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NOTES

The fluorination of methoxy-groups by tungsten hexafluoride

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ALTHOUGH the methoxy- and phenoxy-groups in methylmethoxy- and methylphenoxy-silanes, $Me_nSi(OR)_{4-n}$ (n = 1–3) are completely replaced by fluorine using tungsten hexafluoride under mild conditions[1, 2], the formation of fluorosulphite esters, $ROS(O)F$, (R = Me, Et, or Ph) and dimethylfluorophosphite, $(MeO)_2PF$, from similar reactions with sulphite esters and trimethylphosphite respectively[3] indicate the replacement is not always complete. The overall reactions may be complicated by steps involving the alkoxytungsten(VI) fluorides that are formed initially, for example methoxytungsten(VI) pentafluoride readily looses a Me^+ cation in the presence of $(MeO)_3P$ or $(MeO)_2SO$[3, 4]. The present work was undertaken to determine if other RO-containing compounds would be fluorinated by WF_6 and how far the F, OR exchange processes would be complicated by additional reactions.

EXPERIMENTAL

All operations were carried out in a conventional vacuum system or in a dry box. Mixtures of reactants, in pyrex ampoules fitted with P.T.F.E., glass stop-cocks, were allowed to react under appropriate conditions. Volatile products were removed and subjected to fractional distillation; in most cases it was not possible to separate mixtures of involatile products, but unambiguous identification of the components was usually possible by spectroscopic methods. NMR spectra were recorded at 33°C using a Perkin–Elmer R.10 spectrometer at 60·0 MHz (^1H), 56·4 MHz (^{19}F), and 24·3 MHz (^{31}P), with internal Me_4Si, internal CCl_3F, and external 85% H_3PO_4 as references. A positive chemical shift indicates that resonance occurred at a lower applied field. IR spectra were obtained using Perkin–Elmer 457 or 257 spectrometers, the spectra of authentic samples of BF_3, MeF, SiF_4, PF_3, and POF_3 being used for comparison, and UV visible spectra using a Pye–Unicam SP800D spectrometer. Mass spectra were obtained using an A.E.I. MS12 instrument. Tungsten was determined as WO_3 using cinchonine hydrochloride and other analyses were performed by A. Bernhardt, Elbach-u-Engelskirchen, and Laboratorium Beller, Göttingen.

Tungsten hexafluoride (Allied Chemical Co.) was purified by low temperature trap-to-trap distillation over NaF. WF_5OMe was prepared from WF_6 and $(MeO)_2SO$[3] and titanium tetramethoxide from titanium tetraisopropoxide and methanol[5]. Other reactants and solvents were commercial products and were purified by distillation and storage over 4A molecular sieves or by vacuum drying as appropriate.

RESULTS AND DISCUSSION

The reactions of WF_6 with $M(OMe)_n$ (M = B, n = 3; M = Si, n = 4; M = Nb, n = 5) and with some phosphorus esters are shown in Tables 1 and 2. Only in the WF_6, tetramethoxy-silane system is simple exchange observed. The degree of substitution at tungsten depends on the reactant stoichiometry but the other product is always SiF_4 even when an excess of $Si(OMe)_4$ is used. Although BF_3 and WF_5OMe are formed from WF_6 and trimethoxyborane when the mole ratio is $\geq 3:1$ at lower mole ratios the major product is an involatile liquid, which from its NMR spectra appears to contain MeO-groups (five singlets in the range 3·55–7·1 ppm), F–W (singlet at 67 ppm, half-height width = 20 Hz.) and F–B groups (singlet at −150 ppm, half-height width = 90 Hz). WF_5OMe is partially decomposed to WOF_4 and MeF in the presence of BF_3, possibly as the co-ordination of BF_3 at the

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Table 1. Reactions with $M(OMe)_n$

	Reaction conditions			
Reactants (m-mole)	(°C)	(hr)	Identified products (m-mole)	
WF_6(17·0) + $B(OMe)_3$(5·9)	20	20	BF_3, MeF(a) WF_5OMe(b)*	Wt. of BF_3 + MeF = 0·31 g Unchanged WF_6 recovered
WF_6(9·9) + $B(OMe)_3$(4·7)	20	20	BF_3, MeF(a) WF_5OMe(c)	A viscous, yellow liquid from which BF_3 and MeF were evolved on standing was also formed
WF_6(18·4) + $B(OMe)_3$(18·5)	20	20	BF_3, MeF(a)	Ratio C:H:B:F ≈ 6:18:1:12
WF_6(32·3) + $Si(OMe)_4$(5·2)	20	12	SiF_4(4·2)(d) WF_5OMe(20·8)(e)†	Unchanged WF_6 recovered
WF_6(13·1) + $Si(OMe)_4$(13·0)	20	12	SiF_4(12·2)(d) *cis*-$WF_2(OMe)_4$(10·0)(f)‡	
WF_6(4·2) + $Nb(OMe)_5$(2·1)	20	2	MeF(a)	Mixture of a white solid and an involatile, brown liquid was formed

*Calcd. for CH_3F_5OW: C, 3·9; H, 1·0; F, 30·7; W, 59·3. Found: C, 2·5; H, 1·0; F, 27·2; W, 58·35

†Calcd. for CH_3F_5OW: C, 3·9; H, 1·0; F, 30·7; W, 59·3. Found: C, 3·6; H, 1·0; F, 29·0; W, 58·7.

‡Calcd. for $C_4H_{12}F_2O_4W$: C, 13·9; H, 3·5; F, 11·0; W, 53·1. Found: C, 12·7; H, 3·0; F, 11·6; W, 52·6.

(a)By IR and NMR spectroscopy.

(b)By NMR spectroscopy[3] and analysis. The ^{19}F spectrum also contained a singlet at 68 ppm, half-height width = 60 Hz, which is tentatively assigned to WOF_4.

(c)By NMR spectroscopy[3].

(d)By i.r. spectroscopy and molecular weight. Found 103; required 104.

(e)By NMR spectroscopy[3] and analysis.

(f)By NMR spectroscopy[1] and analysis.

oxygen atom facilitates the loss of a Me^+ cation, and it is suggested that the liquid results from the decomposition of WF_5OMe and its reaction with further $B(OMe)_3$, to give species possibly containing B–O–W bonds. No free methoxydifluoroborane, which has been previously prepared from BF_3 and $B(OMe)_3$[6], was observed in these reactions, but it may be present in the liquid.

A similar liquid is the major product from WF_6 and pentamethoxyniobium(V); its ^1H and ^{19}F NMR spectra comprised five singlets in the range 4·0–5·1 ppm and a singlet at 70 ppm, half-height width = 60 Hz. However, there is no evidence for the formation of niobium and tungsten methoxyfluorides and the characteristic behaviour of WF_6 towards $Nb(OMe)_5$, $Ti(OMe)_4$, and $M(OPr^i)_4$ (M = Ti or Zr) is the formation of ill-defined adducts from which the appropriate alkyl fluoride is readily eliminated. This contrasts with the formation of $TiF_{4-n}(OEt)_n$[7] and $MF_{5-n}(OEt)_n$ (M = Nb or Ta)[8] from reactions of TiF_4 and MF_5 with the corresponding alkoxides.

Both MeO groups in dimethyl methylphosphonate can be replaced by F using WF_6. The reaction is not quantitative as further reactions occur between WF_5OMe and $(MeO)_2P(O)Me$ to give products similar to those obtained from WF_6 and $(MeO)_3P$[3]; a separate NMR experiment confirmed that the $[(MeO)_3PMe]^+$ cation is present in a solution of WF_5OMe in $(MeO)_2P(O)Me$. The reaction of WF_6 with trimethyl phosphate is similar but the yield of POF_3 is very low and the PF_6^- anion is present in the involatile product mixture. The major signal in its ^{19}F NMR spectrum, a doublet with doublet satellite bands is tentatively assigned to tungsten oxotetrafluoride complexed by trimethyl phosphate,

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Table 2. Reactions with phosphorus esters

Reactants (m-moles)	Reaction conditions		Identified products (m-moles)	
	(°C)	(hr)		
WF_6(17·9) + $(MeO)_2P(O)Me$(17·6)	20	0·5	$MeP(O)F_2$(3·8)(a) MeF(2·15)(b) $WOF_4 \cdot OP(OMe)_2Me$(c) $[(MeO)_3)PMe^+][W_2O_2F_9^-]$(c)	Using a 1 : 2 mole ratio (MeO)(Me)P(O)F and unchanged $(MeO)_2P(O)Me$ were identified by NMR spectroscopy [9]
WF_6(7·8) + $(MeO)_2P(O)H$(8·5)	−80	0·2	PF_3, SiF_4(d)	An involatile, colourless liquid which rapidly turned blue at 20°C was also formed
WF_6 + $(MeO)_3PO$ mole ratios in the range 3 : 1–1 : 1 gave the same results	20	2	POF_3, MeF(e) WF_5OMe, PF_6^-, $W_2O_2F_9^-$(f) $WOF_4 \cdot OP(OMe)_3$(?)(g)	
WF_6(10·1) + $(PhO)_3PO$(7·5)	20 in C_6F_6	0·5	$WF_6 \cdot [OP(OPh)_3]_n$(h)	Unchanged WF_6(9·0) recovered

(a) By i.r., NMR [9] and mass spectroscopy. Molecular ion peak at $m/e = 100$.

(b) By i.r. spectroscopy and molecular weight. Found 34·2; required 34·0.

(c) By ^1H, ^{19}F, and ^{31}P NMR spectroscopy [4].

(d) By i.r. spectroscopy and molecular weight. Found 91·8; PF_3 requires 88·0, SiF_4 requires 104.

(e) By i.r. spectroscopy.

(f) By ^1H, ^{19}F, and ^{31}P NMR spectroscopy [3, 4, 10].

(g) Tentatively identified from its NMR spectrum; $\delta(Me) = 4{\cdot}2$, $\delta(F) = 62$, $\delta(P) = 2$ ppm; $J(MeOP) = 11$, $J(FW) = 69$, $J(FP) = 4$ Hz.

(h) Calcd. for $WF_6 \cdot 12{\cdot}8OP(OPh)_3$: C, 61·9; H, 4·3; F, 2·5; P, 8·9; W, 4·1. Found C, 60·3; H, 4·3; F, 2·4; P, 8·7; W, 4·1.

by analogy with $WOF_4 \cdot OP(OMe)_2Me$ (see Table 2). A separate experiment indicated that this species, MeF, and PF_6^-, are formed also from WF_5OMe and $(MeO)_3PO$. Although no direct evidence was obtained for the presence of the $(MeO)_4P^+$ cation [10] in these reactions a doublet at 3·90 ppm, $J(MeOP) = 10$ Hz. and a broad singlet at 0 ppm in the ^1H and ^{31}P NMR spectra of the involatile mixture are assigned to both free $(MeO)_3PO$ and $(MeO)_4P^+$. Exchange between free and co-ordinated $(MeO)_3PO$ is unlikely due to the observation of ^{19}F-^{31}P coupling in the ^{19}F signal assigned to $WOF_4 \cdot OP(OMe)_3$. The formation of PF_6^- suggests that fluorination of the P=O group has occurred, possibly to give $(MeO)_2PF_3$ which exists both in the solid state and in solution as $[(MeO)_4P]^+[PF_6]^-$ [10]. Fluorination of the P=O group in dimethyl phosphite is also suggested to account for the formation of PF_3 as PF_4H, which would be the initial product, readily decomposes to PF_3 and HF [11].

Exchange between F and PhO– groups is not observed in the WF_6, triphenyl phosphate system at 20°C, although a red solid is formed. Its analysis, ^1H and ^{19}F NMR spectra in C_6F_6 (singlets at 6·70 and 163 ppm, half-height width = 90 Hz), and electronic spectrum in Me_4Si (high energy bands characteristic of $(PhO)_3PO$ and a broad band at 27,300 cm^{-1}, $\epsilon_{molar} \sim 10^4$) indicate that a weak complex is formed whose colour is probably due to a charge transfer interaction [12].

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From these reactions it is apparent that WF_5OMe is decomposed both by strong Lewis acids and by Lewis bases, ionic species being formed when the base is capable of accepting Me^+. Some evidence for the fluorination of P=O groups by WF_6 has also been obtained. The absence of exchange between WF_6 and $(PhO)_3PO$ and its presumed absence in WF_6, transition metal alkoxide systems may be due to the inability of the *R*O– groups to co-ordinate to tungsten. A similar explanation has been advanced to explain why no reaction occurs between $SiCl_4$ and WF_6 even at 150°C, whereas halogen exchange is observed between Me_3SiCl and WF_6 at −30°[13].

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$Ba_3Y_2MoO_9$, a new molybdate with perovskite structure

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INVESTIGATING the systems MeO–Y_2O_3–MoO_3, with Me = Ca, Sr, Ba, Mg, Zn or Cd, a new compound was found, viz. $Ba_3Y_2MoO_9$. This compound was prepared by heating an intimate mixture of luminescent grade $BaCO_3$, Y_2O_3 and MoO_3 (samples of 5g) for 2 hr at 1200°C in air; after the heating process the reaction product was ground, sieved and heated a second time for 2 hr at 1300°C.

The X-ray diffraction of the reaction product only showed the diffraction lines of a cubic perovskite with $a = 4{\cdot}260 \pm 0{\cdot}002$ Å. No superlattice lines were found, even after annealing at 1000°C; this is probably caused by the nearly equal scattering factors of the Y- and Mo-ions.

$Ba_3Y_2MoO_9$ has a bright yellow body colour. Its diffuse reflection spectrum is given in Fig. 1, together with that of Y_4MoO_9. The latter phase was recently described by Fournier *et al.*[1] and was

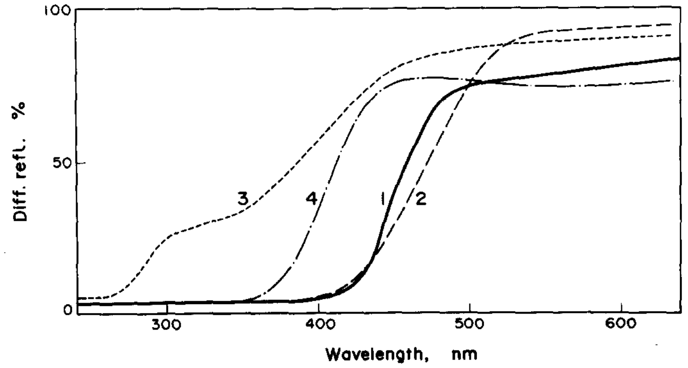

Fig. 1. Diffuse reflection spectra of $Ba_3Y_2MoO_9$ (curve 1), Y_4MoO_9 (curve 2), $BaMoO_4$ (curve 3) and Y_2MoO_6 (curve 4).

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