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THE FLUORINATION OF SULPHITE ESTERS BY SULPHUR TETRAFLUORIDE AND TUNGSTEN HEXAFLUORIDE

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Sulphur tetrafluoride has been widely used as a fluorinating agent for organic compounds (1) but tungsten hexafluoride is generally regarded as having no fluorinating properties (2). We wish to report the preparation of alkylfluorosulphites by the reactions of dialkylsulphites with these fluorides. Metal salts of fluorosulphurous acid are well known (3) but the corresponding esters have not been reported previously.

Sulphur tetrafluoride reacts with alkylsulphites, $(RO)_2SO$, R = Me, Et, at 130°-140° in a sealed tube according to the equation $(RO)_2SO + SF_4 = ROS(O)F + SOF_2 + RF$; the yields of ROS(O)F being better than 90%. SOF_2 and RF, identified by their infrared spectra and separated from ROS(O)F by vacuum distillation at -115° are produced in stoichiometric amounts. Since rigorous precautions were taken to exclude moisture from the reaction mixtures the formation of SOF_2 by hydrolysis can be eliminated. We suggest that SF_3OR is the product other than the alkylfluorosulphite and that it is unstable with respect to decomposition to SOF_2 and RF.

Tungsten hexafluoride reacts with alkylsulphites at 0° in a sealed tube giving ROS(O)F in approx. 40% yield based on the weight of sulphite used. The other products are small amounts of RF and an orange involatile liquid the ^{1}H and ^{19}F nuclear magnetic resonance spectra of which are consistent with a mixture of $WOF_4OS(OR)_2$ and $(RO)_3S^+WOF_5^-$. Tungsten oxytetrafluoride complexes have been shown to result from the reactions of tungsten hexafluoride with ethers but no organofluorine compounds were detected (4).

The alkyl fluorosulphites are colourless volatile liquids which are readily hydrolysed. They have been characterised by analysis, molecular weight, and mass, infrared and nuclear magnetic resonance spectroscopy (Table). For methylfluorosulphite, found C, 11·96; H, 3·00; F, 19·14; S, 32·75; O (by difference), 33·15; mol. wt. 98·9. CH_3FO_2S requires C, 12·24; H, 3·08; F, 19·37; S, 32·69; O, 32·62; Mol. wt. 98·1. For ethylfluorosulphite, found Mol. wt. 111·8, mass measurement of mass spectrometer peak $^m/_e$ 112, 111·99904, of peak $^m/_e$ 111, 110·99161. $C_2H_5FO_2S$ requires mol. wt. 112·1; $C_2H_5FO_2{}^{32}S$ requires $^m/_e$ 111·99942; $C_2H_4FO_2{}^{32}S$ requires $^m/_e$ 110·99160. Peaks in the infrared spectra of the fluorosulphites at 1266(Me) and 1260 cm^{-1}(Et) are assigned to ν(S=O) and at 700(Me) and 696 cm^{-1}(Et) to ν(S–F). The methylene protons of $C_2H_5OS(O)F$ are magnetically nonequivalent due to anisotropy with respect to rotation about the C–O–S bonds A similar effect has been observed in diethylsulphite (5).

It has been shown that $\equiv$Si–N$=$ bonds can be cleaved by sulphur fluorine compounds (6). $CH_3OS(O)F$ reacts with $(CH_3)_3Si{\cdot}N(C_2H_5)_2$ at 20° to give $(CH_3)_3SiF$ and a colourless liquid shown by analysis and its ^{1}H nuclear magnetic resonance

TABLE

^{1}H and ^{19}F NMR Spectra at 33•5°

Compound (neat liquid)	Chemical Shifts (ppm) and Multiplicity			$^{1}H-^{19}F$ Coupling Constants (Hz)
	$CH_3-^{(a)}$	$-CH_2-^{(a)}$	$-F^{(b)}$	
$CH_3OS(O)F$	−3•85 (doublet)		−55•6 (quartet)	1•3
$C_2H_5OS(O)F$	−1•35 (triplet)	−4•35 (c)	−59•8 (triplet)	1•3

(a) w.r.t. TMS interval

(b) w.r.t. CCl_3F interval

(c) two overlapping quartets (separation ~1 Hz) each peak further split due to $^{1}H-^{19}F$ coupling.

spectrum to be, the alkoxysulphinamide $CH_3OS(O)N(C_2H_5)_2$. Found C, 39•58; H, 8•54; N, 9•32; S, 20•96; O(by difference) 21•60. $C_5H_{13}O_2SN$ requires C, 39•73; H, 8•60; N, 9•27; S, 21•17; O, 21•23. The methylene protons are magnetically non equivalent as two overlapping quartets (separation 3 Hz) and are observed centred at −3•16 ppm from external TMS. Signals due to the CH_3O- (singlet) and CH_3- (triplet) groups occur at −3•39 and −1•10 ppm respectively.

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