SYNTHESIS AND REACTIONS OF N,N,N',N'-TETRAKIS(TRIMETHYLSILYL) DIAMINOSULFIDE

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The diamide of sulfoxylic acid (diaminosulfide), H_2NSNH_2 , is of theoretical interest and also of potential applicability in inorganic and organometallic synthesis. From a synthetic viewpoint both the parent diaminosulfide as well as its tetrakis(trimethylsilyl) derivative would be of practical utility. The Si-N bond is easily cleaved using elemental halides, for instance, from the VIB and VB subgroups [1], and confers a synthetic advantage, in that the secondary reaction byproducts are the easily separated Me₃SiHal compounds, rather than reactive HHal derivatives.

In the present paper we describe the synthesis of N,N,N',N'-tetrakis(trimethylsilyl) diaminosulfide (I), as well as its reactions with various chalcogen halides and oxohalides, such as S,S-dichloro-N-pentafluorophenylsulfimide and pentafluorophenyldichlorophosphine. It was anticipated that reaction of (I) with SF₄ would proceed in part via a nonequilibrium polycondensation mechanism [2] to give a polymeric sulfur nitride $(SN)_X$; this material is a molecular metal and superconductor [3, 4], and the indicated reaction would constitute a new and simpler [5-7] method for its preparation. It was also anticipated that reaction of (I) with SeCl₄ and TeCl₄ would lead to polymer analogs of $(SN)_X$ in which every second S atom of the polythiazyl was replaced by a Se or Te atom, respectively. Similar polymers, intermediate between $(SN)_X$ on the one hand, and $(SeN)_X$ and $(TeN)_X$, on the other, are of considerable interest, since, in analogy with $(SeN)_X$.

A previous communication reported, without experimental detail, that compound (1) could be prepared in low (<10%) yield via the reaction of sulfur dichloride with sodium N,N-bis (trimethylsilyl)amide [9]. We have found that (I) can be obtained in 56% yield by treatment of SCl₂ with lithium N,N-bis(trimethylsilyl)amide in ether at -80°C. When this reaction was carried out at 0°C, a highly colored oil was obtained and was not studied any further; compound (I) was not formed under these conditions. The yield of (I) increases as the reaction temperature is lowered (10-15% at -50°C), and reaches a maximum at -80°C.

A secondary product of the reaction of lithium N,N-bis(trimethylsilyl)amide with sulfur dichloride is bis(trimethylsilyl)thiodiimide.



Compound (I) is a white crystalline substance which sublimes readily under vacuum and is stable to store under conventional conditions; it is very soluble in ethers, including cyclic ones, as well as in chloroform. Thermogravimetric analysis revealed that, in a helium atmosphere, compound (I) is easily vaporized at 180-200°C without decomposition. Vaporization in air, on the other hand, is accompanied by vapor-phase combustion (see Fig. 1).

*Deceased.

*With the exception of $(SN)_x$, other chalcogen nitride polymers are unknown. This is evidently related to the idea that it is hardly possible to synthesize $(SeN)_x$ and $(TeN)_x$ along the pathway of $(SN)_x$ because of the instability and explosion hazard of the initial nitrides $(SeN)_x$ and $(TeN)_x$. Alternative synthetic pathways are not suggested.

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Fig. 1. Behavior of compound (I) upon heating in air (a), and of compounds (I), (V), and (VI) upon heating in a helium atmosphere: b) (I); c) (V); d) (VI).

In contrast to our expectations, reaction of (I) with SF₄ as well as with a 1:1 SF₄pyridine complex gave only cyclotetraazathiene, $(SN)_4$ (II), and none of the linear polymer $(SN)_X$. It is interesting to note that attempts to prepare $(SN)_X$ from 1,7-bis(trimethylsily1)-1,3,5,7-tetraaza-2,4,6-trithia-1,2,5,6-heptatetraene (III) and SCl₂ also proved unsuccessful, and gave only compound (II) [10].

It is known that cyclization is often accompanied by linear polycondensation [2]. The appearance of (II) as the reaction product of (I) with SF_4 leads to the conclusion that the tetramer undergoes cyclization. If polycondensation occurred in the (I)- SF_4 reaction system, a portion of the molecules, resulting, for example, from the reaction of dimer + trimer, would bypass the tetramer stage, which is necessary for cyclization, and thus would be converted into linear (SN)_x polymer. No trace of the latter was detected however. It is also assumed that intramolecular cyclization occurs already at the dimer stage to generate the unstable cyclodiazathiene (SN)₂ (IV), which under dilute solution conditions stabilizes itself via dimerization to give (II).

Compound (II) was also formed upon treatment of (I) with S_2Cl_2 and SCl_2 . N,N'Bis(thiosulfinyl)diamino- and dithionitrososulfides, respectively, are probably involved as intermediates in these reactions. In analogy to the behavior observed with SF₄, reaction of (I) with SeCl₄ and TeCl₄ also leads to inorganic heterocycles [compounds (V) and (VI), respectively], and not to linear polymers. The following structures are proposed for the crystalline forms* of compounds (V) and (VI) based on the results of elemental and IR spectroscopic analysis (the available data do not allow one to distinguish among different isomers or between covalent and ionic structures).

In analogy to the behavior observed with SF4, reaction of (I) with SeCl4 and TeCl4 also leads to inorganic heterocycles [compounds (V) and (VI), respectively], and not to linear polymers. The following structures are proposed for the crystalline forms* of compounds (V)

*According to x-ray analysis; details of the x-ray analyses will be published separately.

and (VI) based on the results of elemental and IR spectroscopic analysis (the available data do not allow one to distinguish among different isomers or between covalent and ionic structures).



The well-known tendency of inorganic azathienes to form heterocycles [11, 12] has thus been shown to be applicable to other azachalcogens systems as well.

Thermogravimetric analysis of compound (V) in a helium atmosphere revealed that the material starts to decompose at 135°C, and that it loses 48% of its weight by 373°C, at which point the same weight remains constant up to 460°C. The weight then begins to diminish again after this temperature. The DTA curve exhibits an endothermic effect with a maximum temperature of 460°C, corresponding, apparently, to fusion of elemental tellurium, which has separated as a result of thermal decomposition (see Fig. 1, mp of Te 452°C [13]).

Thermal decomposition of compound (V) is more complex. Upon heating in a helium atmosphere this material begins to decompose at 120°C (which corresponds to the maximum of an exothermic effect on the DTA curve). Two endothermic effects with maxima at 230°C and 320°C are also observed; the first of these probably corresponds to fusion of elemental selenium (see Fig. 1; mp of Se 220°C [13]).

Exposure of (V) and (VI) to the atmosphere results in the appearance of the vibrational bands of the ammonium ion in the IR spectra over a period of several days; ammonium ion probably results from hydrolysis due to atmospheric moisture. The color of (VI) changes at the same time to gray.

Treatment of (I) with imino derivatives of chalcogen tetrahalides, such as for instance S,S-dichloro- or S,S-difluoro-N-arylsulfimides, should preclude cyclization, and the reaction products should be acyclic azathienes. In fact, reaction of (I) with S,S-dichloro-N-pentafluorophenylsulfimide generated 1,7-bis(pentafluorophenyl)-1,3,5,7-tetraaza-2,4,6-trithia-1,2,5,6-heptatetraene (VII) in 7% yield [(VII) has been synthesized previously on 0.6% yield from N,N-bis(trimethylstannyl)pentafluoroaniline and 1-chlorocyclo-3,5-diaza-1,2,4-trithienium chloride [14]). The major reaction products are bis(pentafluorophenyl)thiodiimide and (II). These compounds are assumed to result from further reactions and interconversions of (VII), of which the following pathways seem most reasonable.

1. Intramolecular electrophilic attack of the spiro C atom of the pentafluorophenyl ring attached to the N atom in position 1 at the N atom in position 5, which contains an unshared pair of electrons in an sp^2 hybridized atomic orbital (the valence angles around the N atoms of the thiodiimide group [15, 16] are consistent with sp^2 hybridization). This generates a six-membered ring transition state structure containing a spiro C atom, decomposition of which leads to bis(pentafluorophenyl)thiodiimide and (IV). The latter then dimerizes to give (II) (see path A in the following scheme).

2. Decomposition of (VII) in an electronically excited state would generate two molecules of pentafluorobenzene and a nonlinear acyclic intermediate (NSN) (VIII). Dimerization of this thionitroso compound followed by extrusion of S from the dimer would give bis(pentafluorophenyl)thiodiimide.* According to nonempirical quantum-mechanical calculations, intermediate (VII) should decompose easily to give elemental N and atomic S [18]. Reaction of the latter with another molecule of (VIII) would give (IV), which is further converted to (II) via pathway B.

^{*}The intermediate involvement of thioanalogs of nitroso compounds in reactions leading to thiodiimides has been postulated previously (cf. [17] and references cited therein).



Reaction of (I) with $SOCl_2$ gives N,N'-disulfinyldiaminosulfide. This compound has been synthesized earlier from dichloromonosulfide and N-sulfinyltrimethylsilylamine [19] and also from (II) and $SOCl_2$ [20].

Compound (I) does not react with pentachlorophenyldichlorophosphine, even after refluxing for 3 h in dioxane.

EXPERIMENTAL

¹H and ¹³C NMR spectra were recorded on a Tesla BS-567 spectrometer at 100 and 25.142 MHz, respectively, for CHCl₃ solutions (versus HMDS as internal standard). ¹⁹F NMR spectra were obtained on a Varian A56/60A spectrometer (56.4 MHz) for CCl₄ solutions (versus C_6F_6 as internal standard). ¹⁵N and ²⁹Si NMR spectra were taken for CCl₄ solutions on a Bruker CXP-300 spectrometer (at 30.42 and 59.61 MHz, respectively) at neutral isotopic composition only (versus liquid NH₃ and TMS as external standards). A relaxation agent, namely, chromium acetylacetonate, was added to the solutions. IR spectra were recorded on a Bruker IFS-113 Fourier-transform spectrophotometer and also on an IR-75 apparatus; Roman spectra were obtained on a Coderg PH-1 apparatus using a Spectra Physics-125 helium-neon laser (λ_{exc} 6328 Å) as the excitation source. Electronic spectra of heptane solutions were obtained on a Specord UV-VIS spectrophotometer. Thermal gravimetric analyses were conducted on an MOM derivatograph at a heating rate of 5°/min. Diffraction data were collected on a URS-50M x-ray diffractometer using characteristic Cu-filtered irradiation. Samples were placed in a glass cuvette which was sealed airtight by covering with a fluoroplastic film (5 µm thickness).

Lithium N,N'-bis(trimethylsilyl)amide, S_2Cl_2 , SCl_2 , $SeCl_4$, and $TeCl_4$ were prepared according to [21], $C_6F_5N=SCl_2$, according to [22], $C_6F_5PCl_2$, according to [23], and complex C_6H_5N -SF₄ according to [24]; SOCl₂ was purified as in [25]. Ether, THF, and dioxane were distilled from sodium benzophenone ketyl. All of the synthetic reactions described below were carried out under an argon atmosphere.

N,N,N',N'-Tetrakis(trimethylsilyl)diaminosulfide(I). A stirred suspension of 10.02 g (0.06 mole) of lithium N,N-bis(trimethylsilyl)amide in 75 ml of ether at -80°C was treated dropwise with a solution of 3.09 g (0.03 mole) of freshly prepared sulfur dichloride in 10 ml of ether. The mixture was stirred for 1 h at -80° C, then warmed over 2.5 h to -55° C, and finally the cooling bath was removed. After reaching 20°C the light-yellow solution was filtered and the precipitate was washed with ether. The solution was concentrated on a rotary evaporator, and the last traces of solvent were removed under vacuum and the material collected in a trap cooled in liquid nitrogen. The light-yellow crystalline (or easily crystallizable oil) was distilled twice under vacuum. Yield of compound (I), a white crystalline substance, 5.90 g (56%), mp 65°C. Found: c 40.60; H 9.92; N 7.77; S 9.17; Si (by difference) 32.54%. C₁₂H₃₆N₂SSi₄. Calculated: C 40.91; H 10.23; N 9.75; S 9.09; Si 31.82%. ¹H NMR spectrum (δ, ppm): 0.18 s. ¹³C NMR spectrum (δ, ppm): 1.57 s. ¹⁵N NMR spectrum (δ , ppm): 13.1. ²⁹Si NMR spectrum (δ , ppm): 9.3. IR spectrum (4000-400 cm⁻¹ range, KBr pellet; 400-40 cm⁻¹ range, polyethylene pellet, v cm⁻¹): 2955 s, 2890 m, 1437 w, 1395 ml, 1292 sh, 1241 vs, 904 vs, 842 vs, 785 s, 753 s, 718 s, 670 s, 638 m, 612 n, 485 w, 455 w, 364 w, 351 s, 304 s, 282 s, 240 s, 174 s. Raman spectrum (v, cm^{-1}): 700 w 656 m, 498 w. UV spectrum: no absorbance bands $\lambda \ge 200$ nm.

After the frozen trap contents had thawed, the ether was removed at atmospheric pressure, and the residue was distilled <u>in vacuo</u>. Bis(trimethylsilyl)thiodiimide was

obtained as a colorless liquid, bp 60°C (12 mm). Yield 1.0 g. Its ¹H NMR and IR spectra were identical with those of a sample prepared according to [26].

<u>Reaction of Compound (I) with SF_4 , S_2Cl_2 , and SCl_2 </u>. a) A vigorously stirred solution of 3.52 g (100 mmoles) of (I) in 10 ml of THF was contained in a flask cooled to $-10^{\circ}C$ and fitted with a gas inlet tube up to the solution level; a stream of 1.1 g (10 mmoles) of SF_4 was added slowly to the solution. The mixture was stirred 1 h at $-10^{\circ}C$, 2 h at $0^{\circ}C$, and 4 h at $\sim 20^{\circ}C$. The THF was removed on a rotary evaporator, and the residue was recrystallized from benzene and distilled under vacuum. Compound (II) was obtained as bright orangeyellow crystals, mp 186°C, yield 0.72 g (78%). The material was identified by its mp and IR spectrum, which agreed with the literature data [27, 28], and also by TLC comparison with an authentic sample, prepared according to [27].

b) A vigorously stirred solution of 3.52 g (10 mmoles) of (I) in 30 ml of ether at 0°C was treated with 1.87 g (10 mmoles) of a C_5H_5N -SF₄ complex. The mixture was stirred for 2 h at 0°C and an additional 8 h at \sim 20°C. Ether was removed on a rotary evaporator. Purification and identification of (II) were carried out as described above. Yield 0.64 g (70%).

c) A vigorously stirred solution of 1.76 g (5 mmoles) of (I) in 30 ml of $CHCl_3$ at 0°C was treated with a solution of 10 mmoles S_2Cl_2 or SCl_2 in 5 ml of $CHCl_3$. The mixture was stirred 10 h at ~ 20 °C. The solution was filtered, chloroform was removed on a rotary evaporator, and the residue was subjected to column chromatography on silica gel using benzene eluent [29]. The crystalline product remaining after removal of the eluent was distilled under vacuum. Yield of (II), 0.26-0.28 g (56-60%), identified as described above.

<u>Treatment of Compound (I) with SeCl₄.</u> A stirred solution of 0.96 g (3 mmoles) of SeCl₄ in 25 ml of dioxane was treated with a solution of 1.06 g (3 mmoles) of (I) in 15 ml of dioxane at 50°C. The mixture was stirred for 8 h at this temperature. After cooling to room temperature the precipitate was removed by filtration under an argon atmosphere, washed with dioxane, and dried under vacuum. Yield of (V), bright gold-brown powder, 0.37 g. Found: N 9.30; S 20.24; Cl 20.97; Se (by difference) 49.49%. $Cl_2N_2S_2Se_2$. Calculated: N 8.72; S 19.94; Cl 22.12; Se 49.22%. IR spectrum (ν , cm⁻¹, KBr): 1410 s, 982 m, 950 m, 620 s, 592 w.

<u>Treatment of Compound (I) with TeCl</u>₄. A stirred solution of 0.81 g (3 mmoles) of TeCl₄ in 15 ml of dioxane at 50°C was treated with a solution of 1.06 g (3 mmoles) of (I) in 10 ml of dioxane. The reaction mixture was stirred 6 h at this temperature. After cooling to room temperature the precipitate was removed by filtration under argon, washed with dioxane, and dried under vacuum. Yield of (VI), brown powder, 0.52 g. Found: N 5.11; S 5.76; Cl 14.22; Te (by difference) 74.91%. $Cl_2N_2STe_3$. Calculated: N 5.43; S 6.21; Cl 13.78; Te 74.59%. IR spectrum (ν , cm⁻¹, KBr): 1400 vs, 1110 m, 1037 m, 940 m, 864 m, 607 s, 587 s.

<u>Reaction of Compound (I) with S,S-Dichloro-N-pentafluorophenylsulfimine</u>. A stirred solution of 1.76 g (5 mmoles) of (I) in 25 ml of ether at \sim 20°C was treated dropwise with a solution of 2.84 g (10 mmoles) of S,S-dichloro-N-pentafluorophenylsulfimine in 15 ml of ether. The mixture was stirred for 10 h, and then the solvent was removed on a rotary evaporator. The solid residue was distilled under vacuum (1 mm). Bis(pentafluorophenyl)thiodiimide was collected at 40-45°C and purified by a second distillation; orange-yellow crystals, mp 52-53°C (see [22]), yield 1.58 g. IR, UV, and ¹⁹F NMR spectra were identical with those published previously [22, 30]. A mixture of (II) and (VII) distilled at 80-85°C. Compound (VII) was extracted into CCl₄, solvent was distilled under vacuum, and the residue was distilled again. A crystalline purple substance was obtained, mp 100°C (see [14]). Yield 0.17 g (7%). ¹⁹F NMR and IR spectra were identical with those published in [14]. Compound (II), which was not soluble in CCl₄, was purified by a repeat distillation, yield 0.36 g, and was identified as described above.

<u>Reaction of Compound (I) with Thionyl Chloride</u>. A stirred solution of 1.76 g (5 mmoles) of (I) in 15 ml of benzene at 20°C was treated dropwise with a solution of 1.19 g (10 mmoles) of $SOCl_2$ in 15 ml of benzene. After heating for 3 h at 60°C the solution was concentrated to dryness under vacuum at 20°C, and the solid residue was distilled twice under vacuum. N,N'-Disulfinyldiaminosulfide was obtained as a bright yellow crystalline substance, sensitive to atmospheric moisture, yield 0.67 g (83%), mp 99-100°C (see [19]). The IR spectrum agreed with that published earlier [19].

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CONCLUSIONS

1. A method has been developed for the synthesis of N,N,N',N'-tetrakis(trimethylsilyl) diaminosulfide.

2. Reaction of N,N,N',N'-tetrakis(trimethylsilyl)diaminosulfide with chalcogen tetrahalides leads to inorganic heterocyclic compounds, and not to linear polymers.

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