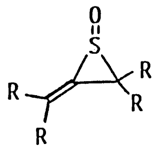
CHEMISTRY LETTERS, pp. 1501-1504, 1988.

Oxidation of Allene Episulfide.
Selective Sulfur Oxidation and Novel Isomerization of Resulting S-Oxide

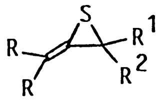
Norihiro TOKITOH, Akihiko ITAMI, and Wataru ANDO*
Department of Chemistry, University of Tsukuba,
Tennohdai 1-1-1, Tsukuba, Ibaraki 305

Oxidation of several kinds of substituted allene episulfides was investigated using peracid and singlet oxygen to show an interesting substituent effect on the oxidation products. Thermal and acid-catalyzed isomerization of resulting allene episulfide S-oxide was also described.

Although the oxidation of thiiranes has been widely explored to provide a general method for the preparation of thiirane S-oxides,$^{1)}$ little is known for the chemistry of allene episulfide S-oxides,$^{2)}$ which are an interesting molecule as a new class of strained small ring system and a methylene homologue of thiirane S-oxide. Oxidation of allene episulfide also attracts much attention from a standpoint of comparing with that of methylenecyclopropane and its heteroatom analogues.$^{3)}$



Allene Episulfide S-Oxide



1

1a; R = ^{t}Bu, R^1 = R^2 = Ph
1b; R = Ph, R^1 = R^2 = ^{t}Bu
1c; R = ^{t}Bu, R^1 = H, R^2 = CO_2Et
1d; R = $SiMe_3$, R^1 = R^2 = Ph

Recently, we have described a facile formation of stable substituted allene episulfides (**1a**, **1b**, **1c**, and **1d**) and investigated their thermal and acid-catalyzed isomerization in order to elucidate the nature of intermediary thioxyallyl species.$^{4)}$ We wish to present here the peracid oxidation and photooxygenation reaction of these allene episulfides together with the characteristic valence isomerization of the resulting allene episulfide S-oxides.

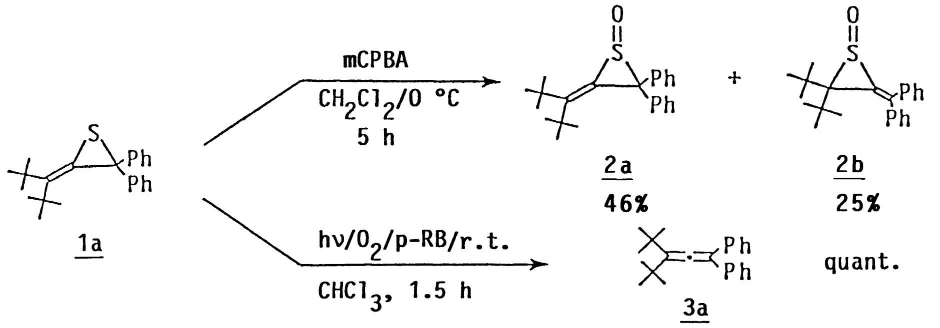
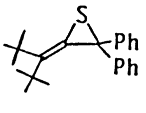
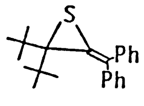
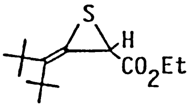
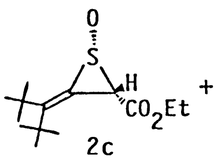
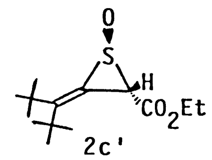
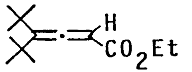
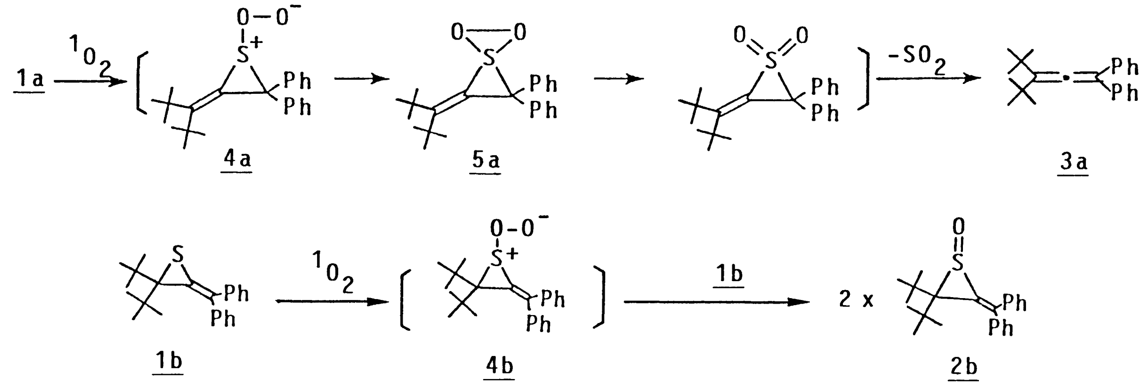


Table 1. Oxidation of Substituted Allene Episulfides

Substrates	Oxidation method	Products (Yield/%)
 1a	mCPBA/CH_2Cl_2/0 °C/5 h	2a (46) + 2b (25)
	hν/O_2/p-RB[a]/r.t./1.5 h	3a (quant.)
 1b	mCPBA/CH_2Cl_2/0 °C/5 h	2b (82)
	hν/O_2/p-RB[a]/r.t./14 h	2b (95)
 1c	mCPBA/CH_2Cl_2/0 °C/5 h	 2c +  2c' (90) (1:1)
	hν/O_2/MB[b]/r.t./2 h	 3c (85) + 2c and/or 2c' (11)

a) Polymer Rose Bengal. b) Methylene Blue.

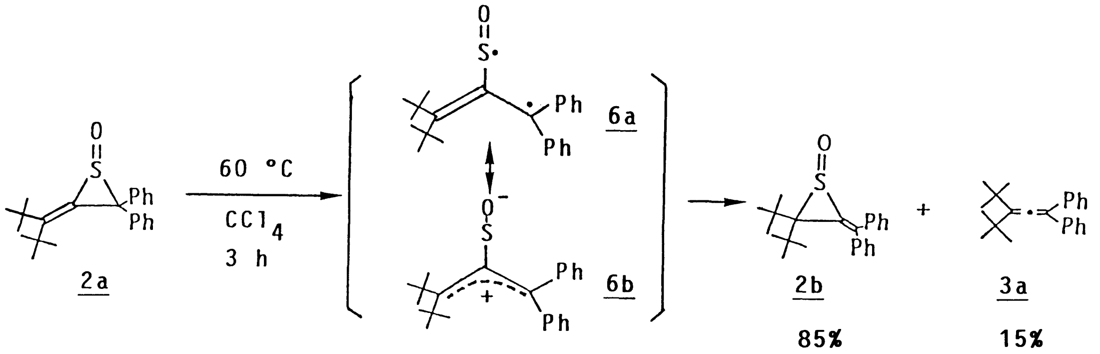
When the allene episulfide (**1a**) was treated with equimolar amount of m-chloroperbenzoic acid (mCPBA) in dichloromethane at 0 °C for 5 h, the S-oxide (**2a**, 46%) was isolated along with the isomerized S-oxide (**2b**, 25%) after silica gel chromatography. The other allene episulfides (**1b** and **1c**) except for **1d**, which decomposed to give a complex mixture under the similar oxidation conditions, also afforded the corresponding S-oxides (**2b**, **2c**, and **2c'**) as listed in Table 1.[5] In contrast, the oxygenation of these allene episulfides with photochemically generated singlet oxygen gave quite different results. **1a** and **1c**



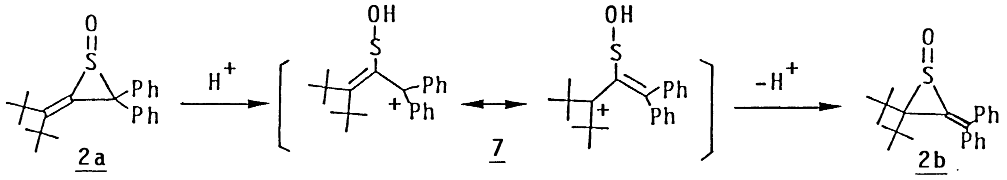
were readily photooxygenated at room temperature in chloroform with polymer Rose Bengal as a sensitizer and use of two 500 W halogen lamps to give the corresponding allenes (**3a** and **3c**) in excellent yields, while **1b** was oxidized very slowly under the same conditions affording the S-oxide (**2b**) quantitatively.

Since the oxidation potentials of **1a** and **1b** showed values adequate for the photooxygenation (E_{ox} = 1.14 and 1.40 V vs. SCE for **1a** and **1b**, respectively), the striking contrast between **1a** and **1b** might be attributable to their difference in the steric hindrance around the allene episulfide unit. The bulky substituents supressed alternative oxygenation onto the exomethylene bond of allene episulfide and resulted in a selective oxidation of its sulfur atom.6) The formation of allenes (**3a** and **3c**) is well interpreted with the initially formed persulfoxide intermediate (**4**) leading to an unstable allene episulfide S,S-dioxide formation via the spirodioxathiirane intermediate (**5**) as the case in the photooxygenation of adamantylideneadamantane episulfide.1d) It seems to us that the higher steric repulsion of the persulfoxide (**4b**) may allow the intermolecular oxidation of unreacted allene episulfide (**1b**) exceeding the intramolecular cyclization into dioxathiirane intermediate.

Next, we have investigated the thermal and acid-catalyzed isomerization of allene episulfide S-oxide (**2a**) into **2b** with a view to comparing the nature of the ring-opened reactive species such as **6a** or **6b** with that of thioxyallyl intermediate in the isomerization of allene episulfides.



The thermolysis of the S-oxide (**2a**) at 60 °C in carbon tetrachloride was monitored by ^{1}H-NMR, and shown to be completed within 3 h affording the isomerized S-oxide (**2b**, 85%) and the corresponding allene (**3a**, 15%). This remarkably facile isomerization relative to that of allene episulfide may be rationalized not only with the resonance stabilization of the ring-opened zwitterionic intermediate such as **6b** but also with the increased nucleophilicity of the sulfur atom of **6b** in the recyclization step leading to the S-oxide (**2b**).



Isomerization of the S-oxide (**2a**) via thioxyallyl cation-type intermediate (**7**) was achieved by the action of acid catalyst such as trifluoroacetic acid in CCl_4 resulting in a quantitative formation of **2b**. Concerning the electronic structure of the allylic part of the ring-opened intermediate, the mechanism of the thermal isomerization of allene episulfide S-oxide (**2a**) seems to have closer resemblance to its acid catalyzed isomerization rather than the thermal valence isomerization mechanism of non-oxidized allene episulfides (**1a** and **1d**).

References

1) a) C. D. Dittmer and G. C. Levy, J. Org. Chem., 30, 636 (1965); b) K. Kondo, A. Negishi, and M. Fukuyama, Tetrahedron Lett., 1969, 2461; c) K. Kondo and A. Negishi, Tetrahedron, 27, 4821 (1971); d) W. Ando, H. Sonobe, and T. Akasaka, Tetrahedron Lett., 27, 4473 (1986), and references cited therein.

2) E. Schaumann and H. Behr, Tetrahedron, 37, 219 (1981); H. Behr, Ph. D. Thesis, University of Hamburg, FRG (1981).

3) W. Ando, Y. Hanyu, Y. Kumamoto, and T. Takata, Tetrahedron, 42, 1989 (1986).

4) W. Ando, A. Itami, T. Furuhata, and N. Tokitoh, Tetrahedron Lett., 28, 1787 (1987); N. Tokitoh, N. Choi, and W. Ando, Chem. Lett., 1987, 2177.

5) All the products newly obtained in this paper gave satisfactory spectral data as follows:

2a: ^{1}H-NMR(CDCl$_3$) δ 1.18(s, 9H), 1.72(s, 9H), 7.1-7.8(m, 10H); IR(CHCl$_3$) 1080(S=O) cm^{-1}; MS, m/z 352(M$^+$); HRMS Found: 352.1855, Calcd for $C_{23}H_{28}OS$: 352.1861.

2b: ^{1}H-NMR(CDCl$_3$) δ 1.12(s, 9H), 1.39(s, 9H), 7.2-7.8(m, 10H); IR(CHCl$_3$) 1050(S=O) cm^{-1}; MS, m/z 352(M$^+$); HRMS Found: 352.1861, Calcd for $C_{23}H_{28}OS$: 352.1861.

2c: ^{1}H-NMR(CDCl$_3$) δ 1.34(s,9H), 1.42(t, J=7.2 Hz, 3H), 1.53(s, 9H), 3.53(s,1H), 4.28(q, J=7.2 Hz, 2H); IR(CCl$_4$) 1085(S=O) cm^{-1}; MS, m/z 272(M$^+$); HRMS Found: 272.1474, Calcd for $C_{14}H_{24}O_3S$: 272.1446.

2c': ^{1}H-NMR(CDCl$_3$) δ 1.39(s, 9H), 1.44(t, J=7.2 Hz, 3H), 1.52(s, 9H), 3.68(s, 1H), 4.15(q, J=7.2 Hz, 2H); IR(CCl$_4$) 1080(S=O) cm^{-1}; MS, m/z 272(M$^+$), HRMS Found: 272.1432, Calcd for $C_{14}H_{24}O_3S$: 272.1446.

3c: ^{1}H-NMR(CDCl$_3$) δ 1.23(s, 18H), 1.26(t, J=7.1 Hz, 3H), 4.26(q, J=7.1 Hz, 2H), 5.50(s, 1H); ^{13}C-NMR(CDCl$_3$) δ 14.28(q), 31.78(q), 35.21(s), 60.19(t), 89.02(d), 125.60(s), 167.05(s), 212.21(s); IR(CCl$_4$) 1930(C=C=C) cm^{-1}; MS, m/z 224(M$^+$); HRMS Found: 224.1806, Calcd for $C_{14}H_{24}O_2$: 224.1776.

6) Sterically less hindered allene episulfide derivatives such as 1,1,3,3-tetramethylallene episulfide and 1,1,4,4-tetramethyl-1,2,3-butatriene 2-episulfide were readily reacted with photochemically generated singlet oxygen at their exomethylene bonds to afford acetone as the expected oxidation product, see Ref. 3a. The photooxygenation of vinyl sulfides has been established to undergo the selective oxidation of their olefinic parts; W. Ando, J. Suzuki, T. Arai, and T. Migita, Tetrahedron, 29, 1507 (1973); W. Ando, K. Watanabe, J. Suzuki, and T. Migita, J. Am. Chem. Soc., 96, 6766 (1974).

(Received June 8, 1988)