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Competitive oxidations of dibenzyl trisulfide *vs.* substituted aryl polysulfides

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The competitive oxidations of dibenzyl trisulfide and several substituted aryl polysulfides were conducted using *meta*-chloroperoxybenzoic acid as the oxidizing agent. The reaction products were determined and analyzed using ^{1}H NMR spectroscopy. The results indicate that aryl trisulfides are not competitive in oxidation rates with dibenzyl trisulfides, the latter are oxidized much faster. However, aryl disulfides containing strong electron-donating groups are competitively oxidized and an *aryl substitution effect* was observed. The decomposition products of dibenzyl trisulfide 1-oxide were determined to be dibenzyl tetrasulfide and dibenzyl disulfide-1,1-dioxide.

Keywords: disulfides; trisulfides; trisulfide 1-oxides; polysulfide oxidation; decomposition

1. Introduction

Trisulfide oxidations are both interesting and challenging to study because of their resulting product regiochemistry and the relative instability of the oxidized derivatives. Both acyclic alkyl and aryl trisulfides have been shown (*1*) to be preferentially oxidized to trisulfide 1-oxides by numerous oxidizing agents (Scheme 1). Trisulfide 2-oxides, R-SS(O)S-R, have been produced by oxidation of cyclic alkyl polysulfides [for selected review articles see ref. (*2*)], but are generally synthesized using thionyl chloride, $SOCl_2$, and 2 equivalents of a thiol (*3*). Derbesy and Harpp (*1*) have accounted for the trisulfide 1-oxide regiochemistry by suggesting that an *alkyl substitution effect* operates and that the more electron donating the R group attached to the terminal sulfur, the faster oxidation occurs (*4*). [Furthermore Block showed that the more electron rich sulfur atom in unsymmetrical alkyl substituted disulfides was more likely to be oxidized by a peroxyacid.] In fact, Harpp demonstrated that when an equivalent amount of di-*t*-butyl disulfide, diisopropyl disulfide, and dibenzyl disulfide are competitively oxidized using 0.33 equivalents of *meta*-chloroperoxybenzoic acid (*m*-CPBA) the corresponding 1-oxide product distributions are 60, 38, and 2%. Harpp argued that the electronic character of the terminal sulfur appears to be more influential than steric effects because the dibenzyl disulfide was barely oxidized.

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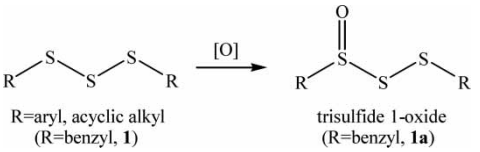


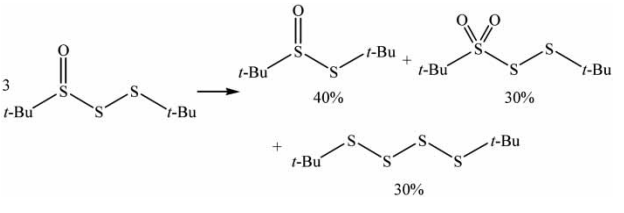
Scheme 1.

A second important factor when considering the oxidative reactivities of polysulfides is the number of sulfur atoms in the polysulfide linkage. As a general rule, as the number of sulfurs in the linkage increases, the reactivity of the terminal sulfur atoms toward an oxidant decreases. Derbesy and Harpp (*5*) have demonstrated a *sulfur chain length effect* by showing that di-*t*-butyl sulfide reacted 20 times faster than di-*t*-butyl disulfide. The rate of oxidation was also greater for disulfides than trisulfides and tetrasulfides, but diminished as more sulfurs were added to the chain (Scheme 2). Harpp and Derbesy suggested that adding sulfur atoms to the linkage decreases the electron density of the terminal sulfur, therefore decreasing the rate of oxidation.

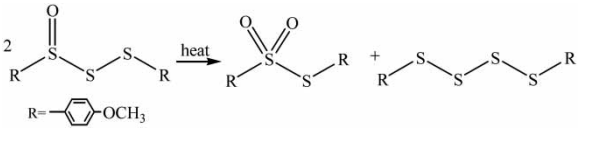
t-Bu-S-Bu-*t* >> *t*-Bu-SS-Bu-*t* > *t*-Bu-SSS-Bu-*t* > *t*-Bu-SSSS-Bu-*t*

Scheme 2.

A complicating factor in the study of oxidation reactions of trisulfides is the relative instability of the resultant trisulfide 1-oxides. Derbesy and Harpp (*6, 7*) and Clennan and Stensaas (*8*) have documented the subsequent decomposition products of di-*t*-butyl 1-oxide (Scheme 3) and bis(*p*-methoxyphenyl) trisulfide 1-oxide (Scheme 4). The alkyl and aryl 1-oxides produced different mixtures of decomposition products. Harpp proposed steric hindrance as a reason for the complicated mixture of products with di-*t*-butyl trisulfide 1-oxide.



Scheme 3.



Scheme 4.

Aryl trisulfide oxidations have received less attention (*6, 8, 9*) than their alkyl counterparts. We are interested in investigating whether an *aryl substitution effect* will operate in substituted aryl polysulfides and if electron-withdrawing substituents will promote production of trisulfide 2-oxide products. Furthermore, we are interested in whether phenyl substituents in dibenzyl trisulfides will affect their oxidation rates. Since this has been demonstrated in alkyl systems previously, we

would expect a faster rate of oxidation in the presence of electron-donating substituents. Studying the stability of the trisulfide 1-oxides is also important for further application of polysulfides. In fact, several substituted dibenzyl trisulfide derivatives have been found to be potent anti-tumor agents (*10*).

2. Results and discussion

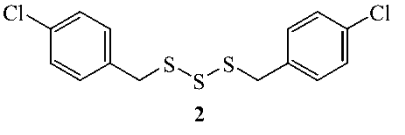
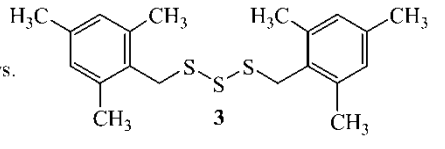
2.1. *Competitive oxidations of substituted dibenzyl trisulfides*

To investigate the oxidative reactivity of substituted dibenzyl trisulfides, we synthesized bis(4-chloro-α-toluene) trisulfide (*11*) (**2**) and bis(2,4,6-trimethylbenzyl) trisulfide (**3**) according to the literature methods. The competitive oxidation of dibenzyl trisulfide (**1**) and **2** (a 1:1 mixture) using 1 equivalent of *m*-CPBA as the oxidizing agent was conducted and the corresponding 1-oxide products (**1a, 2a**) were analyzed using ^{1}H NMR. Table 1 shows the percentage of 1-oxide products found in each reaction mixture. It should be noted that only 1-oxide products were formed, even with the inductive electron-withdrawal of the chlorine substituent in **2**.

The results were somewhat surprising and indicate that **1** and **2** are oxidized at the same rate since their 1-oxide products (**1a** and **2a**) were formed in equal amounts. Even though an electron-withdrawing chlorine has been added to the phenyl group in **2**, the nucleophilicity of the terminal sulfur does not appear to change. Furthermore, **3** was competitively oxidized directly against **2** using the same reaction conditions and the result was the same; the product mixture contained 50% of the 1-oxide **2a** and 50% of the 1-oxide **3a** (Table 1).

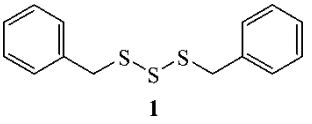
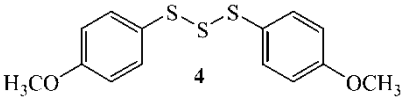
The results indicate that the terminal sulfurs in substituted dibenzyl trisulfides are not susceptible to electronic effects due to substituents on the phenyl group. The –CH_2– group appears to dampen the electronic effect most likely by blocking the resonance of the electron pair on the terminal sulfur with the aromatic ring. Not allowing conjugation of the benzyl trisulfide terminal sulfur with the aromatic ring would account for the lack of a substituent effect toward oxidation. The literature shows (*5*) that alkyl disulfides are responsive to differences in the alkyl group, specifically the rate of oxidation of di-*t*-butyl disulfide produced 60% 1-oxide product, whereas diisopropyl disulfide only produced 38% 1-oxide. Clearly, the electronic character of the terminal sulfur is important in determining the regiochemistry of oxidation in polysulfides. However,

Table 1. Percentage of 1-oxide products formed from 1-equivalent *m*-CPBA competitive oxidations.

Benzyl trisulfide competition	% of 1-oxides formed
1 vs.  **2**	50% **1a**, 50% **2a**
2 vs.  **3**	50% **2a**, 50% **3a**

The benzylic signals were identified using ^{1}H NMR (acetone-d_6). δ CH_2: **1** (4.09), **1a** (4.12, 4.40), **2** (4.09), **2a** (4.10, 4.43), **3** (4.25), **3a** (4.25, 4.33, 4.35, 4.65).

Table 2. Percentage of 1-oxide products formed from 1-equivalent *m*-CPBA competitive oxidation of **1** and **4**.

Trisulfide	% of 1-oxides formed
 **1**	>99% **1a**
 **4**	<1% **4a**

The methoxy signals were identified using ^{1}H NMR (acetone-d_6). δ OCH_3: **4** (3.81), **4a** (3.84, 3.90).

substituted dibenzyl trisulfide systems are different in that the electron-donating ability of the substituted phenyl group does not control the oxidative reactivity of compounds **1–3**. Furthermore, it also appears that for **1–3** steric factors are not important toward their susceptibility of oxidation.

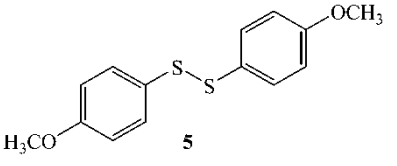
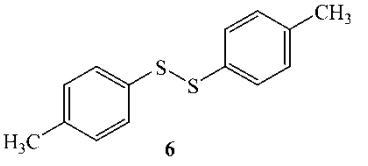
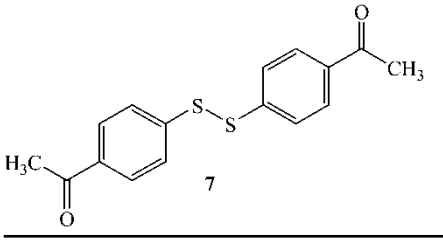
2.2. *Competitive oxidation of dibenzyl trisulfide 1 and aryl trisulfide 4*

If the $-CH_2-$ hinders the electronic effect of the phenyl substituent on the terminal sulfur's oxidative reactivity in benzylic trisulfides, then how would competitive oxidation of a substituted aryl trisulfide *vs.* dibenzyl trisulfide compare? Using the same reaction conditions as above, bis (*p*-methoxyphenyl) trisulfide (**4**) was competitively oxidized against **1** and the results are shown in Table 2. The results indicate that **4** is not competitive with **1** even when a strong electron-donating group like methoxy is used. Therefore, it appears that the alkyl donating effect of the benzyl group in **1** is much more important than the *p*-methoxyphenyl group in **4** for determining the nucleophilicity of the terminal sulfur in trisulfides. Furthermore, the decreased nucleophilicity of the terminal sulfur in **4** can be attributed to resonance with the aromatic ring.

2.3. *Competitive oxidations of substituted aryl disulfides* vs. *dibenzyl trisulfide (1)*

Since aryl trisulfide **4** was not competitive with **1**, we conducted a comparative study with the following aryl disulfides: bis(*p*-methoxyphenyl) disulfide (**5**), bis(*p*-tolyl) disulfide (**6**), and bis (*p*-acetylphenyl) disulfide (**7**). Compounds **5–7** were individually oxidized *vs.* **1** using the same reaction conditions as above, and the results are listed in Table 3. The results indicate that there is a difference in the oxidative reactivity depending on the electron donating ability of the substituent on the aryl disulfide. The molecule with the strongest electron-donating ability, **5**, formed 59% of the 1-oxide product **5a** and the methyl substituted **6** only formed <5% 1-oxide product **6a** when oxidized against dibenzyl trisulfide **1**. As expected, the acetyl substituted compound **7** was not competitive against **1** and did not form any oxidized product under our conditions. Based on this data, it appears that only aryl disulfides with very electron-rich sulfur atoms will exhibit the nucleophilicity required to compete with dibenzyl trisulfide for oxidation. Trisulfide **4** was not competitive with **1**, but the *sulfur chain length effect* allowed the corresponding disulfide **5** to be competitive. Furthermore, due to the ability of the terminal sulfurs in **5–7** to resonate with their aromatic rings, substituents greatly affect susceptibility towards oxidation.

Table 3. Percentage of 1-oxide products formed from 1-equivalent *m*-CPBA oxidation of **5–7** *vs.* dibenzyl trisulfide **1**.

Aryl disulfides	% of 1-oxides formed
 **5**	59% **5a**, 41% **1a**
 **6**	<5% **6a**, >95% **1a**
 **7**	0% **7a**, 100% **1a**

The methoxy, methyl, and acetyl proton signals were identified using ^{1}H NMR: (acetone-d_6). δ OCH_3: **5** (3.80), **5a** (3.87, 3.90), δ CH_3: **6** (2.29), **6a** (2.38, 2.42) ($CDCl_3$) δ $C(O)CH_3$: **7** (2.56), **7a** (2.63, 2.64).

2.4. *Decomposition products of dibenzyl trisulfide 1-oxide (1a)*

Thermal decomposition of trisulfide 1-oxides has been reported in the literature. Harpp noted that di-*t*-butyl trisulfide 1-oxide took 12 hours at 45 °C to decompose and Clennan and Stensaas reported that 95% of **4a** decomposed within 5 hours at 25 °C. The general trend appears to be that alkyl groups attached to the trisulfide linkage lend stability to the system.

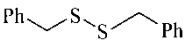
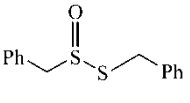
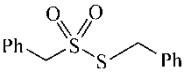
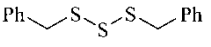
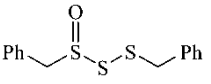
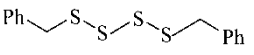
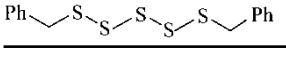
To investigate the stability of **1a**, a 0.80 equivalent *m*-CPBA to **1** oxidation was conducted. Under these conditions only **1a** was produced (δ 4.11, 4.40) with remaining unoxidized **1** (δ 4.09). Table 4 provides a list of proton chemical shifts for the benzylic hydrogens of several benzylic polysulfides and oxidized derivatives. The analysis of the decomposition products of **1a** was conducted by allowing a sample to remain at 25 °C in acetone-d_6 and monitoring the benzylic protons using ^{1}H NMR after 23, 47, 119, and 163 hours. **1a** was completely decomposed after 163 hours.

After 23 hours, the appearance of two new major peaks δ 4.22 and 4.51 occurred. These new peaks grew in at the expense of the two initially formed benzylic peaks from the oxidation (δ 4.11, 4.40) assigned to **1a**. The new peaks correspond to the disulfide-1,1-dioxide **8** (δ 4.23, 4.51) and the tetrasulfide **9** (δ 4.22). Two minor peaks also started to grow in at δ 3.70 and δ 4.28 which have been assigned to dibenzyl disulfide **10** and dibenzyl pentasulfide **11**, respectively. These minor peaks continue to grow even after the disappearance of the 1-oxide and appear to be produced from the presence of the unoxidized trisulfide and forming tetrasulfide. Steudel and Kustos (*2*) have noted that polysulfide decomposition (Scheme 5) is catalyzed by numerous factors.

$$2\ R_2S_n \rightleftharpoons R_2S_{n+x} + R_2S_{n-x}$$

Scheme 5.

Table 4. Proton benzylic chemical shifts for benzylic polysulfides and oxidized derivatives and melting points.

Compound		δ (CH_2)	MP (°C)
	**10**	3.70	71–72 (*15*)
	**12**	4.10, 4.29	130 (*11*)
	**12**	4.23, 4.51	106 (*11*)
	**12**	4.09	49–50 (*11*)
	**1a**	4.11, 4.40	–
	**9**	4.22	52–53 (*20*)
	**11**	4.28	–

Proton NMR in acetone-d_6.

To investigate the acidic stability of dibenzyl trisulfide and further verify the formation of tetrasulfide **9** and disulfide **10** from this decomposition, **1** was dissolved in CH_2Cl_2 and a few drops of concentrated HCl were added. The mixture was stirred and refluxed at 90 °C for 10 hours. The decomposition products were an equal mixture of **9** and **10** with only a 9% conversion of **1**. This result indicates that dibenzyl trisulfide is fairly stable to catalytic acidic conditions.

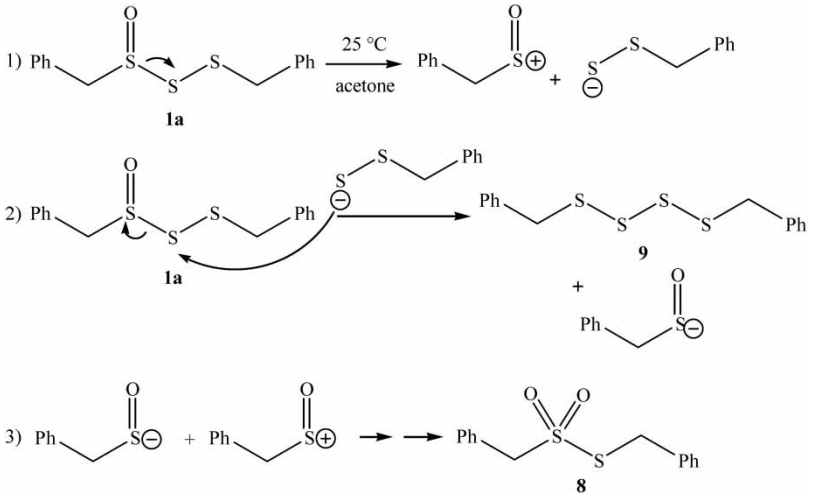
Production of **8** and **9** from the decomposition of **1a** is interesting because Harpp previously showed (*6, 7*) that the di-*t*-butyl trisulfide 1-oxide produces a more complicated mixture of products [Scheme 3]. To our knowledge, this is the first example of an alkyl trisulfide 1-oxide that produces the same decomposition mixture as an aryl trisulfide 1-oxide [Scheme 4]. This result is not completely unexpected since the steric demands in the dibenzyl system are not as great as the *t*-butyl system.

Clennan and Stensaas previously (*8*) suggested the mechanism depicted in Scheme 6 for this decomposition. The first step involves heterolytic cleavage, forming two charged species. In step 2, the anion attacks a second molecule of **1a**, forming tetrasulfide **9** and a sulfinyl anion. Step three involves combination of the sulfinyl anion and cation to initially form the disulfide 1,2-dioxide which subsequently rearranges to product **8** via a well-documented mechanism (*6, 7*). Derbesy and Harpp suggested a more complicated mixture of products because in step 3 the *t*-butyl sulfinyl anion and cation face steric hindrance toward combination.

3. Experimental

3.1. *General experimental*

Dibenzyl trisulfide (**1**), bis(*p*-tolyl) disulfide (**6**), dibenzyl disulfide (**10**), 4-chloro-α-toluene thiol, 2,4,6-trimethylbenzyl mercaptan, *p*-methoxyphenyl thiol, benzyl mercaptan, (phenylthio)acetic



Scheme 6. Proposed mechanism for decomposition of dibenzyl trisulfide 1-oxide (1a)

acid, nitrobenzene, aluminum trichloride, carbon disulfide, acetyl chloride, phosphorus pentachloride, m-CPBA, acetone-d_6, deuterated chloroform, and tetramethylsilane (TMS) were purchased from Aldrich Chemical and used as received. Hydrogen peroxide (30%) and sodium bicarbonate were obtained from Fisher and used as received. Sulfur dichloride, SCl_2, was distilled into a flask containing phosphorus pentachloride immediately prior to use. Sulfur monochloride, S_2Cl_2, was distilled immediately before use. Pyridine, dimethyl sulfoxide, diethyl ether, and dichloromethane were used as received.

3.2. *Instrumentation*

^{1}H NMR spectra were recorded on either a JEOL Eclipse 400 MHz FT-NMR or a Varian EM 360-L 60 MHz spectrometer and referenced internally to TMS. Melting points were taken in open capillaries on a Mel-Temp II apparatus and are uncorrected. Thin layer chromatography was carried out on 250 μm layer silica gel flexible plates and column chromatography was carried out with SilicAR CC-4 silica gel obtained from Mallinckrodt.

3.3. *General oxidation procedure for polysulfides*

The oxidations were carried out according to a literature procedure (*5*). One equivalent of polysulfide was dissolved in dichloromethane with stirring in a round bottom flask submerged in an ice bath and also attached to an addition funnel. *m*-CPBA (0.67–1.0 equivalent) dissolved in dichloromethane was added dropwise over a 15 minute period. The solution was allowed to stir for an additional 45 minutes. The reaction mixture was worked up by washing with two 20 mL portions of water, three 20 mL portions of 2 M NaOH, and 20 mL portions of water until neutral to pH paper. The pH was approximately 8–9 during the base washes. The organic layer was separated, dried with anhydrous $MgSO_4$, filtered, and the solvent evaporated. Under these conditions, the 1-oxide is the expected major product along with some remaining unreacted polysulfide. The oxidations were run both in the presence and absence of 1 equivalent of sodium bicarbonate to neutralize acid formed in the reaction. The results were the same whether bicarbonate was added or not. NMR spectra were taken immediately following workup.

Spectral data for *polysulfide 1-oxides* (acetone-d_6): **(1a)** ^{1}H NMR: δ 4.12 (s, 2H), 4.40 (s, 2H), 7.25–7.40 (m, 10H). ^{13}C NMR: δ 44.65, 62.15, 127.87, 128.48, 128.70, 128.78, 129.78, 130.63, 130.66, 136.54.
(2a) ^{1}H NMR: δ 4.10 (s, 2H), 4.43 (s, 2H), 7.31 (d, 2H, $J = 8.4$ Hz), 7.43 (d, 2H, $J = 8.4$ Hz), 7.63 (d, 2H, $J = 8.4$ Hz), 7.93 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR: δ 43.49, 61.11, 128.74, 128.82, 131.50, 132.28, 133.23, 133.27, 135.68, 136.24.
(3a) ^{1}H NMR: δ 2.22 (s, 3H), 2.23 (s, 3H), 2.36 (s, 6H), 2.40 (s, 6H), 4.25 (d, 1H, $J = 11.4$ Hz), 4.33 (d, 1H, $J = 11.4$ Hz), 4.35 (d, 1H, $J = 13.4$ Hz), 4.65 (d, 1H, $J = 13.4$ Hz), 6.86 (s, 2H), 6.91 (s, 2H). ^{13}C NMR: δ 19.04, 19.23, 20.11, 20.25, 40.09, 57.54, 125.28, 128.90, 129.18, 129.34, 137.57, 137.72, 137.95, 138.30.
(4a) ^{1}H NMR: δ 3.84 (s, 3H), 3.90 (s, 3H), 7.00–7.70 (m, 8H).
(5a) ^{1}H NMR: δ 3.87 (s, 3H), 3.90 (s, 3H), 7.01 (d, 2H, $J = 8.3$ Hz), 7.13 (d, 2H, $J = 8.3$ Hz), 7.44 (d, 2H, $J = 8.3$ Hz), 7.63 (d, 2H, $J = 8.3$ Hz). ^{13}C NMR: δ 55.97, 56.16, 115.44, 115.81, 121.32, 126.97, 136.62, 138.22, 162.84, 163.47.
(6a) ^{1}H NMR: δ 2.38 (s, 3H), 2.42 (s, 3H), 7.27 (d, 2H, $J = 8.0$ Hz), 7.41 (d, 2H, $J = 8.0$ Hz), 7.45 (d, 2H, $J = 8.4$ Hz), 7.62 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR: δ 20.48, 20.62, 124.23, 126.89, 129.77, 130.17, 135.19, 135.39, 140.88, 142.43. Mp: 91–92 °C.
(7a) ^{1}H NMR ($CDCl_3$): δ 2.63 (s, 3H), 2.64 (s, 3H), 7.49 (d, 2H, $J = 8.4$ Hz), 7.68 (d, 2H, $J = 8.4$ Hz), 7.90 (d, 2H, $J = 8.4$ Hz), 7.99 (d, 2H, $J = 8.4$ Hz).

3.4. *General competitive oxidation procedure*

The competitive oxidations were carried out using a 1:1 molar equivalent of **1** and the appropriate trisulfide/disulfide. The following example is representative. Compounds **7** (0.103 mmol) and **1** (0.104 mmol) were dissolved and stirred in 15 mL of CH_2Cl_2 in an ice bath. *m*-CPBA (0.127 mmol, 1 equivalent) dissolved in CH_2Cl_2 was added dropwise with stirring. The rest of the procedure is the same as described above. Under these conditions only one of the polysulfides could be completely oxidized to the 1-oxide product.

3.5. *Common trisulfide syntheses and/or spectral data*

3.5.1. *Dibenzyl trisulfide (**1**)*

This was purchased from Aldrich. Mp: 47–48 °C [lit. (*12*) 49 °C]. ^{1}H NMR (acetone-d_6): δ 4.09 (s, 4H), 7.35 (m, 10H). ^{13}C NMR (acetone-d_6): δ 42.66, 127.56, 128.60, 129.54, 137.00.

3.5.2. *Bis(4-chloro-**α**-toluene) trisulfide (**2**)*

This was synthesized according to the literature procedures (*11*). One equivalent of distilled sulfur dichloride and 2 equivalents of pyridine were added to 25 mL of diethyl ether in a round bottom flask. Two equivalents of 4-chloro-α-toluene thiol was dissolved in 25 mL of diethyl ether in an addition funnel and added dropwise over a period of 30 minutes with stirring. The reaction mixture was submerged in an ice bath and stirred for 2 hours. The reaction mixture was then added to a separatory funnel and washed with two 25 mL portions of ice water, two 25 mL portions of 2 M NaOH, and two 25 mL portions of ice water until neutral to pH paper. The organic layer was separated, dried with anhydrous $MgSO_4$, filtered, and evaporated. White crystals formed which were recrystallized with hexanes.

Mp: 84–85 °C. ^{1}H NMR (*13*) (acetone-d_6): δ 4.09 (s, 4H), 7.37 (m, 8H) [(*10*), reports in $CDCl_3$ δ 3.98 (s, 4H), 7.22 (d, 4H, $J = 8.4$ Hz), 7.29 (d, 4H, $J = 8.4$ Hz). We did not observe a doublet

of doublets using acetone-d_6 as the solvent]. ^{13}C NMR (acetone-d_6): δ 41.62, 128.65, 131.26, 132.90, 136.08.

3.5.3. *Bis(2,4,6-trimethylbenzyl) trisulfide (**3**)*

This was synthesized using the same method. Feathery white crystals were produced in a 97% yield and were recrystallized using hexanes. Mp: 107–108 °C. ^{1}H NMR (acetone-d_6): δ 2.20 (s, 6H), 2.38 (s, 12H), 4.25 (s, 4H), 6.85 (s, 4H). ^{13}C NMR (acetone-d_6): δ 19.00, 20.18, 38.14, 129.09, 129.12, 137.31, 137.36.

3.5.4. *Bis(p-methoxyphenyl) trisulfide (**4**)*

This was synthesized using the same method. The yellow crystals were recrystallized using hexanes in a 64% yield. Mp: 73–74 °C [lit. (*14*) 73–74 °C]. ^{1}H NMR (acetone-d_6): δ 3.81 (s, 6H), 6.90 (m, 4H), 7.50 (m, 4H). ^{13}C NMR (acetone-d_6): δ 55.87, 115.79, 127.65, 134.82, 161.77.

3.6. *Common disulfide syntheses and/or spectral data*

3.6.1. *Bis(p-methoxyphenyl) disulfide (**5**)*

This was synthesized in a 70% yield according to the literature procedure (*15*). Mp: 43–44 °C [lit. (*16*) 44–45 °C]. ^{1}H NMR (acetone-d_6): δ 3.80 (s, 6H), 6.93 (d, 4H, $J = 8.3$ Hz), 7.42 (d, 4H, $J = 8.3$ Hz). ^{13}C NMR (acetone-d_6): δ 55.84, 115.74, 128.75, 133.39, 161.28.

3.6.2. *Bis(p-tolyl) disulfide (**6**)*

This was purchased from Aldrich. Mp: 45–46 °C [lit. (*12*) 47 °C]. ^{1}H NMR (acetone-d_6): δ 2.29 (s, 6H), 7.17 (d, 4H, $J = 8.4$ Hz), 7.40 (d, 4H, $J = 8.4$ Hz). ^{13}C NMR (acetone-d_6): δ 20.19, 128.43, 130.00, 133.50, 137.81.

3.6.3. *Bis(p-acetylphenyl) disulfide (**7**)*

This was synthesized according to the literature procedures (*17*). *p*-Acetyl(phenylmercapto) acetic acid was first synthesized from acylation of (phenylthio)acetic acid in a 60% yield. Mp: 155–157 °C [lit. (*17*) 156–158 °C]. **7** was synthesized from *p*-acetyl(phenylmercapto) acetic acid and hydrogen peroxide under acidic conditions. The oily brown product was triturated with 1.5 M NaOH to form a crystalline product. Recrystallization with aqueous methanol produced white crystals in a 11% yield (not optimized). Mp: 91–93 °C [lit. (*17*) 96–97 °C]. ^{1}H NMR ($CDCl_3$): δ 2.56 (s, 6H), 7.54 (d, 4H, $J = 8.4$ Hz), 7.89 (d, 4H, $J = 8.4$ Hz).

3.6.4. *Dibenzyl disulfide (**10**)*

This was purchased from Aldrich. Mp: 71–72 °C [lit. (*15*) 71–72 °C). ^{1}H NMR (acetone-d_6): δ 3.70 (s, 4H), 7.31 (m, 10H). ^{13}C NMR (acetone-d_6): δ 42.63 127.42, 128.52, 129.51, 137.73.

3.7. *Dibenzyl disulfide 1,1-dioxide (8)*

This was synthesized using a 2 equivalent *m*-CPBA oxidation of dibenzyl disulfide and worked up according to the procedure described above. Mp (*12*): 106 °C. ^{1}H NMR (acetone-d_6): δ 4.23 (s, 2H), 4.51 (s, 2H), 7.35–7.42 (m, 10H). ^{13}C NMR (acetone-d_6): δ 40.27, 67.96, 128.57, 128.67, 129.00, 129.48, 130.44, 131.62, 132.90, 134.09. Solvent effects are substantial for **8** when comparing benzylic chemical shifts in acetone-d_6 and $CDCl_3$. ^{1}H NMR (*18*) ($CDCl_3$): δ 4.02 (s, 2H), 4.19 (s, 2H).

3.8. *Dibenzyl tetrasulfide (9)*

This was synthesized according to a literature procedure (*19*). Mp (*20*): 52–53 °C. ^{1}H NMR (acetone-d_6): δ 4.22 (s, 4H), 7.40 (m, 10H). ^{13}C NMR (acetone-d_6): δ 43.21, 127.72, 128.70, 129.65, 136.72

3.9. *Dibenzyl pentasulfide (11)*

This was not independently synthesized but appeared often as a polysulfide decomposition product. A tentative assignment has been made based on the spectral data. ^{1}H NMR (acetone-d_6): δ 4.28 (s, 4H), 7.43 (m, 10H). ^{13}C NMR (acetone-d_6): δ 43.77, 127.85, 128.77, 129.71, 136.40.

3.10. *Dibenzyl disulfide 1-oxide (12)*

This was synthesized using a 1-equivalent *m*-CPBA oxidation of dibenzyl disulfide and worked up according to the procedure described above. Mp (*12*): 130 °C. ^{1}H NMR (acetone-d_6): δ 4.10 (s, 2H), 4.29 (s, 2H), 7.35–7.40 (m, 10H). Solvent effects are substantial for **12** when comparing benzylic chemical shifts in acetone-d_6 and $CDCl_3$. ^{1}H NMR (*18*) ($CDCl_3$): δ 4.23 (s, 2H), 4.27 (s, 2H).

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