Singlet Oxygen.[1] Conformational Requirements for the Decomposition of Sulphur Substituted Dioxetans

By Wataru Ando* and Kazuo Watanabe
(*Department of Chemistry, The University of Tsukuba, Niiharigun, Ibaraki* 300-31, *Japan*)
and Toshihiko Migita
(*Department of Chemistry, Gunma University, Kiryu, Gunma* 376, *Japan*)

Summary Photosensitized oxygenation of 1-ethylthiocyclohexene gave a C–C bond cleavage product *via* an intermediate sulphur substituted dioxetan, but when 1-ethylthio-4-t-butylcyclohexene was used both C–C and C–S cleavage products were produced; the relative cleavage of the C–S and C–C bonds was affected by the conformation of the intermediate dioxetans.

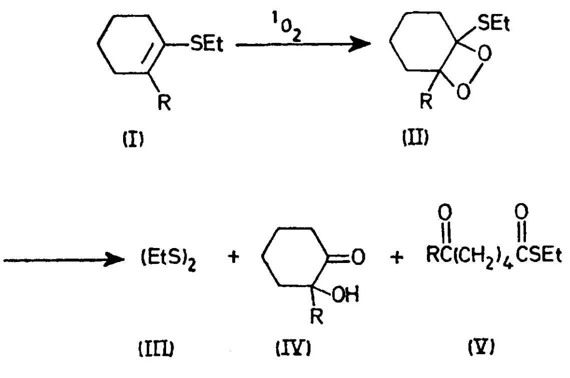
Recently several studies on the decomposition of dioxetan have been reported[2] but they have been restricted to 1,2-dioxetan not involving hetero atoms. We previously found[3,4] that the reaction of various vinyl sulphides with singlet oxygen gave C–S and C–C cleavage products of intermediate sulphur substituted dioxetans. We now report that the ratio of C–S to C–C cleavage is affected by the conformation of the substrate in the decomposition of the sulphur substituted dioxetans.

Table 1. Relative yield[a] of C–S and C–C cleavage products (%) in the reaction of singlet oxygen and 2-substituted 1-ethylthiocyclohexene

	Methanol		Acetone	
	C–S	C–C	C–S	C–C
(Ia); R = H	16	84	8	92
(Ib); R = Me	3	97	2	98
(Ic)[b]; R = Pr^{i}	1	99	1	99
(Id); R = Ph	5	95	1	99

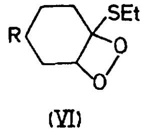
[a] Total yield was 65—85%. [b] 1-Ethylthio-2-isopropyl-4-methylcyclohexene.

Photosensitized oxygenation of 1-ethylthiocyclohexene (I, R = H) gave the C–C cleavage product, ω-formyl thioester (V, R = H) as the major product.[5] When an alkyl or aryl substituent was introduced at the 2-position, C–C cleavage increased relative to C–S cleavage (Table 1).



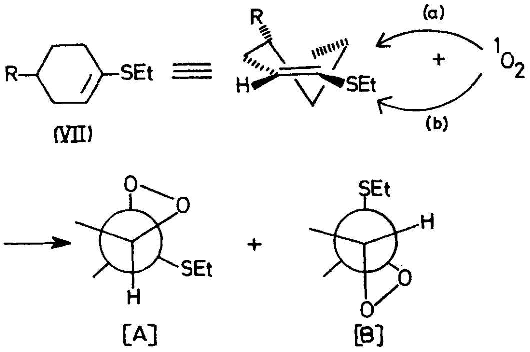
(I) (II)

(III) (IV) (V)



(VI)

However when 1-ethylthio-4-t-butylcyclohexene in methanol was photo-oxidized in the presence of Rose Bengal according to the previous procedures,[4,5] the following products were found after solvent evaporation; diethyl disulphide (18%), 2-hydroxy-4-t-butylcyclohexanone (24%), and ω-formyl thioester (31%). Thus the ratio of C–S to C–C cleavage of (VIb) is influenced by the t-butyl group remote from the centre of 1,2-dioxetan (Table 2).



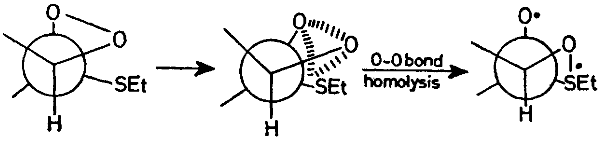
(VII)

[A] [B]

The result can be explained by the conformational requirements of the dioxetan (VI). When singlet oxygen adds to vinyl sulphides (VII), there are two possible conformations of the dioxetan [A] and [B]. In the case of (VIa), these conformations [A] and [B] are interconvertible, and the rate of this interconversion is faster than any dioxetan decomposition which may arise from the more stable conformation [B]. However for (VIb), the interconversion between conformations [A] and [B] is forbidden, and therefore decomposition of (VIb) can arise from both conformations [A] and [B].

Table 2. Relative ratio of C-S and C-C cleavage in the decomposition of the dioxetan (VI)

	C–S cleavage/C–C cleavage	
	Methanol	Acetone
(VIa); R = H	0·19	0·08
(VIb); R = Bu^{t}	0·77	0·62



We can thus predict that decomposition from conformation [A] gives the C–S cleavage product, and from conformation [B] the C–C cleavage product. In conformation [A], the oxygen and sulphur atoms are nearer each other, and neighbouring group participation[6] by sulphur may lead to homolytic cleavage of the oxygen–oxygen bond. C–S cleavage results from homolytic cleavage of the oxygen bond, because the C-S bond energy is lower than the C-C bond energy by 18 kcal mol^{-1}.[7]

C–S cleavage of the sulphur substituted dioxetans might arise by a stepwise mechanism involving oxy-radicals, and C–C cleavage by a concerted mechanism.

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[1] For the previous paper in this series see W. Ando, K. Watanabe, and T. Migita, *Tetrahedron Letters*, in the press.

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