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Sulfur allotrope chemistry—S_{10} an effective two-sulfur transfer reagent

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Abstract

The chemistry of one of the sulfur allotropes has been investigated. Cyclodecasulfur (S_{10}) reacts with conjugated 1,3-dienes and strained olefins to deliver cyclic di- and polysulfides with a better selectivity and under milder conditions than with elemental sulfur (S_8). A radical mechanism is proposed for these sulfuration reactions. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: sulfur allotrope; S_{10}; sulfuration; sulfur heterocycles; olefins; dienes.

Cyclooctasulfur S_8 is the most stable form of sulfur and is commonly referred to as elemental sulfur. It is well-known that sulfur has many allotropic modifications, most of which are also cyclic species. Sulfur homocycles S_n with $n \neq 8$ have been either detected[1] and subsequently isolated from sulfur melts, or independently synthesized.[2] The synthesis and full characterization of these sulfur homocycles continues to be a very active research area. Recently, the preparation of yet another sulfur allotrope, S_{14},[3] was reported and added to an already very substantial list.[4]

Although some sulfur allotropes have been known for a long time, there have been relatively few investigations in terms of their reactivity and to our knowledge, they have never been systematically studied as reagents in organic reactions. One interesting study[5] by Bartlett compared the reactivity of S_6 and S_8 towards triphenylphosphine to form triphenylphosphine sulfide. It was found that S_6 was 25 000 times more reactive towards triphenyl phosphine than S_8.

We and others have been interested for many years in developing new sulfur transfer reagents some of which could be used for the sulfuration of simple alkenes or conjugated alkenes. These sulfuration methods have involved either the use of diatomic sulfur (S_2) transfer reagents[6] or the direct use of elemental sulfur in polar or amine solvents.[7] We believe that certain sulfur allotropes could be used for such transformations and we have focused our attention on S_{10}. It was anticipated that its degradation under appropriate conditions could in fact lead to a net 2 sulfur atom transfer, elemental sulfur S_8 being the only side product of such a process.

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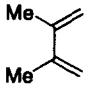
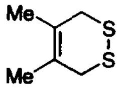
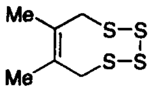
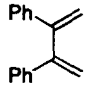
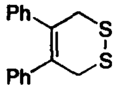
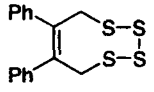
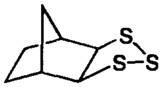
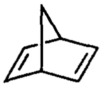
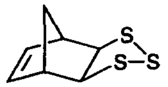
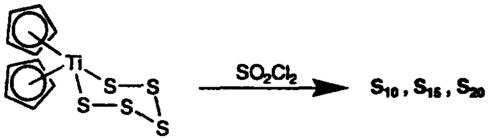
Table 1
Yields of sulfuration products

	Alkene	Conditions (hr)	Product yield	
6a		3[a]	 **1a**, 36%[c]	 **2a**, 6%[c]
6b		2[b]	 **1b**, 38%[c]	 **2b**, 4%[c]
7		3[a]	 **3**, 85%[d]	
8		3[a]	 **4**, 59%[d]	 **5**, 17%[d]

[a] Solvent: toluene/CS_2; temperature *ca.* 90°C (heating mantle).
[b] Solvent: xylenes/CS_2; temperature maintained at 120°C by an oil bath.
[c] Products were isolated as a mixture and the ratio was determined by ^{1}H NMR.
[d] Isolated yield.

The synthesis of S_{10} is easily achieved by a procedure well-established by Steudel and co-workers.[8] When equimolar amounts of titanocene pentasulfide Cp_2TiS_5[9] and sulfuryl chloride (SO_2Cl_2) are reacted together, S_{10} is obtained as the main constituent of a mixture of sulfur homocycles from which it is extracted in pure form (ca. 36%).



(1)

When we first degraded S_{10} in benzene at reflux in the presence of 2,3-diphenyl butadiene, we obtained the expected disulfide (**1b**) and tetrasulfide (**2b**) adducts in moderate yield in a ratio very much in favor of the disulfide adduct (10:1). However, we initially faced some inconsistencies in the reproducibility of this reaction. Impurities in the crude Cp_2TiS_5[10] used to synthesize S_{10} as well as the homogeneity of the reaction medium appeared to variably influence the yields.

We have now optimized the reaction conditions. Isolated yields of the products obtained from the sulfuration of a series of strained olefins and conjugated dienes with S_{10} are reported in Table 1.[11]

In the sulfuration reaction of norbonene **7**, trithiolane **3** was isolated as the unique reaction product. The yield of **3** is comparable to the one reported in the reaction of **7** with diatomic sulfur;[6a] but is quite different from the reaction of S_8 with **7** in polar solvents where Bartlett and Ghosh showed that a significant amount of a pentasulfide cycloadduct was formed.[7b] Similarly, the reaction of S_{10} with norbornadiene **8** produces a trithiolane adduct **4** as well as a new bis-sulfurated compound **5**[12] in good yield. This reaction is again very different from the case of S_8 in polar solvents, where a wide variety of products was isolated.[7b]

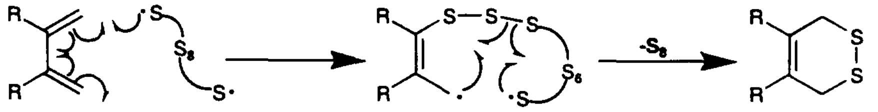
The reaction of S_{10} with conjugated dienes (**6a,b**) proceeds in more moderate yield. Disulfides **1a** and **1b** are formed preferably; high ratios of disulfide versus tetrasulfide adduct (**1/2**) are observed (respectively, 9.5:1 and 6:1).[13] The tetrasulfides **2a** and **2b** in the mixture can then be cleanly transformed into disulfides **1a** and **1b** in ca. 90–95% conversion by treatment with triphenylphosphine.[7d]

Control reactions have been carried out with **6b** and **7** using S_8 as the sulfurating agent. In both cases, only traces (<1% by use of an internal standard) of the expected trapped products were detected.

Sulfur allotropes S_n ($n \neq 8$) are considered to be radical initiators in the process of the polymerization of sulfur melts at ca. 160°C although no radical has ever been detected in sulfur melts below 172°C.[14] However, when BHT was used as a radical scavenger in the sulfuration reaction of **6b** by S_{10}, we observed a 30% reduction in yield of **1b** and **2b**. Moreover, when cumene, a well-known hydrogen donor for thiyl radicals,[15] was used as a solvent for the same reaction, we were able to quench the trapping by ca. 50%. When S_{10} was thermally decomposed in cumene, H_2S was detected;[16] it has been reported to be a decomposition product of sulfanes H_2S_n ($n>1$).[17]

Consistent with these results, we propose a radical mechanism for the sulfuration of conjugated dienes by S_{10} (Eqs. 2 and 3).

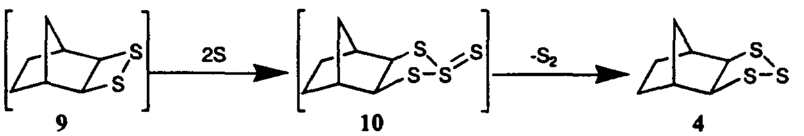
$$S_{10} \xrightarrow{\Delta} \cdot S—S_8—S\cdot \qquad (2)$$



(3)

We believe that the high selectivity of S_{10} to give preferably a disulfide adduct in the sulfuration of conjugated dienes can be rationalized by the cycloelimination of S_8. This process is similar to the one occurring in the depolymerization of polymeric sulfur when long sulfur chains unravel in order to form elemental sulfur. This mechanism is further supported by preliminary trapping experiments with S_{12}. In the case of this allotrope, sulfuration reactions of **6b** produce the tetrasulfide adduct **2b** to a greater extent than the disulfide **1b**.[18]

Such a mechanism is also consistent with the results obtained for the sulfuration of strained olefins. A 2 sulfur atom transfer from the S_{10} chain to norbornene **7** or norbornadiene **8** could lead to an unstable dithietane adduct **9** which could subsequently be sulfurated (2 sulfur addition) to form intermediate **10**. Two of these branch-bonded derivatives could interact to give the more thermodynamically stable trithiolane adduct **4** along with the expulsion of another S_2 molecule (Eq. 4). These elusive intermediates **9** and **10** were first proposed by Steliou and co-workers in the reaction of strained olefins with diatomic sulfur.[19]



9 **10** **4**

(4)

This new reaction process delivers the equivalent of a diatomic sulfur transfer and nicely adds to the growing list of such transfers by having only simple by-products to separate on product purification.

Acknowledgements

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10. S_{10} appears to be very sensitive to traces of base. In order to obtain reproducible results, crude Cp_2TiS_5 is purified by silica gel column chromatography using chloroform as a solvent.
11. A typical experiment is as follows: 1.0 mmol of alkene or conjugated diene is dissolved in 100 mL of toluene and brought to reflux under a nitrogen flow. 1.0 mmol of freshly recrystallized S_{10} is dissolved in carbon disulfide and the solution concentrated to ca. 5 mL on a warm sand bath. The S_{10}/CS_2 solution is then injected on top of the refluxing olefin solution with a syringe over 30 s. An extra 1 mL of CS_2 is used to rinse the flask which contained S_{10} and is subsequently added to the refluxing solution. Reflux is maintained for 2–3 h. The solvent is then evaporated and the residue triturated repeatedly with 3×3 mL of diethyl ether or hexanes and then with smaller portions of CS_2 until no product is detected by TLC. Products are separated on a silica gel chromatographic column using a dry pack in order to load the sample. Typical eluant composition varies from hexanes to hexanes:Et_2O 100:2. Products are obtained in 42–85% yield.
12. ^1H NMR (200 MHz, $CDCl_3$) δ: 1.98 (bs, 2H), 2.63 (t, 2H) and 3.83 (bs, 4H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ: 28.18, 45.61 and 68.63 ppm; HRMS calcd for $C_7H_8S_6$ 283.8950, found 283.8951. This material decomposes over a range starting at 180°C; it is likely that polymerization takes place. It gave a satisfactory carbon and hydrogen analysis albeit the sulfur percentage was low by 2.4%. Anal. calcd for $C_7H_8S_6$ C, 29.55; H, 2.83; S, 67.62. Found C, 29.96; H, 2.88; S, 65.22.
13. In the vast majority of diene sulfuration (Ref. 6c, d), tetrasulfides are formed. Ratios vary but for example **1b**:**2b** ratios are usually between ca. 4:1 (Ref. 7d) and ca. 1:1 (Ref. 6b).
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