

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

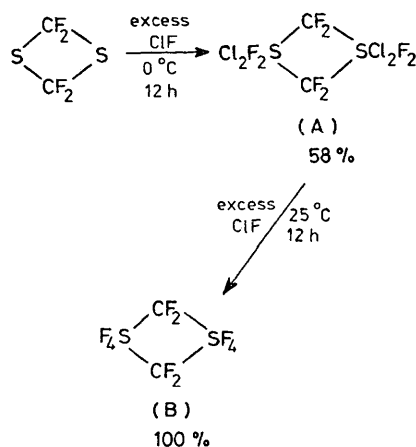
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Summary Chlorine monofluoride oxidatively chloro-fluorinates tetrafluoro-1,3-dithietan to form the first example of a stable fluorine-containing dichlorosulphur compound, $\text{S}(\text{F}_2\text{Cl}_2)_2$; with $\text{LiN}=\text{C}(\text{CF}_3)_2$ and $\text{CH}_3\text{N}[\text{Si}(\text{CH}_3)_3]_2$, the first examples of fluorinated pentaco-ordinate dichlorosulphimides, $[(\text{CF}_3)_2\text{CFN}=\text{S}]\text{Cl}_2\cdot\text{CF}_2$ and $(\text{CH}_3\text{N}=\text{S})\text{Cl}_2\cdot\text{CF}_2$ 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

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 $\delta -148.3$ and 102.2 p.p.m. from internal CFCl_3 . The resonance at $\delta -148.3$, assigned to fluorine atoms bonded to sulphur, occurs in the range reported for equatorially positioned fluorine atoms in a series of $-\text{SF}_n\text{X}$ compounds (SF_6Cl , -125.2 ;⁵ SF_5Br , -145.6 ;⁶ $\text{CF}_3\text{SF}_4\text{Cl}$, -102.17 p.p.m.). The fragment ions at m/e 190 and 192 ($\text{CF}_2\text{SCl}_2\text{F}_2^+$) are present in the mass spectrum.

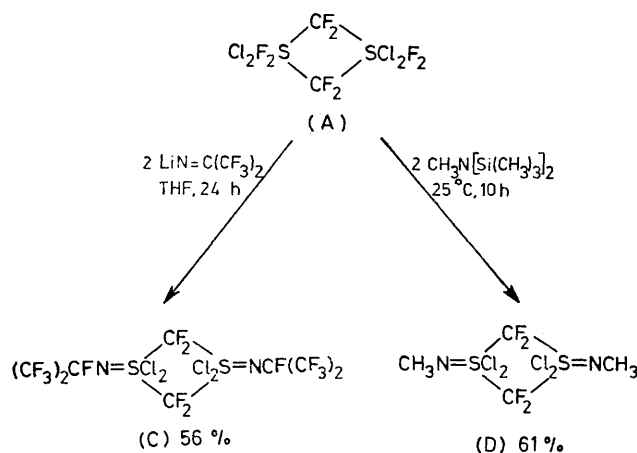


SCHEME 1

fluorination is primarily a function of temperature: the lower the reaction temperature, the larger the yield of the sulphur(iv) compound.

Through the use of appropriate conditions, the tetrachloro-tetrafluoro-intermediate (A) has now been isolated.†

† Satisfactory ($\pm 0.2\%$) 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%.



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 $\text{LiN}=\text{C}(\text{CF}_3)_2$ [in tetrahydrofuran (THF)] and $\text{CH}_3\text{N}[\text{Si}(\text{CH}_3)_3]_2$ (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 $\text{LiN}=\text{C}(\text{CF}_3)_2$, was obtained by

evaporation of solvent *in vacuo*, and recrystallized from THF, m.p. 121–123 °C; ^{19}F n.m.r. δ 144.8 (CF), 98.2 (CF₂), and 71.5 (CF₃) p.p.m., intensity ratio 2:4:12, respectively. The (CF₃)₂CF resonance at δ 144.8 is a multiplet owing to coupling with the CF₂ (J 10.6 Hz) and CF₃ 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 (CF₂SCl₂CF₂SCl₂⁺) and at 164 (C₃F₆N⁺, C₂S₂F₄⁺). Compound (D), the product of reaction with CH₃N[Si(CH₃)₃]₂, was obtained in 61% yield following recrystallization from CHCl₃, m.p. 156–157 °C; n.m.r. (CDCl₃): ^1H , τ 8.31 (s); ^{19}F , δ 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 SF₆.⁸ 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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