Sulphur-containing Esters of Perfluoropinacol

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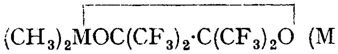
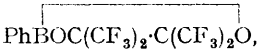
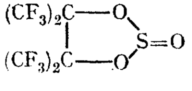
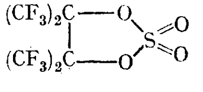
THE reductive dimerisation of hexafluoroacetone to perfluoropinacol has recently been reported by ourselves[1] and others.[2] The formation of the stable ionic disodium alkoxide of perfluoropinacol, $[(CF_3)_2CO{\cdot}CO(CF_3)_2]^{2-}$ 2 Na^+, by the action of sodium on hexafluoroacetone in donor solvent (*e.g.*, tetrahydrofuran) provides a reactive reagent for the preparation of linear or cyclic fluorinated alkaloxides of various elements by reaction with the appropriate halides or dihalides. We have in this way prepared such compounds as  $(CH_3)_2MOC(CF_3)_2{\cdot}C(CF_3)_2O$ (M = Si, Ge or Sn),  $PhBOC(CF_3)_2{\cdot}C(CF_3)_2O$, and $Ph_2POC(CF_3)_2{\cdot}C(CF_3)_2{\cdot}OPPh_2$.

We now report a novel product arising during an investigation of sulphur-containing esters of perfluoropinacol. Reaction of the disodium alkoxide of perfluoropinacol with thionyl chloride produced as expected the sulphite ester (I), b.p. 120°, while sulphuryl chloride gave the sulphate (II), b.p. 120—122°.



(I)



(II)

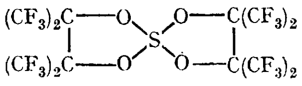
Reaction with sulphur dichloride was also tried, and proceeded readily to give a white crystalline material, m.p. 51—53°, which sublimed at 20° *in vacuo*. Its elemental analysis suggested the formula $C_{12}F_{24}O_4S$, and this was confirmed by mass-spectroscopic examination. The peak corresponding to the molecular ion (*M* 696) was not observed, the heaviest ion being at *M* 677. The Table shows all peaks observed for which $M \geqslant 300$, intensities being relative to 100 for the peak at *M* 231 ($C_5F_9^+$).

TABLE

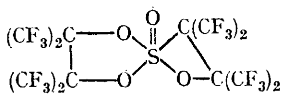
	Mass	Intensity	Formula
(i)	696	—	$C_{12}F_{24}O_4S^+$
(ii)	677	0·5	$C_{12}F_{23}O_4S^+$
(iii)	627	37	$C_{11}F_{21}O_4S^+$
(iv)	511	5	$C_9F_{17}O_3S^+$
(v)	364	19	$C_6F_{12}O_2S^+$
(vi)	311	1	$C_5F_9O_3S^+$
(vii)	300	6	$C_6F_{12}^+$

Peaks (ii) and (iii) correspond to the loss of F^- and CF_3^-, respectively, from the parent molecule, while peaks (iv) and (v) arise through loss of one hexafluoroacetone molecule from (ii) or two molecules from (i). Peak (vi) is consistent with a fragment differing from the sulphite structure (I) by loss of a CF_3^- ion, while peak (vii), the heaviest fluorocarbon fragment observed, corresponds to the ion $[(CF_3)_2C{=}C(CF_3)_2]^+$. All peaks below *M* 300 could be ascribed to fragments derived from perfluoropinacol; the only sulphur-containing ions observed in this region were SOF^+, SO_2^+, and SO^+.

The formula $C_{12}F_{24}O_4S$ is consistent with either structure (III) or (IV).



(III)



(IV)

We suggest that structure (III), perfluoropinacol orthosulphite, is by far the more likely of these two. Infrared-spectroscopic examination of the cyclic perfluoropinacol derivatives we have prepared previously has shown that the five-membered ring is characterised by absorptions near 1100, 1000, 950, 880, and 740 cm.$^{-1}$, and the sulphur compound shows these at the frequencies 1111, 1003, 969, 886, and 750 cm.$^{-1}$. The ^{19}F n.m.r. spectrum shows two rather broad absorptions of equal intensity, having the appearance of poorly resolved septets, at 10·5 and 12·2 p.p.m. (at 56·4 Mc./sec., downfield from $CF_3{\cdot}CO_2H$ external). This is consistent with structure (III), assuming that the sulphur atom, which carries a non-bonding electron pair, is not tetrahedrally surrounded by the four oxygen atoms, but is, to a first approximation, at the apex of a pyramid above the oxygen atoms. Such a structure leads to a division of the eight trifluoromethyl groups into two groups of four in different environments, their interconversion being possible only by inversion of the entire molecule about the sulphur atom.

Neither the infrared nor the n.m.r. spectrum gave any evidence in favour of structure (IV), and, considering also the low probability of going from the five- to the four-membered ring system, we feel that this structure may be excluded. A molecule of structure (III) might be expected to form an adduct with boron trifluoride through use of the nonbonding electron pair on the sulphur atom (as does SF_4); this we have found does not occur, but construction of a model shows that the surrounding trifluoromethyl groups would provide considerable steric hindrance to the approach of any Lewis-acid molecule.

The formation of a sulphur(IV) derivative by the reaction of sulphur(II) chloride with a sodium salt is not unprecendented, since sulphur(IV) fluoride may be made in this way using sodium fluoride.[3] In both cases, presumably, disproportionation of sulphur(II) to give sulphur(IV) and sulphur(0) is occurring, and, consistent with this, we find elemental sulphur as a reaction product.

However, there seems to be no precedent for the isolation of a stable compound in which a sulphur(IV) atom is linked to four oxygen atoms, since no ester of the type $(RO)_4S$ has been reported previously. Determination of the configuration of the oxygen atoms around sulphur in perfluoropinacol orthosulphite should be of some interest, and is now being investigated.

Satisfactory analytical data have been obtained for all new compounds mentioned above.

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[1] A. F. Janzen, P. F. Rodesiler, and C. J. Willis, *Chem. Comm.*, 1966, 672.

[2] C. L. Frye, R. M. Salinger, and T. J. Patin, *J. Amer. Chem. Soc.*, 1966, **88**, 2343.

[3] C. W. Tullock, F. S. Fawcett, W. C. Smith, and D. D. Coffman, *J. Amer. Chem. Soc.*, 1960, **82**, 539.