Direct Insertion of a Nitrogen Atom into the S–S Link of a 1,2,3,5-Dithiadiazole Ring in a D.C. Nitrogen Glow Discharge

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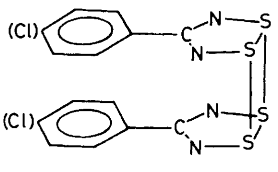
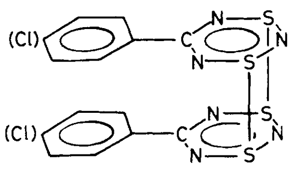
Solid crystalline bis(4-aryl-1,2,3,5-dithiadiazole), $(\mathrm{R\overline{CNSSN}})_2$ combines with two radical nitrogen atoms and/or excited nitrogen molecules in a low pressure nitrogen plasma to give bis(5-aryl-1,2,3,4,6-dithiatriazine), $(\mathrm{R\overline{CNSNSN}})_2$ in high yield (R = Ph and p-$\mathrm{ClC_6H_4}$).

Recently there has been an increasing interest in the use of nitrogen plasma particularly in polymer film formation, in the fabrication of silicon nitride films for the micro-electronics industry, and in the nitridation of metals in general.[1,2] In contrast, although nitrogen plasmas have been used in the preparation of pyrrole from buta-1,3-diene,[3] and of phosphorus nitrides[4] it has been little used for molecular syntheses because yields are usually low.

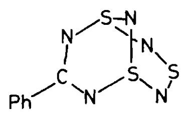
We report the first example of a high yield molecular synthesis in a plasma–solid reaction, in which the title



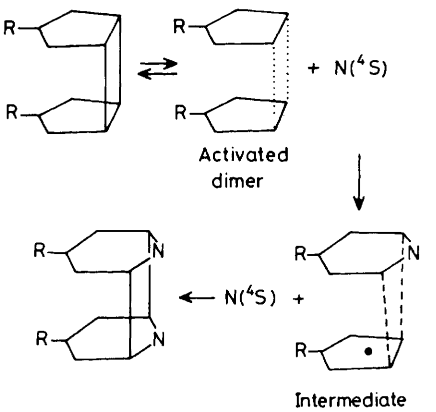
(1), (1′)



(2), (2′)



(3)



Scheme 1

heterocyclic ring undergoes ring expansion by incorporating one nitrogen atom into the disulphide bond. In sulphur chemistry, a few reactions between singlet atomic nitrogen generated in a microwave discharge and various divalent sulphur compounds have been investigated[5] but significant yields were only obtained with S_2Cl_2 which gave $(NSCl)_3$. Since simpler routes are usually available, plasma methods are not normally preferred for such molecular syntheses. The title reaction is a simple convenient preparation of compounds $(RCN_3S_2)_2$.

$(Ph\overset{\frown}{CNSSN})_2$ (**1**) was prepared according to the literature.[6] After purification by vacuum sublimation (80 °C) it was obtained as bundles of needle-shaped crystals and these were used for the plasma reaction. The *p*-chlorophenyl derivative, (**1′**) was synthesised in an analogous way from *p*-ClC_6H_4CN. Approximately 0.25 g (0.7 mmol) of (**1**), loosely heaped in a quartz boat, was immersed in the positive column of the discharge. Purified nitrogen was bled *via* a needle valve into the discharge tube through a capillary. A pressure of *ca.* 1 Torr was maintained throughout the reaction with a flow rate of *ca.* 70 Torr $cm^3\ s^{-1}$. The optimum reaction temperature of 45 °C (60 °C for R = *p*-ClC_6H_4) was kept constant by an external heater. With the tube current at 2 mA and *ca.* 1 kV across the electrodes the completion of the reaction required approx. 10 h. The typical yields of $(Ph\overset{\frown}{CNSNSN})_2$, (**2**) were 80%. The product was the buff-to-brown coloured air stable compound (**2**) covered by a layer of a black porous polymeric veneer. A continuous polymeric film (brown in transmitted light) also formed on the walls of the discharge tube. In a control experiment with argon plasma the starting material (**1**) remained completely unchanged.

The main contaminant of the product (**2**) was some unreacted (**1**) and this was easily washed out with liquid SO_2 [in which (**2**) is only sparingly soluble]. For instance, after continuous refluxing of 0.1 g (**2**) with SO_2 in a closed system[7] at room temperature during 14 days only 0.015 g of (**2**) were extracted, which crystallised in the form of flat thin brown transparent needles. The residual (**2**) was unaffected by the prolonged exposure to liquid SO_2.

The pure product (**2**) was characterised by chemical analyses, i.r., *X*-ray power photographs, mass spectrometry, and differential scanning calorimetry. All these results unambiguously confirmed that (**2**) was identical with the compound recently obtained by Boeré *et al.*[8] in a three-step chemical synthesis.

Differential scanning calorimetry (4 °C/min, in a sealed aluminium capsule under N_2) of pure (**2**) showed the onset of melting at 118 °C (sharp endotherm) followed immediately by decomposition (sharp exothermic peak at 123 °C) leaving a purple melt. (*Cf.* m.p. 115 °C in ref. 8a.)

A small amount (0.112 g) of SO_2 washed (**2**), placed at the bottom of a straight Pyrex tube, was heated to 85 °C *in vacuo* ($\leq 10^{-6}$ Torr). The tube (12 mm in diameter) was subdivided by sealable constrictions (*ca.* 1 mm internal diameter) into three sections kept at constant temperatures so as to afford fractionation of the volatiles. After 48 h the distribution of the products in the individual sections (figures in square brackets give relative amounts by weight and average temperatures of the sections in which the products formed) was: (i) microcrystalline sublimate of $(PhCN_3S_2)_2$ (**2**) [3—5%, 70 °C], (ii) yellow-orange crystals of $PhCN_5S_3$ (**3**)† [27%, 60 °C], (iii) $(PhCN_2S_2)_2$ (**1**) [66%, 20 °C]. In addition a blue $(SN)_x$ film and a black silvery polymeric film (together representing *ca.* 5%) formed in the liquid N_2 trap on warming to room temperature. The composition of the residue (0.050 g) in this 48 h vacuum thermolysis was largely unaltered (**2**).

Scheme 1 outlines a possible mechanism of the plasma nitrogenation. It is most probable that the overall rate of the reaction is determined primarily by the diffusion of the reactive nitrogen species through the solid microcrystalline product (**2**) to the advancing product/reactant interface. Several selected crystals of (**1**) *ca.* 1 mm in size were removed and examined after partial nitrogenation; they all exhibited a central core of unreacted (**1**) with a well defined interface. Although the reactant (**1**) exists in the solid form largely as the dimer as indicated in Scheme 1, e.s.r. powder studies[9] have also shown that there is always some monomer present on the surface and in the dimer lattice as crystal defects. It is likely therefore that some reaction occurs by direct combination of atomic nitrogen with the monomer.

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References

1 'Applications of Plasma Processes to VLSI Technology,' ed. T. Sugano, J. Wiley & Sons, New York, 1985.
2 S. Veprek in 'IEEE Transactions on Plasma Science,' 1974, Vol. PS-2, No. 1.
3 A. Tsukamoto and N. N. Lichtin, *J. Am. Chem. Soc.*, 1962, **84**, 1601.
4 S. Veprek, Z. Iqbal, J. Brunner, and M. Scharli, *Philos. Mag. B*, 1981, **43**, 527.
5 J. J. Smith and W. L. Jolly, *Inorg. Chem.*, 1965, **4**, 1006.
6 A. J. Banister, N. R. M. Smith, and R. G. Hey, *J. Chem. Soc., Dalton Trans.*, 1984, 1379.
7 R. W. H. Small, A. J. Banister, and Z. V. Hauptman, *J. Chem. Soc., Dalton Trans.*, 1984, 1379.
8 (a) R. T. Boeré, A. W. Cordes, and R. T. Oakley, *J. Chem. Soc., Chem. Commun.*, 1985, 929; (b) R. T. Boeré, C. L. French, R. T. Oakley, J. A. J. Privett, S. L. Craig, and J. B. Graham, *J. Am. Chem. Soc.*, 1985, **107**, 7710.
9 S. A. Fairhurst, K. M. Johnson, L. H. Sutcliffe, K. F. Preston, A. J. Banister, Z. V. Hauptman, and J. Passmore, *J. Chem. Soc., Dalton Trans.*, 1986, 1465.

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† $PhCN_5S_3$ (**3**), here formed by the thermal splitting and rearrangement of (**2**) is a known bicyclic compound prepared by Boeré *et al.* (ref. 8a,b).