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Rearrangements of Sulphurimide Anions: 1,4-bis-(trimethylsilyl)hexasulphur-diimide from Heptasulphurimide

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In his pioneering work on the anions derived by deprotonation of the sulphur imides, $S_x(NH)_{8-x}$, where x = 6 or 7, Olsen concluded that the S_7N^- and $S_2N_2^{2-}$ anions were in equilibrium with an open chain isomer [1]. This conclusion was reinforced by the work of Jolly [2] who showed that, above *ca.* –40 °C, the equilibrium between S_7N^- and the open chain form is quite facile. Clarification of this problem became possible when Chivers and Drummond [3] demonstrated the formation of the S_4N^- anion. Subsequently, in an elegant study of the thermolysis of $S_4N_5^-$, Chivers and Oakley (4) succeeded in isolating $(Ph_3P)_2N^+S_4N^-$; a crystallographic study showed that the anion adopts a planar sickle-shaped geometry for which no single valence bond structure is entirely satisfactory [4]. This result prompts us to report some data which we obtained several years ago but were not able to rationalise mechanistically.

Results and Discussion

In connection with another project we had need for the S_7N^- anion and, to check for its formation, it was decided to trap it at –60 °C with Me_3SiCl in the expectation of obtaining an acceptable yield of S_7NSiMe_3. To our surprise, we obtained upon work-up none of the anticipated product but instead a modest yield of $S_6N_2(SiMe_3)_2$, along with some S_8 and the alkylpolysulphides typical of these reactions. Hydrolysis of the $S_6N_2(SiMe_3)_2$ with ice-water and subsequent thin layer chromatography on silica gel gave exclusively the 1,4-isomer of $S_6N_2H_2$.

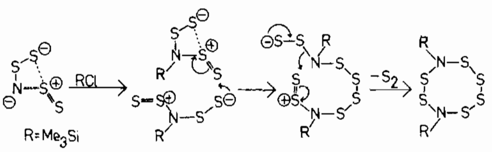
Chivers [5] has suggested the equilibrium (eqn. 1) to account for Olsen's observation [1] of the formation of S_7NCH_3 from 1,3-$S_6N_2^{2-}$ and CH_3I.

$$S_7N^- \rightleftarrows S_4N^- + 3/8\ S_8 \rightleftarrows \tfrac{1}{2}(S_6N_2^{2-}) + \tfrac{1}{2}\ S_8 \qquad (1)$$

Our original intention had been to suppress this equilibrium by working at –60 °C and so maximise the formation of S_7NSiMe_3, but the experimental result clearly shows that such was not the case. One might suggest that at –60 °C the equilibria were spread over the three anions and that the kinetic product (*i.e.*, the one derived from 1,4-$S_6N_2^{2-}$) was the one produced. However, one would expect similar activation energies from both S_7N^- and $S_6N_2^{2-}$ anions; furthermore, Olsen [1] has shown that the reaction rates of these anions are retarded when bulky groups are involved. It is also necessary to rationalise the production of only the 1,4-isomer of $S_6N_2(SiMe_3)_2$.

We believe these difficulties are readily overcome by invoking attack on the Me_3SiCl, at this low temperature, exclusively by the less sterically demanding S_4N^- species. Now, removal of the S_4N^- disturbs the equilibrium and leads to its further production. We had considered these ideas some years ago, but the then prevailing tentative proposal of S_4N^- as the perthionitrate anion required a plethora of rearrangement processes which were not mechanistically appealing. Now, however, Chivers' establishment of the correct S_4N^- structure is entirely compatible with the exclusive formation of the required 1,4-isomer. In the scheme we propose a mechanistic rationale in which one extreme canonical form of S_4N^- is chosen to represent the structure, and the product arises via dimerisation of S_4N-$SiMe_3$.

In the light of these results, one can now rationalise the data of Mendelsohn and Jolly [2] who reported consistently high carbon and hydrogen analytical values on their S_7NSiMe_3. It is now apparent that their product contained about 10% $S_6N_2(SiMe_3)_2$.



Scheme: The formation of 1,4-$S_6N_2(SiMe_3)_2$ from S_4N^- and Me_3SiCl.

Experimental

Heptasulphurimide (4.3 g, 18 mmol), prepared as described elsewhere [6], in dry tetrahydrofuran (100 ml) under a nitrogen atmosphere was treated with an equimolar quantity of butyllithium at –60 °C and the solution turned blue. A three-fold excess of

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chlorotrimethylsilane was added to the cold solution which was stirred for an hour at this temperature. The now orange-red solution was allowed to attain room temperature and was stirred overnight. The solvent was removed *in vacuo*, the residue taken up in hexane and chromatographed on a silica gel column (Baker 60–200 mesh). Elution with hexane gave S_8, recovered S_7NH (20%) and a yellow oil (A) (15–20% in a typical reaction). Elution with 5% benzene gave a vile-smelling yellowish oil (B), identified mass spectrometrically (see below) as a mixture of dibutyl polysulphides. The quoted mass spectral intensities include contributions from corresponding peaks containing ^{34}S.

The yellow oil (A) showed infra-red absorptions (neat liquid between two KBr plates) at: 2950(s), 2850(s), 1460(m), 1410(m), 1390(w), 1290(w), 1265(m), 1250(s), 1215(m), 875(s), 840(s), 800(m), 755(m), 740(m), 685(m) and 630(m) cm^{-1}, and a ^1H nmr singlet at δ 0.31. The mass spectrum (Perkin Elmer Hitachi Model RMU-6A) of (A) showed major peaks at m/e (%): 366, $C_6H_{18}N_2S_6Si_2^{\dot{+}}$ (5.2); 302, $C_6H_{18}N_2S_4Si_2^{\dot{+}}$ (1.7); 270, $C_6H_{18}N_2S_3Si_2^{\dot{+}}$ (1.9); 238, $C_6H_{18}N_2S_2Si_2^{\dot{+}}$ (3.0); 215, $C_3H_9NS_4Si^+$ (30.9); 206, $C_6H_{18}N_2SSi_2^{\dot{+}}$ (0.9); 119, $C_3H_9NSSi^+$ (72.0); 87, $C_3H_9NSi^+$ (59.7); 73, $C_3H_9Si^+$ (100).

Treatment of (A) with ice-water followed by ether extraction and thin layer chromatography on 0.1 mm air-dried silica gel plates gave a single spot with R_f value 0.34. Independently synthesised samples of 1,3-, 1,4- and 1,5-$S_6N_2H_2$ gave R_f values of 0.22, 0.34 and 0.24, in close agreement with the literature values [7].

The mass spectrum of the oil (B) showed major peaks at m/e (%): 306, $C_8H_{18}S_6^{\dot{+}}$ (1.0); 274, $C_8H_{18}S_5^{\dot{+}}$ (6.1); 256, $S_8^{\dot{+}}$ (7.8); 242, $C_8H_{18}S_4^{\dot{+}}$ (30.0); 224, $S_7^{\dot{+}}$ (3.5); 217, $C_4H_9S_5^{\dot{+}}$ (8.5); 210, $C_8H_{18}S_3^{\dot{+}}$ (64.0); 192, $S_6^{\dot{+}}$ (9.0); 186, $C_4H_{10}S_4^{\dot{+}}$ (5.0); 178, $C_8H_{18}S_2^{\dot{+}}$ (42.9); 160, $S_5^{\dot{+}}$ (9.3); 154, $C_4H_{10}S_3^{\dot{+}}$ (14.3); 146, $C_8H_{18}S^+$ (5.1); 122, $C_4H_{10}S_2^{\dot{+}}$ (100); 89, $C_4H_9S^+$ (85.7).

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