

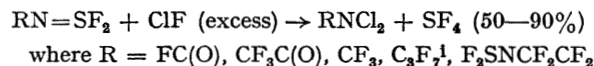
Iminosulphur Difluorides. A New Route to *NN*-Dichloro-compounds

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Summary Perfluoroacyl- and perfluoroalkyl-iminosulphur difluorides react with chlorine monofluoride by the elimination of sulphur tetrafluoride to form the corresponding *NN*-dichloroperfluoro-amides and -amines in high yield.

THE chemistry of the class of compounds $RN=SF_2$ has been limited to sulphur-fluorine reactions, carbon-nitrogen cleavage, and sulphur-nitrogen double bond saturation with accompanying sulphur oxidation.¹ We have found that perfluoroacyl- and perfluoroalkyl-iminosulphur difluorides react with ClF in what is believed to be the first example of direct elimination of SF_4 and formation of the corresponding *NN*-dichloro-compounds.



The reaction of ClF and 1,2-bis(iminosulphur difluoride) tetrafluoroethane yields 1,2-bis(dichloroamino)tetrafluoroethane in greater than 50% yield. Although perfluoroalkyl-dichloroamines are readily accessible by the reaction of perfluoroalkylnitriles and ClF,² this method is restrictive in that the NCl_2 group may only be introduced on to a primary carbon atom. The easy introduction of the NSF_2 group *via* SF_4 reactions,¹ or the photolytic and thermal reactions of $XNSF_2$ ($X = Cl, Br$) with alkenes³ when followed by reaction with ClF, eliminates this restriction.

NN-Dichlorofluoroformamide and *NN*-dichlorotrifluoroacetamide are the first members of the new class of compounds, *NN*-dichloroperfluoroamides, $R_1C(O)NCl_2$. These compounds are light-yellow liquids which are not shock-sensitive in normal handling and which are thermally stable at 125° in Pyrex glass for 24 h.

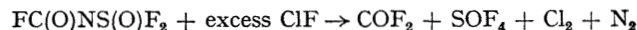
¹ O. Glemser, *Endeavour*, 1967, **28**, 86; O. Glemser and M. Fild, *Halogen Chem.*, 1967, **2**, 1.

² J. B. Hynes and T. E. Austin, *Inorg. Chem.*, 1966, **5**, 488.

³ R. Mews and O. Glemser, *Chem. Ber.*, 1969, **102**, 4188; *Inorg. and Nuclear Chem. Letters*, 1970, **6**, 35.

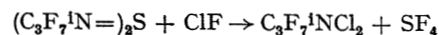
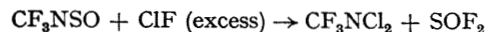
⁴ R. F. Swindell, University of Idaho, personal communication.

Attempts were made to extend this reaction to sulphur(vi) imines and inorganic iminosulphur difluorides with strikingly different results. When $FC(O)N=S(O)F_2$ was treated with ClF, we were unable to isolate $FC(O)NCl_2$ although SOF_4 was formed. Instead the reaction gives rise to the following:



While at -78° very little reaction occurred over 4 h, and the only isolable products were COF_2 and SOF_4 , at 25° the reaction is essentially quantitative. When equal amounts of ClF and $FC(O)NCl_2$ are held at -78° there is only 10–20% decomposition over 4 h and at 25° approximately 50% occurs in 3 h. It therefore seems that $FC(O)NCl_2$ is not an initial product and the reaction may proceed *via* C–N cleavage rather than S=N cleavage. Some inorganic iminosulphur difluorides are still being studied, but work with $NCNSF_2$ and $CNSF_2$ seems to indicate that S=N attack may not be the first step in these reactions.

Although these differences occur, the reaction appears to be general for other sulphur(iv) imines. Both *N*-sulphinyl-trifluoromethylamine and *NN'*-perfluoroisopropylsulphur di-imide⁴ react with ClF to eliminate the sulphur(iv) fluoride and to yield the corresponding dichloroamines



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