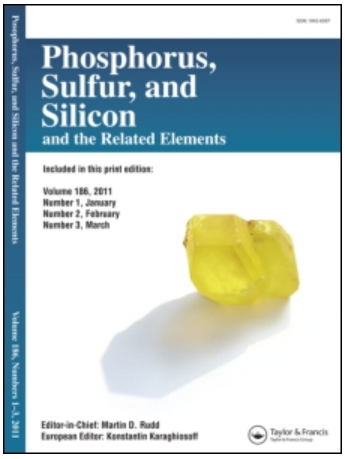

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Preparation of Bis[bis(trimethylsilyl)amino]trisulfane

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PREPARATION OF BIS[BIS(TRIMETHYLSILYL)AMINO]TRISULFANE

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Abstract $(Me_3Si)_2NS_3N(SiMe_3)_2$ has been prepared by two different, but related synthetic routes: The reactions of (a) $(Me_3Si)_2NLi$ with SCl_2 and elemental sulfur, and (b) $(Me_3Si)_2NH$ with S_2Cl_2. The reaction products were identified by elemental analysis, mass spectroscopy, and by ^1H, ^{13}C, and ^{14}N NMR spectroscopy. $(Me_3Si)_2NS_3N(SiMe_3)_2$ reacts with SCl_2 and SO_2Cl_2 to produce S_4N_2 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)].

$$2\ (Me_3Si)_2NLi + SCl_2 + x/8\ S_8 \rightarrow [(Me_3Si)_2N]_2S_{1+x} + 2\ LiCl \qquad (1)$$

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

The ^{13}C 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 $[(Me_3Si)_2N]_2S_3$ in moderate yields [10 and 17 % for the reactions (1) and (2), respectively] by distillation *in vacuo*.

The identity and the purity of $[(Me_3Si)_2N]_2S_3$ was established by elemental analysis {Anal calcd. for $[(Me_3Si)_2N]_2S_3$: H 8.7 %, C 35.0 %, N 6.8 %. Found: H 8.8 %, C 34.7 %, N 6.7 %}, mass spectroscopy, and ^1H, ^{13}C, and ^{14}N 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 ppm, $\delta(^{13}C)$ 2.42 ppm, and $\delta(^{14}N)$ -349 ppm, 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 ppm,[2] $\delta(^{13}C)$ 3.48 ppm, and $\delta(^{15}N)$ -332 ppm;[3] $[Me_3Si)_2N]_2S_2$: $\delta(^1H)$: 0.193 ppm, and $\delta(^{13}C)$ 2.48 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 %).

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

In addition to the singlet at -110 ppm that has previously been assigned to S_4N_2,[4] the ^{14}N NMR spectrum of the raw reaction mixture also showed traces of S_4N_4 [$\delta(^{14}N)$ -255 ppm [4]]. The ^{14}N 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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