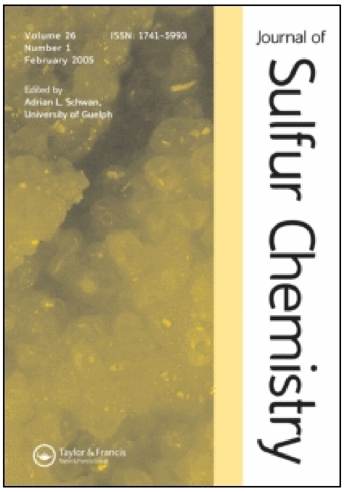

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Interesting Errors in Sulfur Chemistry, 3

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INTERESTING ERRORS IN SULFUR CHEMISTRY, 3

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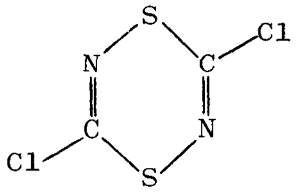
3,6-DICHLORO-1,4,2,5-DITHIADIAZINE

In 1963 it was found that trichloromethanesulfenyl chloride and ammonia could be made to react with elimination of hydrogen chloride according to (1):[1]

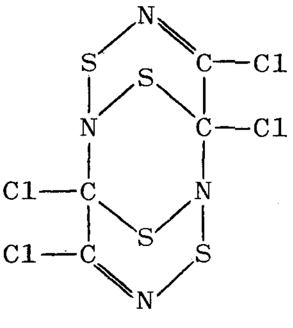
$$n\ CCl_3SCl + n\ NH_3 \longrightarrow \underset{\mathbf{1}}{(CClNS)_n} + 3\ n\ HCl \qquad (1)$$

By standard procedures, including an ebullioscopic molecular weight determination, the product of the reaction, m.p. 200.5–201.5°C, was assigned the structure of 3,6-dichloro-1,4,2,5-dithiadiazine **2** equivalent to **1** ($n = 2$).



2

Three years later the compound originally regarded as **2** was subjected to further chemical[2] and crystallographic[3] scrutiny and unequivocally shown to possess the structure of 2,3,7,8-tetrachloro-5,10,11,12-tetrathia-1,4,6,9-tetraazatricyclo-[5.3.1.1^{2,6}]dodeca-3,8-diene **3** equivalent to **1** ($n = 4$).



3

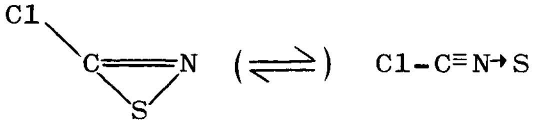
An obvious way to rationalize the formation of **3** (which in all probability must involve **2** as a transient intermediate) is to assume a reaction path via the sulfenamide **4** and the monomer **1** ($n = 1$) which then oligomerizes in more or less discrete steps:[2]

$$\mathrm{CCl_3SCl} + \mathrm{NH_3} \longrightarrow \underset{\mathbf{4}}{\mathrm{CCl_3SNH_2}} + \mathrm{HCl} \tag{2}$$

$$\underset{\mathbf{4}}{\mathrm{CCl_3SNH_2}} \longrightarrow \underset{\mathbf{1}\ (n\,=\,1)}{\mathrm{CClNS}} + 2\ \mathrm{HCl} \tag{3}$$

$$4\ \underset{\mathbf{1}\ (n\,=\,1)}{\mathrm{CClNS}} \longrightarrow \underset{\mathbf{3}\,=\,\mathbf{1}\ (n\,=\,4)}{(\mathrm{CClNS})_4} \tag{4}$$

The intermediate **1** ($n = 1$) is probably 3-chlorothiazirine **5** or cyanogen chloride N-sulfide **6** or an equilibrating mixture of both:



5 **6**

The relationship between nitrile N-sulfides and thiaziridines has been investigated in depth.[4] Though the postulated intermediate **4** was subsequently synthesized according to (2) and fully characterized[5] (as were the related compounds **7**[6] and **8**[6]) **2** has eluded synthesis up to the present day and no more light has been shed upon the intriguing reaction (1).

$$\underset{\mathbf{7}}{(\mathrm{CCl_3S})_2\mathrm{NH}} \qquad \underset{\mathbf{8}}{(\mathrm{CCl_3S})_3\mathrm{N}}$$

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