Thermal Stability and Fluxional Behaviour of Bicyclic Sulphur–Nitrogen Structures of Formula EN_5S_3 (E = CR, PR_2, or SO_2^-)

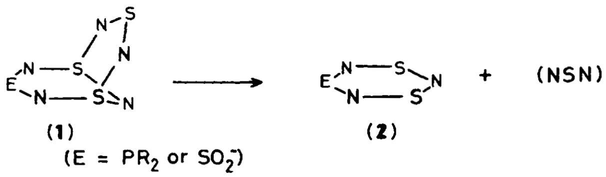
René T. Boeré, Richard T. Oakley,* and Maurice Shevalier

Guelph Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada

Two thermally induced N–S bond cleavage processes are available to EN_5S_3 heterocycles: (i) an irreversible loss of NSN to form EN_3S_2 (for E = PR_2 and SO_2^-) and (ii) a pseudo-degenerate 1,3-nitrogen shift which exchanges all nitrogen atoms (for E = CPh).

The often explosive thermal instability of binary sulphur–nitrogen compounds is a well recognised but poorly understood feature of their chemistry. In order to gain a deeper insight into the mechanisms of these decompositions, we are currently exploring the relationships between the thermal stabilities and the molecular and electronic structures of closely related compounds. Herein we compare the kinetic stabilities of heterocyclic derivatives based on the bicyclic framework EN_5S_3. We also report ^{15}N n.m.r. spectroscopic evidence for nitrogen atom scrambling in $PhCN_5S_3$, an effect hitherto unobserved in sulphur-nitrogen chemistry.

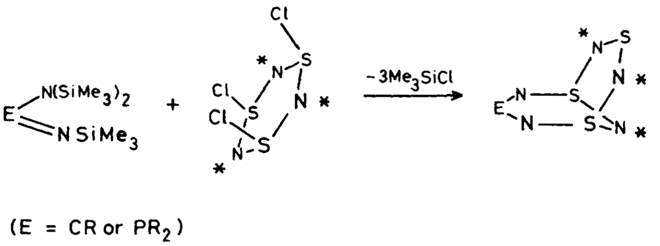
Recently we reported a kinetic analysis of the thermal decomposition of $Ph_2PN_5S_3$ (**1**) (E = PPh_2) to the corresponding dithiatriazine $Ph_2PN_3S_2$ (**2**) (E = PPh_2) (Scheme 1).[1] An analogous decomposition pathway is observed for the anion $SO_2N_5S_3^-$ (**1**) (E = SO_2^-), which is easily prepared as its



(1) (2)

(E = PR_2 or SO_2^-)

Scheme 1



Scheme 2

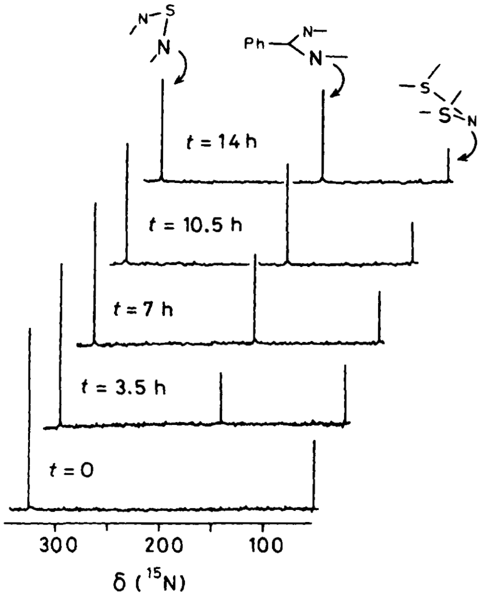


Figure 1. Time dependence of the ^{15}N n.m.r. spectrum of $PhCN_2{}^*N_3S_3$ (in $CDCl_3$). The $t = 0$ case refers to data collected at −20 °C (where fluxional behaviour is frozen out).

yellow $(Ph_3P)_2N^+$ salt† by oxidation of $(Ph_3P)_2N^+SO_2N_3S_2^-$ with $PhICl_2$ in acetonitrile to yield $(Ph_3P)_2N^+SO_2N_3S_2Cl_2^-$,† followed by treatment with $(Me_3SiN)_2S$ (overall yield 59%). Thus, gentle warming of solutions of $(Ph_3P)_2N^+SO_2N_5S_3^-$ in acetonitrile effects the reversion of the bicyclic anion to the monocyclic $SO_2N_3S_2^-$ species,[2] which can be isolated in 60% yield.

In comparison to the above EN_5S_3 derivatives, the isoelectronic species $PhCN_5S_3$[3] (1) (E = CPh) is more thermally stable. It can be sublimed without decomposition at 80 °C and 0.1 Torr, and although it does slowly decompose on prolonged reflux in acetonitrile, the dithiatriazine $PhCN_3S_2$ (2) (E = CPh) is not formed; instead the major isolable products are S_4N_4 and benzonitrile. Similar results have been noted when E = CNR_2.[4] The resistance of RCN_5S_3 derivatives to thermolysis is surprising in view of the long SN bonds to the bridging NSN unit,[3—5] but may be related to the differences in the electronic structures of dithiatriazines where E = CR and E = PR_2 or SO_2^-. While the latter are known to possess singlet ground states,[2,6] $^3\pi$ ground states have been predicted for a variety of RCN_3S_2 structures.[4,7,8] Accordingly formation of RCN_3S_2 *via* the concerted elimination of a singlet[9] NSN fragment from the RCN_5S_3 structure would be symmetry forbidden.

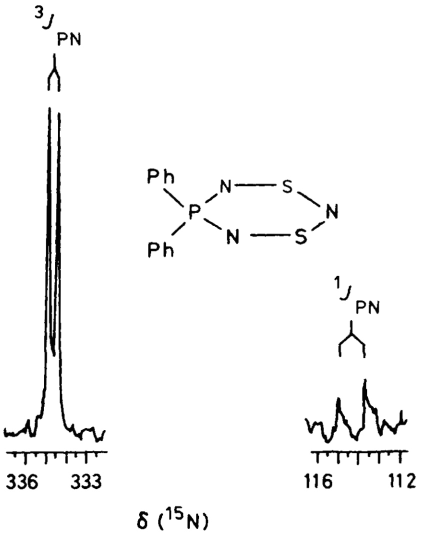
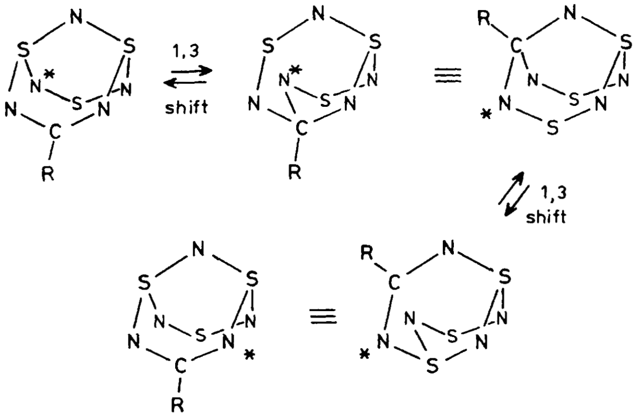


Figure 2. ^{15}N N.m.r. spectrum (in $CDCl_3$) of $Ph_2PN_2{}^*NS_2$ prepared by the thermolysis of $Ph_2PN_2{}^*N_3S_3$.



Scheme 3

In order to examine more carefully the structural stability of $PhCN_5S_3$ we prepared the specifically ^{15}N labelled[10] derivative $PhCN_2{}^*N_3S_3$ (*N = 99% ^{15}N) by the method illustrated in Scheme 2. Consistently with the expected labelling pattern the ^{15}N n.m.r. spectrum‡ (at −20 °C) of the material prepared at −20 °C shows two signals at δ 330.1 (2N) and 54.9 (1N). However, when the solution is warmed to room temperature a third signal (at δ 176.1), generated by the slow incorporation

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† The elemental composition of this compound has been confirmed by elemental analysis.

‡ ^{15}N N.m.r. spectra were recorded at 40.5 MHz on a Bruker WH-400 spectrometer, using 30 s pulse delays and a pulse width of 33 µs. Chemical shifts are reported with reference to liquid ammonia at 25 °C.

of ^{15}N into the carbon-bound nitrogen sites, slowly emerges from the base line. Figure 1 illustrates the progress of this nitrogen exchange over a 14 h period. The limiting spectrum exhibits the 2:2:1 intensity pattern expected for complete scrambling of ^{15}N and ^{14}N nuclei. In contrast to the above behaviour $Ph_2PN_2{}^*N_3S_3$ (also prepared according to Scheme 2) undergoes no observable nitrogen exchange at room temperature; only two signals at δ 322.0 (2N) and 79.2 (1N) are present, although after 16 h some decomposition to $Ph_2PN_2{}^*NS_2$ is apparent. Furthermore, ^{15}N n.m.r. analysis of the phosphadithiatriazine isolated from the thermolysis of $Ph_2PN_2{}^*N_3S_3$ in refluxing toluene shows (by comparison with the known ^{15}N n.m.r. spectrum of $Ph_2P{}^*N_3S_2$)[6] only small amounts of ^{15}N incorporation into the phosphorus-bound nitrogen sites (Figure 2).

While the observation of nitrogen scrambling in $PhCN_5S_3$ is without precedent in sulphur–nitrogen chemistry, the possibility of such a phenomenon was recognized some years ago by Bartetzko and Gleiter for the isoelectronic $S_4N_5{}^+$ cation.[11] Accordingly the fluxional process that leads to interchange of all nitrogen atoms in $PhCN_5S_3$ can be viewed as involving a series of pseudo-degenerate 1,3-nitrogen shifts, as depicted in Scheme 3. While further theoretical and experimental studies are required to establish the activation barriers for such 1,3-shifts in EN_5S_3 structures, and the relative rates of the nitrogen exchange and NSN elimination pathways, the present results indicate that the scrambling process predominates when E = CR. When the NSN elimination channel is allowed, and when the 1,3-shift mechanism involves a high energy intermediate (*e.g.* a five-co-ordinate phosphorus or sulphur), only thermal decomposition to EN_3S_2 is observed.

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