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PHOTOINDUCED REACTIONS. LXXII. REACTIVITY OF SINGLET OXYGEN TOWARD CYCLIC OLEFINS1)

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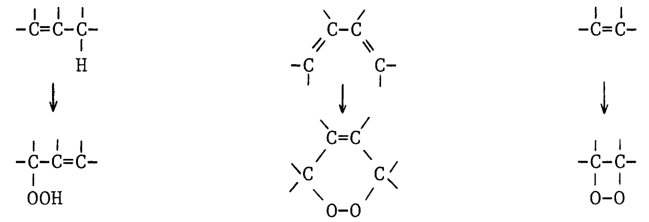
The relative reactivities of various cyclic olefins toward singlet oxygen generated by photosensitized oxygenation were determined. The differences in reactivity are mainly rationalized in term of the conformational requirements of olefins for the concerted "ene" mechanism.

It is generally accepted that singlet molecular oxygen is the reactive species in the dye-sensitized photooxygenation of olefins having an allylic hydrogen, conjugated dienes, and highly electron-rich olefins to give allylic hydroperoxides ("ene" reaction), 1,4-endo-peroxides, and dioxetanes, respectively.2) Kopecky and Reich pointed out the electrophilic nature of singlet oxygen on the basis of the fact that the more electron-rich such substrates, the faster they react with singlet oxygen.3) The reactivity of singlet oxygen toward organic substrates, such as simple olefins and conjugated dienes,4,5) methoxybenzenes,6) and substituted trimethylstyrenes,7) was also examined.



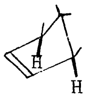
There are several possible factors controlling the rate of "ene" reaction, which most likely proceeds by the concerted "ene" mechanism2a,2b,8) although stepwise mechanisms have also been claimed.2c) (i) The lower the ionization potential of olefins, the higher is the rate within a homologous series of compounds.2c) This implies the relative importance of charge-transfer interaction between singlet oxygen and an olefin in the initial stage which has also been supported by a theoretical consideration.8c) (ii) Singlet oxygen attacks predominantly on the less hindered side of an olefin molecule.2b) (iii) The most favorable conformation of an allylic hydrogen for the "ene" reaction of cyclohexene derivatives and acyclic olefins is axial-like.2b) Therefore, in a conformationally flexible system the reactivity should be dependent upon whether or not such conformational requirements are satisfied. (iv) The reaction rate may be accelerated with increasing the steric strain of olefins, since it is known that strained olefins suffer electrophilic attack more easily than unstrained ones.[9] The present work was undertaken in order to explore factors controlling reactivity of cyclic olefins, for which only the limiting experimental data are available.

Relative rates for the disappearance of various cyclic olefins in the photosensitized oxygenation were determined by competition reactions according to the method described by Foote and coworkers.[4,7] The results are listed in the Table. The reactivities of cycloalkenes 1-7, which can undergo "ene" reaction,[10] are markedly dependent upon ring size. The reactivities show no significant correlation with their ionization potentials. For example, the difference in the ionization potentials of 1 (9.02 eV), 2 (8.95), and 8 (8.81)[11] cannot account for the large difference in their reactivities.

The order of reactivities, 1>2≈3>4>5 for the addition of singlet oxygen, is quite different from those, 4>3>1≫2≈5 for the addition of hexachlorocyclopentadiene[12] or diethylaluminum hydride,[13] 2>1>3≫4 for the addition of hydrogen bromide,[14] and 4>1>3>2 for the addition of some free radicals,[15] to the series of cis-cycloalkenes 1-5, indicating that the nature of the addition of singlet oxygen differs from those of cycloaddition and electrophilic and free-radical additions.

The reactivities of 1-5 were compared with their heats of hydrogenation (Table) which may reflect the steric strain of each olefin.[16] Although a fairly good correlation that reactivity is decreased with decreasing heat of hydrogenation is seen, this does not hold in case of highly strained olefins 8 and 9 which are unreactive in spite of their high heat of hydrogenation. The resistibility of 8 and 9 may be explained by the fact that their π-plane and allylic C-H bond are nearly coplanar so that they could not reach to the transition state for the concerted "ene" mechanism [2b] in which an axial-like C-H bond is necessary.

The differences in reactivities of simple cyclic olefins can be now most satisfactorily rationalized by considering conformational requirements for the concerted "ene" mechanism.[2b] In the most stable conformation of 1,[17] 2,[18] and 3[19] (see figures below), which show relatively higher reactivity than other cycloalkenes, conformational requirements are satisfied; namely they have at least two axial-like hydrogens. The highest reactivity of 1 may be due to the additional effect of its higher ring strain[20] compared with 2 and 3.



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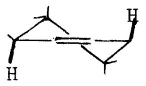

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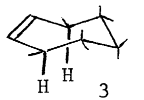

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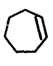
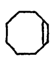
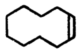
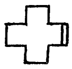
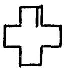
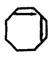
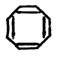
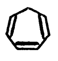
The prefered conformations of medium-size cycloalkenes 4, 5, 6, and 7 are uncertain, rendering difficulty to analyze the results in detail. However, inspections of scale models reveal that, in

Table. Relative reactivities of cyclic olefins toward singlet oxygen[a]

Olefin							
	1	**2**	**3**	**4**	**5**	**6**	**7**
Relative reactivity	115[b]	7.1[c]	7.2[c]	(1.0)[c]	0	0.16	0.56
Heat of hydrogenation -ΔH (kcal/mole)[d]	26.92	27.1	25.9	23.0	20.7	—	—
Olefin							
	8	**9**	**10**	**11**	**12**	**13**	**14**
Rel. reat.	0	0.26	8.0	54	0.7	0	8.7
-ΔH	33.1	68.1	—	—	—	—	—

[a] Rose bengal/hν/O_2/methanol. [b] Calculated from data given in ref. 4). [c] Methylene blue/hν/O_2/methylene chloride. [d] Taken from H. A. Skinner, "Experimental Thermochemistry", Vol. 2, p. 221, Interscience Publ. (1962)

most of their possible prefered conformations, one side of the double bond of cis-olefins **4**,**5**, and **6** is blocked by the polymethylene group of the molecule, and that on the other side of the double bond only one or no allylic hydrogen can take an axial-like conformation because of the nonbonded interaction between β and β' hydrogens with respect to the double bond.[21] In case of cyclododecenes, **7** is known to be thermodynamically more stable than **6**,[22] indicating that the difference of their reactivities should not be due to the higher ring strain of **7** but to the conformational requirements.[23]

The results obtained with a series of eight-membered cyclic olefins are also informative. In a series of **4**, **10**, and **11**, which predominantly undergo "ene" reaction to give hydroperoxides,[10] the greater the interaction between π-bonds the higher is the reactivity. This suggests that the reactivity increases with increasing the strength of the internal π-interaction, provided that the difference in their conformational factors is small. It should be emphasized that it is rather meaningless to compare the difference of reactivities between groups (**4**, **10**, and **11**) and (**12**, **13**, and **14**), since the latter group of compounds is known to undergo [4 + 2] cycloaddition with singlet oxygen (or no reaction) to give a 1,4-endo-peroxide.[10,24]

It should be noted that recently Nickon and coworkers presented evidence that the transition state of the "ene" reaction resembles the starting olefin.[25]

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