Chlorofluorination Reactions of Sulphur(IV) Fluorides

By J. I. DARRAGH and D. W. A. SHARP*

(*Chemistry Department, University of Glasgow, Glasgow, W.2*)

Summary Trifluoromethylsulphur chloride tetrafluoride, CF_3SF_4Cl, results from the action of chlorine on CF_3SF_3 in the presence of caesium fluoride, and $CH_3N:SF_2$ reacts with chlorine to give $CH_2ClN:SF_2$, $CHCl_2N:SF_2$, and $CF_3N:SCl_2$.

SULPHUR CHLORIDE PENTAFLUORIDE, SF_5Cl, is readily prepared from sulphur tetrafluoride by the action of chlorine in the presence of caesium fluoride,[1] suggesting that substituted derivatives of SF_5Cl could result from the corresponding reaction using substituted derivatives of sulphur tetrafluoride. Trifluoromethylsulphur trifluoride reacts with chlorine in the presence of caesium fluoride at room temperature to give trifluoromethylsulphur chloride tetrafluoride, CF_3SF_4Cl. The product has been characterised by n.m.r. and mass spectrometry; the configuration about the sulphur atom is *trans*-octahedral so that all four fluorines attached to sulphur are equivalent. Most[2] of the known disubstituted derivatives of sulphur hexafluoride have a *cis*-configuration, but difluoroaminotrifluoromethylsulphur tetrafluoride, $CF_3SF_4NF_2$, also has the *trans*-configuration;[3] the mass spectra of the two *trans* derivatives, CF_3SF_4Cl and $CF_3SF_4NF_2$, show very similar cracking patterns. Trifluoromethylsulphur chloride tetrafluoride is a colourless volatile liquid, stable at room temperature.

Dimethylaminosulphur trifluoride[4] reacts with chlorine

to give sulphur tetrafluoride as the major product; it is possible that the reaction proceeds by intermediate formation of sulphur chloride trifluoride, SF_3Cl, which undergoes reorganisation. Dimethylaminosulphur trifluoride reacts with chlorine and caesium fluoride to give sulphur chloride pentafluoride; it is probable that the reaction proceeds by initial formation of sulphur tetrafluoride.

N.m.r. data

(a) ClF_3SF_4Cl
^{19}F (p.p.m.)[a] J_{FF}Hz.
+ 67·3 (quintet) − 102·1 (quartet) 24
(b) $X_3CN:SY_2$ derivatives

Compound	^1H (p.p.m.)[b]	^{19}F (p.p.m.)[a]	J_{HF} Hz.
$H_3CN:SF_2$	−2·3 (triplet)	−67·3 (bs)	9·5
$ClH_2CN:SF_2$	−5·12 (triplet)	−59·7 (bs)	8·2
$Cl_2HCN:SF_2$	−7·19 (triplet)	−53·6 (bs)	6·9
$F_3CN:SCl_2$	—	+56·1 (s)	—

[a] Chemical shift with respect to internal CCl_3F
[b] Chemical shift with respect to internal Me_4Si.
bs broad singlet.
s singlet.

In contrast to the behaviour of dimethylaminosulphur trifluoride, methyliminosulphur difluoride,[5] $CH_3N:SF_2$, reacts with chlorine at room temperature with substitution of chlorine into the methyl group. The products are chloromethyliminosulphur difluoride, $CH_2ClN:SF_2$, dichloromethyliminosulphur difluoride, $CHCl_2N:SF_2$, and hydrogen chloride; the proportion of products depends upon the relative proportion of starting materials. In the presence of excess of chlorine, trifluoromethyliminosulphur dichloride, $CF_3N:SCl_2$, is also formed; trichloromethyliminosulphur difluoride, $CCl_3N:SF_2$, has not been identified among the products of this reaction. There is no marked change in the products when caesium fluoride is present. Trifluoromethyliminosulphur dichloride has been previously reported[6] to result from the action of aluminium trichloride on trifluoromethyliminosulphur difluoride. It would appear from these results that the C–H bonds in the methyliminosulphur group undergo very ready substitution by chlorine. Once substitution to the trichloromethylimino group is complete fluorination of the C–Cl bonds by the S–F groups occurs. This latter stage is similar to that observed in the chlorofluoromethylsulphenyl fluorides, $CF_nCl_{3-n}SF$, which rapidly change to the isomeric sulphenyl chlorides, $CF_{n+1}Cl_{2-n}SCl$, at room temperature.[7]

(*Received, June 12th*, 1969; *Com.* 841.)

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