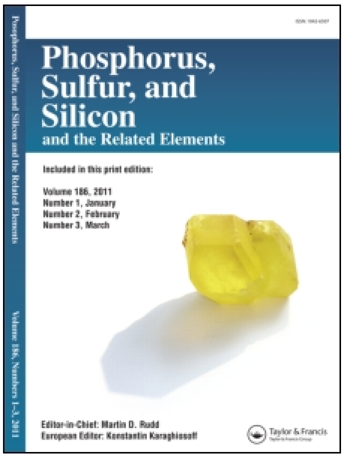

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Ivan P. Parkin[a]; J. Derek Woollins[a]
[a] Imperial College of Science Technology and Medicine, London

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NEW SYNTHETIC ROUTES TO S_4N_4 and S_7NH. REACTION OF Li_3N WITH $S_3N_3Cl_3$ AND SCl_2

IVAN P. PARKIN and J. DEREK WOOLLINS†
Imperial College of Science Technology and Medicine, South Kensington, London SW7 2AY

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Reaction of a suspension of $S_3N_3Cl_3$ in thf with an equimolar amount Li_3N at 0°C produces S_4N_4 in good yield (*ca* 64%). Reaction of Li_3N with SCl_2 in thf generates $[S_4N^-]$ which on acidic work up produces S_7NH.

Key words: Sulfur-nitride; synthesis; heterocycle; lithium nitride.

INTRODUCTION

S_4N_4, discovered in 1835, is one of the oldest and most studied inorganic heterocycles.[1] It undergoes a multitude of chemical reactions, from formation of metal complexes[2] (e.g. $Pt(S_2N_2)(PR_3)_2$, $Ti(S_3N_4)(C_5H_5)_2$ and $W(N_3S_2)Cl_2)$ and Lewis base adducts[3] ($S_4N_4{\cdot}CuCl_2$), to organic incorporation in trithiadiazapenes[4] and main group inorganic compounds[5] such as (SN_x) and $[S_5N_5]Cl$. Despite its central significance in sulphur-nitrogen chemistry and its appearance as a side product in numerous reactions, few synthetic routes are commonly used in its preparation.

The most common preparation of S_4N_4 is reaction[6] of 'SCl_3' with ammonia in CCl_4. The S_4N_4 obtained is contaminated with sulphur and sulphur imides and requires multiple recrystalisations to obtain a pure product.

The preparation of $[S_3N_2Cl]Cl$ by the method of Jolly and Maguire[7] and its subsequent conversion[8] by chlorine to $S_3N_3Cl_3$ is effectively quantitative from cheap starting materials. Hence a conversion of $S_3N_3Cl_3$ to S_4N_4 would be advantageous. This transformation can be achieved by the use of Fe filings or certain transition metal salts. However, the yields are not high and the isolation and purification of the product is non trivial.[9].

Here we report the convenient (*ca* 1–2 g) synthesis of reasonably high purity S_4N_4 from the reaction of $S_3N_3Cl_3$ and Li_3N. A new synthesis of S_7NH from a reaction of Li_3N is also reported.

RESULTS AND DISCUSSION

Reaction of lithium nitride with $S_3N_3Cl_3$ yields high purity S_4N_4 in good yield (Equation 1); the driving force for the reaction being salt formation and nitrogen

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† Author to whom all correspondence should be addressed.

evolution.

$$4Li_3N + 4S_3N_3Cl_3 \xrightarrow[\text{(THF/0°C)}]{} 3S_4N_4 + 12LiCl(s) + 2N_2(g). \qquad (1)$$

This reaction has significant advantages over earlier preparations[9] in that S_4N_4 is the only SN compound formed (no S_8) and is easily recovered. However, the pyrophoric nature of Li_3N will limit the use of this reaction to small scale preparations, where a relatively quick reaction producing high quality S_4N_4 is required.

In CCl_4 or toluene the reaction produced S_4N_3Cl and little S_4N_4, the Li_3N being recovered largely unreacted. This is probably due to thermal decomposition of $S_3N_3Cl_3$ which is known to give S_4N_3Cl[10]. In thf, $S_3N_3Cl_3$ may exist as the solvated monomer $NSCl.thf_x$[11] and it is probable that this species reacts with Li_3N to produce S_4N_4 by a series of salt eliminations (LiCl) followed by coupling of the SN fragments.

Reaction of Li_3N with SCl_2 in thf generates the S_4N^- ion in solution, as shown by the U.V. maximum at 580 nm (an intense blue colour) which compares well with the literature value.[12] Attempted precipitation of the salt with PPh_4Cl or $(^nPr)_4NBr$ failed. The only stable salt of S_4N^- so far isolated is formed by thermal decomposition of an $S_4N_5^-$ salt[12] and numerous attempts to isolate S_4N^- directly from solution have failed.[13] It is well known that S_4N^- is very sensitive to traces of oxygen and moisture decomposing to uncharacterised oxyanions of sulphur. Thus we were not able to isolate S_4N^- directly. However, it has been reported that when S_7NH is deprotonated in strongly basic media the S_4N^- ion is generated via the equilibrium shown in Equation 2.[14]

$$S_7N^- = S_4N^- + \tfrac{3}{8}S_8. \qquad (2)$$

Protonation with HCl by analogy with the published route[15] enabled isolation of S_7NH from the S_4N^- solution. The yield of S_7NH produced (28% based on sulphur) is comparable with the standard preparation. Indeed the purification was relatively easy as other contaminating sulphur imides ($S_6(NH)_2$, $S_4N_4H_4$) were not observed.

EXPERIMENTAL

SAFETY NOTE: S_4N_4 is explosive and should be handled with care! Li_3N is extremely water sensitive and can ignite in air especially if contaminated with traces of Li metal.

All glasswear was flame dried and reactions performed under a nitrogen atmosphere. Solvents were dried and distilled by standard procedures. $S_3N_3Cl_3$ was prepared by the literature method[8] and recrystalised from CCl_4 prior to use. Sulphur dichloride (Aldrich) was distilled before use. Li_3N (Foote or Koch-Light) was used as supplied. IR spectra were obtained on a Perkin-Elmer 1720X as Nujol mulls between CsI plates. Mass spectra were performed on a Varian VG 2020 in the E.I. mode. Microanalysis were undertaken by the departmental service at Imperial College.

Preparation of S_4N_4. To a suspension of $S_3N_3Cl_3$ (4.6 g, 0.018 mol) in THF (30 ml) at 0°C was added over 1 hr Li_3N (0.61 g, 0.018 mol), generating a brown solution and suspension. The suspension was stirred for 16 hr, allowed to warm to room temperature to produce an orange/red solution and an orange precipitate. The solvent was decanted and the precipitate washed with EtOH (15 ml), water (2 × 15 ml), diethylether (3 × 15 ml) and dried *in vacuo*. The precipitate was found to be S_4N_4 (1.89 g, 0.010 mol); i.r. = 927 s, 720 s, 705 s, 560 s, 340 cm^{-1}; Mass Spec. *M/e*, 184(S_4N_4); T.L.C, R_f = 0.80 in CH_2Cl_2. (No S_8 or other SN species was detected by these methods). Further work up of the filtrate was by reduction in volume of the solvent *in vacuo* to give further ppt, which was washed with water and diethylether to give 0.24 g of S_4N_4. Overall yield 2.13 g, 64%.

Preparation of S_7NH. To a stirred suspension of Li_3N (0.28 g, 8.4 mmol) in THF (15 ml) at 0°C was added SCl_2 (1.2 g, 0.012 mol) in THF (20 ml) dropwise over 15 min. The initial purple suspension turned orange/red and after 10 min deep inky blue. This solution was stirred for 24 hr and allowed to slowly warm to RT. The U.V. of this solution had a maximum at 580 nm corresponding to S_4N^-. 5 ml of 10% HCl (aq) was added at 0°C giving a cloudy solution and a brown oil. Extraction of the oil with 3 × 50 ml of diethyl ether and drying over Na_2SO_4 followed by filtration and reduction in volume gave S_7NH (120 mg, 0.5 mmol, 28% based on sulphur). Microanalysis (Calculated values in parenthesis) N = 6.1, (5.8); H = 0.4, (0.5). Mass spec. *M/e* 239(S_7NH^+), 160(S_5^+), 143(S_4NH^+), 128(S_4^+), 111(S_3NH^+), 78(S_2N), 64(S_2). I.r. 3257s, 814s, 722m, 500m, 456m, 428m, 357w, 277m cm^{-1}.

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