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Synthesis of New Cyclic Thionosulfites

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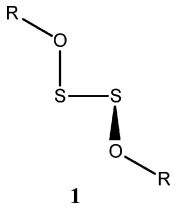
The reaction of a series of 1,2-diols with S_2Cl_2, 1,1′-thiobisbenzimidazole (**4a**), and 1,1′-dithiobisbenzimidazole (**4b**) provides the corresponding thionosulfites, ROS(S)OR (**2**), in moderate to good yield.

Molecules containing the O−S−S−O linkage have been known since 1895;[1] however, debate has ensued with respect to the bond connectivity in these compounds. It was not until 1964 that Thompson and co-workers[2,3] were able to confirm that this functionality could potentially exist in two separate constitutional forms, namely dialkoxy disulfides **1** and a branch-bonded arrangement as thionosulfites **2**. Other isomers such as the thiosulfonate ester (RSO_2SR) previously proposed by Zinner[4] were readily ruled out by their ^{1}HNMR spectra, while other work[5−8] failed to fully distinguish **1** from **2**.



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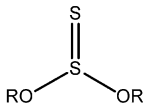

2

Variable-temperature NMR studies[9] for R = Et as well as an analogous EtOS−SNR_2[10] system reveal a reversible coalescence phenomenon from an ABX_3 (with respect to the ethyl group) to an A_2X_3 pattern. This result pointed to one of two conclusions: either the diastereotopicity resulted from an inversion about the tetrahedral sulfur center as could exist with analogous sulfoxide and sulfite[11] systems or an unexpected high barrier to rotation about the S−S bond such as is observed for amide linkages or biphenyl systems.[12,13] Tetrahedral inversion is unlikely because the analogous sulfites have a much higher barrier than that observed for this system.[9] The S−S barrier (*ca*. 18 kcal/mol)[9,14−16] was eventually deemed responsible; subsequent calculations confirmed this conclusion.[17]

In 1965, Thompson treated *dl*-2,3-butanediol with S_2Cl_2 and NEt_3; the unstable product did not exhibit coalescence of the AB pattern and was proposed to exist as a thionosulfite (form **2**).[2] Evidence for this conclusion derived from the close similarities between the ^{1}H NMR of this class of compounds compared to the sulfite analogue as well as similar UV and IR data; in general, compounds **2** are not shelf-stable.[17] Indeed, compounds containing branch-bonded sulfur systems have been hypothesized[18] to exist assuming that the atom immediately adjacent to the sulfur atom was strongly electronegative as in the well-studied S_2F_2 system.[19−24] Further, alkyl branch-bonded structures have been proposed as reactive intermediates in sigmatropic processes.[25,26]

Over 20 years ago, we[27] unequivocally determined the existence of thionosulfites when **3** was synthesized and the first X-ray structure of this class was determined. Compound **3** contains an extremely short S−S bond (1.901 Å)[27] that is quasi-axial with respect to the five-

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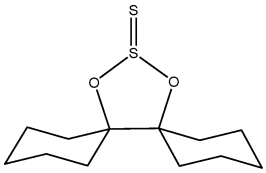
TABLE 1. Yields of Thionosulfites

entry	R_1	R_2	R_3	R_4	diol	product	yield (%)
1	$-(CH_2)_5-$		$-(CH_2)_5-$		**5a**	**3**	50,[a] 41[b]
2	$-(CH_2)_4-$		$-(CH_2)_4-$		**5b**	**6b**[c]	21,[a] 80[b]
3	$-(CH_2)_6-$		$-(CH_2)_6-$		**5c**	**6c**	47[b]
4	$-(CH_2)_7-$		$-(CH_2)_7-$		**5d**	**6d**	14[b]
5	$-(CH_2)_5-$		Me	Me	**5e**	**6e**[c]	72[b]
6	$-(CH_2)_6-$		Me	Me	**5f**	**6f**	77[b]

[a] Method A: 1:1 diol/**4a** in refluxing CCl_4. [b] Method B: 1:1 diol/**4b** in refluxing CCl_4. [c] ^1H NMR data is missing for these two entries; the characterization is therefore incomplete, although the existing data is consistent with the assigned structures.

membered ring core. The shortness of the sulfur−sulfur bond suggests considerable double-bond character similar to the S_2 (1.890 Å),[28] S_2O (1.884 Å),[29] S_2F_2 (1.860 Å),[30] and S_2NR_2 (1.898 Å)[31] systems.



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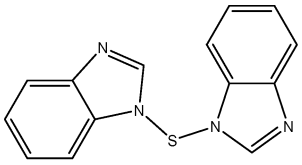
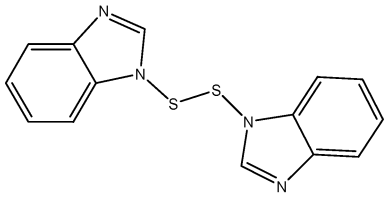
To better understand this fascinating[32] class of compounds, we have synthesized other analogues with the hope that they might eventually provide insight through structural and calculational analysis on the origins of the valence-bond isomerism of **1** and **2**.

A series of 1,2 diols were reacted with with 1,1′-thiobisbenzimidazole (**4a**) and 1,1′-dithiobisbenzimidazole (**4b**);[33] the resulting thionosulfites were then characterized (Table 1).



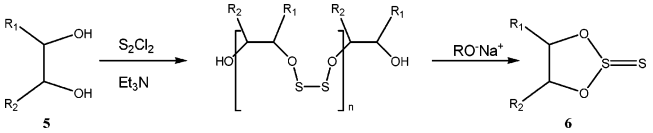
4a



4b

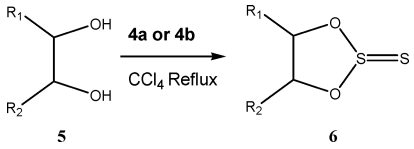
The precursor diols, **5**, were prepared according to a method advanced by Corey.[34] This allowed for both

SCHEME 1. Proposed Mechanism for the Formation of Thionosulfites



5 **6**

SCHEME 2. Synthesis of Thionosulfites Using Either Method A or B (cf. Table 1)



5 **6**

symmetric and asymmetric pinacolic coupling in moderate yield (10−57% for symmetric diols and 37−45% for asymmetric diols). In general, the yields for the diols decreased with increasing size of R_1-R_4 in **5**.[35]

Thompson had initially proposed that the reaction pathway involved the formation of a polymer under high dilution conditions of sulfur monochloride. He suggested[2] (Scheme **1**) that alkoxide-catalyzed unzipping of the proposed polymeric intermediate would yield a thionosulfite as a cyclic monomeric product.

Our method[27] of preparation resulted in similar yields but with no polymeric side products (Scheme 2). We have investigated this procedure using both **4a** and **4b** as effective sulfur transfer reagents. In this manner, thionosulfites **3** and **6b**−**f** were synthesized (Table 1). The monosulfur transfer reagent **4a** produced thionosulfites in moderate yield (21−50%) while the disulfur transfer reagent **4b** was generally more effective (14−80%) and was used for all the diols examined (**5a**−**f**). For all thionosulfites, column chromatography was sufficient to obtain analytically pure samples. While isolable, some of the thionosulfites were nevertheless unstable at room temperature or upon extended exposure to light.

The mechanism of the transformation of **5** to **6** remains unclear particularly with respect to the involvement of *mono*sulfur reagent **4a**. The lack of polymeric side products leads to the conclusion that the mechanism for the process in Scheme 2 is different than that originally advanced by Thompson (Scheme 1). No evidence for the formation of a sulfoxylate ester (ROSOR) intermediate has been found. Moreover, the only byproduct observed was that of benzimidazole.

From desulfurization experiments using triphenyl phosphine on **4b**,[36] this reagent does not cleanly donate two sulfur atoms but nevertheless desulfurizes more rapidly than **4a**. A rearrangement mechanism from the corresponding dialkoxydisulfide isomer **1** is another possible pathway but calculations have suggested that like the sulfur monofluoride (S_2F_2) system (23−46 kcal/mol),[19,37] the unimolecular barrier to isomerization is high (32−38 kcal/mol)[17] making this avenue to thionosulfite formation unlikely.

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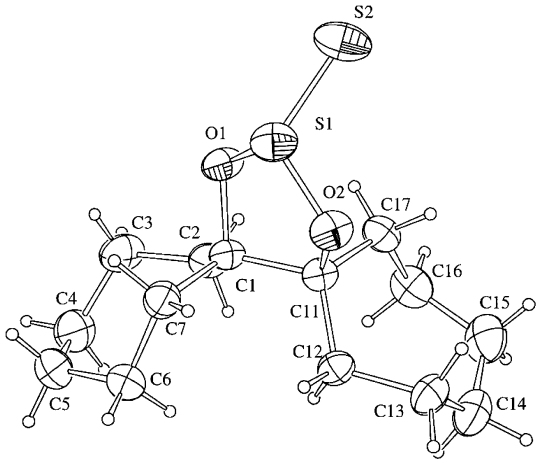

FIGURE 1. ORTEP structure of **6c**.

SCHEME 3. Formation of Sulfites

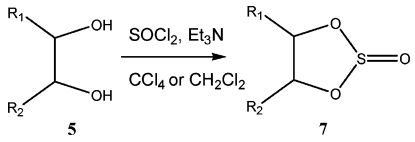

TABLE 2. Yields of Sulfites

entry	R_1	R_2	R_3	R_4	sulfite	yield (%)
1	$-(CH_2)_5-$		$-(CH_2)_5-$		**7a**	60
2	$-(CH_2)_6-$		$-(CH_2)_6-$		**7c**	64

The proton-decoupled ^{13}C NMR spectra of thionosulfites **3** and **6b**−**f** reveal the expected magnetic anisotropy. There is a lack of degeneracy as each carbon is now anisochronous. This is due to the tetrahedral nature of the branched sulfur in the thionosulfite. The extent of the influence of the branch-bonded sulfur atom is hypothesized to be due to its pseudoaxial position with respect to the five-membered ring core as well as its diffuse electron cloud. Indeed, Steudel and co-workers showed *via* calculations that the branched sulfur−sulfur bond is in fact polarized, with the terminal sulfur being negatively charged.[38] This is evidenced by the observed downfield shift of the signal of carbon atoms four-carbons away from the sulfur−sulfur moiety as compared with the parent diol.

We were able to obtain a crystal structure of thionosulfite **6c** (Figure 1). As expected, the geometric features of this molecule differ little with that of the first thionosulfite crystal structure of **3**[27] with a S−S bond distance of 1.910 Å. This distance is much shorter than standard disulfide bond lengths of *ca*. 2.03 Å.[39] There is a twist to the five-membered ring with an O−C−C−O dihedral angle of 45°. This twisting was also observed in **3**.

Although very similar, the NMR spectra of the thionosulfites are distinct from the analogous sulfites, prepared according to Scheme 3 and Table 2. In addition, the absence of a strong band between 1180 and 1240 cm^{-1} indicates the absence of the sulfite moiety. A consistent feature in the infrared spectra of the thionosulfites synthesized is the presence of a strong band at 655 cm^{-1} indicating an S−S stretch; this is in clear agreement with the literature.[17]

Mass spectrometric data provides further evidence to support the existence of new thionosulfites **3** and **6b**−**f**. One characteristic feature of the MS common to all the thionosulfites is the base peak representing the loss of the HS_2O_2 (*m/e* 97) moiety from the parent ion.

Thionosulfites have been regarded as curios until we discovered they could be routinely prepared. The use of reagent **4b** results in a reliable preparation of thionosulfites **3** and **6b**−**f** in moderate yield with no side products and easy purification *via* column chromatography.

Experimental Section

General Experimental Procedures. All reagents were commercially available and were used without further purification save for the following exceptions. Methylene chloride (CH_2Cl_2) and hexamethyldisilazane ($C_6H_{19}NSi_2$−HMDS) were distilled over calcium hydride. Carbon tetrachloride (CCl_4) was dried over 4 Å molecular sieves. Sulfur monochloride (S_2Cl_2) was distilled over sulfur and activated charcoal according to a procedure adapted from Fieser and Fieser,[40] while sulfur dichloride (SCl_2) was fractionally distilled over phosphorus pentachloride (PCl_5). All glassware was oven-dried. Flash chromatography[41] was conducted using 230−400 mesh silica gel. NMR spectra were recorded at 300, 400, or 500 MHz for ^1H NMR and 75 or 101 MHz for ^{13}C NMR. Deuterated chloroform ($CDCl_3$), dried over 4 Å molecular sieves, was used as the solvent of record and spectra were referenced to tetramethylsilane (TMS) or to the solvent peak. Melting points (mp) are uncorrected.

1-Trimethylsilylbenzimidazole. This was prepared on a large scale according to the literature.[33] Yield: 69%. This intermediate was used immediately in the following reactions. ^1H NMR ($CDCl_3$) δ: 8.12 (s, 1H), 7.45 (m, 4H), 0.06 (s, 9H). ^{13}C NMR δ: 145.56, 136.76, 122.75, 122.20, 120.16, 112.45, 97.45, −0.60. MS (EI) *m/z*: 190 ($M^{\bullet+}$), 175, 118, 91. HRMS: calcd for $C_{10}H_{14}N_2Si$ 190.0926, found 190.092(9).

Bis(benzimidazole) Sulfide, 4a. This was prepared on a large scale according to the literature.[33] White powder. Yield: 79%. Recrystallized from CH_2Cl_2/hexanes. Mp: 187−190 (lit.[33] mp 180−185 °C). ^1HNMR ($CDCl_3$) δ: 8.18 (s, 2H), 7.90 (d_{obs}, 2H, J = 7.90 Hz), 7.75 (d_{obs}, 2H, J = 7.90 Hz), 7.47 (td, 2H, J_{AB} = 7.60 Hz, J_{BC} = 1.20 Hz), 7.34 (td, 2H, J_{AB} = 7.60 Hz, J_{BC} = 0.93 Hz). MS (EI) *m/z*: 266 ($M^{\bullet+}$), 118, 91. HRMS: calcd for $C_{10}H_{10}N_4S$ 266.0626, found 266.063(2).

Bis(benzimidazole) Disulfide, 4b. This was prepared on a large scale according to the literature.[33] White powder. Yield: 100%. ^1HNMR ($CDCl_3$) δ: 7.80 (d, 2H, J_{AB} = 8.10 Hz), 7.77 (s, 2H), 7.31, (t_{obs}, 2H, J = 7.65 Hz), 7.20 (t_{obs}, 2H, J = 7.65 Hz), 7.06 (d, 2H, J_{AB} = 8.10 Hz). MS (EI) *m/z*: 298 ($M^{\bullet+}$), 181, 118. HRMS: calcd for $C_{10}H_{10}N_4S_2$ 298.0347, found 298.035(5).

General Synthesis of Thionosulfites 3 and 6b−f Using Method B. A solution of diol **5a** (3.26 g, 16.44 mmol) and **4b** (4.98 g, 16.69 mmol) was dissolved in 150 mL of CCl_4 and heated to reflux under a nitrogen atmosphere for 48 h (the product appeared after 6 h by TLC, 20% EtOAc/CH_2Cl_2). The solution was vacuum filtered through a fine frit, and the solvent was removed under reduced pressure. The resulting oil was flash chromatographed[41] (20% EtOAc/CH_2Cl_2). Yields are reported with respect to the use of method B as described above.

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3. Stable white powder. Yield: 41%. Mp: 100−101 °C (lit.[27] mp 100−101 °C). ^{1}H NMR δ: 2.41 (d, 4H), 1.55 (m, 16H). ^{13}C NMR δ: 94.51, 31.83, 31.15, 25.26, 22.11, 21.96. IR (KBr): 2933, 2861, 1445 (CH_2), 652(s) (S═S). MS (FAB) *m*/*z* (rel intensity): 261 (15), 228 (5), 163 (100).

6b. Clear yellow liquid which solidified in the freezer and decomposed readily in air or $CDCl_3$ to yield an acidic oil with an odor of H_2S. Yield: 80%. Mp: 31−33 °C. ^{1}H NMR is unavailable. ^{13}C NMR δ: 101.86; 34.81, 34.62, 23.82, 23.67. IR (neat): 2965, 2873, 1441 (CH_2), 661(s) (S═S). MS (CI) *m*/*z* (rel intensity): 233, 200 − S, 168 − S_2, 153 − S_2O, 135 − S_2O_2. Anal. Calcd for $C_{10}H_{16}S_2O_2$: 233.06703. Found: 233.06700.

6c. Stable white powder. Yield: 47%. ^{1}H NMR δ 1.40−2.55 (m, CH_2). ^{13}C NMR δ :98.71, 35.24, 34.74, 29.64, 29.53, 23.59, 23.26. IR (KBr): 2923, 2854, 1459, 1445 (CH_2), 651(s) (S═S). MS (CI) *m*/*z* (rel intensity): 289 (2), 256 (1) − S, 224 (2) −S_2, 209 (17) − S_2O, 191 (100) − S_2O_2. Anal. Calcd for $C_{14}H_{24}S_2O_2$: 289.12966. Found: 289.12960. Crystal Structure: $M = 288.45$, monoclinic, space group $P21/c$, $a = 16.854(11)$ Å, $b = 7.000(5)$ Å, $c = 12.77(2)$ Å, $\alpha = 90°$, $\beta = 93.76(9)°$, $\gamma = 90°$, $U = 1503(2)$ Å^3, $T = 293(2)$ K, $D_c = 1.275$ g cm^{-3}, $Z = 4$, μ(Cu Kα) = 0.333 mm^{-1}, 11220 reflections ($11 < \theta < 16.5°$), 2954 unique ($R_{int} = 0.031$), used in all calculations. The final agreement factors are wR2(F^2) = 0.1386 and R1 = 0.0851 for all data. Selected bond distances (Å) and angles (deg): S(1)−O(1) 1.644(2), S(1)−O(2) 1.626(3), S(1)−S(2) 1.910(3), O(1)−C(1) 1.484(3), O(2)−C(11) 1.490(3), C(1)−C(11) 1.557(4), O(2)−S(1)-O(1) 94.23(10), O(1)−S(1)-S(2) 106.08(9), O(2)−S(1)-S(2) 111.45(11), C(1)−O(1)-S(1) 109.8(2), C(11)−O(2)-S(1) 112.7(2), O(2)−S(1)-O(1)−C(1) 20.9(2), O(1)−S(1)-O(2)−C(11) 9.5(2), S(2)−S(1)-O(1)−C(1) 134.6(2), S(2)−S(1)-O(2)−C(11) −99.6(2), S(1)−O(1)-C(1)−C(11) −42.4(2), S(1)−O(2)-C(11)−C(1) −34.2(2).

6d. Solid which decomposes quickly in air or $CDCl_3$. Yield: 14%. ^{1}H NMR δ: 1.40−2.50 (m, CH_2). ^{13}C NMR δ: 98.65, 30.54, 30.26, 27.80, 27.73, 24.84, 22.35, 22.11. IR (neat): 2921, 2851, 1477, 1445 (CH_2), 660(s) (S═S). MS (FAB) *m*/*z* (rel intensity): 317 (6), 307 (16), 289 (12), 273 (11), 237 (18), 219 (94), 154 (100), 136 (82). Anal. Calcd for $C_{16}H_{28}S_2O_2$: 317.16085. Found: 317.16090.

6e. Stable clear oil. Yield: 72%. ^{1}H NMR is unavailable. ^{13}C NMR δ: 93.87, 92.68, 32.23, 31.63, 25.64, 24.47, 23.72, 22.66, 22.49. IR (neat): 2937, 2853, 1445 (CH_2, CH_3), 1386, 1371 (*gem*-CH_3), 655(s) (S═S). MS (FAB) *m*/*z* (rel intensity): 221 (41), 188 (53) − S, 141 (41), 123 (100), 81 (34). Anal. Calcd for $C_9H_{16}S_2O_2$: 221.06702. Found: 221.06700.

6f. Clear oil with minor decomposition in $CDCl_3$. Yield: 77%. ^{1}H NMR δ: 1.45−2.40 (m, 12H), 1.56 (s, 3H), 1.34 (s, 3H). ^{13}C NMR δ: 97.88, 93.33, 35.27, 34.64, 29.34, 29.27, 23.59, 23.08, 22.88. IR (KBr): 2930, 1457 (CH_2, CH_3), 1391, 1374 (*gem*-CH_3), 654(s) (S═S). MS (FAB) *m*/*z* (rel intensity): 235 (11), 202 (15) − S, 155 (21), 137 (100), 95 (28), 81 (39). Anal. Calcd for $C_{10}H_{18}S_2O_2$: 235.08258. Found: 235.08265.

General Synthesis of Sulfites 7a,c. A solution of diol **5a** (99.5 g, 0.50 mmol) was dissolved in 10 mL of CH_2Cl_2. Triethylamine and NEt_3 (140 μL, 1.00 mmol) were added followed by $SOCl_2$ (40 μL, 0.55 mmol). The yellow solution was stirred for 0.5 h at room temperature. The solvent was removed under reduced pressure. The resulting oil was flash chromatographed[41] (60% CH_2Cl_2/hexanes) to yield a crystalline solid.

7a. Yield: 60%. Mp: 58−59 °C. ^{1}H NMR δ: 1.70 (m, CH_2). ^{13}C NMR δ: 92.95, 32.10, 31.54, 25.09, 22.04, 21.99. IR (neat): 2934, 2862, 1447 (CH_2), 1202(s) (S═O). MS (CI) *m*/*z*: 262 ($M^+ + 18$), 245 ($M^+ + 1$), 181 ($M^+ - SO_2 + 1$), 163 ($M^+ - SO_3H_2 + 1$). Anal. Calcd for $C_{12}H_{20}SO_3$: 245.12110. Found: 245.12114.

7c. Yield: 64%. ^{1}H NMR δ: 1.90 (m, CH_2). ^{13}C NMR δ: 97.64, 34.94, 34.60, 29.21, 22.84, 22.69. IR (neat): 2979, 2857, 1462 (CH_2), 1199(s) (S═O). MS (CI) *m*/*z*: 290 ($M^+ + 18$), 273 (M^+), 209 ($M^+ - SO_2$), 191 ($M^+ - SO_3H_2 + 1$). Anal. Calcd for $C_{14}H_{24}SO_3$: 273.15254. Found: 273.15244.

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Supporting Information Available: A crystal structure report for **6c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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