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Diselenide-assisted sulfuration of dienes

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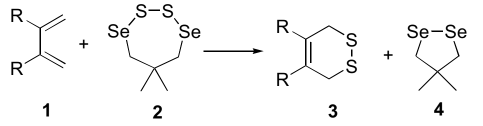
Abstract—Various diselenides assist in the sulfuration of dienes giving cyclic di- and tetrasulfides as main products. The reaction requires a 2-fold excess of diselenides to be efficient. Catalytic amounts of diselenides result in lower yields. This is likely due to secondary reactions (polymerization, aromatization) occurring during extended reaction times under catalytic conditions. It was verified that the sulfur-transferring properties of diselenatetrasulfides are virtually identical to those of diselenides combined with sulfur. Contrary to previous claims, not only the cyclic diselenatetrasulfide but also linear diselenatetrasulfides ($RSeS_nSeR$) transfer sulfur to dienes. A mechanism is proposed and its implications to the nature of diatomic sulfur are discussed.

Singlet diatomic sulfur is generally seen as a selectively reacting species converting dienes into disulfides in a Diels–Alder fashion.[1] One of the more interesting ways to transfer sulfur to dienes **1** was reported by Schmidt and Görl.[2] It involves use of a cyclic seven-membered ring 1,4-diselenatetrasulfide **2** as a 2-sulfur transfer reagent. Upon heating, heterocycle **2** contracts, releasing a two-sulfur unit (possibly $^1S_2$) subsequently trapped by a diene **1** (R = alkyl, aryl) providing **3** accompanied by diselenide **4** (Eq. 1).



(1)

While the reaction was not particularly efficient and resulted in the formation of other products like thiophenes, for years it has been considered a model method for generating diatomic sulfur.[1]

We were interested to extend the original Görl and Schmidt method to linear diselenatetrasulfides. Although the authors commented on the linear 1,4-diselenatetrasulfides as unsuitable for sulfur transfer purposes, no details were provided.

Recently, we have developed a simple and efficient method to prepare both cyclic **2** and acyclic diselenatetrasulfides, **5a**–**f** from corresponding diselenides **4**, **6a**–**f** and trityl thiosulfenyl chloride Ph_3CS_2Cl (Eq. 2).[3]

This easy access to such interesting compounds allowed us to study them as sulfur transfer reagents; we have examined this area and report our findings. In a comparative study, chlorobenzene solutions of 2,3-diphenylbutadiene (**1A**) and various 1,4-diselenatetrasulfides **5** were refluxed under conditions similar to these reported by Schmidt (Eq. 3). To maximize the yields, a 2-fold excess diselenatetrasulfides **5** to diene was used instead of stoichiometric amounts; the results are presented in Table 1.

$$\underset{\textbf{6a-f}}{R'SeSeR'} \xrightarrow{Ph_3CS_2Cl} \underset{\textbf{5a-f}}{R'SeS_2SeR'} \qquad (2)$$

a R' = Ph
b R' = $PhCH_2$
c R' = $O_2NC_6H_4CH_2$
d R' = $MeOC_6H_4CH_2$
e R' = $MeOC_6H_4$
f R' = $O_2NC_6H_4$

The most striking observation was the significant formation of trapped products in the case of linear diselenatetrasulfides **5** (entries 1–3). Yields of cyclic disulfides exceeding 40% were typically observed and were higher than those obtained for cyclic diselenatetrasulfide **2**.

Keywords: Sulfur transfer reactions; Diselenatetrasulfides; Diatomic sulfur; Cyclic disulfides.

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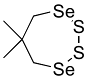
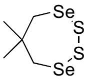
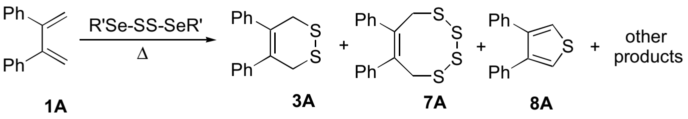
Table 1. Sulfuration of 2,3-diphenylbutadiene (**1A**, R = Ph) with diselenatetrasulfides. Yields determined with bibenzyl as the internal standard

Entry	Time [h]	Diselenatetrasulfide	Equivalents of **5** (**2**)	% **3** + **7**	**3**/**7**	% unreacted diene	% of **8** and other products
1	4	**5a** $(PhSeS)_2$	2	42	5	10	48
2	4	**5b** $(PhCH_2SeS)_2$	2	56	10	9	35
3	4	**5c** $(O_2N–C_6H_4CH_2SeS)_2$	2	44	10	2	55
4	4	**2** 	2	51	0.7	21	28
5[a]	1.5	**2** 	1	23	0.5	75	2
6	4		1	32	0.7	49	19

[a] Results obtained from the reaction repeated under the reported conditions.



1A **3A** **7A** **8A** (3)

In our hands, sulfuration of 2,3-diphenylbutadiene (**1A**) with **2** gave only 23% of sulfur transfer products **3A** and **7A** (entry 5) with not much better results after 4 h (entry 6).[4] Curiously, it was only under our conditions that a substantial amount of **3A** formed (entry 4).

Another remarkable difference between cyclic and acyclic diselenatetrasulfides was the relatively high yield of tetrasulfide (**7A**) using reagent **2**. These yields were expressed as disulfide/tetrasulfide ratios (determined by NMR) as the compounds are difficult to separate. Although important mechanistically, a high **3**/**7** ratio is not essential from a preparative point of view as tetrasulfides **7** are easily converted to disulfides **3** by a treatment of the crude reaction mixture with triphenylphosphine as required.[5]

In general, diselenatetrasulfides are thermally unstable. Their decomposition concomitant with the formation of various selenachalcogenides and S_8 led to the premise that S_2 could be generated that way.[2] Using ^1H NMR to follow the reaction progress, we observed that the bulk of diselenatetrasulfides were transformed into the corresponding diselenides in less than 4 min, that is, long before much of the diene reacted. In spite of that, the sulfuration continued suggesting that the diselenides might be also involved in that process. To test this possibility, 2,3-diphenylbutadiene (**1A**) was treated with a mixture of 2 equiv of dibenzyl diselenide (**6b**) and 4 equiv of elemental sulfur (building blocks of diselenatetrasulfide **5b**). The results compared to those obtained with compound **5b** are shown in Figure 1. Surprisingly, the results with original sulfur transfer reagent were almost identical to those where a mixture of dibenzyl diselenide and elemental sulfur was used. This can be reasonably explained by invoking a very rapid convergence of the reactive selenium species in both reaction mixtures.

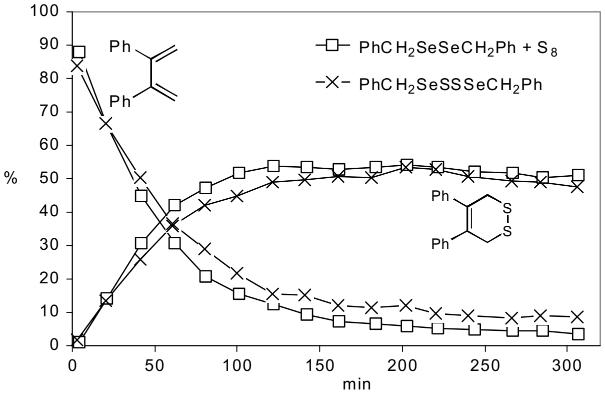


Figure 1. Sulfuration with pure $PhCH_2SeSSSeCH_2Ph$ (**5b**) and with a mixture of $PhCH_2SeSeCH_2Ph$ (**6b**) + elemental sulfur.

Thus, a major part of diselenatetrasulfide **5b** converted rapidly (in less than 5 min) to the corresponding diselenide **6b**. The reverse process in which sulfur inserted to the Se–Se bond of diselenides was also observed but to a lesser extent resulting in a formation of up to 10% of various $RSeS_nSeR$ species. While all diselenides including the dibenzyl ones, underwent sulfur insertion to varying degrees, only the latter were observed to lose selenium. Thus, upon loss of selenium, diselenide **6b** equilibrated with the corresponding monoselenide $PhCH_2SeCH_2Ph$ to reach 26% and 32%, respectively, in both reaction mixtures.

The optimal sulfuration conditions employ 2 equiv of diselenides. There was no benefit in increasing this amount. On the other hand, 1 equiv of diselenide resulted in both lower reaction rate and ca. 5% lower overall yield. Catalytic amounts of diselenides gave expected products but were inefficient, resulting in a lower sulfuration rate and more importantly, in lower yields. A comparison of the efficiencies of various diselenides as sulfur transfer reagents under optimized conditions is presented in Figure 2.

The slowest rate (and lowest yield) was observed in the case of cyclic diselenide **4**. Benzylic diselenides **6b** and

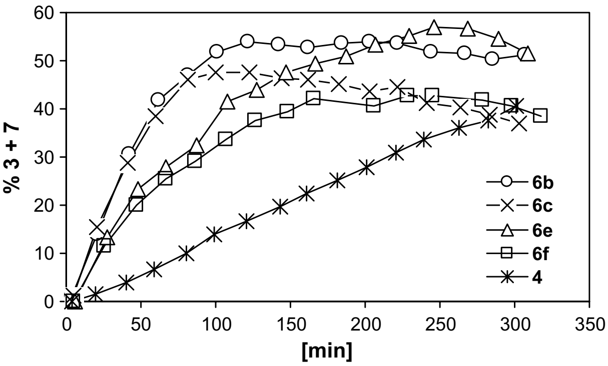


Figure 2. The combined yields of di- and tetrasulfide obtained from the sulfur transfer in the presence of various diselenides **6b**, **6c**, **6e**, **6f**, and **4**.

6c were the fastest. Aromatic diselenides **6e** and **6f** were less active than the benzylic ones but significantly more so than **4**. Interestingly, although the substituents attached to the aromatic ring did not significantly affect the reaction rate, the sulfuration yields were determined by them. Nitro-substituents (**6c** and **6f**) resulted in a decrease as compared to their more electron-rich counterparts **6b** and **6e**.

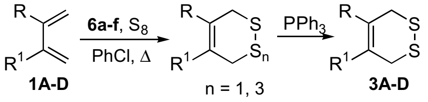
The role of light in sulfuration of dienes with diselenide/S_8 mixtures was tested. To this end, two reactions were carried out; one in the dark and another one irradiated by a 300W sun lamp (50cm from the flask). In fact, both rate and yield were virtually the same as those of the control experiment indicating a marginal role of light in the sulfuration.

Diselenides are known to form radicals but they add to dienes with difficulty.[6] However, when a photolytic addition to dienes is carried out in the presence of disulfides, the formation of mixed sulfide selenide adducts results.[6] As the C–Se bonds dissociate easily, the mixed adducts were easily converted to corresponding thioethers (Eq. 4).[7]

In our control experiment, paralleling dithiolation reported by Ogawa et al.,[7] we replaced elemental sulfur with 2equiv of diethyl disulfide. Under our conditions, diene **1A** remained unchanged.

Finally, the efficiency of various diselenides in sulfur transfer reactions was tested with dienes **1A–D** (Eq. 5). The results are shown in Table 2.

(4)

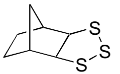


(5)

A: R, R^1 = Ph; **B**: R, R^1 = $PhCH_2$, **C**: R, R^1 = Me;
D: R = $Me_2C{=}CHCH_2CH_2$; R^1 = H

The sulfuration yields were in the 40–65% range with dienes containing aromatic groups showing the best results (including a new dibenzyl substituted disulfide **3B**).[9] A relatively low yield of disulfide **3C** might be explained by a high volatility of the corresponding diene **1C** preventing it from reacting efficiently under the applied conditions.

Similarly as in the case of diselenatetrasulfides, significant amounts of other products formed. Their ^1H NMR spectra show broad peaks in 3.9–4.3ppm region suggestive of some oligomeric species. The addition of a 24-equivalent excess of sulfur blocked oligomer production and resulted in the formation of cleaner products. For the efficient separation of a desired product by column chromatography the diselenide should have a different polarity from that of the product (for the choice of diselenides, see Table 2).



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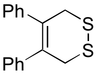
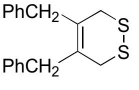
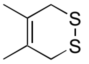
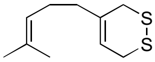
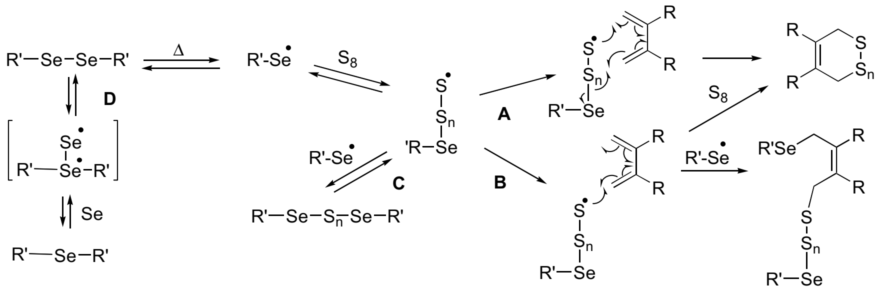
An attempt to extend the method to norbornene **9** was thwarted by a low, 25% yield of the corresponding

Table 2. Yields of sulfuration products obtained from various dienes and norbornene[8]

Sulfuration product		6	Equivalents of sulfur	Time [h]	Yield[a,b] [%]
	**3A**	**a**	24	5	50
		c	6	5	42 (53)
		e	6	5	(48)
	**3B**	**a**	24	2	67
		c	6	2	(50)
		e	6	2	(65)
	**3C**	**e**	6	2	38
		e	24	2	41
	**3D**	**e**	6	2	(28)
		e	24	2	36

[a] Tetrasulfides were desulfurized with PPh_3 prior to the purification.

[b] Values in brackets show the amounts of product in cases when complete purification could not be achieved—determined with the internal standard.



Scheme 1.

trisulfide **10** obtained under optimized conditions (2 equiv of PhSeSePh and 24-excess of elemental sulfur).[10]

The sulfuration appears to be a thermally controlled homolytic process, that is, only slightly enhanced by light (up to 5% higher sulfur transfer yields). Most likely, it implies a cleavage of the diselenides to form reactive radicals ($R'Se^{\cdot}$) as reported by Ogawa[6,7] and Chu.[11] Other radicals likely do not form as we do not observe any $R'S_nR'$-type product. The selenide radicals can generate radical sulfur species that might follow three reaction paths (Scheme 1). In path A, sulfur is transferred to dienes to form the expected sulfuration products. In path B, unsymmetric addition results in the formation of a mixed adduct similarly to what was reported by Ogawa et al.[7] This path seems to be redirected to the formation of sulfur transfer products when massive amounts of elemental sulfur are added. Finally, in path C, the sulfur radical species reversibly converts to diselenapolysulfides. It is by following this path that diselenatetrasulfides convert to radical sulfur species. Benzylic diselenides tend to lose selenium upon heating (path D). It seems that this process is not a prerequisite in sulfuration as even diselenides that do not deselenize (aromatic **6a**, **6e** and **6f** and cyclic **4**) efficiently assist in sulfuration.

Once formed, the sulfuration products **3** and **7** can undergo some subsequent reactions decreasing their yield. Aromatization of **3** and **7** under the sulfuration conditions was reported earlier.[5] In this work we have usually observed very small amounts of **7**. A separate experiment helped us to determine that this effect is due to presence of diselenides that attack **7** converting it to thiophene and some unidentified polymeric species with only 20% left after keeping it under typical reaction conditions.

Acknowledgements

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References and notes

1. Steliou, K.; Gareau, Y.; Harpp, D. N. *J. Am. Chem. Soc.* **1984**, *106*, 799–801; Steliou, K.; Salama, P.; Brodeur, D.; Gareau, Y. *J. Am. Chem. Soc.* **1987**, *109*, 926–927; For reviews see: Harpp, D. N. *Phosphorus, Sulfur, and Silicon and Rel. El* **1997**, *120*, 41–59.
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3. Hou, Y.; Rys, A. Z.; Abu-Yousef, I. A.; Harpp, D. N. *Tetrahedron Lett.* **2003**, *44*, 4279–4282.
4. Likely, there is a typographic error in Ref. 2, as the reaction times for 2,3-dimethylbutadiene and 2,3-diphenylbutadiene seem to be reversed. The latter, known for its lower reactivity in D–A reactions, was reportedly treated with compound **2** for only 1.5 h while the former for 4 h.
5. Rys, A. Z.; Harpp, D. N. *Tetrahedron Lett.* **1998**, *39*, 9139–9142.
6. Ogawa, A.; Tanaka, H.; Yokoyama, H.; Obayashi, R.; Yokoyama, K.; Sonoda, N. *J. Org. Chem.* **1992**, *57*, 111–115.
7. Ogawa, A.; Obayashi, R.; Sonoda, N.; Hirao, T. *Tetrahedron Lett.* **1998**, *39*, 1577–1578.
8. Typical procedure: a mixture of a diene 0.4 mmol, diselenide 0.8 mmol and 12.8 mmol (410 mg) of sulfur in 4 mL of PhCl was refluxed for 2–5 h under nitrogen. The reaction mixture was poured into 15 mL of MeOH, cooled in the freezer and filtered. Five millimoles of PPh_3 were dissolved in the solution upon warming. After 10 min the excess of PPh_3 was eliminated by addition of 1.2 mmol of sulfur, warming and stirring at rt for 1 h. The solvent was then removed, the residue was extracted five times with hexanes (total ca. 25 mL). Solvent was removed and the residue was chromatographed with 0–1% of EtOAc in hexanes.
9. Properties of **3B**: white solid; 79 mg (67%) yield; mp 37–38 °C; ^{1}H NMR ($CDCl_3$): δ 3.31 (s, 4H); 3.62 (s, 4H); 7.1–7.4 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 32.9; 39.9; 126.4; 128.3; 128.6; 130.4; 138.6. HRMS: calc. for $C_{18}H_{18}S_2$ 298.08499, obt. 298.08437.
10. Norbornene trisulfide is known to undergo polymerization, likely initiated when treated with PPh_3; see: Baran, T.; Duda, A.; Penczek, S. *J. Polym. Sci.* **1984**, *22A*, 1085–1095.
11. Chu, J. Y. C.; Lewicki, J. W. *J. Org. Chem.* **1977**, *42*, 2491–2493.