Fascinating Organosulfur Functionalities: Polychalcogens As Diatomic Sulfur Sources

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ABSTRACT: *Recent work on the chemistry of dialkoxy disulfides is summarized. It includes various aspects of their structure and relationship to the isomeric thionosulfites as well as their use as diatomic sulfur precursors.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:449–459, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20341

INTRODUCTION

Organic sulfur compounds occupy a special place in the myriad of known chemicals. In general, they can be oxidized, reduced, undergo concatenation, coordination and can form wide-ranging and fascinating functionalities. Even elemental sulfur has numerous natural and man-made allotropes. One that has attracted considerable attention including our own (for more than 20 years) is diatomic sulfur.

Unlike O_2 which is stable at biological temperatures, S_2 is extremely reactive and labile, concatenating readily to S_8; for instance, S_2 photodissociates in 7.5 min at earth's heliocentric distance [1]. In fact, S_2 is the prevailing sulfur allotrope at elevated temperatures (>500°C) but in the triplet form. Diatomic sulfur has been reported as a blue-violet gas [2] at these elevated temperatures and has been detected celes-

tially. Its relevance in our own solar system manifests in its detection (MW and near IR) in the volcanic plumes of the Jovian moon Io [3,4]; the red color of the moon surface being attributed to energy transitions resulting from ejected S_2 gas, which instantly cools upon landing on the surface and quickly rearranges to more stable allotropes [5,6].

Diatomic sulfur can be trapped at low temperatures by rare gas matrices [7] or synthetically generated and subsequently trapped by dienes as Diels–Alder adducts (Scheme 1) [8]. The generation and trapping of diatomic sulfur has been well reviewed in the literature [9–13]. The Diels–Alder trapping of $^1S_2$ is symmetry allowed by Woodward–Hoffmann rules [14] and mirrors analogous reactions with singlet oxygen [9,15,16]; it is the singlet state of diatomic sulfur that is its excited state (about 13 kcal mol^{-1} above that of the ground state) [17].

A continuing topic of interest in our group is the development of bench-stable sources of S_2 by sequestering the reactive two-sulfur fragment within an organic framework. Within this context, we reported more than 10 years ago that dialkoxy disulfides (ROSSOR **1**) at elevated temperatures efficiently (>75% trapped using 2,3-diphenylbutadiene) deliver a two-sulfur unit [18]. We had originally suggested that such S_2 generation results from the concerted disproportionation of the parent dialkoxy disulfide, (Scheme 2) [18,19] though the actual source of sulfur in these thermolysis reactions has been questioned [20]. Thompson and coworkers [19] observed that the origin of the R group of the dialkoxy disulfide affected their thermal stability (secondary > primary > allyl > propargyl). This observation provided the sole evidence for the cyclic
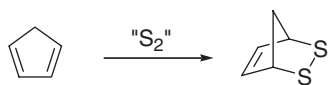
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SCHEME 1 Synthetic trap using cyclopentadiene.

transition shown in Scheme 2. Recently (vide infra), we [21] demonstrated that a radical mechanism was likely operative in the thermal decomposition of dialkoxy disulfides.

Our discovery that dialkoxy disulfides could serve as efficacious two-sulfur sources also serendipitously led us to investigate the unusual physical properties of this class of compound and its related structural isomer, the thionosulfite (ROS(=S)OR, **2**).

Dialkoxy disulfides (**1**) have been known since the late 19th century [22]. In 1964, Thompson and coworkers [19,23,24] confirmed that compounds possessing the molecular formula ROSSOR could potentially exist in two separate constitutionally isomeric forms, namely linear dialkoxy disulfides **1** and branch-bonded arrangement, the thionosulfites **2**. Isomers such as thiosulfite **3** or thiosulfonate ester (RSO$_2$SR) **4** proposed by Zinner [25] were readily ruled out by ^{1}H NMR spectroscopy.
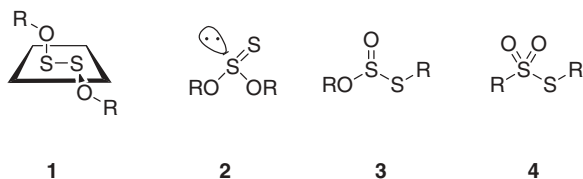
Room temperature ^{1}H NMR spectra of diethoxy disulfide exhibited a characteristic magnetic nonequivalence of the methylene protons. The compound could have connectivity of form **2**, in which case there would be an associated high-thermal barrier to pyramidal inversion [26–28] about the branched sulfur as does exist with analogous sulfite [29–32] and sulfoxide [33–42] systems. Conversely, an inherently high barrier about the sulfur–sulfur bond could be responsible for the anisochronous

signal. Here, the compound would adopt a *gauche* conformation in the ground state and would have form **1** [43]. A coalescence of the ABX$_3$ pattern to that of a simple A$_2$X$_3$ pattern for **1** was observed at 100°C suggesting the connectivity of **1** over that of the branched **2**.

Since Thompson's original work, few investigations into the physical properties of dialkoxy disulfides have been published [44–48]. The chemistry of thionosulfites is even less well understood and studied [49]. Foss [50] had originally suggested that valence expansion of the branched sulfur could be stabilized by adjoining electronegative atoms (F, O). Those of form **2** are rare, having been characterized [23,51–53] only four times until recently (vide infra), with each of the thionosulfites contained within a five-membered ring core (**2a**) as verified crystallographically [51–53].


2a
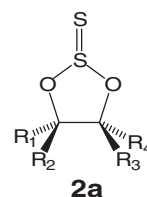
DIALKOXY DISULFIDE SYNTHESIS

As part of our wider interests in the physical properties of dialkoxy disulfides, we have synthesized and characterized several dialkoxy disulfides (derived from the corresponding alcohols **3**) according to a modification of the procedure used by Thompson and coworkers [19] (Scheme 3, Table 1) [21]. Dilute conditions and freshly obtained sulfur monochloride (S$_2$Cl$_2$) are key in attaining high yields and purity.

Although Thompson prepared several aliphatic examples in [19], the series in Table 1 is more varied. Yields were generally high, but phenols and alcohols bearing a trityl group did not couple.
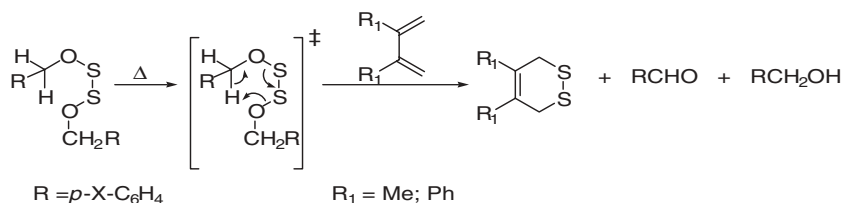

**SCHEME 2** Proposed mechanism in the thermolysis of dialkoxy disulfides.
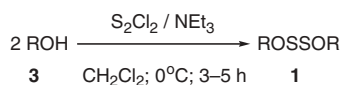
SCHEME 3

Compounds **1a–d, 1f**, and **1h–i** were conveniently stored at $-10°C$ for months with only minor decomposition. Compound **1j** decomposed to a brown solid upon reduced pressure solvent removal but could be stored in CH_2Cl_2 for weeks. Braverman and coworkers also observed the same solution stability [54]. All the dialkoxy disulfides synthesized possess a distinct sweet-fruity aroma.

As part of our investigation of the isomeric preference between thionosulfites and dialkoxy disulfides, using similar conditions to those developed for acyclic analogs, we isolated the *first* cyclic dialkoxy disulfides, one contained within an eight-membered ring (**4**) and its dimeric byproduct contained as a 16-membered macrocycle (**5**) [55]. Synthesis of **4** from 1,2-benzenedimethanol occurs readily, and **4** was isolated in 96% yield. The isolation of **5** proved much more difficult, and its yield was only 8% under optimized conditions.
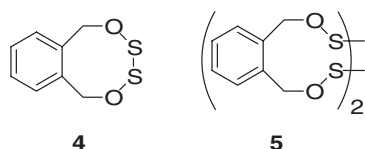

The corresponding dialkoxy disulfide **6** resulting from the S_2Cl_2 coupling of 2,2′-biphenyldimethanol was also isolated, albeit in low yield (25%).

6
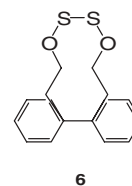
THIONOSULFITE SYNTHESIS

In his original thionosulfite synthesis paper, Thompson et al. [56] proposed that the reaction pathway involved the formation of a polymer under high-dilution conditions of S_2Cl_2. He suggested (Scheme 4) that an alkoxide-catalyzed unzipping of the proposed polymeric intermediate would yield a thionosulfite as a cyclic monomeric product.
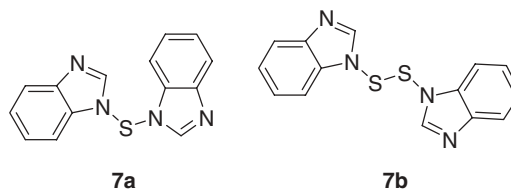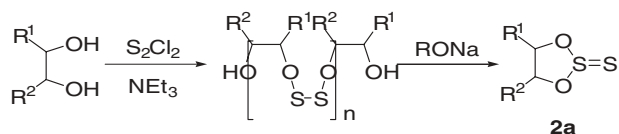

Our method [52] of preparation, using benzimidazole-based sulfur transfer reagents

TABLE 1 Yields of Dialkoxy Disulfides

Compound	R	Yield (%)	Compound	R	Yield (%)
1a	O_2N—⟨aryl⟩—CH₂	97			
			1g	Ph₃C–	0^b
1b	(t-Bu)—⟨aryl⟩—CH₂	90			
1c	MeO—⟨aryl⟩—CH₂	93	**1h**	cyclohexyl	69
1d	H—⟨aryl⟩—CH₂	83	**1i**	allyl	82
1e	Me₂N—⟨aryl⟩—CH₂	0^a	**1j**	propargyl	57
1f	Ph₂CH–	81	**1k**	(Me)—⟨aryl⟩—	0^b

^{a}Complex mixture of products.
^{b}Only starting material detected.

SCHEME 4 Proposed mechanism for the formation of thionosulfites.

7a and **7b**, resulted in similar yields but with no polymeric side products (Scheme 5). While both **7a** and **7b** were effective sulfur transfer reagents in the synthesis of thionosulfites, they proved quite ineffective for the synthesis of isomeric dialkoxy disulfides. In this manner, thionosulfites **2b–g** were prepared (Table 2). The *mono*sulfur transfer reagent **7a** produced thionosulfites in moderate yield (21–50%), whereas the *di*sulfur transfer reagent **7b** was generally more effective (14–80%) and was used for all the precursor 1,2-diols examined. While isolable, some of the thionosulfites were nevertheless unstable at room temperature or upon extended exposure to light.

The mechanism of the formation of thionosulfites remains unclear, particularly with respect to the involvement of *mono*sulfur reagent **7a**. The lack of polymeric side products or sulfoxylate ester (ROSOR) intermediates indicates that the different mechanisms postulated by Thompson et al. [56] and Nakayama and coworkers [53] are not operative in our case.

2h   **2i**
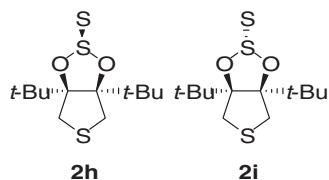
Most recently, using our procedure (solvent: MeCN at RT), Nakayama and coworkers [53] reported the synthesis of a fused 5,5-bicycle containing thionosulfite moiety in two diastereomeric forms. These were isolated by column chromatography then by HPLC to afford **2h** 45% and **2i** 10%.
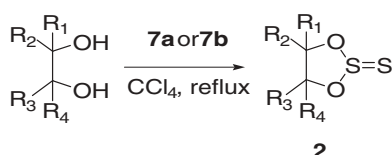
SCHEME 5 Synthesis of thionosulfites.

TABLE 2 Yields of Some Thionosulfites

	Diol					
Entry	R^1	R^2	R^3	R^4	Product	Yield (%)
1	—(CH$_2$)$_5$—		—(CH$_2$)$_5$—		**2b**	50^a; 41^b
2	—(CH$_2$)$_4$—		—(CH$_2$)$_4$—		**2c**	21^a; 80^b
3	—(CH$_2$)$_6$—		—(CH$_2$)$_6$—		**2d**	47^b
4	—(CH$_2$)$_7$—		—(CH$_2$)$_7$—		**2e**	14^b
5	—(CH$_2$)$_5$—		Me	Me	**2f**	72^b
6	—(CH$_2$)$_6$—		Me	Me	**2g**	77^b

^{a}Method A: 1:1 diol:**7a** in refluxing CCl$_4$.
^{b}Method B: 1:1 diol:**7b** in refluxing CCl$_4$.

BARRIER TO ROTATION ABOUT THE S—S BOND IN DIALKOXY DISULFIDES

Dialkoxy disulfides possess a very short S—S bond: X-ray analysis for MeOS-SOMe, r(S—S) = 1.972 Å [46]; for dicubyloxy disulfide, r(S—S) = 1.970 Å [57]; for p-NO$_2$-BnOS-SOBn-p-NO$_2$, r(S—S) = 1.968 Å [58]; for p-Cl-BnOS-SOBn-p-Cl, r(S—S) = 1.933 Å [59]; for **4**, r(S—S) = 1.959 Å [55]; and for **5**, r(S—S) of 1.964 Å [55]. The ϕ(OS—SO) for all of these examples is about 90°, which is unremarkable for XSSX systems [60], but θ (O—S—S) of about 108° is larger than θ(C—S—S) in standard disulfides. The stabilization of the 90° conformation has been determined computationally and is mainly due to the presence of two observed "generalized anomeric effects" resulting from the 2 n(S) → σ^*(S—O) MO interactions [47,55].
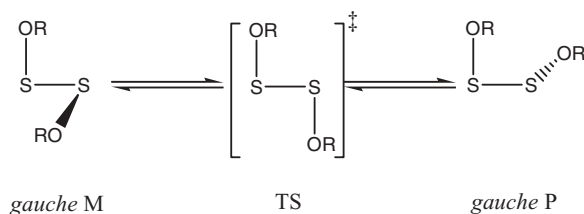

4   **5**
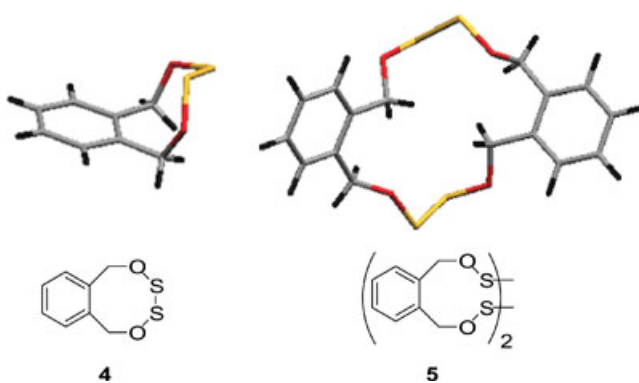
A manifestation of this bond shortening is the high-torsional barrier about the S—S bond. Although Thompson first concluded that this rotational barrier was similar to that of disulfides ($E_a = 8.6 \pm 1.7$ kcal mol^{-1}) [19], such a low value would require an unexpectedly [61] large negative $\Delta S^{\ddagger}$. Subsequent work has shown that the reported value is erroneous [62].

**TABLE 3** S—S Torsional Barrier of Some Related Polychalcogens

Compound	Barrier (kcal mol^{-1})	References
MeS-SMe	6.8	[63]
MeOS-SN(Me)$_2$	14.5	[64]
EtOS-SOEt	18.4	[47]

SCHEME 6 Interconversion of enantiomers of **1**.

Seel et al. [62] demonstrated that the barrier for dimethoxy disulfide was much higher ($\Delta G^{\ddagger} = 17.8 \pm 0.1$ kcal mol^{-1}). Lunazzi and coworkers [47] determined the thermodynamic properties for bis(*p*-nitrobenzyloxy) disulfide in perchloroethene at 105°C ($\Delta G^{\ddagger} = 19.0 \pm 0.2$ kcal mol^{-1}, $\Delta H^{\ddagger} = 20 \pm 1$ kcal mol^{-1}, $\Delta S^{\ddagger} = 2 \pm 5$ eu). Similar activation parameters for other dialkoxy disulfides were also determined indicating within the series, that substitution pattern about the OSSO moiety has a negligible effect on the overall rotational barrier. Restricted rotation in **1** appears to arise entirely from electronic modulation of the S—S σ-bond. The degree of this electronic effect manifests itself through electron-withdrawing elements immediately adjacent to the S—S bond (Table 3).

Rotation between the two enantiomeric *gauche* atropisomers proceeds through a trans transition state (Scheme 6), which was found computationally to be about 3 kcal mol^{-1} less energetically demanding than the cis transition state for MeOSSOMe (Fig. 1).

The barrier to conformational interconversion of the eight-membered ring in **4** was measured by NMR spectroscopy and was found to be 18.8 ± 0.2 kcal mol^{-1} using approximations developed by Gutowsky and Holm [65,66]. The benzyl proton AB spin system coalesced at 114.6°C in *p*-xylene-*d*$_{10}$. This barrier is comparable to those measured [21,47,58,62] and calculated [58,67] for acyclic dialkoxy disulfide analogs; whereas acyclic dialkoxy disulfides interconvert through a trans OS-SO transition state, this is not possible for **4**. The eight-membered ring in **4**, by necessity, switches disulfide chirality by means of a cis transition state. The measured rotational barrier, though similar to the acyclic analog, is due to coupled torsional motions of the C—CH$_2$, CH$_2$—O, and O—S bonds within the ring. The result is an effective lowering of the cis rotational barrier. As such, the 18–19 kcal mol^{-1} value is most likely an underestimate of the energy cost for cis interconversion in an acyclic system.
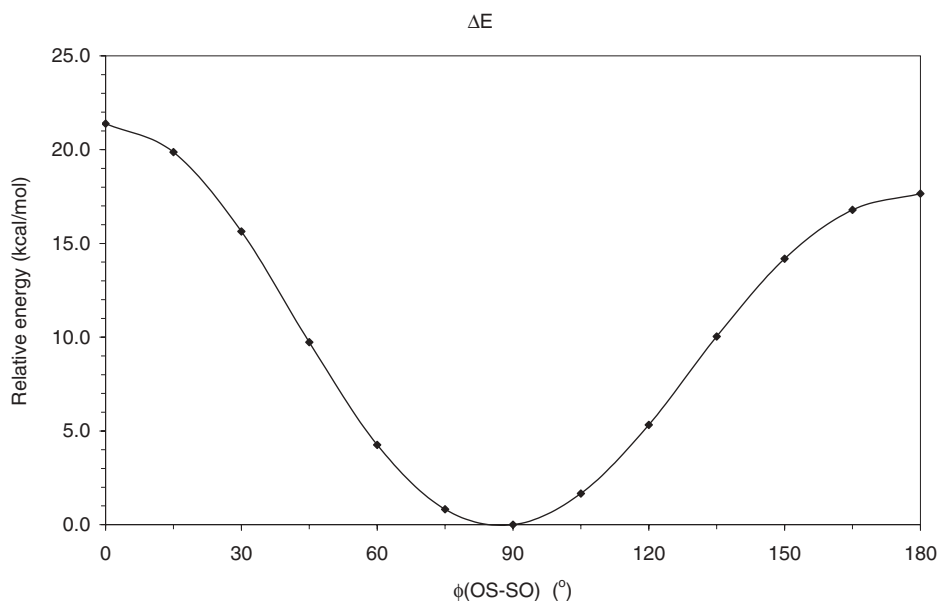
FIGURE 1 Rotational profile of MeOSSOMe based on B3LYP/6-31G(2d) geometries.

We have also measured the activation parameters by VT NMR for a series of 4-substituted bis(benzyloxy) disulfides. Our analysis [21] indicated that subtle modulation of the electronics of the R groups (from NO_2 to MeO) of dialkoxy disulfides insignificantly perturbed the barrier to rotation (18.2–18.4 kcal mol^{-1}). Although our calculations [68] predicted a large dipole moment difference between the ground state *gauche* conformer and that of the trans transition state conformer, barrier height over a series of solvents possessing a large dipole moment range did not appreciably change. Thus, neither substituent size nor electronics nor medium effects significantly perturb the energetics of the S—S rotation barrier.

PHYSICAL PROPERTIES OF FIVE-MEMBERED RING THIONOSULFITES

The proton-decoupled ^{13}C NMR spectra of thionosulfites **2b–g** reveal the expected magnetic anisotropy resulting from the presence of a stereogenic branched-sulfur center. The extent of the electronic influence of the branch-bonded sulfur atom has been hypothesized to be due to its pseudo-axial orientation with respect to the five-membered ring in addition to the polarization that exists within the S—S bond. Indeed, Steudel and Miaskiewicz showed via calculations that the branched sulfur—sulfur bond is polarized, with the terminal sulfur being negatively charged [44]. The observed downfield shift of the signal of the γ-carbon with respect to the S=S bond as compared with the parent diol is a manifestation of this polarization. In fact, the deshielding and shielding zones of the thionosulfite functionality are analogous to that of the sulfite (Fig. 2) [53].
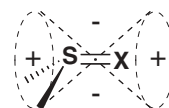

FIGURE 2 Approximate shielding (+) and deshielding (−) zones of sulfites (X = O) and thionosulfites (X = S).

Although quite similar, the NMR spectra of the thionosulfites are distinct from the analogous sulfites. Thionosulfites can be distinguished from sulfites analogs by a comparison of the IR spectra of each. Sulfites posses an IR band between 1180–1240 cm^{-1} associated with the S=O functionality, a consistent feature for thionosulfites is the presence of a strong band at 655 cm^{-1} that has been attributed [58] to the S—S stretch [53,55,69].

One characteristic feature of the MS common to all the thionosulfites is the base peak representing the loss of the HS_2O_2 (*m/z* 97) moiety from the parent ion. The feature common to the MS of dialkoxy disulfides is the initial loss of SO (*m/z* 48) from the parent ion.

More than 20 years ago, we [51] unequivocally determined the existence of thionosulfites when **2d** was synthesized and the first X-ray structure of this class was determined. Compound **2d** contains an extremely short S—S bond (1.901 Å) [51], that is quasi-axial with respect to the five-membered ring core. A later crystal structure of analogs **2e** reveals an r(S=S) of 1.911 Å. The short sulfur—sulfur bond suggests considerable double bond character similar to the S_2 (1.890 Å) [70], S_2O (1.884 Å) [71], S_2F_2 (1.860 Å) [72], and S_2NR_2 (1.898 Å) [73] systems.

2d

2e

8
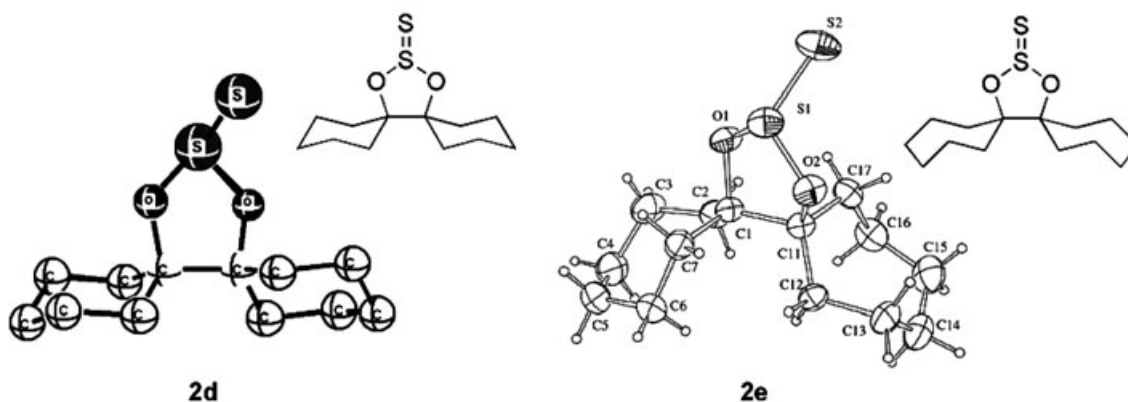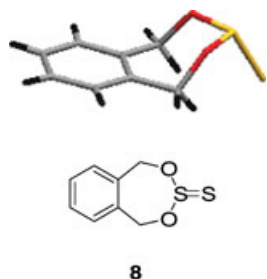
As part of our [55] investigation into the factors that govern dialkoxy disulfide and thionosulfite stability, we were able to isolate and crystallize **8** in 22% yield. Compound **8** possesses C_s symmetry and is the first isolated non-five-membered ring thionosulfite. Thionosulfite **8** has a $r(S{-}S)$ of 1.936 Å, a bond length that is longer than any other reported S=S bond (except gaseous S_2O_2). This is due to the two optimal $n_O \rightarrow \sigma^*_{S=S}$ stereoelectronic donations present in **8**, which contribute to a lengthening of the S=S bond. Greater orbital overlap in **8** versus the other thionosulfites results from the axial orientation of the S=S bond compared to the conformation of the seven-membered ring core.

## THERMOCHEMISTRY OF DIALKOXY DISULFIDES

Recently, we [21] revisited the mechanism behind S_2 delivery during the thermolysis of dialkoxy disulfides. We proposed that dialkoxy disulfides undergo initial asymmetric S—O homolytic bond cleavage to ultimately yield a transient source of diatomic sulfur. Dialkoxy disulfides were found to decompose under first-order kinetics with a $\Delta G^{\ddagger}_{298} = 24$ kcal mol^{-1} (Scheme 7). This stepwise type of decomposition mechanism is not unprecedented. Indeed tetroxides [74–77] and hyponitrites [78–82] have been shown to decompose by analogous mechanisms; some have suggested symmetric homolytic cleavage as the first step [83,84], but it is only the asymmetric cleavage of

tetroxides that leads to product formation. Decomposition appears to proceed via initial S—O bond homolysis and is about 6–8 kcal mol^{-1} more thermally demanding than overcoming the internal S—S rotation barrier.

FACTORS GOVERNING THE CONNECTIVITY IN DIALKOXY DISULFIDES/ THIONOSULFITES

Only two classes of compounds containing both the branched ($R_2S{=}S$) and unbranched (RSSR) constitutionally isomeric motifs have been experimentally verified: FS(S)F [62,85–96] and a small group of thionosulfites [23,51–53,97], compounds containing the OS(S)O moiety along with the better studied dialkoxy disulfides. Although many others [98–121] have suggested the existence of the thiosulfoxide species bound to less electronegative groups as transient intermediates, to our knowledge none of these have been captured as stable species within the temperature ranges common to solution chemistry [122].

Of particular interest is the fact that not only do compounds with the formula S_2F_2 and $R_2S_2O_2$ exist in their branched configurations, but in the latter case they commonly exist as their unbranched dialkoxy disulfide isomers, **1** versus **2** [18,45–47,57–59,123]. Prior to our efforts in the area, the known branched isomers were universally embedded in a five-membered ring, **2a** [23,51–53,56,97,124]. We determined computationally that the primary factor governing isomeric preference is ring size of the heterocycle as evidenced in Fig. 3. Thionosulfites were expected to be preferred in small rings, whereas dialkoxy disulfides were expected to be more stable in larger macrocycles or in acyclic cases (which may be thought of as an infinitely large ring). The trend also suggested that a seven-membered ring thionosulfite would be nearly isoenergetic with its eight-membered dialkoxy disulfide counterpart.

A

B
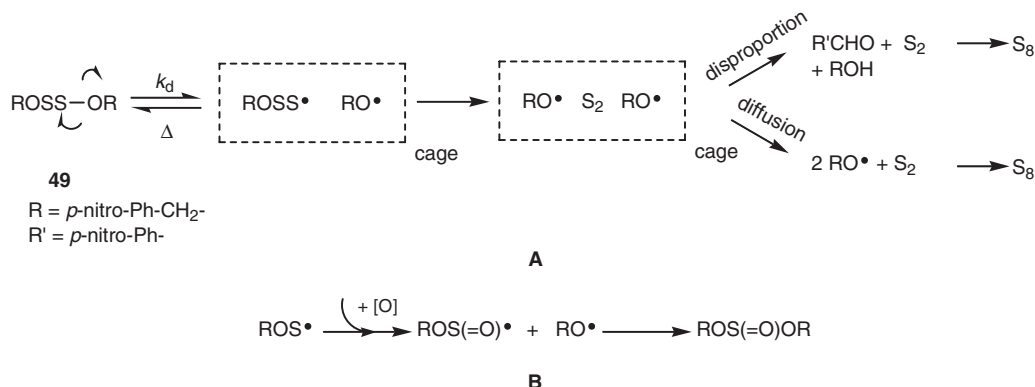
SCHEME 7   Thermally induced radical decomposition mechanism of ROSSOR (R = *p*-NO$_2$-Ph-CH$_2$).

Equilibrium position
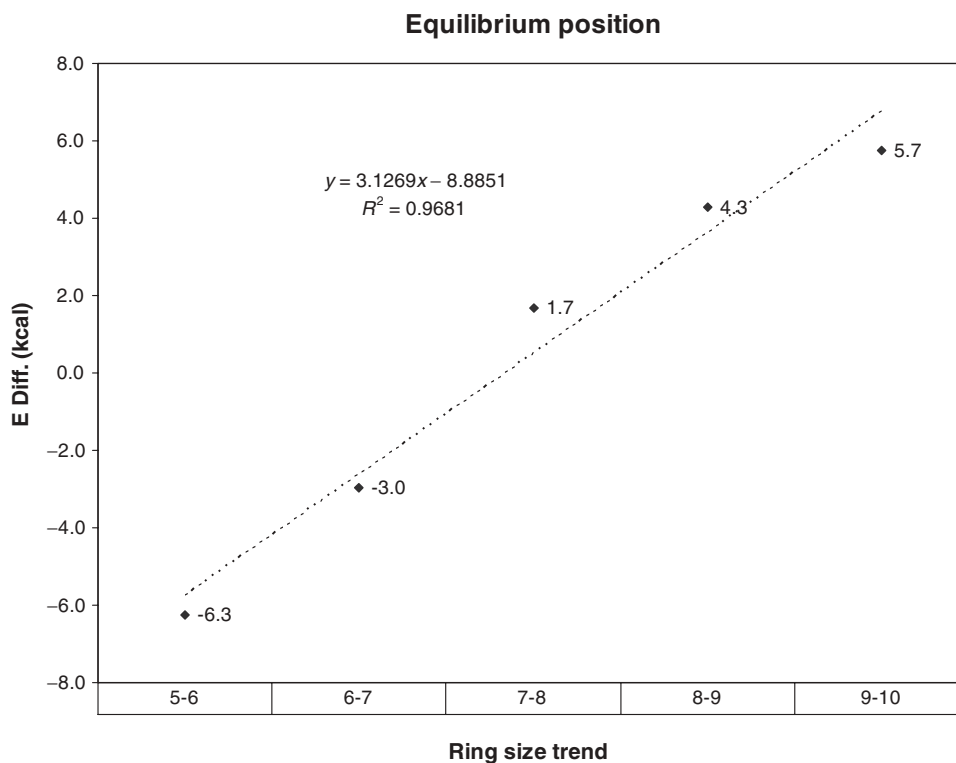

$y = 3.1269x - 8.8851$
$R^2 = 0.9681$

FIGURE 3 Ring-size trend in DFT $\triangle E$s (B3LYP/6-31G(2d)) for increasing ring size of the heterocycle. A positive value indicates that the dialkoxy disulfide isomer is the more stable.

The predicted crossover phenomenon can be understood as a consequence of two opposing effects; one stabilizing and the other destabilizing. The calculated, strained disulfide dihedral angles of six-membered and seven-membered ring ROSSORs of 64.8° and 78.6°, respectively are well below the experimental values observed for acyclic analogs (85–95°) [18,45–47,57–59,123]. The eight-membered ring analog is the minimum ring size required to adopt an optimal ϕ(OS−SO) dihedral angle (94.3°). For the (RO)$_2$S=S system with axial S=S bonds, the near-cis and near-trans LP−O−S=S torsion angles contribute to maximum orbital overlap between the oxygen lone pairs and the $\sigma_{S=S}^*$ antibonding orbital for seven-membered thionosulfites resulting in stabilization of this isomer by negative hyperconjugation [125,126]. Larger rings and acyclic forms elicit less favorable LP-$\sigma_{S=S}^*$ angular interactions. The two
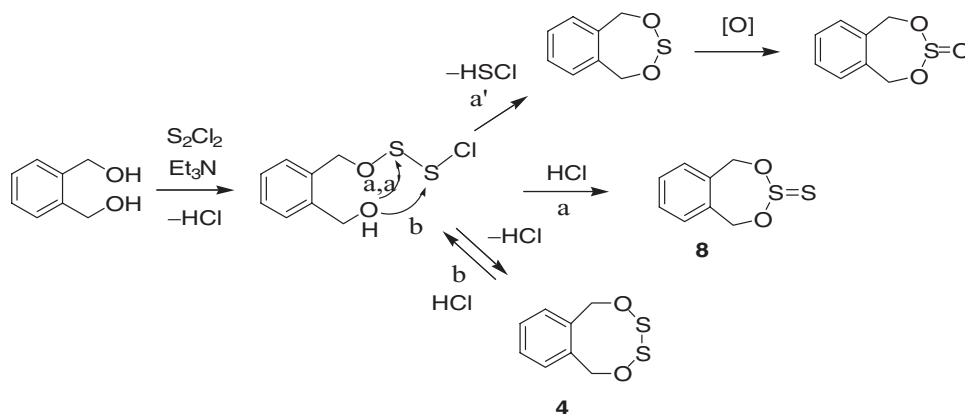
SCHEME 8 Proposed cyclization routes for the formation of either **4** or **8** [55].
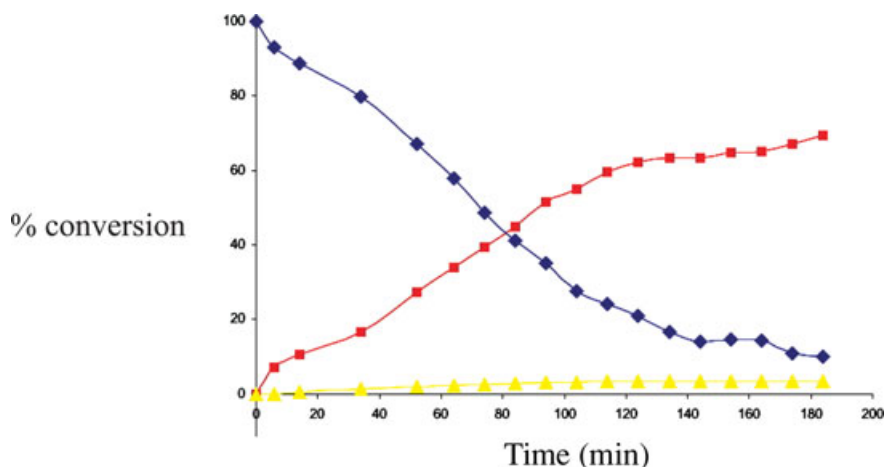
FIGURE 4   Monitoring the conversion of **4** (◇) to **8** (□) and sulfoxylate (△) by ^{1}H NMR (CDCl$_3$, 22°C) in the presence of HCl and tetrabutylammonium bromide with 1,3,5-tri-*t*-butylbenzene as an internal standard.

effects converge at ring sizes of eight and seven, respectively. We targeted this ring system and used 1,2-benzenedimethanol as a model diol. We were able to isolate both constitutional isomers and by varying the reaction conditions, promote the formation of one over the other [55].

What factors determine the formation of **4** and **8**? Initially, it was unclear whether **8** was the result of an isomerization process from **4** or whether **8** formed independently from **4** in the reaction. A plausible mechanism for the conversion of **4** to **8** is suggested in Scheme 8. Although **4** is rapidly formed from 1,2-benzenedimethanol, in acid it reverts to the chloro-alkoxy disulfide intermediate. Apparently, an acid-promoted 7-*exo-tet* S$_N$2' mechanism affords **8**. The same functional group transformation has been reported when a dialkoxy disulfide is treated with SCl$_2$ under carefully controlled conditions [127].

To substantiate these observations further, the acid-promoted conversion of a purified sample of **4** to **8** was monitored by ^{1}H NMR as depicted in Fig. 4. The acid-promoted disappearance of **4** is accompanied by the simultaneous formation of **8** as well as trace sulfoxylate.

One implication of these experiments is that thionosulfite **8** is thermodynamically more stable than dialkoxy disulfide **4**. Qualitatively, this is at odds with the DFT calculations of Fig. 3, which predict the reverse by 0.5–1.7 kcal mol^{-1}. We determined that this is the result of basis set and method choice. The use of larger basis sets inverts the isomeric preference between FS-SF and F$_2$(S=S) [128]. Although we have not examined the considerably larger structures **4** and **8** with the much higher level calculations used by Schleyer, it is likely that a similar stability reversal would be obtained here as well. In spite of the uncertainty in the relatively small DFT energy difference between **4** and **8** using the B3LYP/6-31G(2d)//MM3* model, predicted energy differences between other dialkoxy disulfide/thionosulfite pairs are sufficiently large that the crossover correlation (Fig. 3) is not compromised.

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