

CONTRIBUTION FROM THE CHEMICAL INSTITUTE OF THE
UNIVERSITY OF HEIDELBERG, HEIDELBERG, GERMANY, AND THE
DEPARTMENT OF CHEMISTRY AND LAWRENCE RADIATION LABORATORY,
UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA

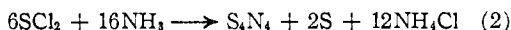
The Synthesis of Tetrasulfur Tetranitride and Trisulfur Dinitrogen Dioxide¹

By WILLIAM L. JOLLY² AND MARGOT BECKE-GOEHRING

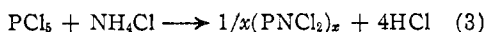
Received March 9, 1961

Tetrasulfur tetranitride (S_4N_4) was prepared by the reaction of S_2Cl_2 vapor with hot ammonium chloride. Trisulfur dinitrogen dioxide ($S_3N_2O_2$) was prepared both by the reaction of $SOCl_2$ vapor with a mixture of hot sulfur and ammonium chloride and by the reaction of a mixture of S_2Cl_2 and $SOCl_2$ vapors with hot ammonium chloride.

Tetrasulfur tetranitride usually is prepared by passing gaseous ammonia into a solution of either S_2Cl_2 or SCl_2 in an inert solvent such as carbon tetrachloride³



It is well known that other nitrogen-containing ring compounds may be prepared by ammonolytic reactions in which ammonium chloride serves as the source of ammonia. For example, the phosphonitrilic chlorides are prepared by the reaction of phosphorus(V) chloride with ammonium chloride.⁴



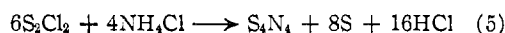
Similarly, trichloroborazine is prepared by the reaction of boron trichloride with ammonium chloride.⁵



It therefore seemed reasonable that one might prepare tetrasulfur tetranitride by an analogous reaction between S_2Cl_2 and ammonium chloride.

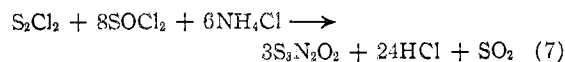
We studied the reaction of S_2Cl_2 with ammonium chloride by passing a stream of air and S_2Cl_2 vapor through hot ammonium chloride pellets. The exit gases passed through an air-cooled condenser wherein a purple-brown solid deposited. This solid was found to be a mixture of S_4N_4 , sul-

fur, and ammonium chloride, together with smaller amounts of $S_3N_2O_2$ and probably traces of S_2N_2 . Large amounts of sulfur were deposited on the ammonium chloride pellets. The formation of S_4N_4 may be accounted for by the reaction



The S_4N_4 may be isolated by extraction of the purple-brown solid with refluxing dioxane⁶ followed by recrystallization from benzene. Total yields of 4 to 9 g. of S_4N_4 may be obtained from 150 g. of S_2Cl_2 in a period of one or two days (corresponding to yields of 12 to 26%, based on equation 5). The method has the advantages that very little attention need be given the apparatus during a run and that a minimum of solvent manipulation is required.

When $SOCl_2$ vapor was passed through hot ammonium chloride pellets, only traces of sulfur-nitrogen compounds formed in the air condenser. However, when the ammonium chloride pellets were mixed with sulfur, or when a mixture of S_2Cl_2 and $SOCl_2$ vapors was used, good yields of $S_3N_2O_2$ were obtained. It is suggested that the following reactions were responsible, respectively, for the formation of $S_3N_2O_2$ in these experiments.



Either of the latter methods is much more convenient than previously described methods for preparing $S_3N_2O_2$.⁷

(6) The compounds $S_3N_2O_2$ and S_2N_2 are partially converted to S_4N_4 by treatment with hot dioxane containing a trace of water. See reference 7 for a discussion of the chemistry of these compounds.

(7) M. Becke-Goehring, *Prog. in Inorg. Chem.*, **1**, 207 (1959).

(1) Presented at the September, 1960, meeting of the American Chemical Society, New York, N. Y.

(2) Work largely done while in Heidelberg during a leave of absence supported by the John Simon Guggenheim Memorial Foundation.

(3) M. Goehring, "Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen," Akademie-Verlag, Berlin, 1957, pp. 144-145; M. Becke-Goehring, *Inorg. Syntheses*, **6**, 123 (1960).

(4) R. Schenck and G. Römer, *Ber.*, **57**, 1345 (1924).

(5) C. A. Brown and A. W. Laubengayer, *J. Am. Chem. Soc.*, **77**, 3699 (1955); H. J. Emelús and G. J. Videla, *J. Chem. Soc.*, 1306 (1959); G. L. Brennan, G. H. Dahl, and R. Schaeffer, *J. Am. Chem. Soc.*, **82**, 6248 (1960).

Experimental

Preparation of Tetrasulfur Tetranitride.—An efficient reaction vessel was constructed from a glass cylinder 9 cm. in diameter and 24 cm. long. A 25-cm. length of tubing was sealed to one end (the entrance) of the cylinder, and the other end (the exit) was furnished with a ground joint, whereby a long glass "air condenser" could be attached. The outside of the cylinder and the entrance tube were wound with resistance wire and then covered with asbestos paper. A glass-sheathed thermocouple was inserted from the entrance side, permitting temperature measurement in any of several zones in the vessel. The vessel was filled with irregular-shaped ammonium chloride particles of 1.5 cm. average diameter. These particles were prepared by baking a mush of ammonium chloride and water to dryness in an oven, then hammering the resulting hard mass into particles of suitable size.

During a run, a stream of air was passed through an efficient KOH-pellet drying tube, a safety trap, a bubbler-flask containing commercial S_2Cl_2 , and then into the pre-heater tube of the reaction vessel. The temperature within the reaction vessel was controlled by adjusting the voltage applied to the resistance wire. At the end of the run, the air condenser was detached and connected above a flask containing about 75 ml. of dioxane. The dioxane was boiled until all the sulfur-nitrogen compounds were washed by reflux into the flask. After evaporation of the dioxane at room temperature, the residue of sulfur-contaminated S_4N_4 was recrystallized from hot benzene.

It was found that sulfur nitrides were formed when the reaction temperature was between 110 and 210°. Below 110°, the reaction was so slow that very poor conversion of the sulfur chloride to sulfur nitrides was achieved. Above 210°, the sulfur nitrides decomposed before reaching the condenser, so only sulfur and ammonium chloride were found in the condenser. In general, a reaction temperature near 160° was employed.

It was found that the best conversions of S_2Cl_2 to S_4N_4 were obtained with air flow rates between 300 and 2000 cc./min. With low flow rates, the sulfur nitrides probably undergo appreciable decomposition because of the long gas residence times. With high flow rates, an excessive fraction of the S_2Cl_2 passes through the vessel without reacting. The sulfur nitride forms partly as a cloud of small particles; consequently, with high flow rates, an appreciable amount of product is lost by passage through the air condenser.

Yields of 26% (calculated from the vaporized S_2Cl_2 on the basis of equation 5) were obtained with a production rate of 4 g. per day, and yields of 12% with a production rate of 9 g. per day. In runs with low flow rates, it was possible to recover 20% of the evaporated S_2Cl_2 by passage of the exit gas through a -78° trap. (It also was found that an appreciable amount of the S_2Cl_2 was oxidized to SCl_2 and SO_2 .) It is suspected that an even greater fraction of S_2Cl_2 passes unreacted in runs with high flow rates.

It was felt that the method would be much more useful if the apparatus could be constructed from readily available laboratory equipment. Therefore a series of runs were carried out using the apparatus pictured in Figure 1, which is almost self-explanatory. The inverted 1000-ml. flask was filled with about 800 g. of 1-g. ammonium chloride pellets, which were kept from falling out by means of a small piece of Monel gauze. Most of the product collected

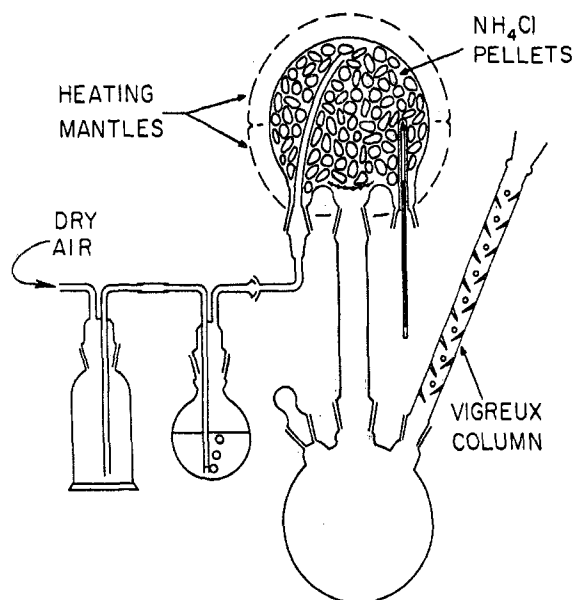


Figure 1.

in the tube immediately beneath the reaction flask. After a run, this tube together with the lower flask and Vigreux column were separated from the reactor and the product was extracted by reflux into 75 ml. of dioxane.

The best results were obtained with reaction temperatures in the range 170–175° and air flow rates near 500 cc./min. Under these conditions, a two-day run yielded 5.0 g. of purified S_4N_4 from 150 g. of S_2Cl_2 .

A portion of the initial purple-brown deposit from a typical run was made into a KBr pellet and the infrared spectrum determined. All bands excepting two very weak ones could be accounted for by S_4N_4 , NH_4Cl , and $S_3N_2O_2$. The presence of S_2N_2 was suspected from the odor of the deposit.

Preparation of Trisulfur Dinitrogen Dioxide.—It was found that when air saturated with $SOCl_2$ at room temperature was passed through a hot ammonium chloride reactor which previously had been used to prepare S_4N_4 , an orange deposit containing considerable amounts of $S_3N_2O_2$ formed in the air condenser. However, in succeeding runs the yields of $S_3N_2O_2$ rapidly dropped off to zero. By performing a run in which sulfur was purposely added to the ammonium chloride, it was made clear that the first runs were successful because of the sulfur which had deposited on the ammonium chloride particles in the previous S_2Cl_2 runs. As this sulfur was removed by reaction 6, the yields of $S_3N_2O_2$ dropped.

Temperatures between 160 and 190° and flow rates around 500 cc./min. were found to be most effective. Only $S_3N_2O_2$ and ammonium chloride were identified in the orange deposit, although traces of other sulfur-nitrogen compounds were present. By extraction with 50 ml. of refluxing benzene and fractional crystallization by room-temperature evaporation in a stream of dry air, the $S_3N_2O_2$ could be isolated; observed m.p. 99–100°; literature,⁸ 100.7°. Using either of the previously described reactors

(8) M. Goehring and J. Heinke, *Z. anorg. u. allgem. Chem.*, **273** 297 (1953).

8–9 g. of purified $S_3N_2O_2$ could be obtained from 200 g. of $SOCl_2$ in a 12-hr. run. These amounts correspond to about 10% yields calculated from the vaporized $SOCl_2$ on the basis of equation 6.

Using pure ammonium chloride pellets, a 3-hr. run was

made using the apparatus shown in Figure 1. A mixture of 303 g. of S_2Cl_2 and 121 g. of $SOCl_2$ was used in the bubbler; during the run 34 g. of this mixture evaporated. Four g. of pure $S_3N_2O_2$ and one g. of crude $S_3N_2O_2$ were obtained from the red material deposited in the air condenser.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASSACHUSETTS

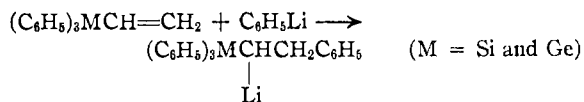
Vinyl Derivatives of Metals. XI. Reaction of Nucleophilic Reagents with Triethylperfluorovinylsilane^{1,2}

BY DIETMAR SEYFERTH AND TADASHI WADA³

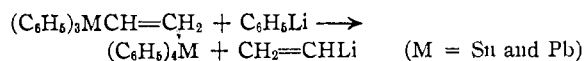
Received August 3, 1961

The reaction of organolithium reagents with triethylperfluorovinylsilane gave *trans*-(C_2H_5)₃SiCF=CFR products (R = *n*-butyl, phenyl, vinyl, allyl, triphenylsilyl, triphenylgermyl, and diphenylphosphino), presumably by an addition-elimination sequence. The action of phenyllithium on α,β -difluoro- β -triethylsilylstyrene resulted in formation of triethylphenylsilane and diphenylacetylene. The possible mechanisms of this reaction are discussed. Treatment of triethylperfluorovinylsilane with sodium alkoxides and mercaptides also produced addition-elimination products, (C_2H_5)₃SiCF=CFOR and (C_2H_5)₃SiCF=CFSR.

Previous studies concerned with the chemical reactivity of vinyl derivatives of Group IV metals have shown that a considerable difference exists between the reactions observed with vinylsilanes and vinylgermanes on the one hand, and vinyltin and vinyllead compounds on the other.⁴ Thus, to cite an example of interest to the present study, triphenylvinylsilane and triphenylvinylgermane react with phenyllithium in the following manner^{5,6}



while triphenylvinyltin and triphenylvinyllead undergo an exchange reaction with phenyllithium⁶



Recent work in these Laboratories has shown that perfluorovinyltin compounds also undergo

an exchange reaction with organolithium reagents to form the rather unstable perfluorovinyl lithium.¹ It therefore was of interest to determine whether an exchange or an addition reaction would be observed on treating perfluorovinylsilanes with organolithium compounds. The results could not be predicted with certainty, since with olefinic silicon compounds both exchange and addition reactions are possible. Which reaction is observed seems to depend mainly on the nature of the unsaturated group. While the addition reaction is observed with vinylsilanes, the exchange reaction was found to occur with β -styryltriphenylsilane⁷ and phenylethynyltriphenylsilane.⁸ Thus an exchange reaction seemed not unlikely with silicon compounds containing the electronegative perfluorovinyl group.

Triethylperfluorovinylsilane⁹ was chosen for this study because of the relative ease of its preparation. Treatment of this compound with a number of organolithium reagents did not result in an exchange reaction; instead, the products isolated were β -organo- α,β -difluorovinyltriethylsilanes

(1) Preliminary communication: D. Seyferth, T. Wada, and G. Raab, *Tetrahedron Letters*, No. 22, 20 (1960).

(2) Part X: D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **83**, 3583 (1961).

(3) On leave from the Shin-Etsu Chemical Industry Co., Ltd., Tokyo, Japan.

(4) For a review see: D. Seyferth, "Vinyl Compounds of Metals" in "Progress in Inorganic Chemistry," Vol. III (F. A. Cotton, ed.), Interscience Publishers Inc., New York, N. Y., in press.

(5) L. F. Cason and H. G. Brooks, *J. Am. Chem. Soc.*, **74**, 4582 (1952); *J. Org. Chem.*, **19**, 1278 (1954).

(6) D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, in press.

(7) H. Gilman, T. C. Wu, and D. Wittenberg, *J. Org. Chem.*, **25**, 596 (1960).

(8) H. Gilman and H. Hartzfeld, *J. Am. Chem. Soc.*, **73**, 5878 (1951).

(9) D. Seyferth, K. A. Brändle, and G. Raab, *Angew. Chem.*, **72**, 77 (1960).