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Cyclohexasulfur monoxide (S_6O) and cyclohexasulfur (S_6) as sulfur-transfer agents

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Cyclohexasulfur monoxide (S_6O) and cyclohexasulfur (S_6) as sulfur-transfer agents

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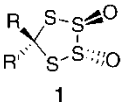
Cyclohexasulfur monoxide (S_6O), prepared *in situ* by the reaction of titanocene pentasulfide with thionyl chloride or the oxidation of S_6 with dimethyldioxirane, reacted with 2,3-diphenyl-1,3-butadiene at room temperature to give the corresponding dihydrodithiin oxide (an S_2O-transfer product), tetrasulfide (an S_4-transfer product), and dihydrodithiin (an S_2-transfer product). S_6O also reacted with *trans*-cyclooctene, cycloheptatriene, and norbornene to provide the corresponding episulfide, trisulfide, and 1,2,3-trithiolane, respectively. The reaction of S_6, prepared by the reaction of titanocene pentasulfide with a small excess amount of SCl_2, with *trans*-cyclooctene gave the corresponding episulfide.

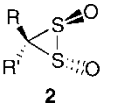
Keywords: cyclohexasulfur; cyclohexasulfur monoxide; sulfur-transfer reaction; butadiene; cyclooctene

1. Introduction

The chemistry of sulfur allotropes (S_n) and their oxides (S_nO_m) has been drawing much attention from the viewpoints of not only fundamental inorganic sulfur chemistry (*1–3*) but also the key, extremely reactive intermediates in organic sulfur-transfer reactions (*4–6*). In 1967, Dodson and Sauers reported the capture of SO, generated by thermolysis of ethylene episulfoxide at 110 °C, with 1,3-butadienes (*4*). Steliou, Gareau, and Harpp succeeded in the generation and the capture of S_2, which was generated by the reaction of $R_3MSSSMR_3$ (M = Si, Ge) and Ph_3PBr_2 through Ph_3PS_3 at 25 °C (*5*). In meantime, several methods have been developed (*6*). In 1999, we reported the generation of S_2O from tetrathiolane 2,3-dioxides **1** and its disproportionation to S_3 and SO_2 (*7*) and the extrusion of SO from dithiirane 1,2-dioxides **2** (*8*). We also revealed that S_8O serves as S_2O or S_3 equivalents (*9, 10*). In this paper, we report the sulfur-transfer reactions from S_6O and S_6 to alkenes.



1



2

R = *t*-Bu, 1-Adamantyl

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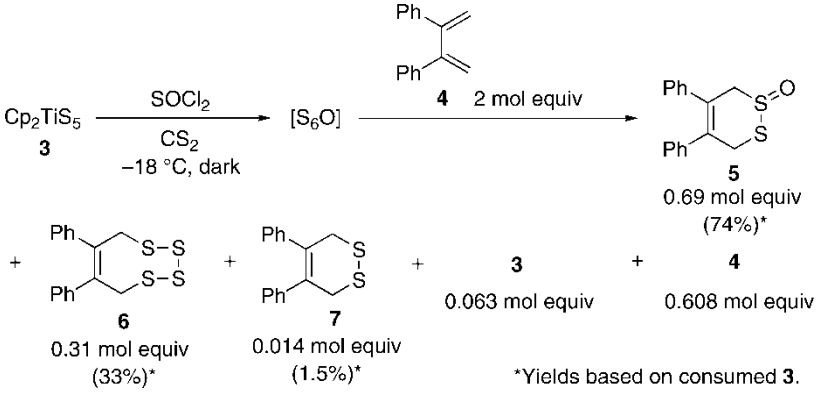
2. Results and discussion

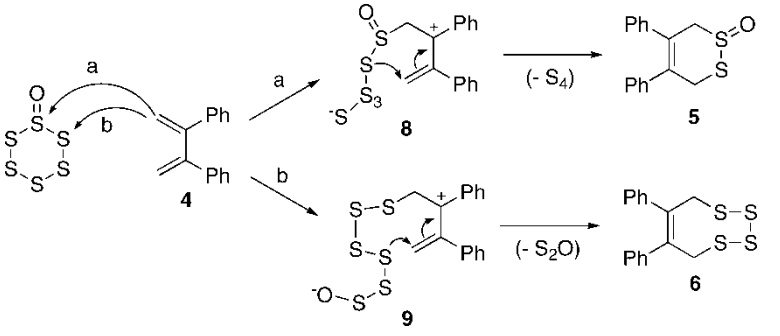
2.1. *Cyclohexasulfur monoxide (S_6O)*

Steudel and Steidel reported that S_6O was prepared by the oxidation of S_6 with CF_3CO_3H, *albeit* in low yield (5%), and was characterized by Raman spectroscopy and X-ray crystallography (*11*). We prepared S_6O *in situ* by the reaction of titanocene pentasulfide **3** (Cp_2TiS_5, Cp = cyclopentadienyl) (*12*) and thionyl chloride ($SOCl_2$) in CS_2 at −18 °C in the dark. When 2,3-diphenyl-1,3-butadiene (**4**) was employed as a reactant, dihydrodithiin oxide **5**, tetrasulfide **6**, and dihydrodithiin **7** were formed in 0.69, 0.31, and 0.014 molar equivalents, respectively, along with recovery of **3** (0.063 molar equiv.) and **4** (0.61 molar equiv.) (Equation 1).



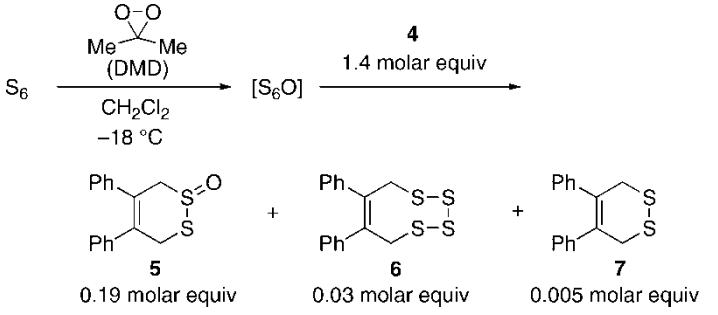
(1)

While we examined this reaction several times, the sum of yields of **5**–**7** did not exceed 1 molar equiv. largely, suggesting that the reactions giving **5**–**7** are operating independently. Thus, the formation mechanisms for the two main products **5** and **6** are speculated as shown in Scheme 1. Butadiene **4** attacks the sulfinyl sulfur (path a) or the neighboring sulfenyl sulfur (path b) of S_6O. The intermediate **8** (path a) cyclizes to give **5** with liberation of S_4, and **9** (path b) is converted to **6** by extrusion of S_2O. S_4 and S_2O in Scheme 1 are not entities and would be taken off by some species. The yields of **5**–**7** based on this idea are given in the parentheses in Equation 1. A radical mechanism was proposed in the S_2-transfer reaction from S_{10} onto 2,3-dimethyl-1,3-butadiene at 90 °C (*6c*). Harpp also reported the hemolytic cleavage of the S−O bond in dialkoxy disulfide (ROSSOR) to generate ROSS· and RO· and then S_2 (*6g*). In the present case, a similar radical process cannot be ruled out.



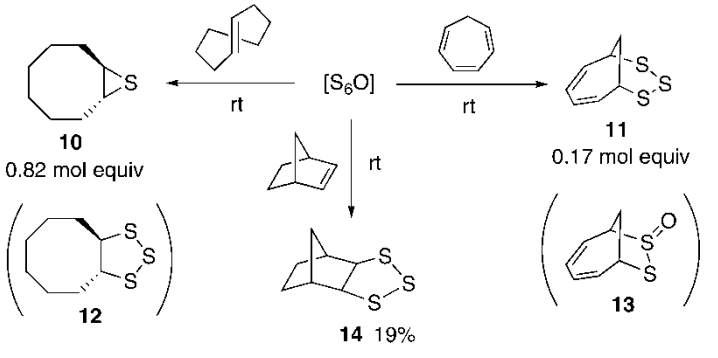
Scheme 1. Plausible formation mechanisms for **5** and **6** in the reaction of S_6O with 2,3-diphenyl-1,3-butadiene (**4**).

We also examined the preparation of S_6O by the oxidation of S_6 (*13*) with an equimolar amount of dimethyldioxirane (DMD) at −18 °C. S_6O thus prepared *in situ* was treated with butadiene **4** (1.4 molar equiv.) to furnish dihydrodithiin oxide **5**, tetrasulfide **6**, and dihydrodithiin **7** in 0.19, 0.03, and 0.005 molar equiv., respectively (Equation 2). This result showed that S_6O was prepared much more effectively by the reaction of Cp_2TiS_5 with $SOCl_2$ than the oxidation of S_6 with DMD.



(2)

Trans-Cyclooctene has been used as an agent abstracting one sulfur atom from 1,2-oxathiolane (sultene) (*14*), $Mo(O)(S_2)(S_2CNEt_2)_2$ (*15*), $Mo(O)[S_2P(OEt)_2]_2$-phenylthiirane (or S_8) (*16*), and 1,2,4-oxadithiolane (*17*). The reaction of S_6O (hereafter prepared by the reaction of Cp_2TiS_5 with $SOCl_2$) with *trans*-cyclooctene (3.3 molar equiv.) yielded *trans*-9-thiabicyclo[6.1.0]nonane (**10**) (0.82 molar equiv.), stereoselectively. The reaction of S_6O with cycloheptatriene gave trisulfide **11** (*10, 18*) (0.17 molar equiv.) (Equation 3). These results are in contrast to those of S_8O giving **12** (*19*) or **13** (*10*), respectively, as the main product. The reaction of S_6O with norbornene gave the corresponding 1,2,3-trithiolane **14** in 19% isolated yield. The formation of **14** was observed as an end product in various sulfuration reactions (*6, 7*). S_6O did not provide identifiable adducts by the reaction with 1,4-diphenyl-1,3-butadiene, 1,3-diphenyl-1,3-butadiene, 1-phenyl-1,3-butadiene, α-methylstylene, or cyclohexene.

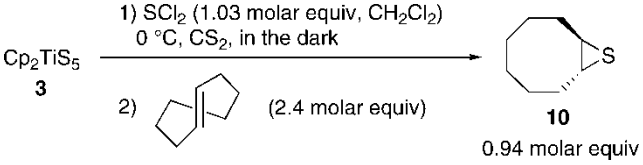


(3)

2.2. *Cyclohexasulfur* (S_6)

The reaction of Cp_2TiS_5 with SCl_2 was reported to afford a mixture of S_6 (87%) and S_{12} (11%) (*13*). We used a solution of S_6 prepared by this reaction, without removal of S_{12}, in the reaction with sulfur-acceptors. Cp_2TiS_5 (**3**) in CS_2 was treated with a small excess amount of SCl_2 (1.03 molar equiv.) at 0 °C and then *trans*-cyclooctene (2.4 molar equiv.) was added to the mixture to furnish 0.94 molar equiv. of episulfide **10** (Equation 4). Interestingly, when an amount less than 1 molar equiv. (0.69 molar equiv.) of SCl_2 was employed, episulfide **10** was not formed at all, suggesting that SCl_2 is necessary for the activation of S_6. In comparison, we examined the reaction of isolated S_6 with *trans*-cyclooctene in the absence or the presence (0.06 molar equiv.) of SCl_2

at room temperature, where the former did not produce episulfide **10** but the latter provided **10** albeit in low yield (0.084 molar equiv.). Thus, SCl_2 was verified to serve as an activator of S_6, but there exist other species such as Cp_2TiCl_2 and S_{12} in the reaction mixture and the details of the mechanism are not clear at present. 2,3-Diphenyl-1,3-butadiene (**4**) or norbornene did not react with S_6.



(4)

3. Conclusion

We found that S_6O, prepared *in situ* by the reaction of Cp_2TiS_5 with $SOCl_2$, transfers S_2O, S_4, and S_2 onto 2,3-diphenyl-1,3-butadiene at room temperature. S_6O also gives S_1 or S_3 to strained alkenes, *trans*-cyclooctene or norbornene, respectively. S_6 reacted with *trans*-cyclooctene to give the corresponding episulfide stereoselectively at room temperature only in the presence of a small amount of SCl_2. S_6O as well as S_8O is a sulfur allotrope activated by oxidation, and S_6O and S_8O exhibit different types of sulfur-transfer reactions toward an atypical, reactive alkene. S_6 itself is much less reactive than S_6O and S_8O. S_6 requires an activator to behave as a sulfur-transfer reagent at room temperature.

4. Experimental

4.1. *Reagents*

The following reagents were prepared by the respective reported methods. Titanocene pentasulfide (**3**) was obtained by the reaction of Cp_2TiCl_2 with S_8-$LiBEt_3H$ (*20*). S_6 was isolated by the reaction of **3** with SCl_2 followed by recrystallization from cold CS_2 as pale brown crystals (m.p. 83–84 °C decomp; lit. 60–80 °C decomp) (*13*). An acetone solution of DMD was prepared by the reaction of acetone and $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (*21*). *Trans*-cyclooctene was obtained by the photochemical isomerization of *cis*-cyclooctene (*22*).

4.2. *Reaction of S_6O, prepared* in situ *by the reaction of Cp_2TiS_5 (3) with $SOCl_2$, with 2,3-diphenyl-1,3-butadiene (4)*

A solution of $SOCl_2$ (38.8 mg, 0.326 mmol) in dichloromethane (1 mL) was added to a solution of Cp_2TiS_5 (104.4 mg, 0.309 mmol) in CS_2 (15 mL) at −18 °C under argon in the dark. After stirring for 30 min, a solution of 2,3-diphenyl-1,3-butadiene (**4**) (124.7 mg, 0.611 mmol) in dichloromethane (10 mL) was added dropwise. The mixture was stirred for 2 h at room temperature and evaporated to dryness. Dibenzyl (34.3 mg, 0.188 mmol) was added to the residue as the internal standard, and the ^{1}H NMR spectrum of the mixture indicated the presence of dihydrodithiin oxide **5** (*6j*) (0.214 mmol, 0.72 molar equiv.), dihydrodithiin **7** (*6j*) (4.3×10^{-3} mmol, 0.014 molar equiv.), tetrasulfide **6** (*6j*) (0.096 mmol, 0.31 molar equiv.), **4** (0.188 mmol, 0.608 molar equiv.), and **3** (0.0194 mmol, 0.063 molar equiv.).

4.3. *Reaction of S_6O, prepared* in situ *by the oxidation of S_6 with DMD, with 2,3-diphenyl-1,3-butadiene (4)*

An acetone solution of DMD (0.0813 M, 1.60 mL, 0.130 mmol) was added to a solution of S_6 (25.7 mg, 0.134 mmol) in dichloromethane (15 mL) at −18 °C under argon in the dark. The mixture was stirred for 1 h, and then a solution of 2,3-diphenyl-1,3-butadiene (**4**) (39.6 mg, 0.194 mmol) in dichloromethane (5 mL) was added dropwise. The mixture was stirred for 2 h at room temperature, and then the solvent was removed under reduced pressure. To the residue was added dibenzyl (14.5 mg, 0.0796 mmol) as the internal standard, and the ^{1}H NMR spectrum was measured to indicate the presence of dihydrodithiin oxide **5** (0.0242 mmol, 0.19 molar equiv.), dihydrodithiin **7** (0.6×10^{-3} mmol, 0.005 molar equiv.), tetrasulfide **6** (4.0×10^{-3} mmol, 0.03 molar equiv.), and **4** (0.0824 mmol).

4.4. *Reaction of S_6O, prepared* in situ *by reaction of Cp_2TiS_5 (3) with $SOCl_2$, with trans-cyclooctene*

A solution of $SOCl_2$ (0.10 mL, 16.8 mg, 0.14 mmol) in CS_2(1 mL) was added to a solution of Cp_2TiS_5 (**3**) (65.4 mg, 0.193 mmol) in CS_2 (5 mL) at −18 °C under argon in the dark. After stirring for 30 min, a solution of *trans*-cyclooctene (52.0 mg, 0.472 mmol) in CS_2 (1 mL) was added. The mixture was stirred for 2 h at room temperature and evaporated to dryness. Dibenzyl (28.3 mg, 0.155 mmol) was added to the residue as the internal standard, and the ^{1}H NMR spectrum was measured to indicate the presence of **3** (0.0827 mmol) and episulfide **10** (*14*, *15*) (0.0904 mmol, 0.82 molar equiv. based on the consumed **3** (0.110 mmol)). Recovered cyclooctene (0.288 mmol, *trans*/*cis* 52/48) was also observed.

4.5. *Reaction of S_6, prepared* in situ *by the reaction of Cp_2TiS_5 (3) with SCl_2, with trans-cyclooctene*

A dichloromethane solution of SCl_2 (1.0 M, 0.20 mL, 0.20 mmol) was added to a solution of Cp_2TiS_5 (**3**) (65.5 mg, 0.194 mmol) in CS_2 (5 mL) at 0 °C under argon in the dark. After stirring for 30 min, a solution of *trans*-cyclooctene (52.0 mg, 0.472 mmol) in CS_2 (1 mL) was added. The mixture was stirred for 2 h at room temperature, and dibenzyl (20.2 mg, 0.111 mmol) was added as the internal standard. The solvent was removed under reduced pressure, and the ^{1}H NMR spectrum of the mixture showed the presence of 0.183 mmol (0.94 molar equiv.) of episulfide **10**. Recovered cyclooctene (0.136 mmol, *trans*/*cis* 65/35) was also observed.

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