Synthesis of New Heterocycles by Halogenation of Tetrasulfur Tetranitride S₄N₄

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Bromine reacts with tetrasulfur tetranitride S₄N₄ in solution in different solvents to give thiodithiazyl dibromide S₃N₂Br₂.

Iodine reacts under the same conditions with S₄N₄ to give trithiazyl iodide (SN)₃I.

The addition of chlorine, bromine or iodine to a mixture of tetrasulfur tetranitride and white phosphorus leads to compounds with the general formula P₃S₄N₄Xₙ, with n = 1 or 3 depending on the nature of X.

Moreover, we obtained also new combinations containing the pattern P₃S₄N₃X by reaction of halogens on a mixture of white phosphorus with tetrasulfur tetranitride.

A. Starting Compounds

Very pure compounds are required to study the reaction of the halogens with tetrasulfur tetranitride. We have been obliged to synthesize some thiacyl chlorides which have been used either as reference or as starting materials for the bromination and iodination reactions.

A.1. Tetrasulfur tetranitride S₄N₄

Numerous authors studied the preparation of S₄N₄. We used the method which has been perfected by BECKE-GOEHRING and revised by VILLENA-BLANCO and JOLLY. 

In this method S₄N₄ is obtained by ammonolysis of disulfur dichloride according to the overall reaction:

\[ 6 \text{S}_2\text{Cl}_2 + 16 \text{NH}_3 \rightarrow \text{S}_4\text{N}_4 + 12 \text{NH}_4\text{Cl} + 8 \text{S} \]

S₄N₄ is little sensitive to moisture. Consequently, it is easy to remove ammonium chloride by water treatment of the product at 0 °C. On the other hand, the separation from sulfur is much more delicate because it is soluble in the same solvents as S₄N₄. After several recrystallisations of the S–S₄N₄ mixture from dioxane and benzene, it is possible to obtain a product enriched in S₄N₄. This is then chromatographed on a column of acid alumina to exclude the residual sulfur.

Introduction

The thiacyl SN radical, the analogue of nitric oxide NO, polymerizes easily owing to the sulfur d-orbitals. The better known of these polymers, tetrasulfur tetranitride S₄N₄, can give SN radicals in the course of reactions, but it is at present impossible to predict how and where SN bond rupture occurs during a given reaction.

The S₄N₄ structure is known. This heterocycle can lead to other cycles with very different shapes. Examples are the structures of the compounds S₃N₃F₄, S₄N₃Cl₃, S₃N₂Cl₂, S₄N₃NO₃, S₃N₃AlCl₆ and S₄N₄F₄.

The large variety of the compounds produced from S₄N₄ shows that it is a good starting material for the synthesis of new combinations.

The action of fluorine on S₄N₄ leads to the compound S₄N₃F₄. The chlorination reaction yields S₄N₃Cl₉, via the intermediate step of S₄N₃Cl₁₀. We studied the bromination and the iodination of S₄N₄. While the bromination of S₄N₄ has been studied by several workers, it is the first time that the iodination reaction is reported.


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IR (KBr pellet) absorptions occurred (cm\(^{-1}\)) at: 925 s, 800 w, 768 w, 760 w, 728 s, 698 vs, 620 m, 550 vs, 528 m, 519 w.

Powder diffraction data (copper radiation) at: 6.33 m, 6.04 m, 4.75 vs, 4.60 vs, 4.37 m, 3.11 m, 2.71 s, 2.56 m Å.

**A.2. Thiodithiazyl dichloride \(S_2N_2Cl_2\)**

Thiazyl chlorides can be prepared from tetrasulfur tetranitride. Ammonium chloride and disulfur dichloride are the preferred starting materials. They react easily according to the scheme:

\[
2 \text{NH}_4\text{Cl} + 4 \text{S}_2\text{Cl}_2 \rightarrow \text{S}_2\text{N}_2\text{Cl}_2 + 8 \text{HCl} + 5 \text{S}. 
\]

The reaction is carried out in presence of sulfur to restrict the disproportionation of disulfur dichloride in sulfur dichloride \(SCl_2\). The compound \(S_2N_2Cl_2\) segregates easily from the reaction mixture by sublimation. Since it is easily obtained, it is used as a starting material for the preparation of the thiazyl chlorides \(S_3N_3Cl\) and \(S_2N_3Cl_3\) instead of \(S_4N_4\).

IR (nujol mull) absorptions occurred (cm\(^{-1}\)) at: 1015 m, 940 s, 582 m, 548 w, 460 w, 398 w.

Powder diffraction data (copper radiation) at: 4.57 vs, 4.28 m, 4.07 s, 3.73 m, 3.42 m, 3.34 m, 2.70 s, 2.68 vs, 2.60 s, 2.51 m, 2.27 m Å.

**A.3. Trithiazyl trichloride \(S_3N_3Cl_3\)**

Trithiazyl trichloride is obtained by chlorination of thiodithiazyl dichloride:

\[
3 \text{S}_2\text{N}_2\text{Cl}_2 + \text{Cl}_2 \rightarrow 2 \text{S}_3\text{N}_3\text{Cl}_3 + 3 \text{SCl}_2. 
\]

It can be separated from \(S_2N_2Cl_2\) due to its solubility in carbon tetrachloride and benzene. The compound \(S_3N_2Cl_3\) is very sensitive to moisture and must therefore be handled in a glove-box.

IR (CsBr pellet) absorptions occurred (cm\(^{-1}\)) at: 1155 s, 992 vs, 670 m, 558 m, 462 vs, 315 s.

**A.4. Thiotrithiazyl chloride \(S_4N_3Cl\)**

Thiotrithiazyl chloride is obtained by reaction between thiodithiazyl dichloride and disulfur dichloride:

\[
3 \text{S}_2\text{N}_2\text{Cl}_2 + \text{S}_2\text{Cl}_2 \rightarrow 2 \text{S}_4\text{N}_3\text{Cl} + 3 \text{SCl}_2. 
\]

The compound is ionic, \(S_4N_3^+ \text{Cl}^-\), and the structure of the \(S_4N_3^+\) ion has been determined using a single crystal of thiotrithiazyl nitrate. Further data are:

IR (CsBr pellet) absorptions occurred (cm\(^{-1}\)) at: 1160 vs, 1125 m, 998 vs, 682 s, 608 m, 565 s, 465 vs, 450 s, 325 s.

Powder diffraction data (copper radiation) at: 5.31 s, 4.56 m, 4.06 s, 3.21 m, 3.06 vs, 2.93 m, 2.71 s, 2.56 m Å.

**A.5. Thiotrithiazyl bromide \(S_4N_3Br\)**

The ionic character of the thiotrithiazyl chloride and the stability of the \(S_4N_3^+\) ion enables the bromide to be obtained by metathesis with potassium bromide:

\[
\text{S}_4\text{N}_3^+\text{Cl}^- + \text{K}^+\text{Br}^- \rightarrow \text{S}_4\text{N}_3\text{Br} + \text{K}^+\text{Cl}^-.
\]

The reaction has been carried out either in water at 0 °C or in formic acid. The thiotrithiazyl bromide precipitates from the solution:

IR (CsBr pellet) absorptions occurred (cm\(^{-1}\)) at: 1155 s, 992 vs, 670 m, 558 m, 462 vs, 315 s.

**B. Study of the Bromination of \(S_3N_4\)**

The first study on the bromination of tetrasulfur tetranitride reported the formation of \((\text{SNBr})_2\). More recently, He\text{al} and Zbor\text{Ilova} concluded that a mixture of products is formed with a composition close to the formula \(S_3N_2Br_2\).

We studied the reaction between \(S_3N_4\) and bromine in carbon disulfide or carbon tetrachloride. It is very important to use moisture free conditions, i.e. strictly anhydrous solvents. Moreover, tetrasulfur tetranitride must be free from sulfur. All manipulations must be carried out in an inert atmosphere and the reaction products are therefore handled in a glove-box. The reaction between \(S_3N_4\) and bromine has been studied at different temperatures.

**B.1. Preparations of \(S_3N_2Br_2\)**

A solution of \(S_3N_4\) and bromine in CS\(_2\) is refluxed for one hour. The precipitate found is thiodithiazyl dibromide. This new compound is a yellow-orange coloured crystalline product.

\(S_3N_2Br_2\) has been obtained also by brominating \(S_2N_2Cl_2\) with HBr. The solid-gas phase reaction proceeds according to the equation:

\[
\text{S}_2\text{N}_2\text{Cl}_2 + 2 \text{HBr} \rightarrow \text{S}_3\text{N}_2\text{Br}_2 + 2 \text{HCl}. 
\]

The formation of HCl is evidenced by IR absorption spectroscopy. Yet, the product is less pure than the \(S_3N_2Br_2\) obtained by bromination of \(S_3N_4\).
Experimental

A 250 ml flask was equipped with a reflux condenser and the top of the condenser was fitted with a drying tube filled with calcium chloride. The reaction temperature was controlled with an electric heating mantle.

The reaction flask was charged with 200 ml of CS₂ or CCI₄ dried with molecular sieves and 1.84 g (0.01 mol) of S₄N₄ recrystallised in C₆H₆ just prior to use. After dissolution of S₄N₄, 3 ml of Br₂ was added. The reaction mixture was allowed to reflux for two hours. Then the S₂N₂Br₂ was collected by filtration in a glove-box, desiccated with P₂O₅, and subsequently washed with dry CS₂. S₃N₂Br₂ was dried in vacuo.

Analysis for S₂N₂Br₂
Calcd  S 33.80  N 9.86  Br 56.34,
Found S 34.1  N 9.94  Br 56.4.

Bromine is titrated by potentiometry, nitrogen by the Kjeldahl’s method and sulfur as barium sulfate.

IR (CsBr pellet) absorptions occurred (cm⁻¹) at:
1160 s, 1010 vs, 1000 s, 675 m, 562 m, 470 vs, 320 s.
Powder diffraction data (copper radiation) at:
5.14 m, 4.84 m, 4.52 m, 3.89 m, 3.48 vs, 3.30 s,
3.09 m, 2.85 m, 2.51 m, 2.42 w Å.

3.09 m, 2.85 m, 2.51 m, 2.42 w Å.

B.2. Study of the reaction of bromination of S₄N₄

We will recall that chlorine and fluorine react with S₄N₄ to give S₃N₃Cl₃ and S₃N₃F₄, and the compound S₄N₃Cl₄ is obtained as an intermediate. On the other hand, bromine does not lead to symmetrical compounds such as S₃N₃Br₃ or S₃N₃Br₂ but yields S₂N₂Br₂ instead.

In order to obtain information on the possible existence of the compound S₂N₂Br₃, S₂N₂Cl₃ was treated with HBr. The reaction takes place with HCl and Br₂ evolution. The yellow S₂N₂Cl₃ turns red rapidly to finally give a yellow-orange coloured product. The X-ray diagram of this latter product is analogous to S₂N₂Br₂. This result can be explained by the formation of S₂N₂Br₃ as an intermediate compound with decomposes at once in S₂N₂Br₂.

In boiling CS₂ (or CCl₄) S₂N₂Br₂ is obtained in a pure state; at room temperature, the bromination of S₄N₄ leads to a mixture of products: S₂N₂Br₂ is obtained admixed with another compound, the elementary analysis of which corresponds to the formula (SN)₂Br. S₂N₂Br₂ is separated from (SN)₂Br by dissolving the latter selectively in liquid SO₂. The compound (SN)₂Br is orange coloured and crystallized.

B.3. Transformation of S₂N₂Br₂ into S₄N₃Br

Thiotrichiazyl bromide S₄N₃Br has been found as an impurity in thiodithiazyl dibromide in the bromination of S₄N₄. It can result either from the hydrolysis of S₂N₂Br₂ or from the presence of sulfur formed in the reaction of bromine on S₄N₄. The thermal decomposition of S₂N₂Br₂ leads likewise to the formation of S₄N₃Br.

S₂N₂Br₂ is very sensible to moisture. It decomposes in the atmosphere giving mainly thiotrichiazyl bromide and ammonium bromide.

The same thiotrichiazyl bromide has been found as an impurity in S₂N₂Br₂ when bromine reacts with a sulfur containing sample of S₄N₄. In this case, bromine reacts both with S₄N₄ and S, the latter forming disulfur dibromide. The formation of S₄N₃Br can then be explained by the reaction of S₂N₂Br₂ with S₄N₃Br₂. In the same way, S₂Cl₂ transforms S₄N₂Cl₂ into S₄N₃Cl₁₆. S₄N₃Br and S₂N₂Br₂ are separated by selective dissolution of S₂N₂Br in liquid SO₂.

At 90 °C and 10⁻¹ torr, S₂N₂Br₂ decomposes according to:
6 S₂N₂Br₂ → 4 S₄N₃Br + S₂Br₂ + 3 Br₂.

C. Study of the Iodination of S₄N₄

The reaction between iodine and S₄N₄ has been studied in an inert solvent at different temperatures. In any case, a precipitate is formed which corresponds to the formula (SN)₂I.

The iodination of S₄N₄:
2 S₄N₄ + 2 I₂ → 4 (SN)₂I

is slow at room temperature but is appreciably accelerated when carried out in boiling solvents.

Experiments in progress show that hydrogen iodide displaces the chlorine atoms from the thiodithiazyl dichloride. The new compound (SN)₂I which is sensible to moisture is dark red. Its X-ray diagram is that of a nearly amorphous compound.

Analysis for (SN)₂I
Calcd  S 36.22  N 15.85  I 47.92
Found S 35.5  N 15.9  I 47.8.

IR (CsI pellet) absorptions occurred (cm⁻¹) at:
962 vs, 755 s, 665 w, 638 m, 590 w, 465 w, 425 m Å.

D. Study of the Halogenation of the Mixture S₃N₃-White Phosphorus

The halogens (chlorine, bromine and iodine) react with a mixture of white phosphorus and tetrasulfur
tetranitride. The reactions are carried out in carbon disulfide which is a solvent of both $S_4N_4$ and white phosphorus.

The reactions are rapid and can be represented as follows:

$$3 \text{S}_4\text{N}_4 + 8 \text{P} + 6 \text{Cl}_2 \rightarrow 4 \text{P}_2\text{S}_3\text{N}_3\text{Cl}_3$$
$$3 \text{S}_4\text{N}_4 + 8 \text{P} + 6 \text{Br}_2 \rightarrow 4 \text{P}_2\text{S}_3\text{N}_3\text{Br}_3$$
$$3 \text{S}_4\text{N}_4 + 8 \text{P} + 2 \text{I}_2 \rightarrow 4 \text{P}_2\text{S}_3\text{N}_3\text{I}$$

The products precipitate from the reaction medium. They are characterized by elementary analysis and mass spectrometry. They are amorphous to X-rays.

Their stability decreases when passing from the iodinated to the chlorinated compound. They decompose below 100 °C. A polymer (PSN)$_n$ is obtained as residue in the decomposition of the iodinated derivate at 95 °C.

**Experimental**

4.96 g (0.16 mol) of white phosphorus, 7.36 g (0.04 mol) of finely ground tetrasulfur tetranitride and 300 ml of inert solvent (CCl$_4$, CS$_2$) were placed in a 500 ml round-bottomed three necked flask. This flask was equipped with a mechanical stirrer, with a nitrogen inlet tube which was used to prevent moisture during the reaction, and with a reflux condenser. The top of the condenser was connected with a drying tube containing calcium chloride, which was replaced with an inlet tube for the adding bromine and iodine solution in CCl$_4$. The chlorine was passed directly through the solution.

The mixture of phosphorus and $S_4N_4$ was allowed to reflux for 4 hours and cooled to room temperature. The solution was brown red. Soon after the start of the halogen adding, the colour turned into yellow. The halogens were added in excess. The compounds precipitated slowly. After 24 hours, the solid was collected by filtration in a glove-box, washed with ether and dried in vacuo.

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