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Diatomic Sulfur Detection By Butadiene And Norbornene: A Cautionary Note[1]

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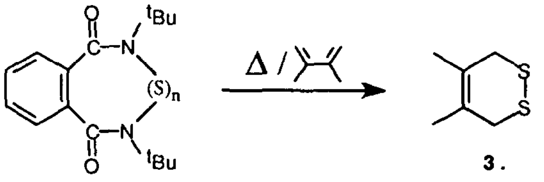
Abstract: In the presence of the recognised S_2 trapping agents, norbornene and 2,3-dimethyl-1,3-butadiene, thermolysis of both benzotrithiadiazacyclononene (1) and the previously reported S_2 precursor dibenzyloxydisulfide (7), generates typical diatomic sulfur trapping products. However the implication that trithiaaryldicarboxiamides are a new class of S_2 precursors must be treated with caution as control experiments, involving thermolysis of elemental sulfur, indicate that detection of the previously accepted S_2 trapping products is not conclusive evidence of the intermediacy of S_2. © 1997 Elsevier Science Ltd.

Diatomic sulfur has been implicated as a significant synthon for the production of organosulfur compounds, many of which are known to display potent biological activity. Due to its high reactivity detection of S_2 is problematic and most studies have relied on Diels-Alder trapping with norbornene and 2,3-dimethyl-1,3-butadiene. To ascertain if benzotrithiadiazacyclononenes (**1**)[2] represent a new class of S_2 precursors we examined the thermolysis of this species with these two trapping reagents and monitored the products by gas chromatography / mass spectroscopy (GC/MS). The sensitivity and low detection limits of this technique permitted accurate and reproducible identification of even trace amounts of the sulfide products (see Table 1).

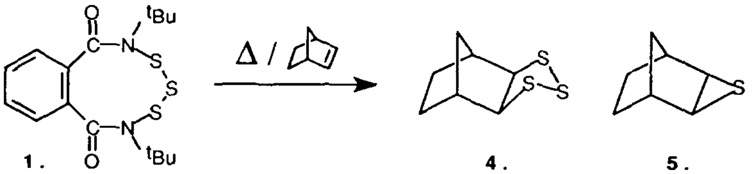


1. n = 3 and **2.** n =1

3.

Scheme 1.

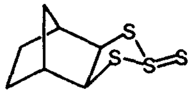
Thermolysis of **1** in the presence of 2,3-dimethyl-1,3-butadiene for 15 minutes at 250° C generated only one trapping product: 1,2-dithia-4,5-dimethyl-4-cyclohexene (**3**) (Scheme 1), which was identified by its mass spectrum. The production of this Diels-Alder adduct of the diene has previously been considered conclusive evidence of the intermediacy of S_2.[3,4,6-10]



1. **4.** **5.**

Scheme 2.

In the presence of norbornene, thermolysis of **1** yielded two main sulfur adducts, each identified by its mass spectrum. Whilst the episulfide **5** was found to be the major trapping product at all temperatures, the trithiolane **4** (usually associated with the Diels-Alder trapping of S_2 by norbornene[4-8]) was also detected in the product mixture. Table 1 illustrates general trends in the production of trapping adducts where the relative yield of adducts increases with thermolysis temperature and reaction time. Note that for experimental simplicity most reactions involved the thermolysis of **1** as a component of a 15:85 mixture with the benzothiadiazacycloheptene **2**. Control experiments using pure samples of **2** generated no sulfur trapping products and **2** was found to be stable to temperatures approaching 300° C with the main decomposition products being phthalimide based compounds (according to their mass spectra) which were not further characterised.



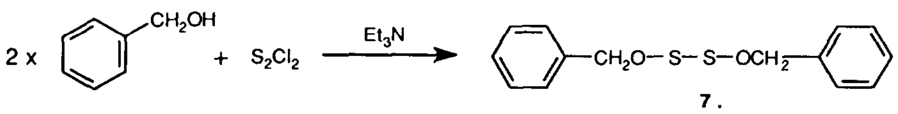
6.

When the thermolysis of **1** was conducted at temperatures higher than 250° C, trace amounts of tetrasulfide and pentasulfide adducts were also detected (reactions 9 and 10). The tetrasulfide may be the thionotrisulfide **6** which has been implicated, but not characterised, as an intermediate in the formation of **4**, via capture of S_2 by the strained norbornene disulfide.[5] However a simple six membered structure cannot be excluded as the ring structure could not be conclusively determined from the mass spectra.

In an attempt to confirm the intermediacy of S_2 in the formation of the observed trapping products, a previously reported S_2 precursor[9], dibenzyloxydisulfide **7**, was synthesised (Scheme 3), and thermolysed under equivalent conditions. Again, butadiene trapped reactions generated adduct **3**, and norbornene trapped reactions produced adducts **4** and **5** as well as the tetrasulfide and pentasulfide. The other reported decomposition products of **7**, benzaldehyde and benzyl alcohol[9], were also observed in the product mixture. By comparing the relative adduct yields of reactions 7 and 11, it can be seen that **7** is a more effective sulfur donor than **1**.

While the production of adducts **3** and **5** is consistent with the generation of S_2 from compounds **1** and **7**, the presence of **4** and the other norbornene/sulfur adducts is not strictly in accordance with clean generation of S_2. While one may envisage mechanisms by which these compounds may be generated in small amounts, either directly or indirectly, through the action of S_2

trapping, Steliou concludes that adducts other than disulfides or trisulfides are more likely to be attributable to activated elemental sulfur than S_2[8].



Scheme 3.

Table 1. Relative Yield[a] of Norbornene Adducts

Reaction No.	Sulfur Source Identity	Sulfur Source Mass /mg	Norbornene Mass /mg	T /°C	Time /min	Yield[a] 4.	Yield[a] 5.
1	1/2	20	58	70	240	-	-
2	1/2	19	46	115	90	<1	-
3	1/2	19	106	150	30	<1	1
4	1/2	22	105	155	30	<1	<1
5	1/2	25	152	200	5	1	3
6	1/2	19	127	200	20	5	7
7	1/2	22	187	250	15	1	2
8	1/2	23	210	250	30	3	11
9	1/2	23	256	250	45	12	10
10	1/2	50	590	>250	30	100	100
11	7	24	1814	240	15	43	9
12	7	5	429	90	90	7	9
13	S_8	3	2077	250	30	35	75
14	S_8	500	500	100	360	<1	<1

[a] An impurity in the norbornene served as an internal standard for the calculation of relative yield of trapping products. The value shown represents the relative yield of sulfur adduct per mole of precursor and is independent of the amount of norbornene present in the reaction mixture although the results with elemental sulfur are therefore slightly amplified. Figures quoted are subject to approximately ± 5% uncertainty.

As a final control experiment, elemental sulfur was heated in the presence of each trapping agent, according to the general thermolysis procedure. Unexpectedly, GC/MS analysis of the products of these experiments confirmed the generation of S_2 type adducts at temperatures as low as 100°C. Trapping with norbornene produced sulfur adducts **4**, **5** and the tetrasulfide - in quite a high relative yield in the case of reaction 13 (see Table 1). It can be seen that elemental sulfur more efficiently donates sulfur to norbornene than **1**, by comparing the relative yields of reactions 13 and 8.

In the presence of 2,3-dimethyl-1,3-butadiene, thermolysis of elemental sulfur generated only the Diels-Alder adduct **3**. This is significant, in that the formation of this adduct has previously not been associated with the action of activated elemental sulfur, even though disulfides have been formed with the phenyl analogue: 2,3-diphenyl-1,3-butadiene[11]. The production of **3** has been considered conclusive evidence of the intermediacy of S_2. In view of these results this empiricism must be treated with caution.

Under the conditions used here, thermolysis of elemental sulfur in the presence of appropriate trapping agents generates adducts previously considered to be exclusive to the trapping of S_2. These adducts were also produced during thermolysis of the benzotrithiadiazacyclononene **1** as well as the previously reported S_2 precursor **7**, and in similar relative yields. Thus, on the basis of the trapping experiments alone, we can neither confirm nor exclude the generation of S_2 in the systems studied. Most importantly however, these results demonstrate that one must exercise caution in making conclusions about the presence of S_2 on the basis of trapping experiments using stained olefins or dienes.

REFERENCES AND NOTES

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