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SINGLET OXYGEN REACTION V. RING SIZE EFFECTS ON THE DECOMPOSITION OF SULFUR SUBSTITUTED 1,2-DIOXETANE[1]

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Electron rich olefins such as enamines[2] and vinyl ether[3] are well known to undergo 1,2-cycloaddition with singlet oxygen to produce 1,2-dioxetanes, which easily decompose to the corresponding carbonyl fragments[4,5]. Recently, in the reaction of a vinyl sulfide with singlet oxygen, we reported that an intermediate sulfur substituted 1,2-dioxetane could decompose by two different paths (C-S bond and C-C bond cleavage)[6-10], because the C-S bond energy is relatively low[7]. Moreover, the ratio of C-S to C-C bond cleavage was found to be subtly variable with a change in the structure of the substrate[7,9]. Here, we wish to report that the ratio of C-S cleavage to C-C cleavage of 1,2-dioxetanes derived from 1-sulfur substituted cycloalkenes depends on the ring size of the substrate, and is closely related to the internal strain of the ring[11].

1-Ethylthiocycloalkene(Ia-f) in acetone was irradiated with a 300W halogen lamp for 30-60 min, while oxygen was bubbled through the mixture in the presence of Rose Bengal. Evaporation followed by glpc gave diethyl disulfide(II), 2-hydroxy cycloalkanone(III) and 1,2-cycloalkanedione(IV) as C-S cleavage products, and ω-formylthioester(V) as a C-C cleavage product. The structural assignments are based on spectral and analytical data by comparison with those of the authentic samples.

The photosensitized oxygenation of 1-ethylthiocyclohexene(Ib, n=6) gave C-C cleavage product V in 59% yield and C-S cleavage product III in 6% yield. On the other hand, the reaction of 1-ethylthiocyclooctene(Id, n=8) gave C-S cleavage product IV in 71% yield and C-C cleavage product V only in 4% yield.

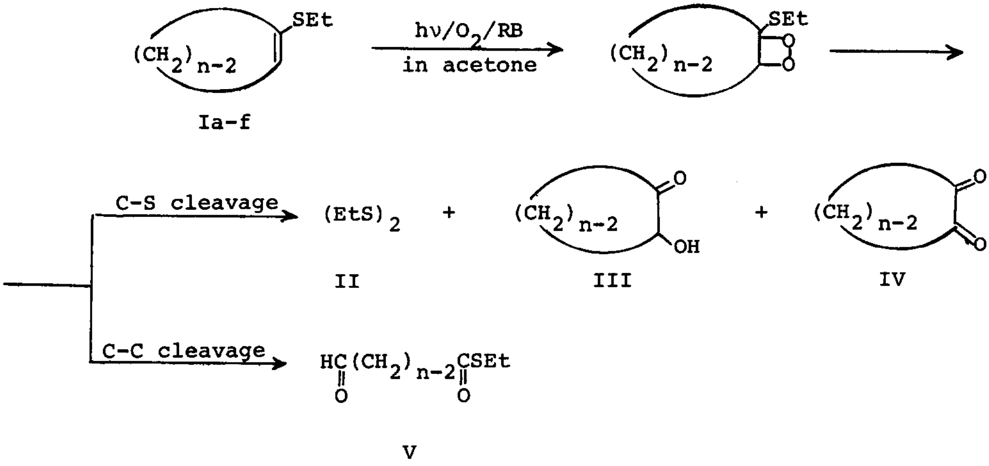

Table I shows that the relative yields of C-S and C-C cleavage products have some relation to the heat of combustion per methylene of the corresponding cycloalkane. Thus, in the photooxygenation of the substrates bearing the six and tweleve membered rings, which are the most stable cycloalkanes, the C-C cleavage products are obtained almost quantitatively.

Table I. Relative Yield of C-S and C-C Cleavage Products in the Reaction of 1-Ethylthiocycloalkenes with Singlet Oxygen(at 20°).

I	n	Relative Yield[12](%)		H[13]
		C-S cleavage[14]	C-C cleavage	-157.4
Ia	5	43	57	1.3
Ib	6	8	92	(0.0)
Ic	7	57	43	0.9
Id	8	95	5	1.2
Ie	10	45	55	1.2
If	12	5	95	0.3
VI[15]	-	20	80	0.0

The appearance of the ring size dependence of the ratio of C-S cleavage to C-C cleavage is also illustrated in Figure 1.

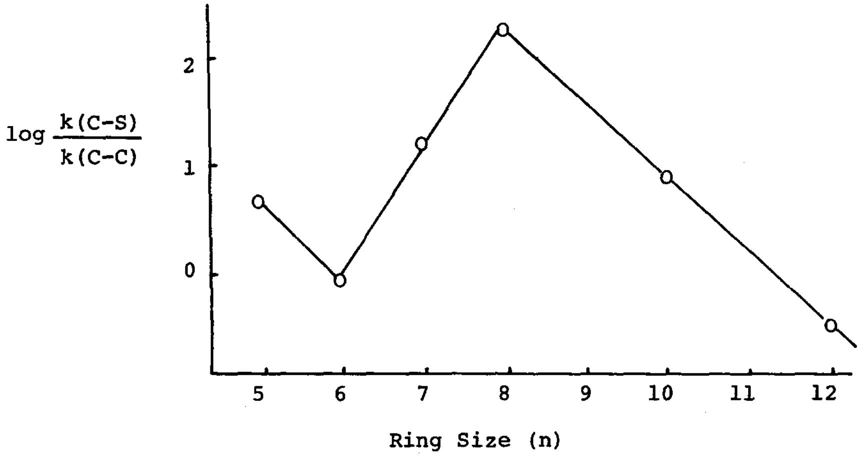

Figure 1. The Effect of Ring Size on the Relative Product Ratio of C-S Cleavage to C-C Cleavage in the Reaction of 1-Ethylthiocycloalkene with Singlet Oxygen.

The tendency of the ring size effect observed is quite similar to those on the relative rates of acetolysis of cycloalkyl tosylates, and of thermolysis of 1-cyanoazocycloalkane[16,17], in which the carbon atoms of the reaction centers are rehybridized from sp^3 to sp^2 during the reactions, as in the case of the present C-S cleavage in the dioxetane decomposition. Accepting that bond opposition will be responsible for this type of ring size effect, the above fact at least shows that bond opposition strain[18,19] can be one of the driving forces for the C-S cleavage in the decomposition of the sulfur substituted 1,2-dioxetanes. The fact that the decomposition path of dioxetanes is under the influence of ring strain also suggests a two step homolysis involving a biradical process[9].

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12. Total yield of products is about 60-80%.
13. Difference in heat of combustion per methylene between the corresponding cycloalkanes, being the value for cyclohexanone taken as standard[11].
14. In Ia, yield of diethyl disulfide is used, because 2-hydroxycyclopentanone could not be detected in clean form under the analytical conditions. In other cases, yields of ketone are used as C-S cleavage.
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