Defluorination of Pentafluorosulphur Chloride and Pentafluorosulphur Bromide by Strong Nucleophiles

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Summary Strong nucleophiles, $(CF_3)_2C{=}NLi$ and $(CH_3)_2NSi(CH_3)_3$, readily defluorinate SF_5Cl and SF_5Br to form $SF_3X{=}NCF(CF_3)_2$, $SFX[{=}NCF(CF_3)_2]_2$, and *trans*-$(CH_3)_2NSF_4X$ ($X = Cl,Br$).

Currently there is considerable interest in the utilization of SF_5Cl[1,2] and SF_5Br[2,3] as reagents for introducing the SF_5 unit into a variety of unsaturated systems under free-radical conditions. However, with the exception of the base hydrolysis of SF_5Cl, little has been reported on the behaviour of SF_5-containing compounds toward nucleophiles. Earlier workers indicated that SF_5Cl was reduced to SF_4 by PhLi,[4] and that it oxidatively fluorinated substituted phosphorus(III) halides to phosphorus(V) fluorides,[5] and oxidized a variety of organic compounds[4].

We now report that both SF_5Cl and SF_5Br undergo smooth reactions with $LiN{=}C(CF_3)_2$, resulting in the replacement of sulphur–fluorine bonds by sulphur–nitrogen multiple bonds, accompanied by fluorine atom shifts [reactions (1) and (2)]. The sulphur–chlorine and sulphur–bromine bonds remain unaffected. This phenomenon of migration of fluorine with concomitant double bond shift occurs frequently in reactions which involve $(CF_3)_2C{=}N^-$.[6–8]

$$SF_5X + LiN{=}C(CF_3)_2 \xrightarrow{-196\text{ to }25\,^{\circ}C} SF_3X{=}NCF(CF_3)_2 \quad (1)$$

$X = Cl$ (74% yield), Br (89%)

$$SF_3X{=}NCF(CF_3)_2 + LiN{=}C(CF_3)_2 \xrightarrow{-196\text{ to }25\,^{\circ}C} SFX[{=}NCF(CF_3)_2]_2 \quad (2)$$

$X = Cl$ (83%), Br (87%)

In typical reactions, SF_5Cl[9] (7 mmol) was condensed into a Pyrex glass vessel which contained $LiN{=}C(CF_3)_2$[7] (5 mmol) at −196 °C. The mixture was allowed to warm slowly to 25 °C and kept 24 h. After separation by trap-to-trap techniques, the colourless liquid, $SF_3Cl{=}NCF(CF_3)_2$, was recovered at −78 °C. $SF_3Cl{=}NCF(CF_3)_2$ (*ca.* 2 mmol) was condensed onto $LiN{=}C(CF_3)_2$ (1·5 mmol) and the reaction allowed to proceed as above. The colourless liquid, $SFCl[{=}NCF(CF_3)_2]_2$, was obtained.

Table

	$\delta^a(SF_A)$ /p.p.m.	$\delta(SF_B)$ /p.p.m.	J_{AB}/Hz
SF_5Cl^b	−61·9	−125·4	148·5
SF_5Br^b	−62·0	−145·2	143·1
$SF_3Cl{=}NCF(CF_3)_2$ ..	−59·5 tr	−120·0 d	128
$SFCl[{=}NCF(CF_3)_2]_2$ ..	−71.6		
$SF_3Br{=}NCF(CF_3)_2$ ..	−59·5 tr	−139·5 d	125
$SFBr[{=}NCF(CF_3)_2]_2$ ..	−91·5		

[a] CCl_3F internal reference. [b] C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, *Inorg. Chem.*, 1962, **1**, 215.

Reactions with SF_5Br[10] were carried out in the same manner. Both bromine-containing derivatives are pale yellow liquids.

These new compounds have been identified and characterised by i.r., n.m.r., and mass spectral techniques as well as by elemental analyses. Fluorine-19 n.m.r. spectral data indicate that the molecular geometry is changed from octahedral (SF_5X) to trigonal bipyramidal [$SF_3X{=}NCF(CF_3)_2$] and to tetrahedral [$SFX({=}NCF\{CF_3\}_2)_2$] (Table).

When mass spectral data are measured at 25 °C, M^+ ions are found for the chloro-derivatives and $(M - F)^+$ ions for the bromo-derivatives.

Also, we find that $(CH_3)_2NSi(CH_3)_3$ attacks SF_5X at −78 °C to replace the axial fluorine atom and form the stable disubstituted sulphur hexafluoride derivative [reaction (3)].

$$SF_5X + (CH_3)_2NSi(CH_3)_3 \xrightarrow{-78\,^{\circ}C} trans\text{-}(CH_3)_2NSF_4X + (CH_3)_3SiF$$

$$X = Cl\ (75\%),\ Br\ (72\%)$$

Typically, SF_5X (3·5 mmol) and $(CH_3)_2NSi\,(CH_3)_3$ (3·0 mmol) were condensed together at −196 °C and allowed to warm slowly to −78 °C and to remain for 12 h. The pure liquid was obtained using trap-to-trap separation.

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[1] N. H. Ray, J. R. Case, and H. L. Roberts, *J. Chem. Soc.*, 1961, **2066**, 2070; R. E. Banks, R. N. Haszeldine, and W. D. Morton, *J. Chem. Soc. (C)*, 1969, 1947; H. W. Sidebottom, J. M. Tedder, and J. C. Walton, *Trans. Faraday Soc.*, 1969, **65**, 2103; *Chem. Comm.*, 1970, 253; F. W. Hoover and D. D. Coffman, *J. Org. Chem.*, 1964, **29**, 3567; R. A. Bekker, B. L. Dyatkin, and I. L. Knunyants, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1970, 2738, (*Chem. Abs.*, 1971, **74**, 99366); D. D. Moldavskii and V. G. Temchenko, *Zhur. Org. Khim.*, 1970, **6**, 185, (*Chem. Abs.*, 1970, **72**, 89678).

[2] A. D. Berry and W. B. Fox, *J. Fluorine Chem.*, 1975, **6**, 175.

[3] A. D. Berry and W. B. Fox, *J. Fluorine Chem.*, 1976, **7**, 449; J. Steward, L. Kegley, H. F. White, and G. L. Gard, *J. Org. Chem.*, 1969, **34**, 760.

[4] H. L. Roberts, *Quart. Rev.*, 1961, **15**, 30.

[5] C. J. W. Fraser, M. E. McCartney, D. W. A. Sharp, and J. M. Winfield, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1455.

[6] R. F. Swindell and J. M. Shreeve, *J. Amer. Chem. Soc.*, 1972, **94**, 5713.

[7] R. F. Swindell, D. P. Babb, T. J. Ouellette, and J. M. Shreeve, *Inorg. Chem.*, 1972, **11**, 242.

[8] J. A. Gibson and R. Schmutzler, *Z. anorg. Chem.*, 1975, **416**, 222.

[9] C. J. Schack, R. D. Wilson, and M. G. Warner, *Chem. Comm.*, 1969, 1110.

[10] T. A. Kovacina, A. D. Berry, and W. B. Fox, *J. Fluorine Chem.*, 1976, **7**, 430.