p.m. (width at half height 60 Hz) and a single sharp peak δ_F 22·1 p.p.m. Similar behaviour has been reported for py,IF_5 in solution.[27]

Reaction of IF_5 *with Other* Me_3SiX *compounds.* These reactions are summarised in Table 4. Mixtures of products were usually obtained, the components of which were identified by i.r., n.m.r., and mass spectroscopy.

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* Footnote as on page 1381.

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