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Reversible Disulfur Monoxide (S_2O)-Forming Retro-Diels−Alder Reaction. Disproportionation of S_2O to Trithio-Ozone (S_3) and Sulfur Dioxide (SO_2) and Reactivities of S_2O and S_3

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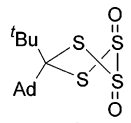
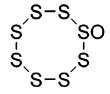
Abstract: 5,6-Di-*tert*-butyl-2,3,7-trithiabicyclo[2.2.1]hept-5-ene 7-endo-oxide (**4**) was prepared by addition of S_2Cl_2 to 3,4-di-*tert*-butylthiophene 1-oxide (**3**) in high yield. The oxidation of **4** with dimethyldioxirane gave a 7:1 isomeric mixture of 5,6-di-*tert*-butyl-2,3,7-trithiabicyclo[2.2.1]hept-5-ene 2-endo-7-endo-dioxide (**5a**) and 2-exo-7-endo-dioxide (**5b**) quantitatively. The thermally labile **5** was shown to undergo a retro-Diels−Alder reaction that produces S_2O and **3** in a reversible way. The resulting S_2O was trapped by Diels−Alder reactions with dienes to give 3,6-dihydro-1,2-dithiin 1-oxides in good yields. In the absence of the dienes, S_2O disproportionates to SO_2 and S_3, and the resulting S_3 underwent a 1,3-dipolar cycloaddition with **3** on its syn-π-face with respect to the S═O bond to give a trithiolane derivative, whereas in the presence of excess norbornene, it produced the 1,3-dipolar cycloadduct with norbornene in good yield. Thus, the retro-Diels−Alder reaction of **5** functions as an S_2O and S_3 source. DFT calculations at the B3LYP/6-311+G(3df,2p) level were carried out in order to explain why S_2O disproportionates to SO_2 and S_3 and why S_2O acts as a dienophile and not a 1,3-dipole, whereas O_3 and S_3 serve as 1,3-dipoles.

Introduction

Disulfur monoxide (S_2O; S═S═O), an analogue of sulfur dioxide (SO_2) which is one of the most common compounds of sulfur, is formally derived from the latter by replacing the oxygen atom by sulfur. S_2O is suspected to be a component of the surface and the atmosphere of Jupiter's moon Io[1] and has been detected in the atmosphere of the planet Venus.[2] Most fundamentally, S_2O is produced by incomplete combustion of sulfur under reduced pressure.[3,4] It is also generated by the pyrolysis of ethylene episulfoxide,[5] electronic discharge of a mixture of SO_2 and sulfur vapor,[6] and reactions of heavy metal oxides or sulfides with elemental sulfur or with gaseous $SOCl_2$.[3,4,7] However, these methods, most of which are vapor phase reactions, require forcing conditions, in addition to special equipment and techniques. Therefore, these are not necessarily convenient to investigate the reactions of S_2O with organic substrates and the application of S_2O to organic synthesis in solution under mild conditions. 4,5-Diphenyl-3,6-dihydro-1,2-dithiin 1-oxide was found to liberate S_2O, though not in a free state, via a transition-metal-assisted retro-Diels−Alder reaction.[8] Recently, we have reported the generation of S_2O by thermal decomposition of tetrathiolane 2,3-dioxide (**1**) (Ad = 1-adamantyl) in solution.[9] The synthesis of **1** is, however, rather laborious. More recently, we also found that readily obtainable octasulfur monoxide (**2**)[10] serves as an S_2O equivalent.[11] Here, we report a new and clean method that generates free S_2O by a hetero retro-Diels−Alder reaction. We also report the computational rationalization of the chemical properties of S_2O.



1



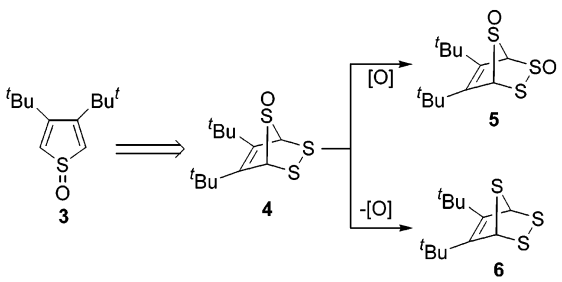
2

Results and Discussion

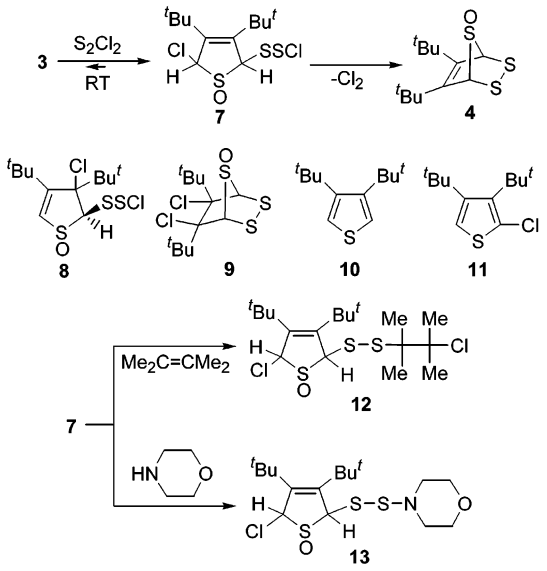
Preparation of 5,6-Di-*tert*-butyl-2,3,7-trithiabicyclo[2.2.1]-hept-5-ene 7-Oxide (4). In our continuing interest in the reactions of 3,4-di-*tert*-butylthiophene 1-oxide (**3**),[12,13] we have

(1) (a) Hapke, B. *Icarus* **1989**, *79*, 56−74. (b) Spencer, J. R.; McEwen, A. S.; McGrath, M. A.; Sartoretti, P.; Nash, D. B.; Noll, K. S.; Gilmore, D. *Icarus* **1997**, *127*, 221−237.
(2) Na, C. Y.; Esposito, L. W. *Icarus* **1997**, *125*, 364−368.
(3) For reviews on the chemistry of S_2O, see: (a) Schenk, P. W.; Steudel, R. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 402−409. (b) Murthy, A. R. V.; Kutty, T. R. N.; Sharma, D. K. *Int. J. Sulfur Chem. B* **1971**, *6*, 161−175.
(4) For the latest review on sulfur-rich oxides S_nO and S_nO_2 ($n > 1$), see Steudel, R. *Top. Curr. Chem.* **2003**, *231*, 203−230.
(5) Dodson, R. M.; Srinivasan, V.; Sharma, K. S.; Sauers, R. F. *J. Org. Chem.* **1972**, *37*, 2367−2372.
(6) Schenk, P. W.; Holst, W. *Z. Anorg. Allg. Chem.* **1963**, *319*, 137−149.
(7) (a) Satyanarayana, S. R.; Murthy, A. R. V. *Z. Anorg. Allg. Chem.* **1964**, *330*, 245−250. (b) Schenk, P. W.; Steudel, R. *Z. Anorg. Allg. Chem.* **1966**, *342*, 253−262. (c) Schenk, P. W.; Steudel, R. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 61.
(8) (a) Urove, G. A.; Welker, M. E. *Organometallics* **1988**, *7*, 1013−1014. (b) Raseta, M. E.; Cawood, S. A.; Welker, M. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8268−8270. (c) Raseta, M. E.; Mishra, R. K.; Cawood, S. A.; Welker, M. E.; Rheingold, A. L. *Organometallics* **1991**, *10*, 2936−2945. (d) Hayes, B. L.; Welker, M. E. *Organometallics* **1998**, *17*, 5534−5539.

Scheme 1



Scheme 2



planned the preparation of compounds **5** and **6** via **4** by use of **3**[12] as the starting material (Scheme 1). Compounds **5** and **6** are expected to generate S_2O and diatomic sulfur $^1S_2$, respectively, by retro-Diels−Alder reactions.

Thus, addition of S_2Cl_2 to **3** was examined in CH_2Cl_2 with the expectation of obtaining adduct **7**, **8**, or **9** as the precursor of **4** (Scheme 2). The addition took place, providing a plethora of curious but interesting observations (see also Experimental Section). When the solvent was removed immediately after a solution of **3** and S_2Cl_2 in CH_2Cl_2 had been stirred for only 1 min, 1,4-adduct **7**[14] was obtained quantitatively as a yellow oil. Neither **8** nor **9** was formed. **7** is highly labile, and thus leaving the crude **7** neat or as a solution at room-temperature brought about the decomposition that produced **4** as a single stereoisomer, the compound of our desire, in addition to thiophenes **10** and **11**, with the product ratio being dependent upon the conditions. Further, either treatment of the crude **7** with water or subjection of **7** to silica gel column chromatography gave **4** in reasonable yields (50−60%) together with **10** and **11** in small amounts. **4** was obtained in an optimized yield of 98% when **7** was treated with aqueous $NaHCO_3$ solution. An additional curious but reproducible observation is the nearly quantitative formation of **10** on treatment of **7** with MeOH, where MeOH acted as a reducing agent. Treatment of **7** with *tert*-BuOH also produced **10** in 78% yield in addition to **4** in 22% yield.

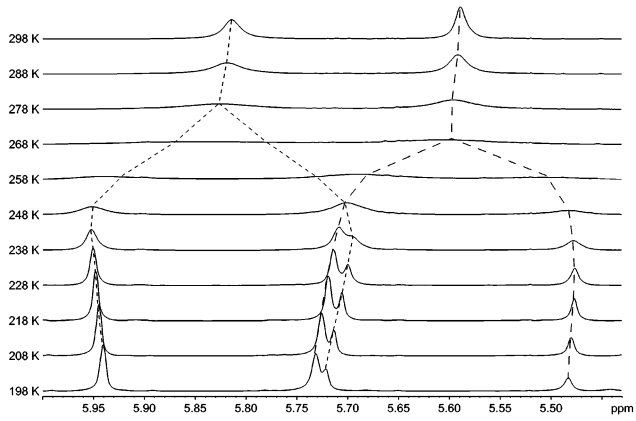


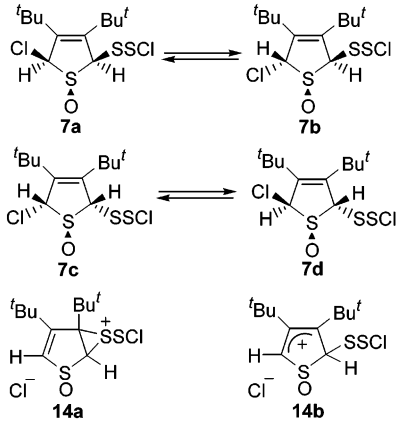
Figure 1. Temperature-dependent ^{1}H NMR spectra of the methine protons of **7** in CD_2Cl_2

We then treated **7** with tetramethylethylene and morpholine with expectation of obtaining a more stable derivative.[15] Although the reactions produced the expected products **12** and **13**, respectively and quantitatively, they are still thermally labile and decomposed completely, when allowed to stand at room-temperature overnight, to give **4** and **10** as the principal products.

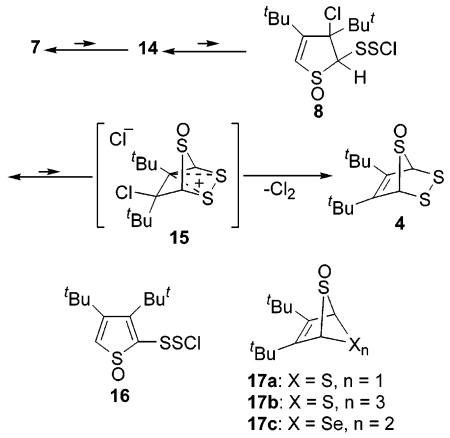
Interestingly, the methyl protons of one of the two *tert*-butyl groups and one of the two methine protons of **7** appeared as broad singlets in the room temperature ^{1}H NMR spectrum. On lowering the temperature, the proton signals for both of the methine and both of the *tert*-butyl groups became quite broad. At −15 °C, each singlet split into two very broad singlets, and at −45 °C, into two clear singlets with the signal intensity ratios of 50:50 at −15 °C and 56:44 at −45 °C in $CDCl_3$ and of 56:44 at −15 °C, 65:35 at −45 °C, and 71:29 at −75 °C in CD_2Cl_2 (Figure 1). The peak-broadening at room temperature and the peak-splitting at low temperatures were also observed for the ^{13}C NMR. These phenomena can best be explained by assuming a rapid equilibrium between two of the four possible stereoisomers **7a**−**7d**, where the equilibrium position, i.e., the isomer ratio is dependent upon the temperature and solvent, and the equilibrium takes place slightly faster than the ^{1}H NMR time scale at room temperature, whereas it becomes slow enough at lower temperatures, allowing us to observe the two isomers as different molecules. The equilibrium between **7a** and **7b** or

(9) (a) Ishii, A.; Nakabayashi, M.; Nakayama, J. *J. Am. Chem. Soc*. **1999**, *121*, 7959−7960. (b) Ishii, A.; Nakabayashi, M.; Jin, Y.-N.; Nakayama, J. *J. Organomet. Chem*. **2000**, *611*, 127−135.
(10) (a) Steudel, R.; Latte, J. *Angew. Chem., Int. Ed. Engl*. **1974**, *13*, 603−604. (b) Steudel, R.; Sandow, T. *Inorg. Synth*. **1982**, *21*, 172−174.
(11) Ishii, A.; Kawai, T.; Tekura, K.; Oshida, H.; Nakayama, J. *Angew. Chem., Int. Ed*. **2001**, *40*, 1924−1926.
(12) Nakayama, J.; Yu, T.; Sugihara, Y.; Ishii, A. *Chem. Lett*. **1997**, 499−500.
(13) (a) Nakayama, J.; Sano, Y.; Sugihara, Y.; Ishii, A. *Tetrahedron Lett*. **1999**, *40*, 3785−3788. (b) Otani, T.; Sugihara, Y.; Ishii, A.; Nakayama, J. *Tetrahedron Lett*. **1999**, *40*, 5549−5552. (c) Otani, T.; Sugihara, Y.; Ishii, A.; Nakayama, J. *Chem. Lett*. **2000**, 744−745. (d) Otani, T.; Sugihara, Y.; Nakayama, J. *Tetrahedron Lett*. **2000**, *41*, 8461−8465. (e) Nakayama, J.; Otani, T.; Sughihara, Y.; Sano, Y.; Ishii, A.; Sakamoto, A. *Heteroatom Chem*. **2001**, *12*, 333−348. (f) Nakayama, J.; Takayama, J.; Sugihara, Y.; Ishii, A. *Chem. Lett*. **2001**, 758−759. (g) Nakayama, J.; Furuya, T.; Ishii, A.; Sakamoto, A.; Otani, T.; Sugihara, Y. *Bull. Chem. Soc. Jpn*. **2003**, *76*, 619−625. (h) Otani, T.; Takayama, J.; Sugihara, Y.; Ishii, A.; Nakayama, J. *J. Am. Chem. Soc*. **2003**, *125*, 8255−8263. (i) Takayama, J.; Fukuda, S.; Sugihara, Y.; Ishii, A.; Nakayama, J. *Tetrahedron Lett*. **2003**, *44*, 5159−5162. (j) Nakayama, J. *J. Synth. Org. Chem., Jpn*. **2003**, *61*, 1106−1115.
(14) Bromine adds to **3** and the related compounds to produce 1,4-*cis*-mode adducts exclusively.[13g] The two 1,4-*cis*-mode bromine adducts (syn- and *anti*-adducts to the S═O bond) to **3** are stable enough to be isolated by usual methods (silica gel column chromatography and crystallization). Therefore, the SSCl group of **7** plays a crucial role to the mutual conversion between the two species, and the carbenium ion **14b** would not be a probable intermediate.
(15) For a recent review on the chemistry of the S_nCl ($n > 1$) group, see Abu-Yousef, I. A.; Harpp, D. N. *Sulfur Rep*. **2003**, *24*, 255−282. A recent paper on reactions of the SSCl group: Mloston, G.; Majchrzak, A.; Senning, A.; Søtofte, I. *J. Org. Chem*. **2002**, *67*, 5690−5695.

Scheme 3



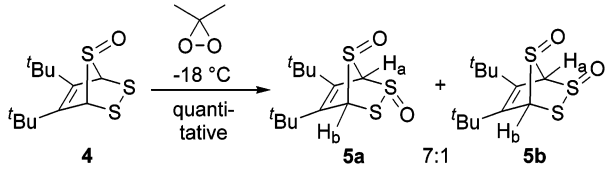
Scheme 4



between **7c** and **7d** is the likely candidate for such an equilibrium, where the equilibrium might be attained through intermediary formation of the episulfonium ion **14a**,[14] although we cannot say which combination is more probable from the NMR data. Other combinations, i.e., the equilibria between **7a** and **7c**, **7a** and **7d**, **7b** and **7c**, and **7b** and **7d**, seem least probable because such equilibria require that inversion of the configuration at >CHSSCl takes place rapidly, i.e., addition of S_2Cl_2 to **3** is a rapid reversible reaction.[16] However, the experimental observation does not fulfill the requirement because the ^{1}H NMR spectrum shows the independent signals of **3** and the product **7**, when **3** and S_2Cl_2 were mixed up in the ratio 1:1 in $CDCl_3$. Isomer **8** is not appreciably involved in the equilibrium because the ^{13}C NMR of **7** shows two sp^2-carbon peaks at δ 143 and 147, reasonable values for sp^2 carbons that carry a *tert*-butyl group.[13g−i,17]

To account for the conversion of **7** to **4**, we suggest the following tentative mechanism. Initially **7** isomerizes to the 1,2-adduct **8** through **14a**. An intramolecular addition in **8** produces the carbenium ion **15**, which is stabilized by neighboring group participation of the two sulfur atoms.[18] Water, through its highly polar nature, probably promotes the formation of **15**. Finally,

Scheme 5



elimination of Cl_2 from **15** produces **4**; the smell witnesses the generation of Cl_2. The hydroxide ion that originates from $NaHCO_3$ is more nucleophilic than is the chloride, and might also abstract chlorine in **15** to promote the formation of **4**. A route involving elimination of HCl from **7** to give **16** is not possible. The direct determination of the stereochemistry of the sulfinyl group in **4** was not possible because the single crystals for X-ray diffraction analysis could not be obtained despite numerous efforts.

Incidentally, attempted syntheses of **17a**−**c** by reactions of **3** with SCl_2, S_3Cl_2, and Se_2Cl_2 were all unsuccessful.

Preparation and Thermal Properties of 5,6-Di-*tert*-butyl-2,3,7-trithiabicyclo[2.2.1]hept-5-ene 2,7-Dioxide (5). The oxidation of **4** by a slight excess of dimethyldioxirane (DMD) at −18 °C, followed by removal of the solvent at −18 °C, furnished 2,7-dioxide **5** quantitatively as a 7:1 mixture of two diastereomers (Scheme 5). These are thermally highly unstable and decompose even at room-temperature both in solution and as the solid. The major diastereomer was isolated by crystallization at −18 °C and the structure determined to be **5a** by X-ray crystallographic analysis (Figure 2). Thus the minor diastereomer was assigned as **5b**. The ^{1}H NMR chemical shift data of the methine protons of **5b** are also in harmony with this structure; for example, H_a of **5a**, located in the deshielding zone of the newly introduced S═O group, is more deshielded (δ 6.28) than both methine protons of **5b** (δ 5.81, 5.93).[19] The same conclusion is also reached by inspection of the chemical shift values of the *tert*-butyl protons. This assignment in turn means that the S═O bond in **4** is syn to the S−S bond.

Brief heating of a crude 7:1 mixture of **5a** and **5b** in boiling $CHCl_3$ gave trithiolane **18** in 43% yield (86% yield based on the sulfur atom) in addition to **3** in 45% yield (Scheme 6). The structure of **18** was determined by X-ray crystallographic analysis (Figure 3). The formation of **18** is easily explainable. The retro-Diels−Alder reaction of **5** gives **3** and S_2O. The resulting S_2O disproportionates to S_3 and SO_2.[9,11,20] Finally, 1,3-dipolar cycloaddition of S_3 with **3** furnishes **18**, by reaction exclusively on the syn-π-face of **3** with respect to the S═O bond consistent with Diels−Alder reactions of **3** which occur on the syn-π-face.[13h−j]

Interestingly, both methine and *tert*-butyl protons of both **5a** and **5b** appeared as broad singlets in the ^{1}H NMR spectrum at 25 °C. This led us to determine variable temperature ^{1}H NMR spectra in the range from −40 to 50 °C. In addition, progress of the decomposition of **5** was followed (Figure 4). Although

(16) Pyramidal inversion at the sulfinyl center would not be the case because such inversion does not take place for the two 1,4-*cis*-mode bromine adducts to **3**.[13g]

(17) Nakayama, J.; Hasemi, R.; Yoshimura, K.; Sugihara, Y.; Yamaoka, S. *J. Org. Chem.* **1998**, *63*, 4912−4924.

(18) For neighboring group participation of sulfur, see Block, E. *Reactions of Organosulfur Compounds*, Academic Press: New York, 1978; pp 141−145, and references therein.

(19) (a) Green, C. H.; Hellier, D. G. *J. Chem. Soc., Perkin Trans. 2* **1972**, 458−463. (b) Green, C. H.; Hellier, D. G. *J. Chem. Soc., Perkin Trans. 2* **1973**, 243−252. (c) Pritchard, J. G.; Lauterbur, P. C. *J. Am. Chem. Soc.* **1961**, *83*, 2105−2110. (d) Green, C. H.; Hellier, D. G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 190−193. (e) Buchanan, G. W.; Hellier, D. G. *Can. J. Chem.* **1976**, *54*, 1428−1432.

(20) On annealing matrix-isolated S_2O decomposes primarily to SO_2 and S_3; Tang, S.-Y.; Brown, C. W. *Inorg. Chem.* **1975**, *14*, 2856−2858. In the gas phase, S_2O survives for several days below 100 Pa and at temperatures below 20 °C.[4]

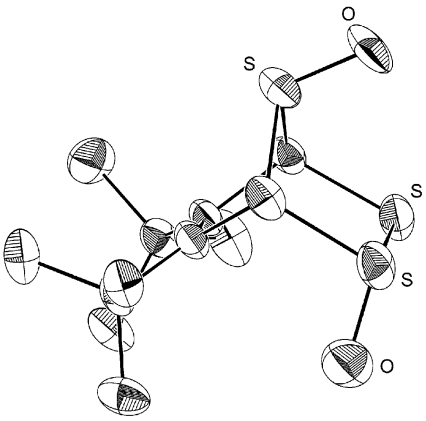
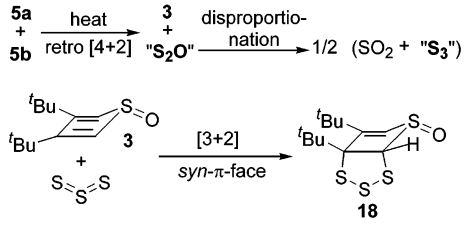


Figure 2. Molecular structure of **5a**.

Scheme 6



discussion here is concentrated only on the signals of the methine protons of **5** and those of **3** and **18**, similar phenomena were observed for the *tert*-butyl protons. Thus, at lower temperatures, for example, at −35 °C, the methine protons of both **5a** and **5b** appeared as clear doublets because of long-range coupling, and the α-protons of **3** that exists as an impurity were observed as a clear singlet (Figure 4a). At 15 °C, the methine proton signals of **5** became broad singlets, while the α-proton signal of **3** became obscure by signal-broadening (Figure 4b). In addition, the methine and vinyl protons signals of **18**, which formed by decomposition of **5**, began to appear. At 25 °C, the methine proton signals of **5** became quite broad (Figure 4c). At the same time, the signal intensity of **18** increased, whereas the α-protons signal of **3** is virtually unseen by signal-broadening notwithstanding that both **18** and **3** are produced by decomposition of **5**. Letting the sample stand at 25 °C for 12 h resulted in the further decomposition of **5** (Figure 4d). This was re-cooled and, again at −35 °C, the methine protons of **5a** and **5b** became clear doublets and the α-protons of **3** a singlet, whereas the signals of **18** appeared as rather broad singlets (Figure 4e). Warming of the sample to 50 °C brought about the decomposition of most **5**, where the α-protons of **3** appeared as very broad singlet, whereas methine protons signals of **5** are unseen because of broadening; the signals of **18** were observed as sharp singlets (Figure 4f). After the decomposition of **5** had been completed, both signals of **3** and **18** appeared as clear singlets at 25 °C (Figure 4g).

The signal-broadening of **5** and **3** can be explained by assuming a reversible reaction[21] between **5** and (**3** + S_2O) that takes place, probably in a solvent cage, at 15 °C or higher temperatures and is frozen at the lower temperatures (Scheme 7). The broadening, brought about by a rise in temperature, cannot be explained by restricted rotation of the *tert*-butyl groups. On the other hand, the signal-broadening of **18** at low temperatures can be explained as a result of either restricted

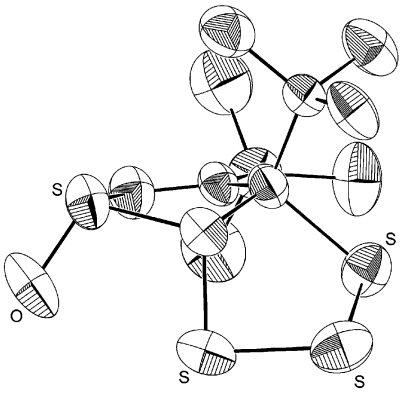


Figure 3. Molecular structure of **18**.

rotation of the *tert*-butyl groups[17] or conformational change of the trithiolane ring.[22]

It is well documented that Diels−Alder reactions of **3** with a great number of dienophiles take place exclusively on the syn-π-face with respect to the S═O bond.[13h,i] If we take this account into consideration, then the ratio 7:1 of **5a** and **5b** in $CDCl_3$ will not change regardless of the number of times the reversible addition of S_2O to **3** occurs (Scheme 7). Indeed, letting a 12:1 mixture of **5a** and **5b** in $CDCl_3$ stand at room temperature gave 9:1 and 7:1 mixtures after 3 and 6 h, respectively.

2,7-Dioxide 5 as the S_2O Source. The above results indicate that the retro-Diels−Alder reaction of **5** serves as a clean source of S_2O. Indeed, when the crude **5** was heated with excess dienes in refluxing CH_2Cl_2, the resulting S_2O reacted with the dienes to give Diels−Alder adducts **19a**,**b**[8,9,11] in high yields (Scheme 8). On the other hand, the reaction of **5** with an equimolar amount of $(Ph_3P)_2Pt(C_2H_4)$ took place quickly even at room temperature to give a platinum complex **20**[23] in 60% yield. Thus, **20** is likely formed directly by reaction of **5** with the metallic reagent; contribution of free S_2O would be small if any.

2,7-Dioxide 5 as the S_3 Source. The retro-Diels−Alder reaction of **5** is also expected to serve as the S_3 source through disproportionation of S_2O. Indeed, decomposition of crude **5** in the presence of excess norbornene provided **21**,[9,11,24] the 1,3-dipolar cycloadduct of S_3 with norbornene, in 82% yield (Scheme 9). The decomposition of **5** in the presence of excess cyclopentadiene produced, the 1,3-dipolar cycloadduct, **22**[25] in 80% yield, and not the Diels−Alder adduct, **24**. This probably means that **24**, even if it formed, undergoes the cycloreversion to S_2O and cyclopentadiene. The reaction also produced **23** in 58% yield, which formed by reaction of cyclopentadiene with **3**, the cycloreversion counterpart of S_2O. The decomposition in the presence of norbornadiene did not give the expected

(21) For some examples of temperature-dependent ^{1}H NMR spectra of the equilibrating systems, see cycloheptatriene-norcaradiene system: (a) Vogel, E.; Wendisch, D.; Roth, W. R. *Angew. Chem.* **1964**, *76*, 432−433. (b) Schröder, G.; Oth, J. F. M.; Merényi, R. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 752−761. (c) Ciganek, E. *J. Am. Chem. Soc.* **1967**, *89*, 1458−1468. Benzene oxide-oxepin system: (d) Vogel, E.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 385−401. Tri-*tert*-butylcyclopropenyl azide: (e) Curci, R.; Lucchini, V.; Kocienski, P. J.; Evans, G. T.; Ciabattoni, J. *Tetrahedron Lett.* **1972**, 3293−3296.
(22) Sugihara, Y.; Abe, K.; Nakayama, J. *Heteroatom Chem.* **1999**, *10*, 638−643.
(23) Ishii, A.; Murata, M.; Oshida, H.; Matsumoto, K.; Nakayama, J. *Eur. J. Inorg. Chem.* **2003**, *20*, 3716−3721.
(24) (a) Bartlett, P. D.; Ghosh, T. *J. Org. Chem.* **1987**, *52*, 4937−4943. (b) Leste-Lasserre, P.; Harpp, D. N. *Tetrahedron Lett.* **1999**, *40*, 7961−7964.
(25) Steliou, K.; Gareau, Y.; Milot, G.; Salama, P. *J. Am. Chem. Soc.* **1990**, *112*, 7819−7820.

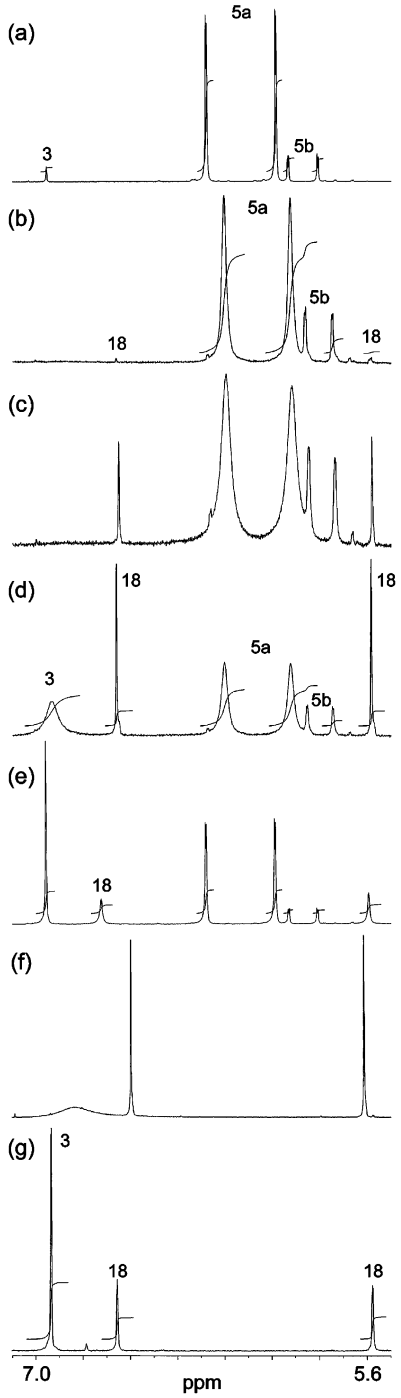
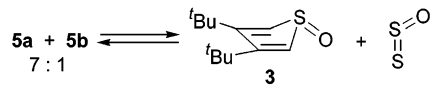


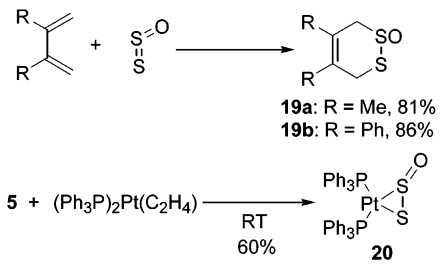
Figure 4. Temperature-dependent ^{1}H NMR spectra of **5**, **3**, and **18** in the region δ 5.5−7.1 and the progress of the decomposition of **5**: (a) at −35 °C; (b) at 15 °C; (c) at 25 °C; (d) at 25 °C after letting stand at 25 °C for 12 h; (e) at −35 °C; (f) at 50 °C after determination of (e); (g) at 25 °C after completion of decomposition of **5**.

[2+2+2] (homo-Diels−Alder) cycloadduct **27**,[26] but instead gave adducts **25** (5%) and **26** (43%). Thus, S_2O is inert to norbornadiene and disproportionates to S_3 and SO_2. The resulting S_3 undergoes a 1,3-dipolar cycloaddition with norbornadiene to provide **25** initially, which then reacts with **3** to give **26**. The formation of **26** by reaction of S_3 with **28**, the adduct of **3** with norbornadiene, is ruled out because a separate experiment showed that the reaction of **3** with norbornadiene did not afford **28** under the above conditions. Incidentally, during the preparation of this paper, the rotational spectrum and geometrical structure of S_3 were communicated in this journal.[27]

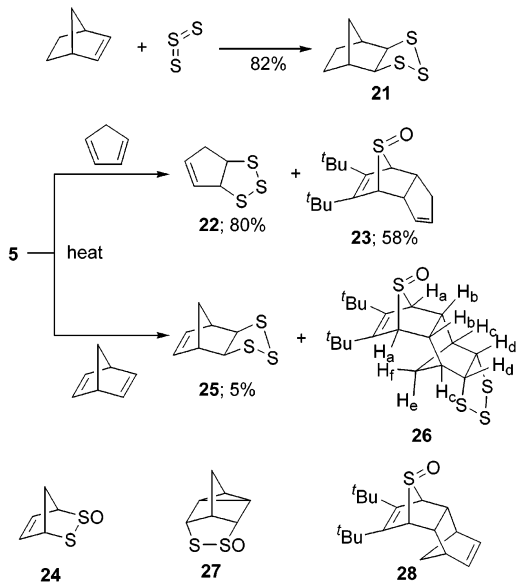
Scheme 7



Scheme 8



Scheme 9



Approach to $^1S_2$ Source, 5,6-Di-*tert*-butyl-2,3,7-trithiabicyclo[2.2.1]hept-5-ene (6). The 7-oxide **4** is thermally stable, in marked contrast to **5**, and shows no tendency, at least under mild conditions, to undergo the retro-Diels−Alder reaction that produces $^1S_2$ and **3**. Meanwhile, **6** might undergo retro-Diels−Alder reaction readily to generate $^1S_2$ because the formation of aromatic **10** serves as the driving force. Consequently, we then attempted conversion of **4** to **6**.

Heating **5** with Lawesson's reagent (LR), a reagent that reduces sulfoxides to the corresponding sulfides,[28] in toluene at 100 °C provided **10** and 1,2,3,4-tetrathiocin **30**[29] in 23% and 31% yields, respectively (Scheme 10). The formation of **30** is

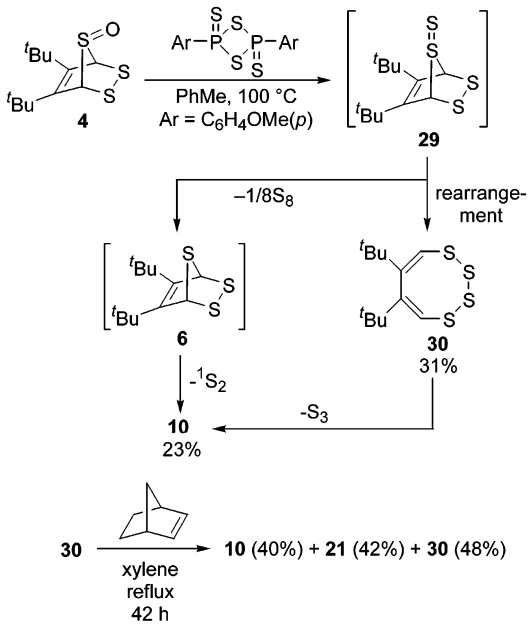
(26) (a) Blomquist, A. T.; Meinwald, Y. C. *J. Am. Chem. Soc.* **1959**, *81*, 667−672. (b) Williams, J. K.; Benson, R. E. *J. Am. Chem. Soc.* **1962**, *84*, 1257−1258.

(27) McCarthy, M. C.; Thorwirth, S.; Gottlieb, C. A.; Thaddeus, P. *J. Am. Chem. Soc.* **2004**, *126*, 4096−4097.

(28) Rasmussen, J. B.; Jørgensen, K. A.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 307−308.

(29) Monocyclic 1,2,3,4-tetrathiocine is a rare class of compounds. For tricyclic 1,2,3,4-tetrathiocines, see (a) Bigoli, F.; Pellinghelli, M. A.; Atzei, D.; Deplano, P.; Trogu, E. F. *Phosphorus, Sulfur* **1988**, *37*, 189−194. (b) Schroth, W.; Felicetti, M.; Hintzsche, E.; Spitzner, R.; Pink, M. *Tetrahedron Lett.* **1994**, *35*, 1977−1980.

Scheme 10



explained by skeletal rearrangement of the initially formed thiosulfoxide intermediate **29**.[30] Meanwhile, **10** could be produced by extrusion of $^1S_2$ from **6** that formed from **29** by loss of the sulfur atom. Competitively, **10** might be also formed from **30** together with S_3. Indeed, heating **30** with norbornene in refluxing xylene afforded **21**, together with **10**, in good yield based on the consumed **30**.[31] The above results are suggestive but not conclusive of the intermediary formation of **6** as the $^1S_2$ source.[31a,32]

Although the reduction of **4** by Me_2SiCl_2/Zn[33] produced **10** in 63% yield, its probable counterpart $^1S_2$ could not be trapped by 2,3-dimethyl-1,3-butadiene. This might mean that $^1S_2$ (or **6**) reacted more quickly with metallic zinc than with the diene, if it had formed. Attempted reduction by Me_3SiCl (or Me_2SiCl_2)/PhSH and by Ac_2O/*iso*-PrOH[34] resulted in the quantitative recovery of **4**.

Computational Rationalization of Properties of S_2O and S_3. We have observed that 1) S_2O disproportionates to SO_2 and S_3, and 2) S_2O acts as a dienophile and not a 1,3-dipole, whereas O_3 and S_3 serve as 1,3-dipoles. To rationalize these observations, we have carried out DFT calculations.

Figure 5 shows the bond angles and bond lengths of SO_2, S_2O,[35] and S_3 obtained by DFT calculations at B3LYP/6-311+G(3df) level.[36,37] For comparison, the experimental bond lengths and bond angles of SO_2, S_2O,[38] and S_3[27] are given in Figure 6. The calculated structures are in good agreement with the experimental ones. The calculations on enthalpy of the reaction predict that the disproportionation ($2S_2O \rightarrow SO_2 + S_3$) is 10.3 kcal mol^{-1} exothermic (see Figure 7). The calculations also revealed that O=S=S and O=S=O are more stable than their isomers S=O=S and O=O=S by 63.8 and 116.5 kcal mol^{-1}, respectively.

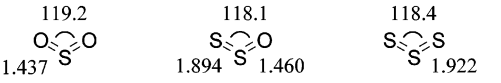


Figure 5. Bond angles (°) and bond lengths (Å) of SO_2, S_2O, and S_3 calculated at B3LYP/6-311+G(3df) level.

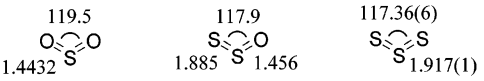


Figure 6. Experimental bond angle (°) and bond length (Å) data of SO_2, S_2O,[36] and S_3[25] in the gas phase.

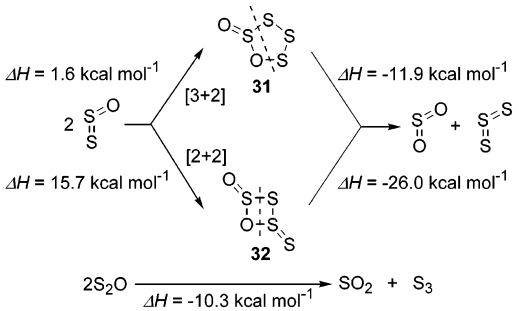


Figure 7. Thermochemistry of the disproportionation of S_2O to SO_2 and S_3.

Previously, the [2+2] self-dimer **32** was proposed as the intermediate of the disproportionation of S_2O.[20] However, the [2+3] dimer **31**, which would be formed by a symmetry allowed 1,3-dipolar cycloaddition, seems to be a more likely intermediate both kinetically and thermodynamically. We then calculated the enthalpy of formation of **31** and **32** at B3LYP/6-311+G(3df) level. The calculations predicted that the formation of **32** is largely endothermic by 15.7 kcal mol^{-1}, whereas the formation of **31** is endothermic only by 1.6 kcal mol^{-1} (Figure 7).[39] Thus, **31** would be more favorable as an intermediate. In addition, the calculations predicted that the [2+3] dimerization is symmetry allowed and the energy gap between $HOMO_\pi$ (−8.83 eV) and $LUMO_\pi$ (−4.27 eV) of S_2O is as small as 4.56 eV (Figure 8).[40] This will render the 1,3-dipolar dimerization

(30) (a) Shimada, K.; Kodaki, K.; Aoyagi, S.; Takikawa, Y.; Kabuto, C. *Chem. Lett*. **1999**, 695−696. (b) Ishii, A.; Yamashita, R.; Saito, M.; Nakayama, J. *J. Org. Chem*. **2003**, *68*, 1555−1558.

(31) The formation of **21** does not necessarily require the involvement of S_3 since **21** is formed by reaction of norbornene with other sulfur species.[23] See also (a) Steliou, K.; Salama, P.; Brodeur, D.; Gareau, Y. *J. Am. Chem. Soc*. **1987**, *109*, 926−927. (b) Okuma, K.; Kuge, S.; Koga, Y.; Shioji, K.; Wakita, H.; Machiguchi, T. *Heterocycles* **1998**, *48*, 1519−1522.

(32) (a) Schmidt, M.; Görl, U. *Angew. Chem., Int. Ed. Engl*. **1987**, *26*, 887−888. (b) Harpp, D. N.; MacDonald, J. G. *J. Org. Chem*. **1988**, *53*, 3812−3814. (c) Steliou, K.; Gareau, Y.; Milot, G.; Salama, P. *J. Am. Chem. Soc*. **1990**, *112*, 7819−7820. (d) Clennan, E. L.; Stensaas, K. L. *Org. Prep. Proced. Int*. **1998**, *30*, 551−600.

(33) Nagasawa, K.; Yoneta, A.; Umezawa, T.; Ito, K. *Heterocycles* **1987**, *26*, 2607−2609.

(34) Numata, T.; Togo, H.; Oae, S. *Chem. Lett*. **1979**, 329−332.

(35) For previous *ab intio* calculation studies on S_2O, see (a) Ivanic, J.; Atchity, G. J.; Ruedenberg, K. *J. Chem. Phys*. **1997**, *107*, 4307−4317. (b) Fueno, T.; Buenker, R. J. *Theor. Chim. Acta* **1988**, *73*, 123−134. A DFT calculation study predicted a cyclic ground-state structure of S_2O.; (c) Jones, R. O. *Chem. Phys. Lett*. **1986**, *125*, 221−224.

(36) The calculations were carried out at both B3LYP/6-311+G(d) and B3LYP/6-311+G(3df) levels, although the results of the latter level calculations are described here; for the former level calculations and the vibrational models and frequencies of these molecules, see Supporting Information.

(37) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98* Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(38) Marsden, C. J.; Smith, B. J. *Chem. Phys*. **1990**, *141*, 325−334.

(39) B3LYP/6-311+G(d) level calculations predicted that the formation of **31** is 1.3 kcal mol^{-1} exothermic.

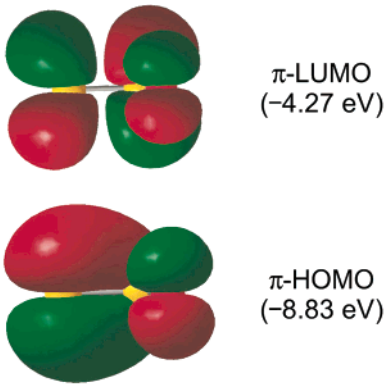
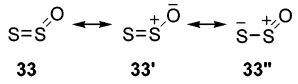


Figure 8. π-HOMO and π-LUMO of S_2O.

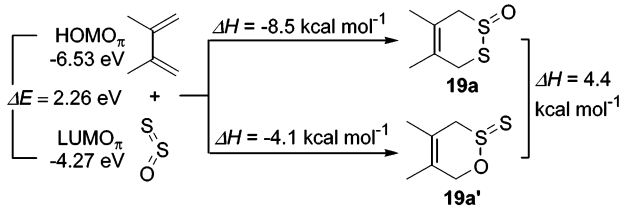
favorable by lowering the transition state energy with effective $HOMO_\pi-LUMO_\pi$ interactions.

Both experimental (1.885 Å) and calculated (1.894 Å) S−S bond lengths in S_2O are shorter than both experimental (1.917 Å) and calculated (1.922 Å) S−S bond lengths in S_3. But the S−O bond length in S_2O is slightly longer than that in SO_2. The S−S bond length of S_2O is also slightly shorter than those of [$(RO)_2S$═S], which are of the order of 1.90−91 Å.[41] These indicate that the S−S bond order in S_2O is greater than that in S_3 because of greater contribution of the canonical structure **33′** than **33″**. The same conclusion is also reached by inspection of the $HOMO_\pi$ of S_2O in which the sulfur atoms are connected by a π-bonding orbital (Figure 8). This would explain why S_2O acts as a dienophile toward dienes, whereas S_3 does not. For another point of view, the energy gap between the $LUMO_\pi$ of S_2O and the HOMO (−6.53 eV) of 2,3-dimethyl-1,3-butadiene is only 2.26 eV because of the low-lying LUMO (−4.27 eV) of S_2O, and thus effective interactions between these orbitals take place to lower the transition state energy of the Diels−Alder reaction.

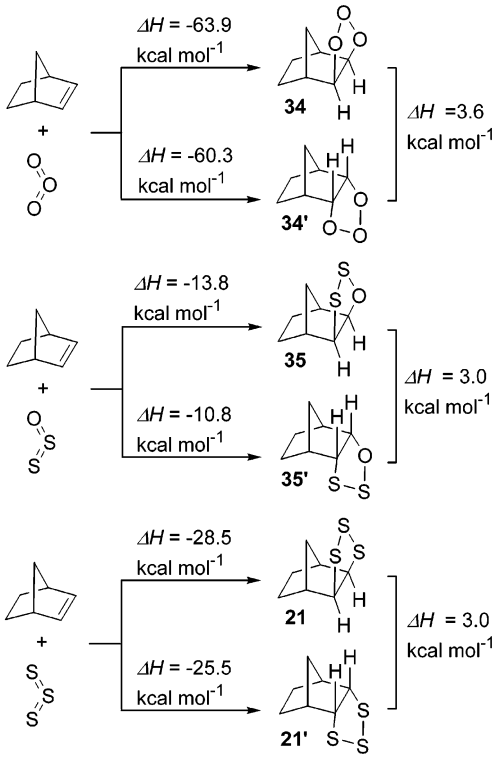


Calculations at B3LYP/6-311+G(3df,2p) level predicted that the Diels−Alder reaction of S_2O with 2,3-dimethyl-1,3-butadiene that forms **19a** is exothermic by 8.5 kcal mol^{-1}, while the reaction that gives **19a′** is less exothermic by 4.1 kcal mol^{-1} (Scheme 11). Thus, the former reaction is thermodynamically more favorable than the latter by 4.4 kcal mol^{-1} in accordance with the exclusive formation of **19a**. However, the **19a**-forming reaction is exothermic only by 8.5 kcal mol^{-1}. This in turn means that **19a**, when heated, can undergo the retro-Diels−Alder reaction that regenerates S_2O. The difference of enthalpy of formation of **19a** and **19a′** is much smaller than we expected, in other words, **19a′** is much stabler than we expected. Thus, thionosulfinate esters R−S(═S)−O−R such as **19a′** may be

Scheme 11



Scheme 12



obtainable as isolable, stable compounds, if we could devise a suitable method for their synthesis.

Finally, we examined the thermochemistry of 1,3-dipolar cycloadditions of O_3, S_2O, and S_3 with norbornene by B3LYP/6-311+G(3df,2p) level calculations. Results of the calculations are summarized in Scheme 12. It is well-known that a number of addition reactions of norbornene take place exclusively at its *exo*-face.[42] The calculations at the enthalpy of adducts predict that *exo*-1,3-dipolar adducts (**34**, **35**, and **21**) are more stable than the corresponding *endo*-1,3-dipolar adducts (**34′**, **35′**, and **21′**) by 3.6, 3.0, and 3.0 kcal mol^{-1}, revealing that the *exo*-selection is in harmony with thermodynamic stability of the adducts. The 1,3-dipolar cycloadditions of O_3 and S_3 at the *exo*-face of norbornene are exothermic by as large as 63.9 and 28.5 kcal mol^{-1}, respectively. Unexpectedly, even 1,3-dipolar cycloaddition of S_2O is 13.8 kcal mol^{-1} exothermic, though less so than that of O_3 and S_3. In the latter case, however, it must be difficult to reach the fully symmetrical transition state by concurrent two-bond formation between S_2O and norbornene because the HOMO lobes of sulfur and oxygen in S_2O are not

(40) (a) Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; John Wiley: New York, 1983; Vol. 1, Chapter 1. (b) Houk, K. N.; Yamaguchi, K. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A. Ed.; John Wiley: New York, 1983; Vol. 2, Chapter 13.

(41) (a) Harpp, D, N.; Steliou, K.; Cheer, C. J. *J. Chem. Soc., Chem. Commun.* **1980**, 825−826. (b) Snyder, J. P.; Nevins, N.; Tardif, S. L.; Harpp, D. N. *J. Am. Chem. Soc.* **1997**, *119*, 12 685−12 686. (c) Zysman-Colman, E.; Abrams, C. B.; Harpp, D. N. *J. Org. Chem.* **2003**, *68*, 7059−7062. (d) Tanaka, S.; Sugihara, Y.; Sakamoto, A.; Ishii, A.; Nakayama, J. *J. Am. Chem. Soc.* **2003**, *125*, 9024−9025.

(42) For the *exo*-selection and enhanced reactivities of norbornene, see (a) Schleyer, P. von R. *J. Am. Chem. Soc.* **1967**, *89*, 701−703. (b) Brown, H. C.; Hammar, W. J.; Kawakami, J. H.; Rothberg, I.; Vander Jagt, D. L. *J. Am. Chem. Soc.* **1967**, *89*, 6381−6382. (c) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054−4061. (d) Huisgen, R.; Ooms, P. H. J.; Mingin, M.; Allinger, N. L. *J. Am. Chem. Soc.* **1980,** *102*, 3951−3953.

of the same size, much greater at the sulfur atom than at the oxygen (Figure 8). This would explain why S_3 undergoes 1,3-dipolar cycloadditions, whereas S_2O prefers to act as a dienophile, even though the difference of the exothermicity described above would not be a negligible factor.

In conclusion, the retro-Diels−Alder reaction of **5** that produces S_2O and **3** is reversible and serves as an excellent source of both S_2O and S_3, and will set the next stage for developing the organic chemistry of these rather little explored species.

Experimental Section

Preparation of 5,6-Di-*tert*-butyl-2,3,7-trithiabicyclo[2.2.1]hept-5-ene 7-Oxide (4) by Reaction of 3,4 -Di-*tert*-butylthiophene 1-oxide (3) with S_2Cl_2. (a) Isolation of the Intermediate 7. 3,4-Di-*tert*-butylthiophene 1-oxide (**3**) (100 mg, 0.47 mol) and S_2Cl_2 (64 mg, 0.47 mmol) were dissolved in CH_2Cl_2 (5 mL) and stirred for only one minute at room temperature. The solvent was immediately removed under reduced pressure to give a yellow oily residue, which was stirred for another 1 min to quantitatively provide the intermediate **7**. For temperature-dependent ^{1}H NMR spectra in CD_2Cl_2, see Figure 1. **7**: yellow oil; ^{1}H NMR (400 MHz); $CDCl_3$ as the solvent at 298 K δ 1.44 (s, Bu^t, 9H), 1.49 (broad s, Bu^t, 9H), 5.61 (s, 1H), 5.85 (broad s, 1H), at 258 K δ 5.57 (s, 0.5H), 5.72 (s, 0.5H), 5.78 (s, 0.5H), 6.03 (s, 0.5H), at 228 K δ 5.60 (s, 0.44H), 5.78 (s, 0.56H), 5.83 (s, 0.44H), 6.06 (s, 0.56H) (*tert*-butyl signals are omitted); CD_2Cl_2 as the solvent at 298 K δ 1.43 (s, Bu^t, 9H), 1.49 (broad s, Bu^t, 9H), 5.62 (s, 1H), 5.85 (broad s, 1H); C_6D_6 as the solvent at 298 K δ 1.01 (s, Bu^t, 9H), 1.36 (broad s, Bu^t, 9H), 4.97 (s, 1H), 5.80 (broad s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) 298 K δ 32.1, 32.2 (broad), 36.4, 36.5, 79.0, 86.0 (broad), 143.4, 146.8 (broad); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) 198 K δ 32.3, 32.7, 36.87, 36.94, 78.2, 90.4, 144.3, 145.1 (major isomer); 32.2, 33.3, 36.6, 37.5, 76.0, 86.3, 147.8, 150.9 (minor isomer); UV/Vis (CH_2Cl_2) λ_{max} (ϵ) 266 nm (3800, shoulder).

The following were observed when the reaction was carried out in $CDCl_3$ and monitored by ^{1}H NMR. On stirring even for 1 h, **3** still remained unreacted, while a slight decomposition of the resulting **7** was observed. **3** was consumed completely after 3 h with considerable decomposition of the resulting **7** that gave rise to 3,4-di-*tert*-butylthiophene (**10**) and 3,4-di-*tert*-butyl-2-chlorothiophene (**11**) in addition to 5,6-di-*tert*-butyl-2,3,7-trithiabicylo[2.2.1]hept-5-ene 7-oxide (**4**). Thus, in a dilute solution the addition of S_2Cl_2 to **3** is rather slow, but seemingly accelerated when the solution was concentrated or the solvent was removed.

(b) Derivation of 12 and 13 from 7. A solution of tetramethylethylene (40 mg, 0.47 mmol) in CH_2Cl_2 (3 mL) was added to **7** (prepared from 0.47 mmol of **3**). Immediately after the addition, the solvent was removed under reduced pressure to give the thermally unstable adduct **12** quantitatively as viscous colorless oil. The reaction of **7** with morpholine (two molar amounts) was done in a similar way to give the thermally unstable adduct **13** quantitatively as viscous colorless oil; the resulting hydrochloride salt of morpholine was removed by filtration. **12**: colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.40 (s, 9H), 1.45 (s, 9H), 1.60 (s, 3H), 1.63 (s, 3H), 1.72 (s, 3H), 1.73 (s, 3H), 5.17 (s, 1H), 5.74 (s, 1H); (C_6D_6, 400 MHz) δ 1.12 (s, 9H), 1.17 (s, 9H), 1.51 (s, 3H), 1.52 (s, 3H), 1.54 (s, 3H), 1.55 (s, 3H), 5.02 (s, 1H), 5.71 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 29.2, 29.3, 31.9, 32.0, 32.7, 33.4, 36.3, 36.4, 53.4, 59.7, 81.2, 83.0, 144.9, 145.4; MS (FAB) *m*/*z* 431 (MH^+). **13**: colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.40 (s, 9H), 1.46 (s, 9H), 2.96−3.01 (m, 2H), 3.05−3.10 (m, 2H), 3.68−3.78 (m, 4H), 5.40 (s, 1H), 5.70 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 32.0, 32.1, 36.3 (overlapping of two peaks), 55.7, 66.8, 80.9, 83.0, 144.7, 145.5.

(c) Optimized Procedure for the Preparation of 4. A solution of S_2Cl_2 (64 mg, 0.47 mmol) and **3** (100 mg, 0.47 mol) in CH_2Cl_2 (5 mL) was stirred only for 1 min at room temperature. The solvent was immediately removed under reduced pressure to give the yellow oily residue, which was stirred for another one minute. The resulting crude **7** was stirred with a aqueous saturated solution of $NaHCO_3$ (15 mL) for a while. The mixture was extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with water, dried over $MgSO_4$, and evaporated. The crystalline residue was washed with a small amount of pentane to give 127 mg (98%) of practically pure **4**. **4**: mp 195−196 °C (dec); pale yellow crystals; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.35 (s, 18H), 5.38 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 32.8, 35.1, 80.0, 141.1; IR (KBr) 1096 cm^{-1} (S═O). Anal. Calcd for $C_{12}H_{20}OS_3$: C, 52.13; H, 7.29. Found: C, 52.37; H, 7.33.

Treatment of the crude **7** (prepared from 0.47 mmol of **3**) with water (10 mL), and not $NaHCO_3$, also gave **4**, but in decreased yield (82 mg, 59%), in addition to a mixture of **10** and **11** (26%). Subjection of the crude **7** (prepared from 0.47 mmol of **3**) to silica gel column chromatography also produced **4**, but in decreased yield (75 mg, 54%), in addition to a mixture of **10** and **11** (35%). Treatment of the crude **7** (prepared from 0.47 mmol of **3**) with MeOH (1 mL) gave **10** (89 mg, 96%).

Preparation of 5,6-Di-*tert*-butyl-2,3,7-trithiabicyclo[2.2.1]hept-5-ene 2,7-Dioxide (5). A 82 mM solution of DMD in acetone (5.0 mL, 0.41 mmol) was added to a solution of **4** (103 mg, 0.37 mmol) in CH_2Cl_2 (3 mL) at −18 °C. After the mixture had been stirred for 3.5 h at −18 °C, the solvent was removed below −18 °C to furnish a 7:1 mixture of **5a** and **5b** quantitatively as crystalline solid. Crystallization of the crude product at −18 °C from CH_2Cl_2/hexane gave 69 mg (63%) of practically pure **5a** as colorless crystals: mp < 90 °C (dec); ^{1}H NMR ($CDCl_3$, 400 MHz, 238 K) δ 1.33 (s, 9H), 1.49 (s, 9H), 5.99 (d, J = 1.9 Hz, H_b), 6.28 (d, J = 1.9 Hz, H_a); ^{13}C NMR ($CDCl_3$, 100.6 MHz, 238 K) δ 31.6, 32.1, 34.4, 36.7, 82.5, 92.6, 138.5, 149.8; IR (KBr) 1093 (S═O), 1078 (S═O) cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_2S_3$: C, 49.28; H, 6.89. Found: C, 49.32; H, 6.54. **5b**: ^{1}H NMR ($CDCl_3$, 400 MHz, 238 K) δ 1.31 (s, 9H), 1.33 (s, 9H), 5.81 (d, J = 2.0 Hz, H_a or H_b), 5.93 (d, J = 2.0 Hz, H_a or H_b). For definition of H_a and H_b, see Scheme 5.

Thermal Decomposition of a 7:1 Mixture of 5a and 5b: Formation of 3 and 18. A solution of a crude 7:1 mixture of **5a** and **5b**, prepared from 44 mg (0.15 mol) of **4**, in $CHCl_3$ (3 mL) was heated at 50 °C for 1 h. After the solvent had been removed, the residue was purified by silica gel column chromatography and then by GPC (gel permeation chromatography) to give 15 mg (45%) of **3** and 21 mg (43% or 86% based on the sulfur atom) of **18**. **18**: mp 132−133 °C (dec); faint yellow crystals (from CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.27 (s, 9H), 1.42 (s, 9H), 5.59 (s, 1H), 6.66 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 30.5, 34.2, 37.7, 40.5, 89.4, 101.1, 135.8, 161.8; IR (KBr) 1032 (S═O) cm^{-1}. Anal.Calcd for $C_{12}H_{20}OS_4$ C, 46.71; H, 6.53. Found: C, 46.82; H, 6.54.

Trapping of S_2O by Dienes: Formation of 19. A solution of a crude mixture of **5a** and **5b**, prepared from 21 mg (0.077 mol) of **4**, and 2,3-dimethylbutadiene (126 mg, 1.54 mmol) in CH_2Cl_2 (3 mL) was heated at 30 °C for 15 h. After the solvent had been removed, the residue was analyzed by ^{1}H NMR with dibenzyl as the internal standard. The analysis revealed the formation of **19a**[9a,11] and **3** in 82% and 86% yields, respectively. Similarly, **19b**[5,11] was formed in 86% yield along with **3** in 80% yield. **19a**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.95 (s, 3H), 2.02 (s, 3H), 3.18 (d, J = 13.7 Hz, 1H), 3.23 (d, J = 13.1 Hz, 1H), 3.76 (d, J = 13.7 Hz, 1H), 3.93 (d, J = 13.1 Hz, 1H). **19b**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.65 (d, J = 13.2 Hz, 1H), 3.65 (d, J = 13.2 Hz, 1H), 4.23 (d, J = 13.2 Hz, 1H), 4.47 (d, J = 13.2 Hz, 1H), 7.10−7.26 (m, 10H).

Formation of Platinum Complex 20. A solution of a crude mixture of **5a** and **5b**, prepared from 11 mg (0.04 mol) of **4**, and $(Ph_3P)_2Pt(C_2H_4)$ (30 mg, 0.04 mmol) in toluene (7 mL) was stirred for 75 min at room temperature. The solvent was removed and the residue was purified by silica gel column chromatography and then by GPC to give

7 mg (79%) of **3** and 19 mg (60%) of **20**.[23] **20**: mp 201−202 °C (dec); faint yellow crystals;^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15−7.23 (m, 12H), 7.26−7.35 (m, 18H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 17.9 [d, $^1J(^{195}\text{Pt-}^{31}\text{P}) = 4366$ Hz, $^2J(^{31}\text{P-}^{31}\text{P}) = 7$ Hz], 18.1 [d, $^1J(^{195}\text{Pt-}^{31}\text{P}) = 3411$ Hz, $^2J(^{31}\text{P-}^{31}\text{P}) = 7$ Hz]; IR (KBr) 1095 (S═O) cm^{-1}.

Trapping of S_3 with Norbornene: Formation of 21. A solution of a crude mixture of **5a** and **5b**, prepared from 34 mg (0.12 mol) of **4**, and norbornene (175 mg, 1.86 mmol) in $CHCl_3$ (7 mL) was heated at reflux for 1 h. After the solvent had been removed, the residue was purified by silica gel column chromatography and then by GPC to give 10 mg (82%) of **21**[9,11,24a] and 22 mg (83%) of **3**. **21**: yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.07 (dt, J = 10.3 Hz, J = 1.9 Hz, 1H), 1.18−1.27 (m, 2H), 1.71−1.76 (m, 2H), 1.94 (dt, J = 10.3 Hz, J = 1.9 Hz, 1H), 2.48 (m, 2H), 3.65 (d, J = 1.9 Hz, 2H).

Trapping of S_3 with Cyclopentadiene: Formation of 22 and 23. A solution of a crude mixture of **5a** and **5b**, prepared from 66 mg (0.24 mol) of **4**, and cyclopentadiene (158 mg, 2.4 mmol) in $CHCl_3$ (5 mL) was heated at reflux for 3 h. The mixture was evaporated and the residue was purified by silica gel column chromatography and then by GPC to give 16 mg (80%) of **22**,[25] 6 mg (11%) of **3**, and 38 mg (58%) of **23**. **22**: yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.51−2.61 (m, 1H), 3.04−3.15 (m, 1H), 4.76 (m, 1H), 5.21 (m, 1H), 5.63 (m, 1H), 5.85 (m, 1H). **23**: mp 150−151 °C; colorless crystals (from CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.19 (s, 9H), 1.24 (s, 9H), 1.99−2.12 (m, 1H), 2.45−2.61 (m, 1H), 3.42−3.45 (m, 1H), 3.89−3.96 (m, 1H), 3.99 (dd, J = 3.9 Hz, J = 1.5 Hz, 1H), 4.05 (dd, J = 4.2 Hz, J = 1.5 Hz, 1H), 5.57−5.68 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 31.6, 32.4, 32.9, 33.7, 34.5, 38.8, 50.8, 68.6, 68.9, 129.4, 132.8, 140.2, 142.8; IR (KBr) 1075 (S═O) cm^{-1}. Anal. Calcd for $C_{17}H_{26}OS$: C, 73.33; H, 9.41. Found: C, 73.26; H, 9.60.

Trapping of S_3 with Norbornadiene: Formation of 25 and 26. A solution of a crude mixture of **5a** and **5b**, prepared from 70 mg (0.25 mol) of **4**, and norbornadiene (233 mg, 2.53 mmol) in $CHCl_3$ (5 mL) was heated at reflux for 8 h. The mixture was evaporated and the residue was purified by silica gel column chromatography and then by GPC to give 2.7 mg (5%) of **25**,[24b,43] 2.5 mg (5%) of **3**, and 44 mg (43%) of **26**. **25**: yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.72 (dt, J = 9.4 Hz, J = 1.9 Hz, 1H), 2.48 (d, J = 9.4 Hz, 1H), 2.91 (m, 2H), 4.06 (d, J = 1.9 Hz, 2H), 6.38 (t, J = 1.9 Hz, 2H). **26**: mp 211−212 °C; faint yellow crystals (from CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.25 (s, 18H), 1.67−1.71 (m, 1H, H_f), 1.80−1.83 (m, 1H, H_e), 2.51−2.52 (m, 2H, H_c), 2.77−2.78 (m, 2H, H_b), 3.81 (d, J = 2.0 Hz, 2H, H_d), 4.02 (dd, J = 2.1 Hz, J = 2.1 Hz, 2H, H_a) (for hydrogen labeling, see Scheme 9); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 29.7, 32.2, 34.4, 42.8, 45.4, 68.4, 71.3, 140.9; IR (KBr) 1079 (S═O) cm^{-1}; MS (EI) m/z 400 (M^+); HRMS (EI) Calcd for $C_{19}H_{28}OS_4$ (M^+): 400.1023, Found: 400.1023.

6,7-Di-*tert*-butyl-1,2,3,4-tetrathiocin (30). A mixture of **4** (50 mg, 0.18 mmol) and Lawesson's reagent (46 mg, 0.11 mol) in toluene (50 mL) was heated at 100 °C for 24 h. The solvent was removed under reduced pressure and the residue was stirred with hexane (10 mL). The insoluble materials were removed and the filtrate was evaporated. The residue was purified successively by silica gel column chromatography, GPC, and HPLC to give 8 mg (23%) of **10** and 16 mg (31%) of **30**. **30**: mp 111−112 °C; faint yellow crystals (CH_2Cl_2/MeOH); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.20 (s, 18H), 6.63 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 31.5, 36.8, 120.7, 164.2; UV/Vis (hexane) λ_{max} (ϵ) 212 (11200, shoulder), 232 (7650, sh), 302 nm (135, sh); MS (EI) m/z 292 (M^+). Anal. Calcd for $C_{12}H_{20}S_4$ C, 49.27; H, 6.89. Found: C, 49.21; H, 6.91.

Thermolysis of 30 in the Presence of Norbornene. A solution of **30** (20 mg, 0.069 mmol) and norbornene (132 mg, 1.4 mmol) in xylene (5 mL) was heated at reflux for 42 h. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography and then by HPLC to give 9.7 mg (48%) of **30**, 5.4 mg (40%) of **10**, and 5.5 mg (42%) of **21**.

X-ray Crystallographic Analysis of 5a and 18. The crystal data were recorded on a Mac Science DIP3000 diffractometer equipped with a graphite monochromator. Oscillation and nonscreen Weissenberg photographs were recorded on the imaging plates of the diffractometer by using Mo−$K\alpha$ radiation (λ = 0.71073 Å), and the data reduction was made by MAC DENZO program system. The cell parameters were determined and refined by using the MAC DENZO for all observed reflections. The structure was solved by direct methods using SIR-97[44] and refined with full-matrix least-squares (SHELXL-97[45]) using all independent reflections. Absorption corrections were done by a multiscan method (SORTAV[46]). The non-hydrogen atoms were refined anisotropically. Crystal data for **5a**: $C_{12}H_{20}O_2S_3$, Mw 292.48, colorless cubes, 0.26 × 0.13 × 0.12 mm^3, orthorhombic, space group *Pbca*, a = 8.6590(14), b = 11.644(2), c = 27.952(5) Å, V = 2789.0(8) Å^3, Z = 8, D_{calcd} = 1.393 g cm^{-3}, μ (Mo-Kα) = 0.52 mm^{-1}, 2819 independent reflections, 155 parameters; R_1 = 0.074 ($I > 2\sigma(I)$, 1522 reflections), wR_2 = 0.195 (for all), S = 1.002; temperature 153 K. Crystal data for **18**: $C_{12}H_{20}OS_4$, Mw 308.55, colorless cubes, 0.22 × 0.13 × 0.12 mm^3, triclinic, space group $P-1$, a = 8.0020(12), b = 9.0860(13), c = 11.798(3) Å, α = 69.516(6), β = 83.248(6), γ = 67.72 (2) °, V = 743.5(2) Å^3, Z = 2, D_{calcd} = 1.128 g cm^{-3}, μ (Mo-Kα) = 0.47 mm^{-1}, 2565 independent reflections, 154 parameters; R_1 = 0.073 ($I > 2\sigma(I)$, 1301 reflections), wR_2 = 0.198 (for all), S = 1.001; temperature 298 K.

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Supporting Information Available: Temperature-dependent ^{1}H NMR spectra of methine protons of **7** in $CDCl_3$, X-ray crystallographic data of **5a** and **18**, and DFT calculation data at B3LYP/6-311+G(d,p) and B3LYP/6-311+G(3df,2p) levels, including the vibrational models and frequencies (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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