

## The General Quantitative Cycloaddition Reactions of the Dithianitronium Cation with Olefins: The Preparation of 1,3,2-Dithiazolium and 1,4-dithia-7-azanorbornylium Cations and the Crystal and Molecular Structure of 1,4-Dithia-7-azanorbornylium Hexafluoroarsenate(v)

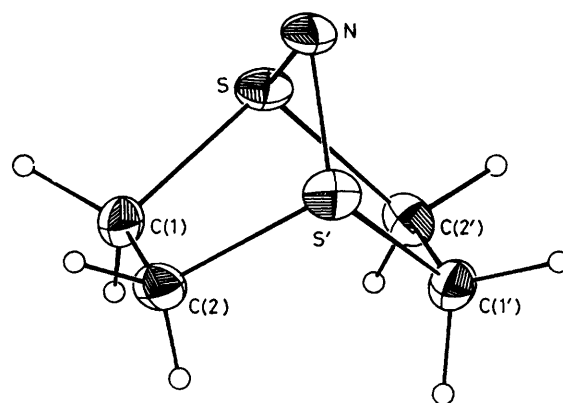
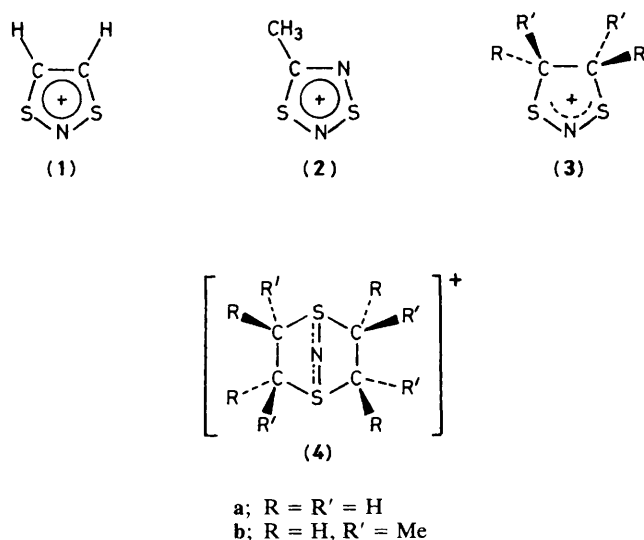
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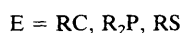
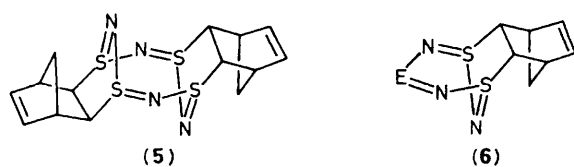
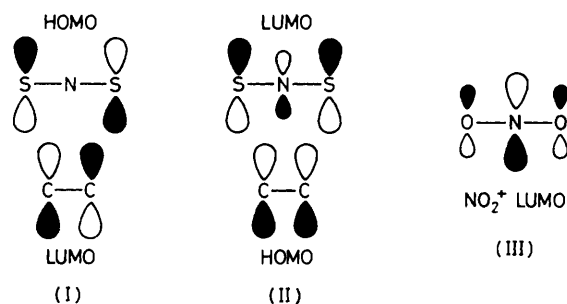
A number of olefins react quantitatively with  $S_2NAsF_6$  via a concerted symmetry allowed cycloaddition to give 1 : 1 and 2 : 1 stoichiometric cationic products: the generality of reaction is rationalised and the X-ray crystal structure determination of the 1,4-dithia-7-azanorbornylium cation is reported.

The proposal by Hoffmann *et al.*<sup>1</sup> that a polymer made up of a (-C-N-S-N)- repeating unit would have conducting properties superior to those of  $(SN)_x$  has prompted a number of investigations into the synthesis of possible precursors. The result has been the discovery of a variety of new organo-sulphur-nitrogen heterocycles which have many unusual physical and chemical properties. However, the preparation of many of these compounds is often complex<sup>2-4</sup> involving many products<sup>3</sup> or giving low yields.<sup>2,4-6</sup> Although improved yields have been achieved by development of rational

syntheses for certain systems,<sup>7,8</sup> these are usually very specific and are not quantitative. In keeping with the opinion that direct syntheses can be more easily developed using simple, small, reactive cations, we have employed the linear  $S_2N^+$  cation, prepared conveniently as  $S_2NAsF_6$ ,<sup>9</sup> to aid in the synthesis of C-S-N heterocyclic polymer precursors and simple S-N species. Halogenation<sup>10</sup> of  $S_2N^+$  and reactions with triple bonds (alkynes and nitriles)<sup>11</sup> have already proven to be straightforward, quantitative processes. The latter resulted in the preparation of the heterocyclic cations (1) and



**Figure 1.** ORTEP drawing of the cation in  $C_4H_8S_2NAsF_6$  (**4a**). Selected bond lengths (Å) and angles ( $^\circ$ ) are: S–N 1.634(4), S–C(1) 1.814(7), S'–C(2) 1.804(7), C(1)–C(2) 1.511(9); S–N–S' 102.4(4), C(1)–S–N 99.0(3), C(2)–S'–N 99.0(3), C(1)–C(2)–S' 107.1(5), C(1)–S–C(2') 96.1(3), C(2)–C(1)–S 106.2(5).



(2) from a concerted, symmetry-allowed 4 + 2 cycloaddition.<sup>11</sup> As an extension of this work we have examined the reactions of  $S_2N^+$  with olefins and report below the quantitative preparation of a number of derivatives of (3), a new five-membered C–S–N heterocyclic cation, indicating further generality for the cycloaddition reactions of  $S_2N^+$ . In addition, (3) undergoes a cycloaddition with excess of olefin to give a quantitative yield of (4), an unusual heterocyclic norbornane cation.

The reaction of *trans*-but-2-ene (0.05 g, 0.89 mmol) with  $S_2NAsF_6$  (0.23 g, 0.87 mmol) proceeded rapidly in liquid  $SO_2$  at room temp. to give an essentially quantitative yield of (3b) (0.26 g, 0.82 mmol, 94%) as a poorly crystalline red solid, m.p. 177–179  $^\circ C$  (decomp.), presumably a mixture of two enantiomers (*trans*-but-2-ene is prochiral). Compound (3b) was characterised by chemical analysis, i.r.,  $^1H$  n.m.r. [ $AA'X_3X'_3$   $\delta(H)$  6.37,  $\delta(CH_3)$  2.86], and mass spectroscopy ( $m/z$  134,  $C_4H_8S_2N^+$ ). A similar reaction of  $S_2NAsF_6$  with norbornene has been studied by  $^1H$  n.m.r. spectroscopy and seems to be quantitative, giving the corresponding derivative of (3).

The rapid and quantitative nature of the cycloaddition reactions of  $S_2N^+$  with olefins is indicative of a concerted, symmetry-allowed process involving one of the degenerate, mutually perpendicular  $\pi$ -systems of  $S_2N^+$  (cf.  $CO_2$ ). This is illustrated from a frontier molecular orbital viewpoint in the plane of the reaction in (I) and (II). The process is further promoted by the predominant contribution of the sulphur centres in both the HOMO and LUMO.† It is interesting that isovalent  $NO_2^+$  and  $CO_2$  have not been observed to undergo a related cycloaddition.<sup>12‡</sup>

Interactions (I) and (II) are identical to those involved in the quantitative adduct cycloaddition reactions reported for  $S_4N_4$ <sup>14</sup> and other S–N heterocycles<sup>15,16</sup> with norbornadiene, leading to (5) and (6) respectively. In all cases a similar, five-membered  $C_2S_2N$  ring is formed.

Recently, Oakley has demonstrated how cycloaddition reactions of S–N compounds, in general, occur *via* a reverse electron demand<sup>16</sup> process (primary interaction is donation from the HOMO of the olefin into the LUMO of the S–N species).<sup>17</sup> This imposes a strong kinetic control on reactions involving neutral S–N compounds, which have a relatively high energy LUMO.<sup>17</sup> Consequently, neutral S–N heterocycles are only observed to react with strained or electron-rich (high-energy HOMO) olefins (recently emphasised by Rees<sup>4</sup>). Our present observations provide support for this hypothesis. The kinetic barrier is significantly reduced in the  $S_2N^+$  system owing to the general stabilisation of all of the MO's afforded by the positive charge carried by the molecule. Consequently, interaction between the LUMO of  $S_2N^+$  and the HOMO of all olefins, nitriles, and alkynes is effective and it is likely that the cycloaddition reaction of  $S_2N^+$  will prove to be even more general.

The formation of (3) is analogous to that of (1) and (2); however, while (1) and (2) have fully delocalised ring  $\pi$ -structures, (3) has a  $\pi$ -system localised on the S–N–S unit of the molecule with the carbon region formally saturated. This allows for a more extensive reactivity than that observed for

† The S 3p orbital is larger than the N 2p orbital and  $S_2N^+$  is one of very few triatomics having relatively electropositive terminal atoms.

‡ This is probably a consequence of the thermodynamic preference of the C–N bond and the kinetic control imposed by the nitrogen based LUMO of  $NO_2^+$  (III), by virtue of the higher electronegativity of oxygen than nitrogen, ref. 13.

(1) and (2).<sup>11,18</sup> The ring framework of (3) has been identified in a neutral radical derivative of the molecule using e.s.r. spectroscopy by Sutcliffe;<sup>19</sup> however this is the first example of (3) obtained on a preparative scale. Compound (3) is conceivably the centre of a number of new synthetic pathways to new C-S-N compounds. This is illustrated by the quantitative reaction of (3) [unlike (1) and (2)] with olefins to give (4).

Compound (3b) (0.33 g, 1.03 mmol) reacted with an excess of *trans*-but-2-ene (0.47 g, 8.38 mmol) in SO<sub>2</sub> at room temp. over 2 h. Following removal of the excess of olefin, a quantitative yield of (4b) was recrystallized from SO<sub>2</sub> as a white crystalline solid (0.35 g, 0.92 mmol, 90%), m.p. 114 °C (decomp.). Compound (4b) was characterised by chemical analysis, i.r., <sup>1</sup>H n.m.r. [ $\delta(\text{CH}_3\text{-endo})$  1.77,  $\delta(\text{CH-exo})$  1.53,  $\delta(\text{H-endo})$  3.54,  $\delta(\text{H-exo})$  3.20], and mass spectroscopy (*m/z* 190, C<sub>8</sub>H<sub>16</sub>S<sub>2</sub>N<sup>+</sup>). By comparison with (3b), attempted preparations of (3a) from S<sub>2</sub>NAsF<sub>6</sub> and ethene gave mixtures of (3a) and (4a), as shown by <sup>1</sup>H n.m.r. spectroscopy. However, reaction of S<sub>2</sub>NAsF<sub>6</sub> (0.56 g, 2.08 mmol) with an excess of ethene (0.27 g, 9.78 mmol) in SO<sub>2</sub> gave a quantitative yield of (4a) (0.67 g, 2.08 mmol, 100%), m.p. 188 °C (decomp.) Compound (4a) was characterised by chemical analysis, i.r., and <sup>1</sup>H n.m.r. [ $\delta(\text{endo})$  2.82,  $\delta(\text{exo})$  3.33, <sup>2</sup>J<sub>HH</sub> 6.7 Hz]. Reaction of S<sub>2</sub>NAsF<sub>6</sub> with an excess of norbornene has also been studied by <sup>1</sup>H n.m.r. spectroscopy and seen to give the respective 2:1 cation.

The crystal and molecular structure of (4a), 1,4-dithia-7-azanorbornylium hexafluoroarsenate has been determined by X-ray crystallography. § An ORTEP<sup>22</sup> view of the cation is shown in Figure 1 with the pertinent bond lengths and angles. The cation adopts a bicyclic norbornane-like structure with the S-N-S unit as the fusion of two five-membered rings and above the plane described by the four carbon atoms, similar to the Si-Si neutral derivative.<sup>23</sup> The nitrogen atom lies on a two-fold axis making the two five-membered rings identical. The C-C and C-S bond lengths are typical for single bonds and the S-N distances are shorter than a single bond indicative of some S-N  $\pi$ -bonding.<sup>24</sup>

The formation of (4) can be viewed as a second 4 + 2 cycloaddition to (3). At the simple Hückel level, the purely  $\pi$ -bonded C<sub>2</sub>H<sub>4</sub> unit of (3) has no effect on the remaining, perpendicular, degenerate  $\pi$ -MO's of the S<sub>2</sub>N<sup>+</sup> unit, which are therefore of identical symmetry and energy to those of the initial free S<sub>2</sub>N<sup>+</sup>, and are available for a second cycloaddition. It is interesting that compounds of the type (1) and (2) do not undergo a related cycloaddition reaction with an excess of alkyne, indicating an inherent thermodynamic stability for (1) and (2) due to the  $\pi$ -interaction between the S-N-S unit and the available  $\pi$ -type orbitals on the C-C unit. Reaction with a second alkyne would require disruption of the  $\pi$ -manifold. Using this Hückel model these  $\pi$ -orbitals are not present on the tetrahedrally bound carbon centres of (3). The relative

thermodynamic stability of (1) and (2) is further demonstrated by the observation that (3b) reacts with ethyne or nitriles to give a mixture of (1) or (2), respectively, along with (4b) and free *trans*-but-2-ene, all identified by <sup>1</sup>H n.m.r. spectroscopy. The olefin has effectively been substituted by the ethyne or nitrile and is then free to react with (3b) to form (4b).

Finally, we note that (4b) is shown by <sup>1</sup>H n.m.r. spectroscopy to be a single species but is presumably a mixture of enantiomers each of which has 6 chiral centres.

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§ *Crystal Data*: C<sub>4</sub>H<sub>8</sub>S<sub>2</sub>NAsF<sub>6</sub>, *M* = 323.16, orthorhombic, space group *Pcca*, *a* = 13.046(3), *b* = 6.965(1), *c* = 10.630(1) Å, *U* = 965.9 Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* 2.22 Mg m<sup>-3</sup>. Data were collected on an Enraf-Nonius CAD-4 automated diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda$  0.710 73 Å) using  $\omega$ -2 $\theta$  scans ( $2\theta_{\text{max}}$  of 50°), and were corrected for absorption. The structure was solved by direct methods (ref. 20) and refined by full matrix least-squares (ref. 21) to residuals of *R* 0.037, *R<sub>w</sub>* 0.038, 0.058, 0.047 including unobserved) for 611 unique reflections [*I* > 3 $\sigma$ (*I*)] (858 total) and 82 parameters. All non-hydrogen atoms were assigned anisotropic thermal parameters and hydrogen atoms were refined with isotropic ones. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.