

N,N'-Bis(perfluoroethyl)thiadiaziridine

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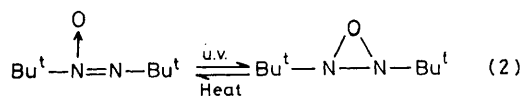
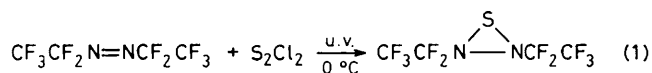
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Photolysis of $\text{CF}_3\text{CF}_2\text{N}=\text{NCF}_2\text{CF}_3$ with S_2Cl_2 at 0°C resulted in the formation of the first thiadiaziridine, $\text{CF}_3\text{CF}_2\text{N}-\text{S}-\text{NCF}_2\text{CF}_3$, in 5% yield.

Heterocycles which contain sulphur and nitrogen have been of considerable interest to chemists since tetrasulphur tetranitride was first prepared in 1835.¹ It has been suggested that the only three-membered rings, other than thiirane derivatives, to be more stable than their ring-opened isomers are the 1,1-dioxides of thiaziridines and of thiadiaziridines.² Such a three-membered ring comprised of heteroatoms, $\text{RN}-\text{SO}_2-\text{NR}$, has been verified by X-ray analysis, where R is $\text{Me}_3\text{CCH}_2\text{CMe}_2$, which helps to stabilize the ring. The tetraco-ordinate sulphur is formally S^{VI} .^{3,4}

We report the synthesis of a three-membered heteroatom ring with dico-ordinate sulphur(II), the first thiadiaziridine [equation (1)]. While the oxygen analogue with t-butyl substituents on nitrogen has been isolated,^{5,6} the oxadiaziridines are somewhat labile reverting to their valence isomers, azoxyalkanes, at room temperature in a few hours [equation (2)].^{5,6}

Probably because of N-S-lone pair repulsive interactions, this moderately stable heterocycle, $\text{N}-\text{S}-\text{N}$, had not been synthesized. This synthesis has now been made possible by placing strongly electron-withdrawing perfluoroethyl sub-

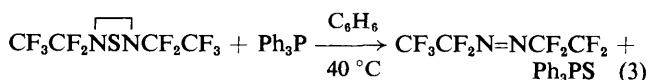


stituents on the nitrogen atoms of the parent diazene and is a rare example of addition across the nitrogen-nitrogen double bond of *N,N'*-bis(perfluoroalkyl)diazene whose synthesis has been described.

When equimolar amounts (1 mmol) of $\text{C}_2\text{F}_5\text{N}=\text{NC}_2\text{F}_5$ and S_2Cl_2 were photolysed in a quartz vessel for 4 h, $\text{CF}_3\text{CF}_2\text{NSNCF}_2\text{CF}_3$ was isolated in about 5% yield. Its vapour pressure is ca. 9 Torr at 25°C . Molecular weight measurements give 291 (theoretical 298). The mass spectrum contains a molecular ion peak at m/z 298. The next highest m/z is at 266 ($M^+-\text{S}$) with other peaks at 247 ($M^+-\text{S}-\text{F}$), 228 ($M^+-\text{S}-2\text{F}$), and 197 ($M^+-\text{S}-\text{CF}_3$), which leads us to suggest a cyclic structure. The i.r. spectrum is as follows: 1245s, 1180s, 1080s, 715vw, and 530vw cm^{-1} . The heterocycle was purified *via* g.c. which precludes the presence of $\text{CF}_3\text{CF}_2\text{N}=\text{NCF}_2\text{CF}_3$

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as an impurity, although complete separation from S_2Cl_2 was not achieved. When $CF_3CF_2NSNCF_2CF_3$ was treated with triphenylphosphine in benzene at 40 °C [equation (3)], $CF_3CF_2N=NCF_2CF_3$ was obtained in quantitative yield which also supports a cyclic rather than an acyclic sulphur di-imide geometry.



The ^{19}F n.m.r. spectrum has two singlets at $\delta -83.3$ (CF_3) and -112.5 p.p.m. (CF_2) in the ratio of 3:2. The chemical shift of the difluoromethylene group in the starting $CF_3CF_2N=NCF_2CF_3$ is at $\delta -122.4$ p.p.m. The only other realistic structural possibility, $CF_3CF_2N=S=NCF_2CF_3$, is known⁷ and its spectral data do not match those of our cyclic compound, e.g., CF_3 $\delta -88.8$ and $CF_2 -94.4$ p.p.m. Also, comparison of chemical shifts for CF_2 in $CF_3CF_2N=SX_2$, $CF_3CF_2N=S=NMe_3$, $CF_3CF_2N=S(O)F_2$, $CF_2ClCF_2N=S=NCH_3$, and $CF_3CF_2N=S(F_2)=NCF_2CF_3$ shows that the range is $\delta -70$ to -97 p.p.m. Thus, the methylene group in the cyclic compound exists in an environment which does not involve a sulphimide link but rather one similar to that in the starting diazene. In a hydrazine derivative, such as $CF_3CF_2N(NF_2)N(F)CF_2CF_3$, where the nitrogen which is bonded to $>CF_2$ is three co-ordinate, the ^{19}F n.m.r. shift for CF_2 is $\delta -110.7$ p.p.m. which is very close to that found for CF_2 in the parent $CF_3CF_2N=NCF_2CF_3$ and in the product $CF_3CF_2N-S=NCF_2CF_3$.

The presence of a thia-azoxy isomer, $CF_3CF_2N(S^-)=NCF_2CF_3$ or of a rapid equilibrium between the latter and the cyclic structure is unlikely based on the i.r. data. The highest bands observed at 1245 and 1180 cm^{-1} must be assigned to $\nu(C-F)$ relegating $\nu(N-N)$ to a band at lower energy. In fluorinated azoxy compounds, $\nu(N=N)$ occurs ca. 100 cm^{-1} higher than in

the corresponding diazenes [$-N(O^+)=N-$ vs. $-N=N-$, 1525 vs. 1425 cm^{-1}]. Yet in the spectrum of $CF_3CF_2NSNCF_2CF_3$ there are no bands higher than those in $CF_3CF_2N=NCF_2CF_3$ where the highest band is at 1346 cm^{-1} .⁸ This would argue against the thia-azoxy structure or any species with a nitrogen-nitrogen double bond. In the thia-azoxy isomer, the CF_2 groups would be chemically nonequivalent but only a single resonance is observed in the ^{19}F n.m.r. spectrum. Such differences are observed in nonfluorinated systems.⁸

By varying the stoichiometry of the reactants, it is possible also to prepare five- and six-membered heterocycles,

$R_fNS_xNR_f$ ($x = 3$ and 4), whose mass spectra show an analogous stepwise loss of sulphur atoms and, also, the parent diazene, $R_fN=NR_f$, is regenerated in reaction with triphenylphosphine. These will be reported in due course.

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