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REACTION OF SINGLET OXYGEN WITH THIIRANE: IMPLICATION FOR A SPIRODIOXATHIIRANE INTERMEDIATE

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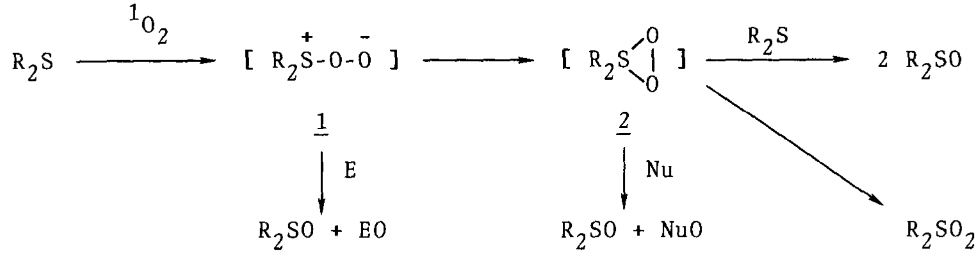
Summary: Photosensitized oxygenation of biadamantylidene thiirane afforded, in addition to the corresponding thiirane oxide, the desulfurization products i.e., biadamantylidene and its oxidized products, dioxetane and oxirane, via a spirodioxathiirane intermediate.

Reaction of singlet oxygen with sulfur compounds has been extensively studies and much attention has been devoted to the structures of peroxidic intermediate.[1-4] The photooxidation of sulfide was first described by Schenck et al.[5] They reported that dialkyl sulfides undergo photosensitized oxygenation to give 2 moles of sulfoxide per mol of absorbed oxygen. The nucleophilic persulfoxide 1 might be of first hypothetical intermediate followed by cyclization to electrophilic dioxathiirane 2 of second one.[2,3] At low temperature in aprotic solvent[6], sulfone formation is accelerated from direct rearrangement of 2. Their structures are, however, not certain yet. Photosensitized oxygenation of thiirane might be an interesting target to clear the characteristic and structure of such intermediates.



In this paper we would like to show that a spirodioxathiirane is genarated as an intermediate in photosensitized oxygenation of biadamantylidene thiirane (3).

Photosensitized oxygenation of thiirane 3 (3.3×10^{-2}M) was carried out at 15°C for 6 hrs in methylene chloride with methylene blue (MB, 1.1×10^{-3}M) as a sensitizer and use of two 500W halogen lamps. When the reaction mixture was chromatographed on silica gel, the corresponding thiirane oxide (4), biadamantylidene dioxetane (5), and biadamantylidene oxirane (6) with a trace amount of biadamantylidene (7) and unreacted thiirane were obtained (Scheme 1). No reaction took place in the absence of light and a sensitizer. This oxidation was inhibited by addition of 0.3 eq of DABCO, a singlet oxygen

Scheme 1.

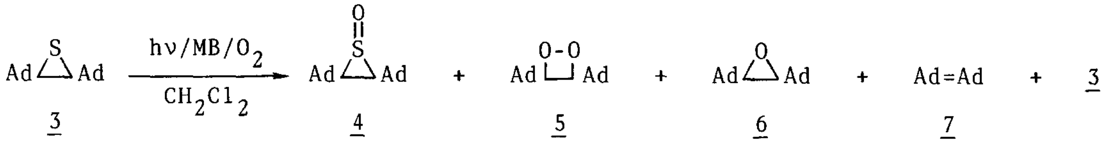
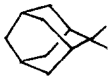


Table 1. Photosensitized Oxygenation of 3



Reaction conditions[b]	Products and Yields[a](%) $\underline{4}^c$	$\underline{5}^d$	$\underline{6}^d$	$\underline{7}^d$
15°C	55.1	17.7	6.5	0.5
-40°C	28.3	7.8	44.3	6.5
MeOH-CH_2Cl_2(10:1),15°C	97.6	trace	0	trace
DMSO(50eq)/CH_2Cl_2,15°C	73.3	12.7	9.2	0.4

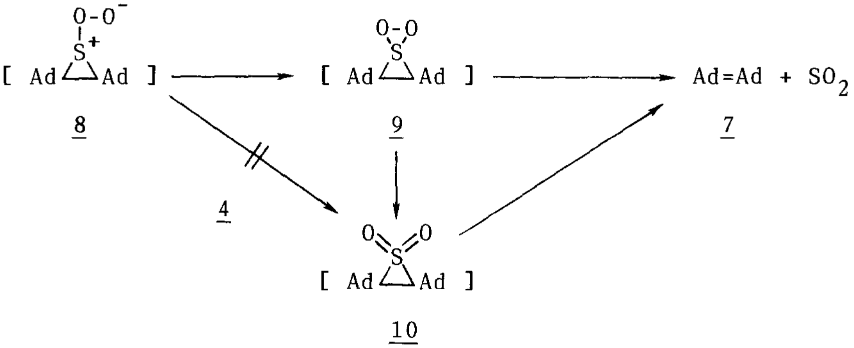
a) Conversion yields. b) hν/MB/O_2/CH_2Cl_2 c) Isolated yields.

d) GLC yields.

quencher.[7] These results clearly show an incorporation of singlet oxygen reaction. Interestingly, the yields of thiirane oxide 4, dioxetane 5, and oxirane 6 depends on solvent, additive and temperature. The results obtained are summarized in Table 1. Addition of methanol and dimethyl sulfoxide accelerated the formation of thiirane oxide 4. As the reaction temperature was decreased from 15°C to -40°C, the yield of oxirane 6 increased dramatically. The formation of thiirane oxide 4 could be explained as follows. Methanol may stabilize a thiirane peroxide intermediate 8 by hydrogen bonding[1-3] and it would decrease the negative charge on an outer oxygen atom making the intermediate more electrophilic. The methanol stabilized 8 could react with thiirane 3 to form 2 moles of 4. 8 also could be trapped by nucleophilic oxygen atom transfer to dimethyl sulfoxide to yield the corresponding thiirane oxide (4) and dimethyl sulfone.[1-3] Without electrophiles thiirane peroxide 8 may collapse to form a spirodioxathiirane intermediate 9 which reacts with another thiirane 3 to give 2 moles of thiirane oxide 4[1-3] and this cyclization seems to be very fast (Scheme 2).

It is quite interesting to note the formation of oxirane 6. The formation of oxirane 6 was enhanced at low temperature in aprotic solvent by suppression of the formation of thiirane oxide 4. This means that instead of intermolecular reaction of a spirodioxathiirane intermediate 9 with thiirane 3,[6] the elimination of sulfur dioxide from a spirodioxathiirane 9 occurs directly and/or through the biadamantylidene thiirane dioxide (10) to produce biadamantylidene (7) which was oxidized to oxirane 6.[8,9] Thiirane dioxide 10 could not be produced from the reaction of thiirane oxide 4 with thiirane peroxide intermediate 8, probably by steric hindrance of the sulfoxide center.

Scheme 2.



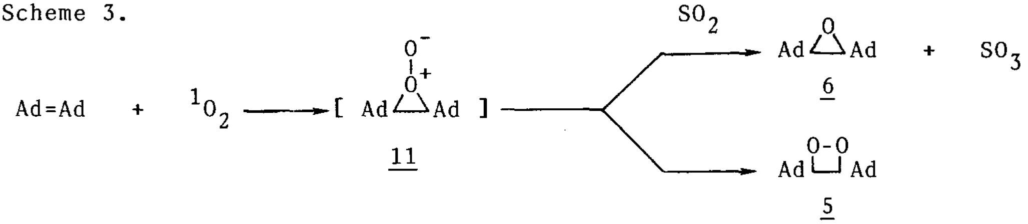
Above results prompted us to study the photosensitized oxygenation of thiirane 3 and biadamantylidene (7) in the presence of sulfur dioxide. The epoxidation occurs very efficiently (Table 2,Entry 1,5)[10,11] which is strikingly contrast with predominant formation of dioxetane 5 in photosensitized oxygenation of 7.[12] Control experiments show that no epoxidation occurred in the absence of sulfur dioxide and methylene blue.[13] Since sulfur dioxide is sufficiently dissolved in the reaction mixture at low temperature,[14] addition of an excess of sulfur dioxide did not alter the yield of 6 (Entry 3). The formation of oxirane 6 can be explained by that a sulfur dioxide captures a nucleophilic oxygen atom of perepoxide intermediate 11, as was in the case of the sulfoxide trapping of 11.[15] Further studies on the effect of SO_2 in the photosensitized oxygenation of olefin are being in progress.

Table 2. Photosensitized Oxygenation of 3 and 7 in the Presence of SO_2.[10]

			Products and Yields[a](%)			
Entry	Substrates	Reaction conditions	4	5	6	7
1	3	MB/15°C/CH_2Cl_2/SO_2	45.9	trace	28.3	12.1
2	3	MB/15°C/CH_2Cl_2	55.1	17.7	6.5	0.5
3	3	MB/-40°C/CH_2Cl_2/SO_2	22.6	trace	39.3	12.0
4	3	MB/-40°C/CH_2Cl_2	28.3	7.8	44.3	6.5
5	7	MB/15°C/CH_2Cl_2/SO_2	——	trace	98.0	——

a) Conversion yields.

Scheme 3.



References;

1) Ando, W.; Takata, T., In " Singlet O_2 ", Frimer, A. A., Ed.; CRC Press: Florida, 1985: Vol. 3, p 1.
2) Gu, C. -L.; Foote, C. S.; Kacher, M. L., J. Am. Chem. Soc., 1981, 103, 5949.; Gu, C. -L.; Foote, C. S., ibid., 1982, 104, 6060.
3) Liang, J. -J.; Gu, C. -L.; Kacher, M. L.; Foote, C. S., J. Am. Chem. Soc., 1983, 105, 4717.
4) Akasaka, T.; Ando, W., Tetrahedron Lett., 1985, 26, 5049; references cited therein.
5) Krauch, C. H.; Hess, D.; Schenck, G. O., unpublished results; quoted by: Gollnick, K., Adv. Photochem., 1968, 6, 1.
6) Foote, C. S.; Peters, J. W., J. Am. Chem. Soc., 1971, 93, 3795.
7) Foote, C. S.; Peterson, E. R.; Lee, K. -W., J. Am. Chem. Soc., 1972, 94, 1032.
8) Zoller, U., In " SMALL RING COMPOUNDS ", Hasser, A., Ed. An Interscience Publication: New York, 1983: Vol. 42, Part 1, p 517; references cited therein.
9) By addition of etheral diazomethane solution to the reaction mixture, sulfuric acid formed by hydration of sulfur trioxide under the reaction condition was detected as dimethyl sulfate by GLC.
10) Sulfur dioxide (Seitetsu Chemical Co.) was used as received. Photosensitized oxygenation of thiirane 3 was carried out in sulfur dioxide (ca. 160 eq)-dissolved methylene chloride.
11) Ando, W.; Sonobe, H.; Akasaka, T., details will be reported in a separate paper.
12) Jefford, C. W.; Boschung, A. F., Helv. Chim. Acta., 1977, 60, 2673.
13) Desulfurization of thiirane 3 did not take place in the absence of oxygen under the reaction conditions.
14) Sano, H., Nippon Kagaku Zasshi, 1968, 89, 36.
15) Schaap, A. P.; Recher, S. G.; Faler, G. R.; Villasenor, S. R., J. Am. Chem. Soc., 1983, 105, 1691.

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