# Reactions of Tetrasulphur Tetranitride with Halides. Part III.[†] Two New Methods of Preparing Trichlorocyclotrithiazene

By **Gulab G. Alange, Arthur J. Banister,*** and (Miss) **Betty Bell,** Chemistry Department, University Science Laboratories, Durham

Trichlorocyclotrithiazene, $(NSCl)_3$, is conveniently prepared by the action of sulphuryl chloride on tetrasulphur tetranitride, $S_4N_4$, or chlorocyclotrithiadiazenium chloride, $S_3N_2Cl^+Cl^-$.

TRICHLOROCYCLOTRITHIAZENE (the cyclic trimer of thiazyl chloride, NSCl), is commonly prepared by the action of chlorine on $S_4N_4$[1,2] or $S_3N_2Cl_2$.[3] Use of sulphuryl chloride instead of chlorine is more convenient and results in a purer product.

## EXPERIMENTAL

The $S_4N_4$ or $S_3N_2Cl_2$ and excess of $SO_2Cl_2$ (*e.g.* 2—3 ml $SO_2Cl_2$ per g of sulphur compound) are stirred under nitrogen for 24 h at room temperature. Evaporation to dryness under reduced pressure and recrystallisation of the yellow product from dry $CCl_4$ (or $SO_2Cl_2$ and filter at $-10°$) gives pale yellow needles (m.p. 91°; lit.[4] m.p. variable between 89 and 98°). Yields based on nitrogen content are 95—100%. I.r. (Nujol mull) absorptions occur at: 1017vs, 698ms, 621w, 514m, 493m, 385m, and 320m $cm^{-1}$. The peaks above 600 $cm^{-1}$ are probably SN ring modes, by analogy with $(NSF)_3$ which absorbs[5] at 1085, 720, and 650 $cm^{-1}$. The broad absorption at 480—520 $cm^{-1}$ is assigned to $\nu_{SCl}$ since this band is missing from the i.r. spectrum of $(NSF)_3$.

## DISCUSSION

Under the microscope the crystals of the product are seen to be identical to the $\alpha(NSCl)_3$ examined by Wiegers[6] and obtained by the action of chlorine on a suspension of $S_4N_4$ in $CCl_4$.[1] However, the latter product contains

---

[†] Part II, A. J. Banister and J. S. Padley, *J. Chem. Soc.* (*A*), 1969, 658.

[1] M. Goehring, 'Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen,' Akademie-Verlag, Berlin, 1957, p. 155.

[2] A. Meuwsen, *Berichte*, 1931, **64**, 2311; H. Schröder and O. Glemser, *Z. anorg. Chem.*, 1959, **298**, 78.

[3] W. L. Jolly and K. D. Maguire, *Inorg. Synth.*, 1967, **9**, 102.

[4] S. A. Lipp and W. L. Jolly, *Inorg. Chem.*, 1971, **10**, 33.

[5] O. Glemser, 'Preparative Inorganic Reactions,' ed. W. L. Jolly, Interscience, New York, vol. I, 1964, p. 236.

[6] G. A. Wiegers and A. Vos, *Acta Cryst.*, 1966, **20**, 192.

crystals of more than one type[7] and, further, its i.r. spectrum is often much more complex than that of the α$(NSCl)_3$ obtained from $S_4N_4$ and $SO_2Cl_2$, especially on unpurified material or the product of recrystallisation from hot solutions. The i.r. spectrum (4000—400 $cm^{-1}$) of the unpurified product from $S_4N_4$ and chlorine shows the peaks characteristic of α$(NSCl)_3$, the five main peaks[8] of $(NSCl)_4$, and numerous other absorptions. Their relative intensity is governed by the solvent used in the preparation, the concentration of $S_4N_4$, the temperature, and the rate and time of passage of chlorine. We conclude that the product is probably a mixture of $(NSCl)_3$ and $(NSCl)_4$ isomers and possibly other products also. The precise composition is determined by the procedures for preparation and purification. During recrystallisation of α$(NSCl)_3$ the solution should not be warmed above *ca.* 60° (the solution turns green) or allowed to stand, since this results in the appearance of extra i.r. peaks and a deepening of the colour of the product. Attempts at sublimation under reduced pressure resulted in depolymerisation to NSCl and some decomposition to $S_3N_2Cl$ (*cf.* refs. **3** and **9**).

We thank the S.C.S. College, Omerga (India) and the S.R.C. for Research Studentships to G. G. A. and B. B. respectively.

[1/2395 *Received*, 13*th December*, 1971]

---

[7] A. C. Hazell, personal communication.

[8] J. Nelson and H. G. Heal, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 429.

[9] R. L. Patton and W. L. Jolly, *Inorg. Chem.*, 1970, **9**, 1079.