

PREPARATION OF SOME PERFLUOROALKYLSULPHINES

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Fluorotrifluoromethylsulphine ($\text{CF}_3\text{CF}=\text{S}=\text{O}$, 1), the first stable perfluoroalkylsulphine has been synthesised recently in our laboratories. An alternative route to (1) and a route to other perfluoroalkylsulphines $\text{R}_f\text{CF}=\text{S}=\text{O}$ arise via the dechlorofluorination of perfluoroalkylsulphonyl chlorides ($\text{R}_f\text{CF}_2\text{SOCl}$, 2), readily available from the corresponding sulphonyl halides.

Thermal dechlorofluorination of the sulphonyl chlorides (2) over copper at approximately 250° gives the corresponding sulphines. In contrast, at temperatures around 200° , the reaction of the sulphonyl chlorides (2) with copper gives the perfluoroalkylthiosulphonates ($\text{R}_f\text{S}\cdot\text{SO}_2\text{R}_f$), which are also prepared from the sulphonyl chlorides (2) and mercury at room temperature.

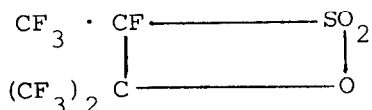
† see footnote on p. 63

PREPARATION AND REACTIONS OF 1,2-OXATHIETAN 2,2-DIOXIDES:
A CONVENIENT ROUTE TO INTERNAL POLYHALOGENOALKENES

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1,2-Oxathietan 2,2-dioxides (β -sultones) are conveniently prepared either by the addition of sulphur trioxide to polyfluoroalkenes or by the addition of polyhalogenoketones to a sulphene. Thus the sulphonyl fluoride ($\text{CF}_3\text{CHF}\cdot\text{SO}_2\text{F}$, 1) reacts with the complex of $\text{Me}_3\text{N}\cdot\text{SiF}_4$, probably to give the sulphene $\text{CF}_3\text{CF}:\text{SO}_2$ which, in the presence of hexafluoroacetone, gives the sultone



Extension of this procedure has yielded a series of β -sultones. Pyrolysis of the sultones eliminates SO_3 and provides an efficient route to internal perfluoroalkenes, whereas photolysis of a sultone yields an oxirane via loss of SO_2 .

The reaction of some of the internal olefins with chloride ion will also be described.

† see footnote on p. 63