Perfluoro(tetramethylene)sulphilimine and Its *N*-Chloro- and *N*-Bromo-derivatives. Perfluoro(tetramethylene)sulphoximine and Its *N*-Chloro-derivative

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Summary Perfluoro(tetramethylene)sulphur difluoride is a useful precursor to the new perfluoro-cyclic sulphilimines $\overline{CF_2CF_2CF_2CF_2S}{=}NX$ (X = H, Cl, or Br) and perfluoro-cyclic sulphoximines $\overline{CF_2CF_2CF_2CF_2S(O)}{=}NX$ (X = H or Cl).

WE have already reported the first member of a new class of stable sulphilimines,[1] the dimeric $(CF_3)_2S{=}N{-}N{=}S(CF_3)_2$, which results from the photolysis of $(CF_3)_2S{=}NCl$. The latter and its *N*-fluoro-analogue can be generated from chlorination or fluorination of $(CF_3)_2S{=}NH$[2] with chlorine or sulphur tetrafluoride, respectively. The parent difluorosulphilimine, $SF_2{=}NH$, is unknown.

A straightforward route is now available for the synthesis of the first perfluoro-cyclic sulphilimine, perfluoro(tetramethylene)sulphilimine, (**1**), which exploits the susceptibility of the sulphur atom in perfluoro(tetramethylene)-sulphur difluoride[3] to nucleophilic attack by $LiNH_2$ in the presence of ammonia with isopentane as the heat sink at 0 °C. Compound (**1**) is a colourless solid with a vapour pressure of 19 Torr at 25 °C.† When the reaction was carried out on a 5 mmol scale, the yield was 78%. The ^{19}F n.m.r. spectrum has resonances at ϕ −130·8 and −133·8 p.p.m. (J_{AB} 266 Hz; CF_2) and at ϕ −116·8 and −118·3 p.p.m. (J_{AB} 231 Hz; CF_2 α to S).‡ The ^1H n.m.r. spectrum has a broad band at δ 2·33, and the mass spectrum contained a molecular ion peak. A new feature of the i.r. spectrum is a medium band at 3315 cm^{-1} assigned to ν_{N-H}.

Chlorination or bromination permits the synthesis of the respective *N*-chloro- or *N*-bromo-compounds (**2**),† *e.g.* reaction (1). In each case the mass spectrum shows a

$$\overline{CF_2CF_2CF_2CF_2S}{=}NH \xrightarrow{X_2,KF} \overline{CF_2CF_2CF_2CF_2S}{=}NX \qquad (1)$$

(**1**) (**2**)

X = Cl, 87%; Br, 23%

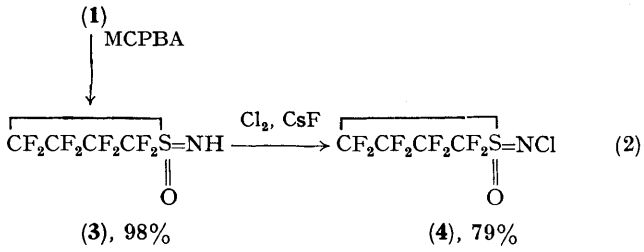
molecular ion peak with the appropriate isotope ratio and the ^{19}F n.m.r. spectrum contains 2 sets of AB patterns.

While the acyclic $(CF_3)_2S(O){=}NH$[4] and difluorosulphoximine, $F_2S(O){=}NH$.[5,6] analogues are known and their

† Satisfactory elemental analyses were obtained.

‡ Positive shifts are downfield from CCl_3F.

reactions have been well studied,[4,7] we report the synthesis of the first fluorinated cyclic sulphoximine and its *N*-chloro-derivative. Oxidation of compound (**1**) with *m*-chloroperbenzoic acid (MCPBA) yields perfluoro(tetramethylene)sulphoximine (**3**) which in turn may be chlorinated in the presence of an alkali metal fluoride. Compound



(2)

(**3**)† is a white solid, m.p. *ca.* 76 °C, b.p. 124·1 °C; ν_{NH} 3395 cm^{-1}, and the mass spectrum shows a molecular ion peak. The *N*-chloro-compound (**4**)† is a colourless liquid which solidifies at −40 °C. The mass spectrum does not show a molecular ion peak, the highest *m/e* value being 262 (M^+ − Cl).

The study of these new sulphilimines and sulphoximines is continuing. Of particular interest are the photolysis reactions of both *N*-chloro-compounds. However, preliminary evidence indicates that ring opening does occur which may preclude the synthesis of the analogues of $(CF_3)_2S{=}N{-}N{=}S(CF_3)_2$.

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