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Preparation of Bis[bis(trimethylsilyl)amino]trisulfane

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PREPARATION OF BIS[BIS(TRIMETHYLSILYL)AMINO]TRISULFANE

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Abstract (Me₃Si)₂NS₃N(SiMe₃)₂ has been prepared by two different, but related synthetic routes: The reactions of (a) (Me₃Si)₂NLi with SCl₂ and elemental sulfur, and (b) (Me₃Si)₂NH with S₂Cl₂. The reaction products were identified by elemental analysis, mass spectroscopy, and by ¹H, ¹³C, and ¹⁴N NMR spectroscopy. (Me₃Si)₂NS₃N(SiMe₃)₂ reacts with SCl₂ and SO₂Cl₂ to produce S₄N₂ in good yield (72.5 %).

 $[(Me_3Si)_2N]_2S$ and $[(Me_3Si)_2N]_2S_2$ are produced when $(Me_3Si)_2NM$ (M = Li, Na) is treated with SCl_2 .¹ We describe here the formation of bis[bis(trimethylsilyl)amino]sulfanes with sulfur chains longer than two by two different, but related routes: The reaction of $(Me_3Si)_2NLi$ with SCl_2 and elemental sulfur [equation (1)], and that of $(Me_3Si)_2NH$ with S_2Cl_2 [equation (2)].

$$2 (Me3Si)2NLi + SCl2 + x/8 S8 \rightarrow [(Me3Si)2N]2S1+x + 2 LiCl$$
 (1)

$$2 (Me_3Si)_2NH + x/2 S_2Cl_2 \rightarrow [(Me_3Si)_2N]_2S_x + 2 HCl$$
 (2)

The ¹³C NMR spectra of the product mixtures in both cases indicate the formation of aminosulfanes with at least up to four sulfur atoms in the chain. In this work we report the isolation of [(Me₃Si)₂N]₂S₃ in moderate yields [10 and 17 % for the reactions (1) and (2), respectively] by distillation *in vacuo*.

The identity and the purity of [(Me₃Si)₂N]₂S₃ was established by elemental analysis {Anal calcd. for [(Me₃Si)₂N]₂S₃: H 8.7 %, C 35.0 %, N 6.8 %. Found: H 8.8 %, C 34.7 %, N 6.7 %}, mass spectroscopy, and ¹H, ¹³C, and ¹⁴N NMR spectroscopy.

The assignment of the 12 eV mass spectrum of $[(Me_3Si)_2N]_2S_3$ was carried out by comparing the calculated isotopic distribution with the observed one. It was thus possible to deduce the molecular ion and the fragmentation pattern from several overlapping alternatives. The 1H , ^{13}C , and ^{14}N NMR spectra all showed single resonances with chemical shift values $[\delta(^1H): 0.19 \text{ ppm}, \delta(^{13}C) 2.42 \text{ ppm}, \text{ and } \delta(^{14}N) -349 \text{ ppm}, \text{ all recorded in } CH_2Cl_2]$ that are reasonable when compared to the known chemical shifts of analogous molecules $\{i.e.\ [(Me_3Si)_2N]_2S: \delta(^1H): 0.252 \text{ ppm}, ^2 \delta(^{13}C) 3.48 \text{ ppm}, \text{ and } \delta(^{15}N) -332 \text{ ppm}; ^3 [Me_3Si)_2N]_2S_2: \delta(^1H): 0.193 \text{ ppm}, \text{ and } \delta(^{13}C) 2.48 \text{ ppm}\}.$

 $[(Me_3Si)_2N]_2S_3$ is a convenient source for S_4N_2 . When treating the trisulfane with SCl_2 and SO_2Cl_2 [equation (3)], S_4N_2 is formed in good yield (72.5 %).

$$[(Me_3Si)_2N]_2S_3 + SCl_2 + SO_2Cl_2 \rightarrow S_4N_2 + 4 Me_3SiCl + SO_2$$
 (3)

In addition to the singlet at -110 ppm that has previously been assigned to S_4N_2 , the ¹⁴N NMR spectrum of the raw reaction mixture also showed traces of S_4N_4 [$\delta(^{14}N)$ -255 ppm ⁴]. The ¹⁴N NMR spectrum of the purified product only showed a singlet at -110 ppm. The IR spectrum of the product was also in good agreement with that recorded previously for S_4N_2 .⁵

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