

Sulfuration of Dienes with Elemental Sulfur

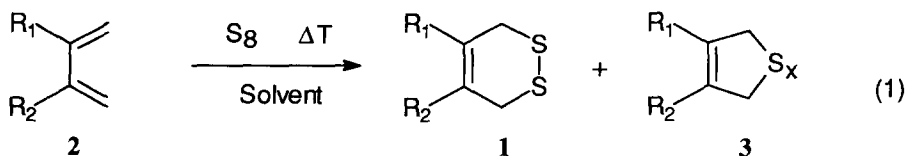
Andrzej Z. Rys and David N. Harpp*

Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6

Abstract: Elemental sulfur reacts with conjugated 1,3-dienes to deliver cyclic di- and polysulfides; the reaction proceeds without any activation other than heat. Treatment of cyclic polysulfide products with triphenylphosphine cleanly converts them to the corresponding disulfide in good overall yield. Additionally, some mechanistic aspects have been examined. The presence of disulfur as an active species in the sulfuration of dienes with S_8 is discussed. © 1997 Elsevier Science Ltd.

Sulfur transfer to acceptors like conjugated dienes and strained olefins has been developed intensively in recent years.¹ The possibility of synthesizing reagents capable of specifically delivering a diatomic sulfur unit (likely in the singlet state) in a Diels–Alder fashion to dienes, parallel to the chemistry of singlet oxygen, has attracted considerable attention.^{1c-i} The use of elemental sulfur has also been examined. Some approaches have been carried out using elemental sulfur activated by ammonia in a DMF-pyridine mixture (30% yield of disulfide from myrcene)² or by a palladium catalyst (formation of open-chain products in the case of butadiene and mono- and disulfide when isoprene was used)³ with modest success. Recently, the synthesis of disulfide **1c** using elemental sulfur with activators was reported by Welker.⁴ We now wish to report our findings in this area of sulfur-transfer chemistry.⁵

We have found that elemental sulfur shows a variable level of activity towards dienes. In solvents of relatively low polarity, the reaction proceeds only at elevated temperatures (*ca.* 130°C). In contrast, DMSO, DMF and pyridine permit the transformation to proceed at lower temperatures (Equation 1).



a, $R_1, R_2 = \text{Me}$; b, $R_1 = \text{H}, R_2 = (\text{CH}_2)_2\text{CH}=\text{C}(\text{Me})_2$; c, $R_1, R_2 = \text{Ph}$

Solvent = DMSO, DMF, PhCl, PhMe, $(\text{CH}_2\text{OEt})_2$; $x = 3, 4$ and higher

It should be emphasized that in these reactions, sulfur does not need separate activation by amines. Tetrasulfides **3a** and **c** ($x = 4$) or trisulfides **3b** ($x = 3$) together with the corresponding disulfides **1**, form the bulk of the product in the sulfuration of **2**. The polysulfides formed are almost quantitatively converted to disulfides with triphenylphosphine.^{14,8} The 1:3 ratios (determined by NMR) of crude material (values in brackets) and some examples of isolated yields of disulfides, along with optimized reaction conditions, are given in the Table.⁶

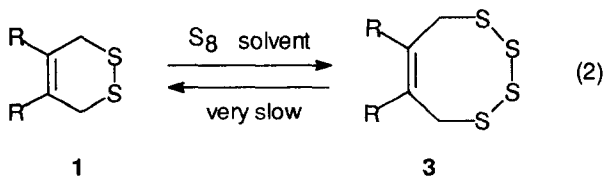
Table. Yields of Disulfides **1** in the Sulfuration of **2**.

Conditions	Disulfides		
	1a	1b	1c
DMSO/125°C	72% (1 : 1.8) 3 h	45% (1 : 1.4) 2 h	80% (4.1 : 1) 6 h
Pyridine/115°C	68% (1 : 1.1) 3 h	52% (1.1 : 1) 3 h	82% (2.1 : 1) 12 h

The best yields are obtained using 2,3-diphenyl-1,3-butadiene **2c**. In the case of the two other substrates, volatility (**2a**) and side reactions (**2b**) resulted in a decrease in the isolated yield. The extent of formation of tetrasulfides is possibly influenced by the repulsion between substituents at positions 2 and 3.

Formation of disulfides along with polysulfides in different ratios encouraged us to consider the mechanistic problem of the reaction. An emphasis was placed on the formation of tetrasulfides **3** ($x = 4$). A mechanism based on S_2 chemistry could rationalize the formation of **3** as a product of insertion of disulfur into a disulfide bond.^{1c,f,i,7a} Experiments with different ratios between diene and sulfur suggest however, that this process is not too important in the formation of tetrasulfides. When the concentration of S_8 was increased 5-fold (the ratio of sulfur/diene varying from 2 to 10), the increase of the 1:3 ratio was not dramatically changed (4.5 to 5.6).

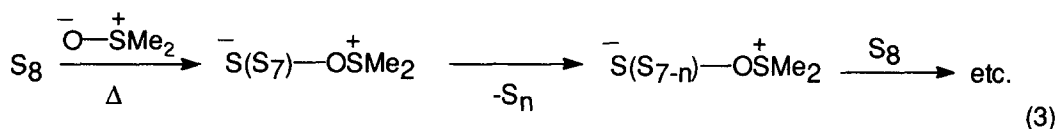
In a series of control experiments, pure disulfides **1a,c** were heated with elemental sulfur in DMSO and PhCl (Equation 2). Although some tetrasulfide **3** formed in each case, it was *ca.* 10-20% of what was observed in the reactions with dienes under identical conditions. About the same extra quantity of **3** formed in experiments with the increased amount of sulfur. Recently, it has been claimed that elemental sulfur dissolved in polar solvents can exist in equilibrium with S_2 .⁸ However, these measurements were carried out at room temperature and may not apply to the conditions described here.



We also examined the possibility that tetrasulfides were formed first in a sulfuration reaction and then were equilibrated in the presence of elemental sulfur. A separate experiment in which a sample of pure tetrasulfide **3c** was heated with an excess of S_8 in DMSO, did not confirm this hypothesis. Only 8% of **3c**

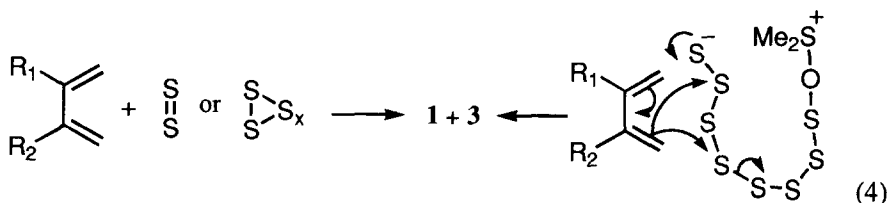
($x = 4$) was converted to **1c**. Both of these experiments suggest that the equilibration does not significantly determine the composition of sulfuration products. Interestingly, equilibration was found to play important role in the chemistry of pentathiepins^{1a,9}

In Equation 3 we offer a working hypothesis rationalizing the behavior of sulfur in a polar medium like DMSO. The S_8 ring could be opened by the solvent and an ionic intermediate could generate discrete sulfur units S_n with $n = 2, 3, 4$ or 5 . This could give a useful explanation as to the formation of tri- and pentasulfides during the addition of sulfur to some dienes like **2b** and to strained alkenes.^{7a}



At this time, S_3 , S_4 and S_5 remain elusive sulfur allotropes whose properties can be suggested only on the basis of MO calculations.¹⁰ It is also conceivable that the opened S_8 ring can act as an actual sulfur transfer reagent as opposed to the some discrete sulfur allotrope transfer. A radical mechanism has been excluded because addition of BHT had little effect on either the yield or the ratio between **1** and **3**.

From the data obtained to date, it can be inferred that formation of both di- and tetrasulfides occurs in a single step (Equation 4). It is possible that two mechanisms can be operating. It seems that the prevalent formation of di- and tetrasulfides for certain dienes depends more on the nature of the diene than on the method of sulfur transfer.



We have carried out experiments determining the formation of certain impurities in the studied reaction, namely thiophene, 2,5-dihydrothiophene, and polymers for dienes with $R_1, R_2 = \text{Ph}$.¹¹ Prolonged heating of pure samples of **1c** and **3c** at elevated temperatures (DMSO at 140°C, in PhCl at 135°C and in xylenes at 145°C) resulted mainly in the formation of the thiophene derivative along with smaller amounts of the dihydrothiophene compound and polymer. Such products have been attributed to "activated sulfur".⁷ This again raises the question about its nature as well as the frontier between S_2 and other forms of sulfur.

Acknowledgments: We thank the Natural Science and Engineering Research Council of Canada as well as the F.C.A.R. (Québec) for financial support of this work.

References and Notes

1. a) Bartlett, P. D. and Ghosh, T. *J. Org. Chem.* **1987**, *52*, 4937; b) Freeman F.; Kim D. S. H. L. and Rodriguez E. *Sulfur Rep.* **1989**, *9*, 207 and references cited therein; c) Steliou K. *Acc. Chem. Res.* **1991**, *24*, 341 and references cited therein; d) Williams, C. R. and Harpp, D. N. *Tetrahedron Lett.* **1991**, *52*, 7651; e) Abu-Yousef, I.A. and Harpp, D. N. *Tetrahedron Lett.* **1994**, *35*, 7167; f) Chew, W. and Harpp, D. N. *Sulfur Lett.* **1993**, *16*, 19; g) Tardif, S. L.; Williams C. R. and Harpp, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 9067; h) English, R. F.; Rakitin, O. A.; Rees, C. W. and Vlasova, O. G. *J. Chem. Soc., Perkin Trans. I* **1997**, 201; i) Harpp D. N. *Phosphorus, Sulfur, and Silicon*, **1997**, in press.
2. Elvidge, J. A. and Jones, S. P. *J. Chem. Soc., Perkin Trans. I* **1982**, 1089.
3. Dzhemilev, U. M.; Baibulatowa, N. Z.; Tkachenko, T. K. and Kunakova, R. W. *Zh. Org. Khim.* **1987**, *23*, 1793.
4. Fulcher B. C.; Hunter M. L. and Welker M. E. *Synth. Commun.* **1993**, *23*, 217.
5. Rys A. Z.; Shaver A. and Harpp D. N. 79th Canadian Chemical Conference, St. John's, Newfoundland, Canada, June, 1996.
6. A typical procedure is as follows: the reagents, 1 mmol of diene and 0.5 mmol of S₈ are added to 4 mL of pyridine. The reaction mixture is refluxed for 3-12 h. An excess, 3 mmol of PPh₃, is added to the still hot solution. The mixture is stirred at room temperature for about 30 min. Next, an excess, 0.2 mmol of S₈, dissolved in a small amount of CS₂ is added and the solution stirred for additional 10 min. After the solvent is removed, the residue is triturated with hexanes. Precipitated PPh₃S was washed 5 times to ensure recovery of disulfide. The solvent is removed and the residue introduced at the top of the chromatographic column (silica gel) with a minimal amount of CS₂. Elution is carried out first with hexanes and then with a mixture of hexanes/Et₂O (100 : 1). The product was obtained in 45-82% isolated yield.
7. a) Steliou, K.; Gareau, Y.; Milot, G. and Salama, P. *J. Am. Chem. Soc.* **1990**, *112*, 7819. A paper has appeared which comments on the mechanism of S₂ and/or "activated sulfur" with dienes; b) see Micallef, A. S. and Bottle, S. E. *Tetrahedron Lett.* **1997**, *38*, 2203
8. Bosser, G. and Paris, J. *New, J. Chem.* **1995**, *19*, 391.
9. Chenard, B. L.; Harlow, R. L.; Johnson, A. L.; Vladuchick, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 3871
10. Salahub, D. R.; Foti, A. E. and Smith, V. H., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 7847; it should be noted that S₃ transfers have been efficiently effected; see Ghosh, T.; Bartlett, P. D. *J. Am. Chem. Soc.* **1988**, *110*, 7499.
11. Rys, A. Z. and Harpp, D. N. unpublished results.

(Received in USA 4 April 1997; revised 8 May 1997; accepted 9 May 1997)