1λ^4,2-Thiazacyclohexa-1,4-dienes

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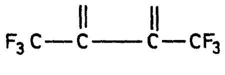
Summary The first [4+2] addition to a formal S≡N triple bond is found in the reaction of perfluorobutadiene with N≡S–F.

Thiazyl fluoride (NSF) (**1**) is known to form polymeric products and a cyclic trimer.[1] Attempts to incorporate the –N=S(F)– unit into heterocycles have been unsuccessful until now, however. Thermal addition of (**1**) to the double bond of hexafluoropropene in the presence of CsF gives linear thiazenes,[2] and reaction with hexafluorobut-2-yne gives the thiadiazole (**2**) and the dithiadiazole (**3**).[3] Alkylbutadienes, *e.g.* 2,3-dimethylbutadiene, react explosively, but with perfluorobutadiene perfluoro-1λ^4,2-thiazacyclo-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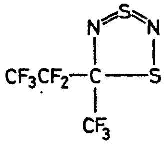
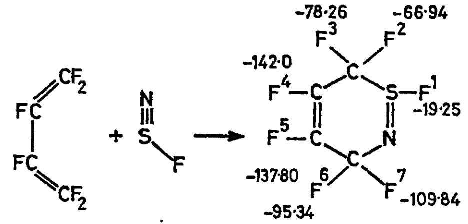

(3)

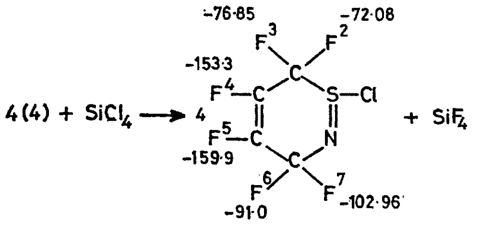
hexa-1,4-diene (**4**) is formed in almost quantitative yield (Scheme 1) in an exothermic [4+2] addition. Compound (**4**) is a stable, colourless, moisture-sensitive liquid, b.p. 89 °C at 748 mmHg. I.r. absorptions (gas phase) at 1743w, 1335s, and 680s cm^{-1} are tentatively assigned to $\nu_{C=C}$, $\nu_{S=N}$, and ν_{S-F}, respectively. In the n.m.r. spectrum the seven fluorine atoms are not magnetically equivalent, with both CF_2 groups showing AB-structures. All the 21 possible coupling constants could be determined. The coupling constants, chemical shifts, and line broadening at room temperature show that the most reasonable assignments are those given on the structural diagram.



(**1**) (**4**)

Scheme 1. δ Values for compound (**4**), in p.p.m. from $CFCl_3$ internal reference; −30 °C; coupling constants: $J_{1,2}$ 36·0, $J_{1,3}$ 12·9, $J_{1,4}$ 0·7, $J_{1,5}$ 5·2, $J_{1,6}$ 20·2, $J_{1,7}$ <1, $J_{2,3}$ 237·0, $J_{2,4}$ 25·8, $J_{2,5}$ 12·4, $J_{2,6}$ 1·8, $J_{2,7}$ 4·0, $J_{3,4}$ 25·8, $J_{3,5}$ 12·9, $J_{3,6}$ 6·3, $J_{3,7}$ <1, $J_{4,5}$ 9·4, $J_{4,6}$ 9·2, $J_{4,7}$ 22·4, $J_{5,6}$ 24·6, $J_{5,7}$ 12·7, and $J_{6,7}$ 253·0 Hz.

Exchange of the sulphur bonded fluorine ligand with retention of the structure is possible; *e.g.* with $SiCl_4$ in 60% yield the *S*-chloro-derivative (**5**), b.p. 124 °C at 740 mmHg, $\nu_{C=C}$ 1745m and ν_{S-N} 1340s cm^{-1}, is formed.



(**5**)

Scheme 2. δ Values for compound (**5**), in p.p.m. from $CFCl_3$ internal reference; −30 °C.

Cleavage of the carbon–sulphur bond of compound (**4**) is effected by halogens (Scheme 3).

$$(\mathbf{4}) + Cl_2 \xrightarrow{u.v.} CF_2Cl[CFCl]_2\cdot CF_2\cdot NSFCl\ (50\%)$$

$$(\mathbf{4}) + XeF_2 \xrightarrow[-Xe]{BF_3} CF_3C(F){=}C(F).CF_2.NSF_2 \qquad + CF_3[CF_2]_3NSF_2$$

(72% *cis*, 15% *trans*) (13%)

Scheme 3

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[1] O. Glemser, H. Meyer, and A. Haas, *Chem. Ber.*, 1964, **97**, 1704.

[2] W. Bludsuss, R. Mews, and O. Glemser, *Israel J. Chem.*, 1978, **17**, 137.

[3] W. Bludssus and R. Mews, unpublished results.