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COMMUNICATIONS

[1 + 2] Cycloadditions of Sulfur Monoxide (SO) to Alkenes and Alkynes and [1 + 4] Cycloadditions to Dienes (Polyenes). Generation and Reactions of Singlet SO?

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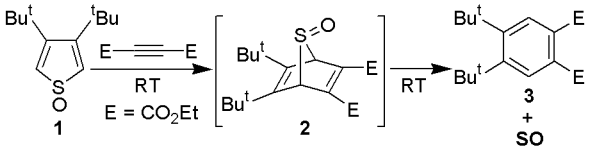
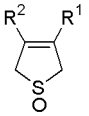
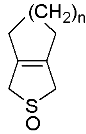
Recently, we reported that the Diels−Alder reaction of 3,4-di-*tert*-butylthiophene 1-oxide (**1**) with dimethyl acetylenedicarboxylate (DMAD) at room temperature affords dimethyl 4,5-di-*tert*-butylphthalate (**3**) in high yield probably through extrusion of sulfur monoxide (SO) from the initial adduct **2**.[1] The SO, generated here, would be singlet if the SO extrusion from **2** takes places and is concerted. We have thus examined a range of chemical trapping experiments of the SO to characterize its reactivities and to compare them with those of SO generated from other organic sources.[2,3]



Thus, the reaction of **1** with an equimolar amount of DMAD was examined at room temperature in the presence of excess diene.[4] 2-Methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 2,3-diphenyl-1,3-butadiene, myrcene, 1,2-dimethylenecyclopentane, and 1,2-dimethylenecyclohexane successfully trapped the SO to give the [1 + 4] cycloadducts **4a**[2f] (49%), **4b**[2a] (74%), **4c**[2a] (28%), **4d**[2k] (27%), **4e** (76%), and **4f** (44%), respectively; the phthalate **3** was isolated in good yield in all cases. Reportedly, SO, generated by thermolysis of thiirane oxide in refluxing toluene, added to each of the three 2,4-hexadiene isomers to provide [1 + 4] adducts, in which the stereochemistry of the dienes was not retained.[2f,g] The authors thus concluded that triplet SO was generated[5] and the addition took place through a radical intermediate. By contrast, the SO generated from **2** failed to add to these dienes, and thus we could not determine the stereochemistry of the addition.

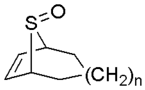


4a: $R^1 = Me, R^2 = H$
4b: $R^1 = R^2 = Me$
4c: $R^1 = R^2 = Ph$
4d: $R^1 = CH_2CH_2CH{=}CMe_2, R^2 = H$

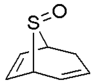


4e: n = 1
4f: n = 2

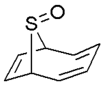
The SO was also trapped by cyclic dienes (polyenes) such as 1,3-cyclohexadiene, 1,3-cycloheptadiene, 1,3-cyclooctadiene, cycloheptatriene, and cyclooctatetraene to give **5a** (68%), **5b** (27%), **5c**[2f] (2%), **5d** (26%), and **5e**[2i] (39%), respectively, although cyclopentadiene failed to give the corresponding adduct. Reportedly, the SO, generated from thiirane oxide in refluxing toluene, gave a mixture of **5e** (23.6%) and **5e′** (4.5%) on reaction with cyclooctatetraene,[2i] whereas in our case, **5e** is the sole adduct. **5e** isomerized to **5e′**, when heated in refluxing toluene, to produce a 9:1 equilibrium mixture of **5e** and **5e′**.[6,7] The other adducts **5a**−**5d** did not undergo such isomerization under the same conditions. Thus, the present [1 + 4] addition is kinetically controlled and results in the stereoselective formation of **5a**−**5e**, where the S=O group is *anti* to the resulting double bond. It was also reported that the SO, generated from thiirane oxide, did not add to cycloheptatriene to give **5d**, but gave 7,7′-dicycloheptatriene probably through hydrogen abstraction by SO.[2b] Any sign of such reaction was not observed in the present case. In addition, throughout this study, [2 + 4] adducts of the SO with dienes never formed, in contrast with reactions of $^1O_2$,[8] diatomic sulfur (S_2),[9] and sulfur dioxide[10] which afford [2 + 4] cycloadducts.



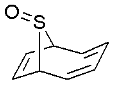
5a: n = 0
5b: n = 1
5c: n = 2



5d



5e

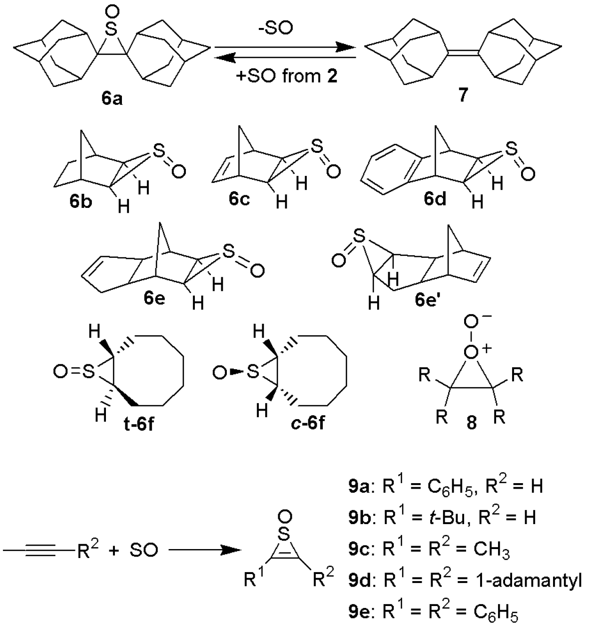


5e'

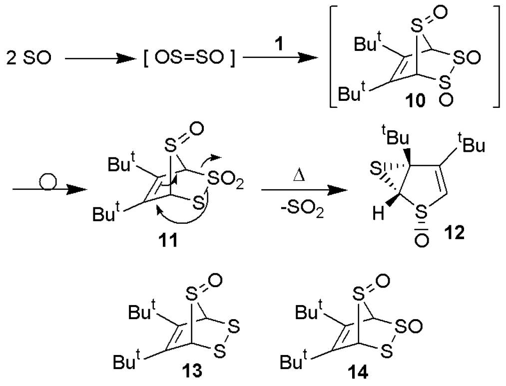
Thiirane oxide **6a** was reported to generate SO with formation of 2,2′-biadamantylidene (**7**).[2j,k] We have now found that the reverse reaction does take place, that is, the SO, generated from **2**, added to **7** affording **6a** in 17% yield. Angle-strained alkenes, norbornene, norbornadiene, and benzonorbornadiene also reacted with the SO to produce **6b**[11] (2%), **6c**[11] (19%), and **6d** (4%), respectively, thus providing a new one-pot conversion of alkenes to thiirane oxides. Dicyclopentadiene gave **6e** (5%) and **6e′** (3%). The SO addition to *cis*- and *trans*-cyclooctene is stereospecific and gave **c-6f** (2%) and **t-6f** (17%) as the sole adduct, respectively, indicating that the addition may occur in a concerted manner.[12] However, more general information on the stereochemistry was not obtained because the SO did not add to *cis*- and *trans*-cyclodecenes and *cis*- and *trans*-3-hexenes. Incidentally, we should note the fact that thiirane oxides correspond to perepoxides **8**, which were often postulated as the intermediates that lead to the formation of dioxetanes and other products for the reactions of $^1O_2$ with alkenes.[13]

Synthetically most important is the addition of the SO to alkynes, which provided a simple synthesis of thiirene 1-oxides.[14] Thus, the SO added to 2-phenylacetylene, 3,3-dimethyl-1-butyne, 2-butyne, di(1-adamantyl)acetylene, and diphenylacetylene to give thiirene 1-oxides **9a** (20%), **9b** (10%), **9c**[15] (17%), **9d**[14e−g] (7%), and **9e**[14a,b] (5%), respectively. **9a** and **9b** are the first examples of monosubstituted thiirene 1-oxides. Even structurally simple thiirene 1-oxides such as **9a**−**c** are much more stable than expected and were satisfactorily purified by silica gel column chromatography, recrystallization, or distillation. In the ^1H NMR spectrum of **9a** and **9b**, the vinyl proton appeared at δ 8.69 and 8.20, respectively, values comparable to those of cyclopropenone (δ 9.0) and methylcyclopropenone (8.6).[16]

10.1021/ja072044e CCC: $37.00 © 2007 American Chemical Society



As described above, the yields of the SO-trapping products are generally low to moderate, though the yield of **3** was more than 80%. The remaining SO is consumed to produce elemental sulfur, sulfur dioxide, and compound **11**. The formation of **11** can best be explained by dimerization of SO and the Diels−Alder reaction of the resulting disulfur dioxide (OS═SO)[3] with **1** that produces *vic*-disulfoxide **10**,[17] which undergoes a 1,2-rearrangement to give **11**. Thus, the reaction of DMAD with 2 molar equiv of **1** gave an increased yield of **11** (46%). **11** was alternatively obtained by oxidation of **13**[18] through the known compound **14**[18] and then **10**. **11** is thermally unstable and converted to **12** by extrusion of SO$_2$.



Evidently the reactivities of the present SO differ from those of SO that was generated from thiirane oxides and other sources and considered to be triplet. Its capability of adding to alkenes and alkynes resembles singlet carbenes. Therefore, seemingly, the singlet SO was generated from **2** and directly involved in the trapping reactions without decay to the more stable triplet.[19,20]

Acknowledgment. This work was supported by a Grant-in-Aid (#16350019) for Scientific Research the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Supporting Information Available: General procedure of the trapping experiments and spectroscopic data for new compounds and a few selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA072044E