

Defluorination of Pentafluorosulphur Chloride and Pentafluorosulphur Bromide by Strong Nucleophiles

By TOMOYA KITAZUME and JEAN'NE M. SHREEVE*

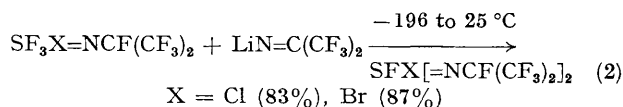
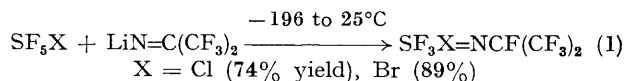
(Department of Chemistry, University of Idaho, Moscow, Idaho 83843)

Summary Strong nucleophiles, $(\text{CF}_3)_2\text{C}=\text{NLi}$ and $(\text{CH}_3)_2\text{NSi}(\text{CH}_3)_3$, readily defluorinate SF_5Cl and SF_5Br to form $\text{SF}_3\text{X}=\text{NCF}(\text{CF}_3)_2$, $\text{SFX}=[\text{NCF}(\text{CF}_3)_2]_2$, and *trans*- $(\text{CH}_3)_2\text{NSF}_4\text{X}$ (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 compounds⁴.

We now report that both SF_5Cl and SF_5Br undergo smooth reactions with $\text{LiN}=\text{C}(\text{CF}_3)_2$, 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 $(\text{CF}_3)_2\text{C}=\text{N}^-$.⁶⁻⁸

In typical reactions, SF_5Cl ⁹ (7 mmol) was condensed into a Pyrex glass vessel which contained $\text{LiN}=\text{C}(\text{CF}_3)_2$ 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, $\text{SF}_3\text{Cl}=\text{NCF}(\text{CF}_3)_2$, was recovered at -78°C . $\text{SF}_3\text{Cl}=\text{NCF}(\text{CF}_3)_2$ (ca. 2 mmol) was

condensed onto $\text{LiN}=\text{C}(\text{CF}_3)_2$ (1.5 mmol) and the reaction allowed to proceed as above. The colourless liquid, $\text{SFCl}[\text{NCF}(\text{CF}_3)_2]_2$, was obtained.

TABLE

	$\delta^a(\text{SF}_A)$ /p.p.m.	$\delta(\text{SF}_B)$ /p.p.m.	J_{AB}/Hz
SF_5Cl^b	-61.9	-125.4	148.5
SF_5Br^b	-62.0	-145.2	143.1
$\text{SF}_3\text{Cl}=\text{NCF}(\text{CF}_3)_2$..	-59.5 tr	-120.0 d	128
$\text{SFCl}[\text{NCF}(\text{CF}_3)_2]_2$..		-71.6	
$\text{SF}_3\text{Br}=\text{NCF}(\text{CF}_3)_2$..	-59.5 tr	-139.5 d	125
$\text{SFBr}[\text{NCF}(\text{CF}_3)_2]_2$..		-91.5	

^a CCl_4F internal reference. ^b C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, *Inorg. Chem.*, 1962, **1**, 215.

Reactions with $\text{SF}_5\text{Br}^{10}$ 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 [$\text{SF}_3\text{X}=\text{NCF}(\text{CF}_3)_2$] and to tetrahedral [$\text{SFX}(\text{NCF}(\text{CF}_3)_2)_2$] (Table).

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.

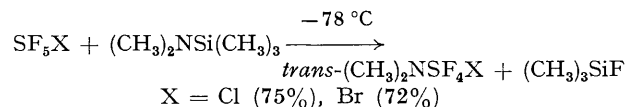
⁸ J. A. Gibson and R. Schmutzler, *Z. anorg. Chem.*, 1975, **416**, 222.

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.

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 $(\text{CH}_3)_2\text{NSi}(\text{CH}_3)_3$ attacks SF_5X at -78 °C to replace the axial fluorine atom and form the stable disubstituted sulphur hexafluoride derivative [reaction (3)].



Typically, SF_5X (3.5 mmol) and $(\text{CH}_3)_2\text{NSi}(\text{CH}_3)_3$ (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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