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SYNTHESIS OF A NOVEL FUSED THIIRENE SULFOXIDE WITH ENDOPEROXIDE AND ITS DIELS-ALDER ADDUCT

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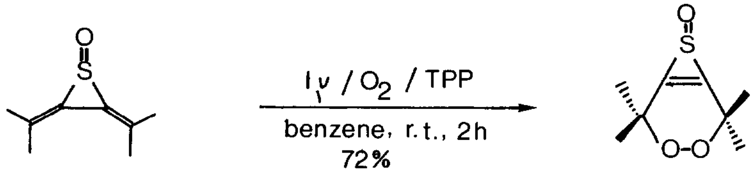
Abstract: Photooxidation of thiiranoradialene sulfoxide afforded a new thiirene sulfoxide fused with an endoperoxide ring, which gave the [2+4]cycloadduct with furan.

In our recent studies Diels-Alder reaction of thiiranoradialene sulfoxide 1[1] has emerged as powerful method for preparing highly strained fused small ring systems.[2] 4-Substituted 1,2,4-triazoline-3,5-dione(TAD) as a dienophile quantitatively afforded a fused thiirene sulfoxide,[2] although strong dienophiles such as tetracyanoethylene, maleinimide, etc. did not react. Therefore, the successful use of TAD demands knowledge of similarity[3] on cycloaddition of singlet oxygen($^1O_2$).

We now report that 1 reacted with $^1O_2$ to afford a novel fused thiirene sulfoxide without any [2+2]cycloaddition, ene reaction and S-oxidation(Eq.1).[4]



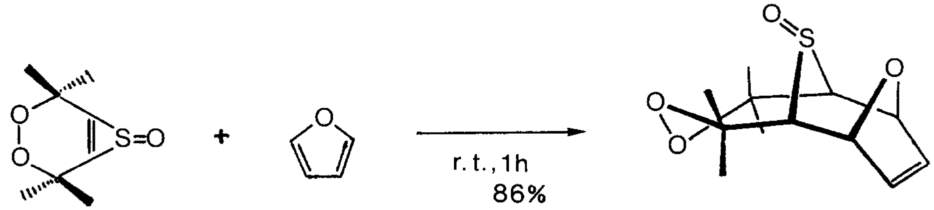
1

2

(1)

Photooxidation of 1 in benzene with a 300W halogen lamp through a Pyrex filter under bubbling oxygen in the presence of tetraphenylporphyrin(TPP) at room temperature, gave colorless crystalline product in 72% yield after purification by preparative high pressure liquid chromatography.[5] Recrystallization from CCl_4 at low temperature afforded genuinely pure product having mp 103°C(decomp). The product was suggested to be a new thiirene sulfoxide 2 fused with endoperoxide ring, from its spectroscopic data.[6,7] Namely, unusually high frequency of S-O absorption at 1115 cm^{-1} in IR and highly down-field shifted carbon resonance at 155.5 ppm in ^{13}C-NMR are characteristic of the fused thiirene sulfoxide.[2] Simple ^1H-NMR of two singlets at 1.63 and 1.67 ppm for four methyl groups also supports the structure 2. It is interesting that 1 favorably undergoes [2+4]cycloaddition in spite of its possible multireactivity toward $^1O_2$.

Since ring fusion generally causes higher reactivity to small ring compounds due to the ring strain, the reaction of the thiirene sulfoxide 2 in furan was studied.

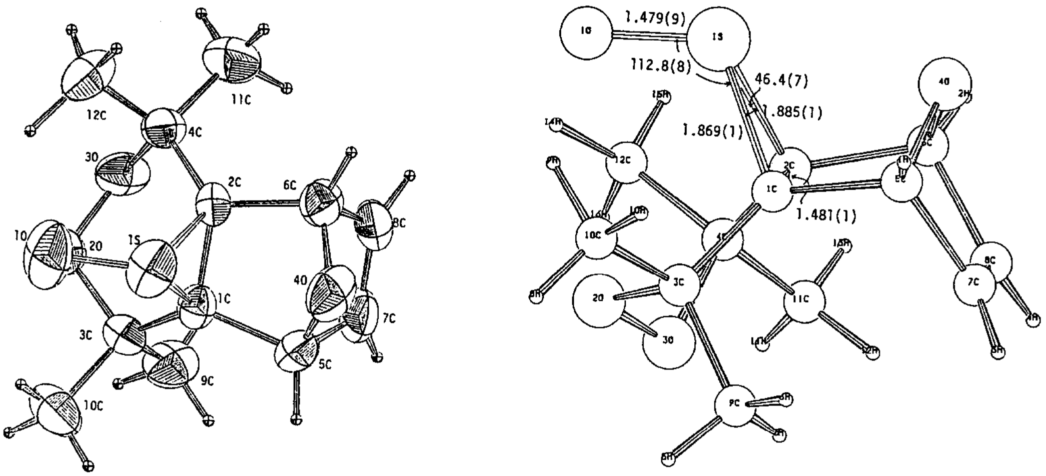


2

3

(2)

When 2 was dissolved in furan and allowed to stand for 1 h at room temperature, colorless crystals were obtained after removal of excess furan (Eq. 2). Chromatographic purification gave only one pure product in 86% yield. The product was enough stable not to decompose at 100°C.[8] Assigned structure 3 as a [2+4]cycloadduct by spectroscopic and elemental analyses,[8] was correctly confirmed by the X-ray crystal structure analysis,[9,10] which could strongly suggest the structure of 2, too(Figure 1). Surprisingly, the X-ray result clearly indicates the reaction is stereospecific with endo



(90° rotated)

Figure 1 ORTEP Presentation of Molecular Structure of One of the Two Independent Molecules of the Cycloadduct 3.[10] Selected Mean Bond Lengths(Å) and Angles(°) of the Two Molecules.

addition.[11] Bicyclo[3.1.0] system containig thiirane sulfoxide moiety is the lowest synthetic limit of the ring size at present time.[12] The formation of 3 owes undoutedly its driving force to the favorable removal of the ring strain of 2 by the cycloaddition.[13] This result was compared with 2,3-diphenylthiirene sulfoxide,[14] only known non-fused one, which was quite unreactive toward furan even at 80°C in a sealed tube.

There has been no X-ray crystal structure analysis for thiirene sulfoxide so far. Inspection of the X-ray crystal analysis data suggests that the thiirane ring of 3 is slightly " lanky " as expected for the first propellane type thiirane sulfoxide 3, in comparison with those of ethylene episulfoxide by microwave analysis.[15] Namely, bond length of 1S-1C(1.869 Å) or 1S-2C (1.885 Å) is ca. 0.05 Å longer whereas 1C-2C(1.481 Å) is 0.02 Å shorter. Therefore, the angle of 1C-1S-2C(46.4°) is 2° smaller. However, S-O bond length(1.479 Å) is comparable to that of ethylene episulfoxide(1.483 Å), as suggested by IR absorption(1067 cm^{-1}).[8]

As for the unique reactivity of some fused thiirene sulfoxides,[2] addition of C-C double bond, ring opening reaction, etc. will be described in the near future.[13]

REFERENCES AND FOOTNOTES

1. Ando, W.; Hanyu, Y.; Takata, T. *Tetrahedron Lett.*, 1981, **22**, 4815 - 6.
2. Ando, W.; Hanyu, Y.; Takata, T.; Ueno, K. *J. Am. Chem. Soc.*, 1982, **104**, 4981 - 2.
3. An example: Adam, W.; De Lucchi, O. *Tetrahedron Lett.*, 1981, **22**, 929 - 32.
4. In contrast, thiiranoradialene[1] seemed to undergo [2+2]cycloaddition with singlet oxygen to give acetone as a detectable product.
5. The product **2** readily decomposed on exposing to silica gel and even neutral alumina.
6. **2**: Colorless crystals, mp 103°C(decomp); ^{1}H-NMR(δ,CDCl$_3$) 1.67(s,6H), 1.63(s,6H); ^{13}C-NMR(δ,CDCl$_3$) 155.5(s), 85.5(s), 23.6(q), 22.8(q); IR (cm^{-1},CDCl$_3$) 1115(S=O).
7. Elemental analysis could not be achieved since **2** slowly decomposed.
8. 3: Colorless crystals, mp 113°C(decomp); ^{1}H-NMR(δ,CDCl$_3$) 6.71(s,2H), 5.22(s,2H), 1.90(s,6H), 1.39(s,6H); ^{13}C-NMR(δ,CDCl$_3$) 137.8(d), 81.6(d), 80.1(s), 62.7(s), 26.9(q), 22.0(q); IR(cm^{-1},KBr) 1067(S=O); MS m/e 208 (M^{+}- SO); Elemental analysis: Calcd for $C_{12}H_{16}O_4S$, C 56.23; H 6.29. Found, C 56.29; H 6.29.
9. The crystal has monoclinic space group $P2_1/n$ with a=16.280(4), b=10.588(6), c=16.117(5), and β=117.81(2) with Z=8. Intensity data were collected on a Rigaku automated four-circle diffractometer with graphite-monochromated Mo Kα radiation. Of 5837 reflections obtained with $2\theta \leq 55°$, 2467 with $|F| > 3\sigma(F)$ were used for structure analysis. The structure was refined to a final value of R=0.053. Final crystallographic coordinates have been deposited with the Cambridge Crystallographic Data Centre.
10. There are two independent molecules in the asymmetric unit. Both of them have essentially the same structure.
11. Endo addition was also observed in the case of cyclopropene derivatives: Wiberg, K. B.; Bonneville, G. *Tetrahedron Lett.*, 1982, 23, 5385 - 8.
12. The product **3** is the second example. First example: Solway, S. B. *U. S. Patent*, 1955, 2,694,072; *Chem. Abstr.*, 1955, **49**, 3645.
13. In addition to **3**, [2+4]cycloadducts of **2** and other thiirene sulfoxides[2] with furan, diphenylisobenzofuran, cyclopentadiene, etc. were also prepared in high yields.
14. Few reactions of the thiirene sulfoxide are known: Carpino, L. A.; Chen, H.-W. *J. Am. Chem. Soc.*, 1979, **101**, 390 - 4.
15. Saito, S. *Bull. Chem. Soc. Jpn.*, 1969, 42, 663 - 6.

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