Fluorinated Dichloro Hexa- and Penta-co-ordinated Sulphur(VI) Compounds

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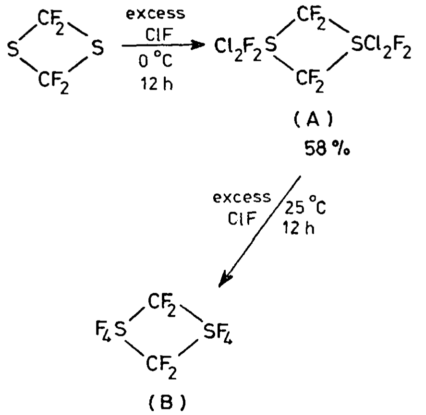
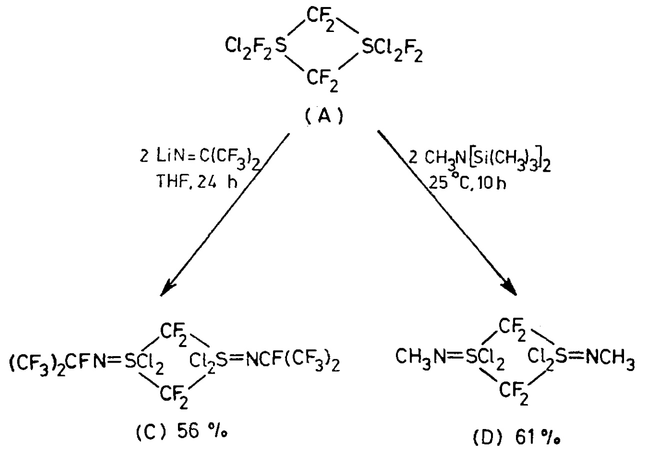
Summary Chlorine monofluoride oxidatively chlorofluorinates tetrafluoro-1,3-dithietan to form the first example of a stable fluorine-containing dichlorosulphur compound, $\overline{S(F_2Cl_2)CF_2S(F_2Cl_2)CF_2}$; with $LiN{=}C(CF_3)_2$ and $CH_3N[Si(CH_3)_3]_2$, the first examples of fluorinated pentaco-ordinate dichlorosulphimides, $[(CF_3)_2CFN{=}]\overline{SCl_2{\cdot}CF_2{\cdot}[(CF_3)_2CFN{=}]SCl_2{\cdot}CF_2}$ and $(CH_3N{=})\overline{SCl_2{\cdot}CF_2{\cdot}(CH_3N{=})SCl_2{\cdot}CF_2}$ are obtained.

We report the synthesis of the first examples of stable fluorine-containing dichlorosulphur(VI) compounds. Earlier we and others demonstrated that chlorine monofluoride readily fluorinates bis(perfluoroalkyl) sulphides or fluorinated cyclic sulphides to the corresponding bis(perfluoroalkyl)sulphur difluorides,[1,2] tetrafluorides,[2,3] or fluorinated cyclic sulphur difluorides or tetrafluorides.[4] The degree of fluorination is primarily a function of temperature: the lower the reaction temperature, the larger the yield of the sulphur(IV) compound.



Scheme 1

Through the use of appropriate conditions, the tetrachloro-tetrafluoro-intermediate (A) has now been isolated.† Compound (A) is prepared (Scheme 1) by allowing a mixture of an excess of chlorine monofluoride and tetrafluoro-1,3-dithietan to warm slowly from −196 to 0 °C during 10 h. Recrystallization of the involatile product from $CHCl_3$ gave (A), m.p. 170—172 °C. Its ^{19}F n.m.r. spectrum consists of two complex multiplets at ϕ − 148·3 and 102·2 p.p.m. from internal $CFCl_3$. The resonance at ϕ − 148·3, assigned to fluorine atoms bonded to sulphur, occurs in the range reported for equatorially positioned fluorine atoms in a series of $-SF_nX$ compounds (SF_5Cl, −125·2;[5] SF_5Br, −145·6;[6] CF_3SF_4Cl, −102·1[7] p.p.m.). The fragment ions at *m/e* 190 and 192 ($CF_2SCl_2F_2^+$) are present in the mass spectrum.



Scheme 2

Compound (A) is fluorinated readily with chlorine monofluoride to form the tetrafluorosulphur derivative (B)[3] quantitatively, which may be collected in a trap at −78 °C upon vacuum distillation. The reactions of compound (A) with nucleophiles, such as $LiN{=}C(CF_3)_2$ [in tetrahydrofuran (THF)] and $CH_3N[Si(CH_3)_3]_2$ (neat), produce two new dichloro-sulphur(VI) compounds (C) and (D) in which the sulphur is pentaco-ordinate (Scheme 2).† Compound (C), the product of reaction with $LiN{=}C(CF_3)_2$, was obtained by

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† Satisfactory (±0·2%) analyses for C and, where appropriate, for H and N were obtained for (A), (C), and (D). Cl analyses were not in such good agreement; for (A), calc., 37·2, found 36·55%; for (C), calc. 22·05, found, 22·9%.

evaporation of solvent *in vacuo*, and recrystallized from THF, m.p. 121—123 °C; ^{19}F n.m.r. ϕ 144·8 (CF), 98·2 (CF_2), and 71·5 (CF_3) p.p.m., intensity ratio 2:4:12, respectively. The $(CF_3)_2CF$ resonance at ϕ 144·8 is a multiplet owing to coupling with the CF_2 (J 10·6 Hz) and CF_3 groups (J 3·6 Hz). The mass spectrum shows a weak molecular ion at *m/e* 670, 672, 674, and fragments at *m/e* 304, 306, 308 ($\overline{CF_2SCl_2CF_2S}Cl_2^+$) and at 164 ($C_3F_6N^+$, $C_2S_2F_4^+$). Compound (D), the product of reaction with $CH_3N[Si(CH_3)_3]_2$, was obtained in 61% yield following recrystallization from $CHCl_3$, m.p. 156—157 °C; n.m.r. ($CDCl_3$): ^1H, τ 8·31 (s); ^{19}F, ϕ 97·6; weak molecular ion at *m/e* 362, 364, 366. The fluorine atoms bonded to sulphur have been displaced leaving the chlorine atoms as is typical in reactions of chloro- and bromo-derivatives of SF_6.[8] A concomitant 1,3 fluorine shift from sulphur to carbon also occurs.[9,10] Reaction of (B) with the same nucleophile allows the preparation of the tetrafluoro-analogue (E) of compound (C). Based on i.r. and ^{19}F n.m.r. spectral data, the fluorine atoms in (E) bonded to sulphur occupy axial positions.[11] Thus, the chlorine atoms in (C) and (D) must be axial, also.

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[1] D. T. Sauer and J. M. Shreeve, *J. Fluorine Chem.*, 1972, **1**, 1.
[2] G. Haran and D. W. A. Sharp, *J. Fluorine Chem.*, 1973/74, **3**, 423.
[3] T. Abe and J. M. Shreeve, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 465; *J. Fluorine Chem.*, 1973/74, **3**, 187.
[4] T. Abe and J. M. Shreeve, *J. Fluorine Chem.*, 1973/74, **3**, 17.
[5] R. K. Harris and K. J. Packer, *J. Chem. Soc.*, 1961, 4736.
[6] C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, *Inorg. Chem.*, 1962, **1**, 215.
[7] J. I. Darragh and D. W. A. Sharp, *Chem. Comm.*, 1969, 864.
[8] T. Kitazume and J. M. Shreeve, *J. Amer. Chem. Soc.*, 1977, **99**, 3690.
[9] R. F. Swindell and J. M. Shreeve, *J. Amer. Chem. Soc.*, 1972, **94**, 5713.
[10] J. A. Gibson and R. Schmutzler, *Z. anorg. Chem.*, 1975, **416**, 222.
[11] T. Kitazume and J. M. Shreeve, *J. Amer. Chem. Soc.*, in the press.