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Short Communication

Oxidation of iodoperfluoroalkylsulphur(VI) pentafluorides with chlorine trifluoride

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Chlorine trifluoride is a useful reagent for the oxidation of perfluoroalkyl iodides to the corresponding perfluoroalkyl-iodine(III) difluorides or -iodine(V) tetrafluorides[1, 2]. Oxidation of the recently reported compounds $SF_5(CF_2)_nI$, where $n = 2$ or 4[3] (for related compounds see ref. 4), should yield fluoroalkanes having both $-SF_5$ and $-IF_4$ or $-IF_2$ substituents as the $-CF_2SF_5$ group is chemically inert[5]. This has been found to be the case.

The reactions are summarised in Table 1. The analytical data suggest that in both cases the products are iodine(V) compounds but their NMR spectra (Table 2) clearly indicate that the product obtained from $SF_5CF_2CF_2I$ is a mixture of $SF_5CF_2CF_2IF_2$ and $SF_5CF_2CF_2IF_4$ in approximately a 1:1 mole ratio. The different behaviour is probably due to the lower solubility of $SF_5(CF_2)_2IF_2$ in the liquid reaction mixture and does not indicate that $SF_5(CF_2)_2IF_2$ is less easily oxidised. Under the conditions used, no side reactions occur.

The compounds are best characterised by their NMR spectra with their mass spectra providing additional support. The NMR spectroscopic equivalence of the fluorine atoms in the $-IF_n$ groups is consistent with a pseudo-octahedral environment for I^V with equatorial F ligands, and a pseudo-trigonal-bipyramidal

TABLE 1

REACTIONS OF ClF_3 WITH $SF_5(CF_2)_nI$

Reactants (mmol)	Reaction conditions	Products
$SF_5(CF_2)_2I$ (4.4) + ClF_3 (6.8)	−65 °C to −30 °C overnight in C_6F_{14} (3.3 g)	$SF_5(CF_2)_2IF_4$ [a] $SF_5(CF_2)_2IF_2$
$SF_5(CF_2)_4I$ (3.7) + ClF_3 (7.6)	−78 °C to −36 °C overnight in C_6F_{14} (3.9 g)	$SF_5(CF_2)_4IF_4$ [b]

[a] Analysis: Found: C, 5.8; F, 57.2; I, 29.85; S, 7.5 %. $C_2F_{13}IS$ requires C, 5.6; F, 57.4; I, 29.5; S, 7.5 %.

[b] Analysis: Found: C, 8.9; F, 60.5; I, 24.3; S, 6.2 %. $C_4F_{17}IS$ requires C, 9.1; F, 60.9; I, 23.9; S, 6.1 %.

TABLE 2

^{19}F NMR PARAMETERS OF THE $-IF_n$ GROUPS

Compound	Chemical shift δ/ppm [a]	Coupling constants $\frac{1}{2}[^3J(FF) + {}^4J(FF)]$/Hz
$SF_5(CF_2)_4IF_4$	-29.9	14
$SF_5(CF_2)_2IF_4$	-33.0	16
$SF_5(CF_2)_2IF_2$	-175.5 [b]	~ 11

[a] Compare $\delta(IF_4) = -32.4$ ppm in CF_3IF_4; $\delta(IF_2) = -172.7$ ppm in CF_3IF_2[2].

[b] Broad signal [width ½ height = 30 Hz] with partially resolved fine structure.

environment for I^{III} with axial F ligands. However the presence of fast intramolecular exchange processes, particularly for the I^{III} compound, cannot be ruled out.

$SF_5(CF_2)_4IF_4$ is a white solid, soluble in CH_3CN and IF_5. The $-IF_4$ group undergoes slow hydrolysis in moist air. The compound melts (66–68 °C) without decomposition and sublimes *in vacuo* at 140 °C. The $SF_5(CF_2)_2IF_4/SF_5(CF_2)_2IF_2$ mixture (m.p. 69–70 °C) has similar properties. The thermal stability of these compounds is in marked contrast to those of CF_3IF_4 and CF_3IF_2 which both decompose readily at 20 °C[2, 6]. We suggest that the $SF_5(CF_2)_n-$ groups reduce the possibility of close intermolecular contacts between $-IF_n$ groups which are believed to promote the decomposition of R_FIF_n species.

Experimental

All operations were carried out in Monel metal or Pyrex vacuum lines or in a Lintott inert-atmosphere box where the H_2O and O_2 concentrations were $\leqslant 10$ ppm. ^{19}F NMR spectra were recorded on a Jeol C60-HL instrument at 56.4 MHz. Chemical shifts are reported as δ values from CCl_3F which are positive to low field of the reference. Mass spectra were recorded on a G.E.C./A.E.I. MS12 instrument at 70 eV with direct sample insertion. Microanalyses were by A. Bernhardt, Elbach über Engelskirken, W. Germany. Chlorine trifluoride (Matheson), perfluoro-n-hexane (Fluorochem) and $SF_5(CF_2)_nI$ (I.C.I. Ltd., Mond Division) were used as received.

Preparation and characterisation of $SF_5(CF_2)_nIF_4$

Oxidations were performed in a Kel-F trap attached to the Monel vacuum system, using techniques described elsewhere[2]. The usual precautions in handling ClF_3 were observed. A small excess of ClF_3 over that required by equation (1) was used in each case (see Table 1)

$$3R_FI + 4ClF_3 \rightarrow 3R_FIF_4 + 2Cl_2 \qquad (1)$$

but in the $SF_5(CF_2)_2I$ reaction some precipitation occurred at −65 °C which resulted in a mixture of products.

Signals attributable to $-SF_5$, $-CF_2-$ and $-IF_n$ groups were easily distinguished from the NMR spectra of the products in CH_3CN. Complete analyses were not undertaken but the $-IF_n$ parameters are given in Table 2. Approximate chemical shifts of the other ^{19}F nuclei were as follows: $SF_5(CF_2)_4IF_4$; $\delta(SF)$ 64, $\delta(SF_4)$ 46, $\delta(CF_2)$ -85 and -94 (tentatively assigned to $-CF_2IF_4$ and $-CF_2SF_5$ respectively), -119 and -121. $SF_5(CF_2)_2IF_4$; $\delta(SF)$ 57, $\delta(SF_4)$ 44, $\delta(CF_2IF_4)$ -90, $\delta(CF_2SF_5)$ -96. $SF_5(CF_2)_2IF_2$; $\delta(SF)$ 57, $\delta(SF_4)$ 46, $\delta(CF_2IF_4)$ -87, $\delta(CF_2SF_5)$ -96 ppm.

The mass spectrum of $SF_5(CF_2)_4IF_4$ was similar to that of the parent iodide with additional peaks as follows [*m/e*, intensity relative to *m/e* 69 (CF_3^+), assignments]: 473, <0.1, $SF_5(CF_2)_4IF^+$; 203, 2, IF_4^+; 184, 2, IF_3^+; 165, 8, IF_2^+; 146, 3, IF^+. Analogous peaks were observed for the $SF_5(CF_2)_2IF_4/SF_5(CF_2)_2IF_2$ mixture.

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REFERENCES

1 C. S. RONDESTVEDT, JR., *J. Amer. Chem. Soc., 91* (1969) 3054.
2 O. R. CHAMBERS, G. OATES AND J. M. WINFIELD, *J. Chem. Soc., Chem. Commun.*, (1972) 839; G. OATES AND J. M. WINFIELD, *J. Chem. Soc. (Dalton Trans.)*, (1974) 119.
3 J. HUTCHINSON, *Abstracts, 4th European Symposium on Fluorine Chemistry, Ljubljana*, 1972, 11–20; *J. Fluorine Chem., 3* (1973/74) 429.
4 G. L. GARD AND C. WOOLF, *J. Fluorine Chem., 1* (1971/72) 487.
5 H. L. ROBERTS, in G. NICKLESS (Ed.), *Inorganic Sulphur Chemistry*, Elsevier, Amsterdam, 1968.
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