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SULFUR NITROGEN CHLORIDES

Thiodithiazyl Dichloride, * $S_3N_2Cl_2$

Thiotrithiazyl Chloride, * S_4N_3Cl

Thiodithiazyl Chloride, * S_3N_2Cl

Trithiazyl Chloride, * $S_3N_3Cl_3$

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William L. Jolly and Keith D. Maguire

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ABSTRACT

The usual directions[1] for preparing sulfur nitrogen chlorides call for the starting material S_4N_4 - a compound that is neither readily available commercially nor easily prepared.[2] It has recently been discovered that $S_3N_2Cl_2$ may be conveniently prepared from the readily available materials ammonium chloride and disulfur dichloride, and that $S_3N_2Cl_2$ may be easily converted to either S_4N_3Cl, S_3N_2Cl, or $S_3N_3Cl_3$.[3] The following procedures are based on the latter reactions.

A. $S_3N_2Cl_2$

$$4\ S_2Cl_2 + 2\ NH_4Cl \longrightarrow S_3N_2Cl_2 + 8\ HCl + 5\ S$$

Procedure

One hundred grams (1.87 moles) of granular ammonium chloride, 100 ml. (168 g. or 1.24 moles) of disulfur dichloride, and 20 g. (0.63 mole) of powdered sulfur are placed in a short-necked 500-ml. round-bottomed flask with a 24/40 ₮ joint. An air condenser (25 mm. o.d., 50 cm. long), the top of which is fitted with a drying tube filled with anhydrous calcium sulfate, is attached to the flask (Fig. 1 A). The ground joints should be lubricated with a grease inert to disulfur dichloride (e.g., Kel-F halocarbon grease*) to prevent "freezing" of the joints. The assembly is placed in a well ventilated hood, and the slurry is heated with an electric heating mantle until the disulfur dichloride begins to boil. The heating is then adjusted so that the upper level of the condensing disulfur dichloride lies just within the bottom joint of the air condenser. During the heating, orange crystals of $S_3N_2Cl_2$ collect in the air condenser. It is important that the heating be adjusted so that the $S_3N_2Cl_2$ collects at the lower end of the air condenser -

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* Manufactured by Minnesota Mining & Manufacturing Co., St. Paul, Minnesota.

close to the flask, but not actually inside the flask. The heating is continued until the disulfur dichloride is almost completely consumed (about 10-12 hrs.). The flask must not be allowed to run completely dry, or ammonium chloride will sublime and contaminate the product. The air condenser is separated from the reaction flask, and the bottom of the condenser is immediately closed off with a small stopper. The top of the air condenser is connected to a vacuum pump via a liquid nitrogen trap. (See Fig. 1 B) The entire operation of replacing the reaction flask with a stopper and making the vacuum connection should take less than 10 seconds. Pumping is continued for 30 minutes at room temperature to remove the volatile impurities, hydrogen chloride and sulfur dichloride. Dry air is admitted to the air condenser, and the condenser is transferred to a dry bag* where the $S_3N_2Cl_2$ is removed from the air condenser by scraping with a metal spatula. The $S_3N_2Cl_2$ should be stored in a glass container with an air-tight

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* A thin polyethylene bag, flushed with dry nitrogen, serves as an effective dry bag. Very convenient and inexpensive dry bags with gloves may be obtained from Instruments for Industry and Research, Cheltenham, Penna.

polyethylene stopper. The yield is 12-14 g. (20-23% based on the disulfur dichloride). Anal. Calcd. for $S_3N_2Cl_2$: S, 49.29; N, 14.36; Cl, 36.36. Found: S, 49.0; N, 14.6; Cl, 36.81.

Analysis

An accurately measured amount (about 0.2 g.) of $S_3N_2Cl_2$ is placed in a 250-ml. Erlenmeyer flask containing 5 g. of potassium hydroxide pellets, 50 ml. of distilled water and 20 ml. of 3% hydrogen peroxide. A small short-stemmed funnel is placed in the mouth of the flask to prevent loss by spattering, and the flask is boiled gently on a hot plate for one hour. The solution is cooled, and the chloride determined by a Volhard titration in the usual manner.

Sulfur is determined gravimetrically by precipitation of barium sulfate after oxidation of an approximately 50-mg. sample by fusion with a sodium peroxide-sodium carbonate mixture in a nickel crucible.

Nitrogen is determined by heating an approximately 100-mg. sample with 1 g. of a 1:1 copper-copper oxide mixture in an evacuated sealed tube at 500° for two hours. A suitable tube consists of a piece of 30 mm. Pyrex tubing, 15 cm. long, provided at one end with an opening for introducing the sample (later

sealed after evacuating), and at the other end with a break-seal and vacuum line connection. After heating, the tube is cooled, transferred to the vacuum line, and opened; the nigrogen gas is measured by Toepler-pumping it into a calibrated gas collection system. Traces of sulfur dioxide are removed by passing the nitrogen through an efficient liquid nitrogen trap.

Properties

Pure $S_3N_2Cl_2$ is an orange crystalline solid that is very sensitive toward moisture, and all manipulations of the compound should be carried out in a suitable dry bag. In the presence of traces of moisture it turns dark red. $S_3N_2Cl_2$ is insoluble in anhydrous organic solvents. It reacts instantly with water yielding sulfur dioxide, ammonium chloride, and sulfur. $S_3N_2Cl_2$ melts (with decomposition) at 90-92° in a sealed capillary.

Although $S_3N_2Cl_2$ has never been observed to decompose explosively, it is recommended that the material be handled with reasonable caution, inasmuch as it is probably thermodynamically unstable.

B. S_4N_3Cl

$$3\ S_3N_2Cl_2 + S_2Cl_2 \longrightarrow 2\ S_4N_3Cl + 3\ SCl_2$$

Procedure

The preparation of $S_3N_2Cl_2$ is carried out as described in Procedure A as far as the removal of volatile impurities by pumping. After the pumping,* the vacuum is broken with dry air, and the top of the air condenser is fitted with a drying tube filled with anhydrous calcium sulfate. The bottom of the air condenser is attached to a 250-ml. round-bottomed flask containing 50 ml. of dry carbon tetrachloride† and 50 ml. of disulfur dichloride. The assembly

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* If the sulfur dichloride and dissolved hydrogen chlorine are not removed a product contaminated with ammonium chloride will result. An alternative procedure to pumping off the volatile impurities is to allow the assembly to stand 48 hours so that the adhering liquids drain into the reaction flask. This procedure is not as efficient as pumping off the impurities, but has the advantage of minimizing exposure of the product to the atmosphere.

† Freshly distilled from anhydrous calcium sulfate after being allowed to stand 48 hours over anhydrous calcium sulfate.

is placed in a well ventilated hood, and the solvent mixture is refluxed gently so that the condensing liquid washes down the solid material. The orange $S_3N_2Cl_2$ turns dark green, and then slowly, upon continued refluxing, it becomes bright yellow as the S_4N_3Cl is produced. The solid tends to stick to the walls of the air condenser, thereby considerably retarding the rate of conversion. If considerable solid remains in the condenser after about 30 minutes of refluxing, the drying tube is removed, and the solid is pushed down into the flask with a long glass rod. The refluxing is continued until the flask contains a bright canary-yellow solid that is completely free of dark green material. This usually requires 4 - 6 hours. The product is filtered while still warm on a medium-porosity sintered glass funnel, washed three times with dry carbon tetrachloride and finally dried in a vacuum desiccator. The yield (7 - 9 g.) corresponds to a quantitative conversion of $S_3N_2Cl_2$ to S_4N_3Cl. Anal. Calcd. for S_4N_3Cl: N, 20.38; S, 62.34; Cl, 17.24. Found: N, 21.0; S, 62.09; Cl, 17.58. Analyses may be performed as described under Section A.

Properties

S_4N_3Cl is a bright canary yellow solid that is stable in dry air but is attacked slowly by moist air. The compound dissolves in ice-cold water to form an unstable solution from which the brick red iodide, S_4N_3I may be precipitated

by the addition of cold aqueous KI. S_4N_3Cl is insoluble in most organic solvents, but appreciable amounts dissolve in anhydrous formic acid. The infrared spectrum (KCl disc.) has peaks at 8·6, 9·9, and 14·7 microns. S_4N_3Cl has been observed to melt with decomposition in the range 180-200°.

Although $S_3N_2Cl_2$ has never been observed to decompose explosively, it is recommended that the material be handled with reasonable caution, inasmuch as it is probably thermodynamically unstable.

C. $S_3N_3Cl_3$

$$3\ S_3N_2Cl_2 + 3\ Cl_2 \longrightarrow 2\ S_3N_3Cl_3 + 3\ SCl_2$$

Procedure

The $S_3N_2Cl_2$ is prepared according to Procedure A. After removing the volatile impurities, dry air is allowed to enter the air condenser. The bottom of the condenser is then connected to a 150-ml. round-bottomed three-neck flask fitted with an inlet tube for chlorine and a vacuum connection (Fig. 2). The vacuum connection on top of the air condenser is replaced with a drying tube containing anhydrous calcium sulfate. The assembly is placed in a hood, the inlet tube is connected to a chlorine cylinder and a slow stream of chlorine is passed through

the air condenser over the $S_3N_2Cl_2$. Soon after the start of the chlorine flow, the $S_3N_2Cl_2$ turns into a dark red-brown slury which falls into the flask. The chlorine is passed for 30 minutes with occasional shaking. At the end of this time the chlorine stream is stopped, stopcock 1 is closed, and the top of the drying tube is closed with a stopper. The flask is then evacuated (to less than 1 mm) via the vacuum connection, and the pumping is continued for 15 minutes. The sulfur dichloride produced in the reaction is thus removed quite quickly and is conveniently collected in a trap cooled with liquid nitrogen. The vacuum is closed off (stopcock 2) and dry air is allowed to enter the apparatus via the drying tube on top of the air condenser. The chlorination is repeated for a further 30-minute period, and the sulfur dichloride is again removed by evacuating the flask. The chlorination procedure is repeated until there is no darkening of the pale yellow product when chlorine is passed over it for 5 minutes. Two chlorinations are usually sufficient, but the size of the pieces of $S_3N_2Cl_2$ in the flask governs the rate of chlorination. When the chlorination is complete, the flask is evacuated and the pumping is maintained for one hour at room temperature. Dry air is admitted to the apparatus via the drying tube, the assembly is placed in a dry bag, and the $S_3N_3Cl_3$ is removed from the flask with a spatula. The

product is a pale yellow crystalline solid. The yield (9·5 - 11 g.) corresponds to a quantitative conversion of $S_3N_2Cl_2$ to $S_3N_3Cl_3$. The product can be recrystallized from dry carbon tetrachloride in a dry atmosphere if a slightly purer material is required. Anal. Calcd. for $S_3N_3Cl_3$: N, 17.81; Cl, 43.49. Found (crude product): N, 17.14; Cl, 43.62. Mol. wt. (cryoscopic in benzene) 244. Calcd. for $S_3N_3Cl_3$ 244.6. Analyses may be performed as described under Section A.

Properties

$S_3N_3Cl_3$ is a pale yellow crystalline solid that is soluble in solvents such as carbon tetrachloride and benzene. The crude product melts at 75° (with decomposition), the recrystallized product at 91° (with decomposition). $S_3N_3Cl_3$ is decomposed by moist air, yielding sulfur dioxide and ammonium chloride; liquid water causes a similar decomposition very rapidly. $S_3N_3Cl_3$ should be stored in a glass container with an air-tight polyethylene stopper.

Although $S_3N_3Cl_3$ has never been observed to decompose explosively, it is recommended that the material be handled with reasonable caution, inasmuch as it is probably thermodynamically unstable.

D. S_3N_2Cl

$$3\ S_3N_2Cl_2 \xrightarrow{80\text{-}90^\circ} 2\ S_3N_2Cl + NSCl + SCl_2$$

Procedure

The pyrolysis of $S_3N_2Cl_2$ is carried out in a chemical vacuum line. A suitable reaction vessel is shown in Fig. 3. The tared reaction vessel is charged with 5 g. of $S_3N_2Cl_2$ in an atmosphere of dry nitrogen in a dry bag. The reaction vessel is weighed, evacuated, reweighed, and then connected to the vacuum line. All the joints and stopcocks should be lubricated with a grease inert to sulfur chloride (e.g., Kel-F halocarbon grease). While continuously pumping on the reaction vessel, the bottom of the vessel is immersed 5 cm. deep in an oil bath and the oil bath is heated over a period of 30 - 40 minutes from room temperature to 80 - 90°. The temperature should not be allowed to exceed 90°. The oil bath is maintained at 80 - 90° for two hours, and during this period sulfur dichloride and NSCl are evolved, and the solid residue turns dark green. The SCl_2 and NSCl are collected in a liquid nitrogen trap between the reaction vessel and the vacuum pump. The reaction vessel is allowed to cool to room temperature, the stopcock is closed,

and the reaction vessel is removed from the vacuum line and weighed. The heating *in vacuo* is repeated for 15-minute periods until the weight of the reaction vessel and contents is constant. The weight of product should be 0.545 times the weight of the original $S_3N_2Cl_2$. *Anal.* Calcd. for S_3N_2Cl: N, 17.54; Cl, 22.24. Found: N, 17.8; Cl, 22.0.

Properties

S_3N_2Cl is dark green and has a metallic luster; it is insoluble in organic solvents and insoluble in water, by which it is hydrolysed slowly. It is stable in dry air. S_3N_2Cl does not have a sharp melting point. When heated *in vacuo* to 120 - 140°, it decomposes, yielding sulfur dichloride, NSCl, and S_4N_3Cl. Although S_3N_2Cl has never been observed to decompose explosively, it is recommended that the material be handled with reasonable caution, inasmuch as it is probably thermodynamically unstable.

REFERENCES

* These names are commonly used in the literature even though in at least one case (S_4N_3Cl) the name implies an incorrect structure. Since systematic names are cumbersome, we refer to the compounds by their formulas.

+ This work was supported by the United States Atomic Energy Commission.

1. M. Goehring, "Ergebnisse und Probleme der Chemie Schwefelstickstoffverbindungen", Akademie-Verlag, Berlin, 1957.

2. M. Becke-Goehring, Inorg. Syn, 6, 123 (1960).

3. W. L. Jolly, K. D. Maguire, and D. Rabinovich, Inorg. Chem., in press.

Figure Captions

Figure 1. Apparatus for the Preparation of $S_3N_2Cl_2$.

Figure 2. Apparatus for the Preparation of $S_3N_3Cl_3$.

Figure 3. Reaction Vessel for the Preparation of S_3N_2Cl.

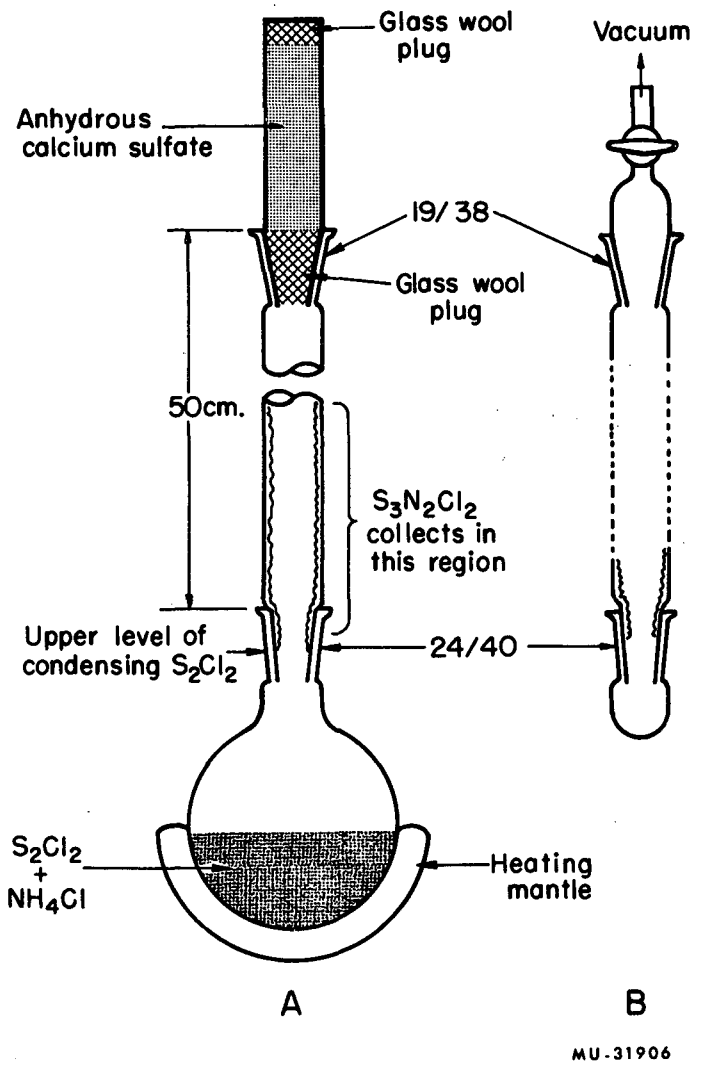

Glass wool plug
Vacuum
Anhydrous calcium sulfate
19/38
Glass wool plug
50cm.
$S_3N_2Cl_2$ collects in this region
Upper level of condensing S_2Cl_2
24/40
S_2Cl_2 + NH_4Cl
Heating mantle
A
B
MU-31906

Fig. 1.

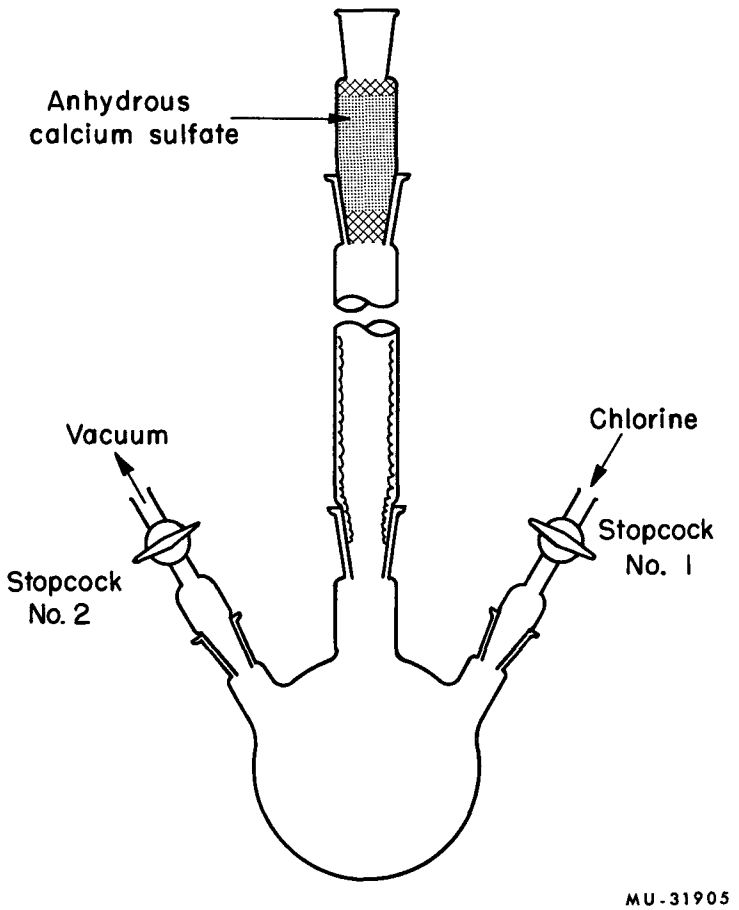
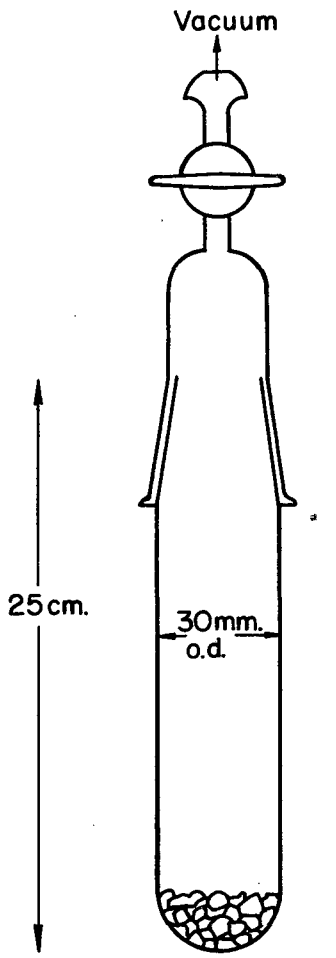

Anhydrous
calcium sulfate
Vacuum
Chlorine
Stopcock
No. 1
Stopcock
No. 2
MU-31905

Fig. 2.



MU-31907

Fig. 3.

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