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**FOUR NEW METHODS FOR PREPARING NSCI**

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FOUR NEW METHODS FOR PREPARING NSCI

K. D. Maguire, J. J. Smith and W. L. Jolly

June 1963

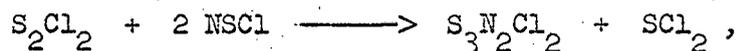
Four New Methods for Preparing NSCl

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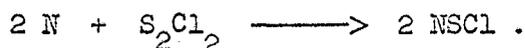
Glemser<sup>1,2</sup> has reported that NSCl may be prepared by the pyrolysis of (NSCl)<sub>3</sub>. We wish to report four additional methods for preparing NSCl.

(1) When a stream of S<sub>2</sub>Cl<sub>2</sub> vapor was passed into a stream of active nitrogen<sup>3</sup>, a blue glow was emitted by the mixture, and yellow-brown solids formed on the walls of the reaction tube. A -196° trap immediately following the reaction tube collected (beside the unreacted S<sub>2</sub>Cl<sub>2</sub>) NSCl, SCl<sub>2</sub>, small amounts of S<sub>3</sub>N<sub>2</sub>Cl<sub>2</sub>, traces of chlorine, and small amounts of an uncharacterized red-brown solid. The S<sub>3</sub>N<sub>2</sub>Cl<sub>2</sub> probably formed as a result of the reaction

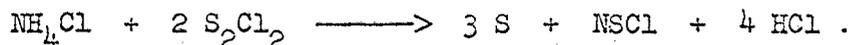


which takes place rapidly in the liquid state.<sup>4</sup> By allowing the trap to stand at room temperature for an hour or so before attempting a separation of the products, it was possible to remove all the NSCl by this reaction. In a typical run, S<sub>2</sub>Cl<sub>2</sub> was added at the rate of 0.18 μmoles sec<sup>-1</sup> to a stream of active nitrogen. (P = 5 mm; N/N<sub>2</sub> = 0.014) in which the flow-rate

of atomic nitrogen was  $3.02 \mu\text{moles sec}^{-1}$ . Sixty-two milligrams of NSCl (calc. from  $\text{S}_3\text{N}_2\text{Cl}_2$ ) formed in a period of 105 minutes, corresponding to a 34% conversion of the  $\text{S}_2\text{Cl}_2$ , based on the equation

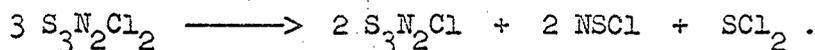


(2) When a suspension of ammonium chloride in excess  $\text{S}_2\text{Cl}_2$  was refluxed for an extended period, the ammonium chloride eventually was consumed, and a solution of sulfur in  $\text{S}_2\text{Cl}_2$  remained. Hydrogen chloride, NSCl and  $\text{S}_2\text{Cl}_2$  were the principal components of the effluent gas. The first two species were probably formed by the reaction



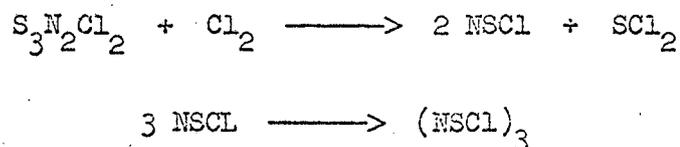
Modifications of this process which permit the isolation of  $\text{S}_3\text{N}_2\text{Cl}_2$  are described elsewhere.<sup>6</sup>

(3) When  $\text{S}_3\text{N}_2\text{Cl}_2$  was heated in vacuo to  $80-100^\circ$ , NSCl and  $\text{S}_2\text{Cl}_2$  were evolved and a greenish-black residue of  $\text{S}_3\text{N}_2\text{Cl}$  was formed:



In one experiment, 4.89 g. of  $\text{S}_3\text{N}_2\text{Cl}_2$  yielded 2.53 g. of  $\text{S}_3\text{N}_2\text{Cl}$  (2.67 g. calc.), 1.36 g. of NSCl (1.61 g. calc.) and 0.74 g. of  $\text{S}_2\text{Cl}_2$  (0.86 g. calc.).

(4) Meuwesen<sup>5</sup> has reported that, by passing chlorine into a carbon tetrachloride suspension of  $S_3N_2Cl_2$ , the compound  $(NSCl)_3$  may be prepared. He postulated that the intermediate NSCl was involved. Indeed, we have found that NSCl (along with  $SCl_2$  and what is presumably  $(NSCl)_3$ ) is formed by the reaction of chlorine gas on  $S_3N_2Cl_2$  at room temperature in the absence of a solvent.



NSCl was identified by its infrared spectrum<sup>1</sup>. In some cases the NSCl was allowed to polymerize to a pale yellow solid (presumably  $(NSCl)_3$ ) which was then analyzed for nitrogen and chlorine. (Calcd. for  $(NSCl)_3$ : N, 17.18; Cl, 43.49. Found: N, 17.14; Cl, 43.62.) This substance melted in the region 73-77° to a dark green liquid which, upon heating to 110-140°, formed an orange solid which melted at 195-198°. These results differ from those of Schröder and Glemser<sup>7</sup>, who reported a melting point of 162.5° for  $(SNCl)_3$ .

This work was supported by the U.S. Atomic Energy Commission.

References

- <sup>1</sup> Glemser, O. & Richert, H., Z. anorg. allgem. Chem., 1961, 307, 313.
- <sup>2</sup> Glemser, O. & Perl, H., Naturwiss., 1961, 48, 620.
- <sup>3</sup> Prepared by passing dry nitrogen gas at low pressures through a microwave discharge.
- <sup>4</sup> Meuwsen<sup>5</sup> has shown that  $(\text{NSCl})_3$  reacts with  $\text{S}_2\text{Cl}_2$  to give  $\text{S}_3\text{N}_2\text{Cl}_2$ .
- <sup>5</sup> Meuwsen, A., Ber., 1932, 65, 1724.
- <sup>6</sup> Jolly, W. L., Maguire, K. D. & Rabinovich, D., to be published.
- <sup>7</sup> Schröder, H. & Glemser, O., Z. anorg. allgem. Chem., 1959, 298, 78.

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