Bis(perfluoroalkyl)sulphur Difluorides and Bis(perfluoralkyl) Sulphoxides

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Summary Bis(perfluoroalkyl)sulphur difluorides result from the fluorination of bis(perfluoroalkyl)sulphides with chlorine monofluoride and react to give bis(perfluoroalkyl)sulphoxides.

Previous attempts to prepare SF_4 derivatives by the fluorination of bis(perfluoroalkyl) sulphides with metal fluorides resulted in either bond cleavage or oxidation to sulphur(VI).[1] We have found a straightforward synthesis for bis(perfluoroalkyl)sulphur difluorides in which the products are formed nearly quantitatively by the ClF fluorination of a bis(perfluoroalkyl) sulphide to the corresponding bis(perfluoroalkyl)sulphur difluoride [reaction (1)].

$$CF_3SR_F + ClF \xrightarrow{-78^\circ} CF_3SF_2R_F + Cl_2 \tag{1}$$

$$R_F = CF_3,\ C_2F_5,\ n\text{-}C_3F_7$$

In a typical reaction, CF_3SCF_3 (3 mmol) and ClF (6 mmol) are condensed into a metal reactor at −183°. The reactor is warmed to −78° and slowly allowed to warm to 25° over 12 h. Fractional condensation, followed by g.c. gives $CF_3SF_2CF_3$ in 90% yield. Similar yields were obtained with $CF_3SCF_2CF_3$ and $CF_3SCF_2CF_2CF_3$.

Bis(perfluoroalkyl)sulphur difluorides prepared in this manner are colourless liquids at room temperature and have been characterized by i.r., n.m.r., and m.s. data. Elemental analyses and vapour pressure data support the structures given.

Oxidation of bis(perfluoralkyl) sulphides to the corresponding sulphoxides has been unsuccessful.[1] Pure $CF_3SF_2CF_3$ held in Pyrex or in the presence of water vapour failed to hydrolyse after one week. However, reaction of $R_FSF_2CF_3$ with HCl, followed by hydrolysis yields the bis(perfluoroalkyl) sulphoxides directly [reaction (2)].

$$CF_3SF_2R_F + HCl \longrightarrow CF_3SCl_2R_F \xrightarrow{H_2O} CF_3S(O)R_F \tag{2}$$

$$R_F = CF_3,\ C_2F_5,\ n\text{-}C_3F_7$$

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No attempt was made to isolate the sulphur dichloride intermediate. Yields range from 40—95% depending on the sulphur difluoride used, but, in general, the yield decreases with increasing complexity of the R_F group. Each of the sulphoxides, $CF_3S(O)CF_3$, $CFS(O)CF_2CF_3$ and $CF_3S(O)CF_2CF_2CF_3$ is a colourless liquid at room temperature and is stable in Pyrex at 25°. In a typical reaction, $CF_3SF_2CF_3$ (3 mmol) and HCl (8 mmol) react at room temperature overnight in Pyrex. Fractional condensation, followed by g.c. separation gives $CF_3S(O)CF_3$ in 95% yield.

The most striking changes in the infrared for the sulphoxides compared to those of the sulphur difluorides are the absence of the band at 675 cm^{-1} and the appearance of a band in the 1230—1245 cm^{-1} region which may be assigned to the S=O stretch. The mass spectra show molecular ions in all cases. Fluorine atoms bonded to the α-methylene carbon atom are non-equivalent due to the presence of an asymmetric centre. Vapour pressure data and elemental analyses also support the assigned structures.

The hydrolytic stability of the sulphur difluorides is not easily understood since such a process is favoured themodynamically and SF_4,[2] as well as perfluoroalkylsulphur trifluorides,[3] rapidly hydrolyses. Steric shielding of the $-SF_2-$ in $CF_3SF_2CF_3$ cannot be advanced to explain this stability as opposed to the case for $[(CF_3)_2CF]_2SF_2$.[4]

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