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PHOTOINDUCED REACTIONS. LXIV.[1)]

REACTION OF α,α'-DIALKYLSTILBENES WITH SINGLET OXYGEN: "ENE" REACTION AND CLEAVAGE TO CARBONYL FRAGMENTS

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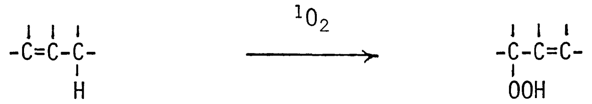
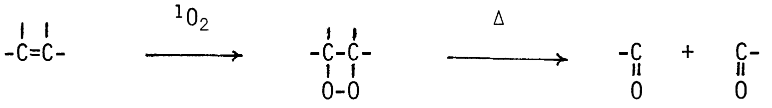
Photosensitized oxygenation (a system generating singlet oxygen) of α,α'-dialkylstilbenes gave exclusively an allylic hydroperoxide, the "ene"reaction product, whereas the introduction of methoxy groups into their para positions causes a competition between "ene" reaction and cleavage to carbonyl fragments. In the latter case, a solvent dependence on the competition was observed.

It is well known that singlet oxygen adds to olefins having an allylic hydrogen to give allylic hydroperoxides[2)] ["ene" reaction; eq. (1)], and that it reacts with electron-rich olefins such as vinyl ethers to undergo cleavage to carbonyl fragments through an dioxetane intermediate which was detected in some cases[eq. (2)].[3-5)] However, relatively few attention has been made to the reaction of singlet oxygen with electron-rich olefins having allylic hydrogen which usually result in the predominant formation of carbonyl fragments.[5)]



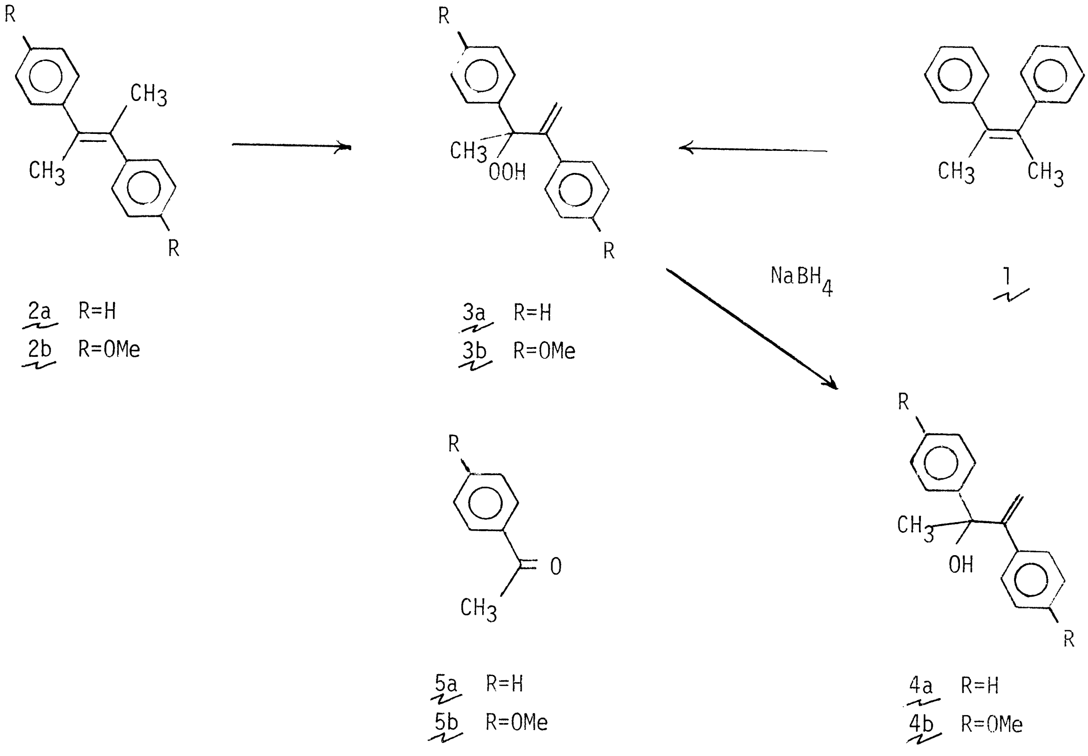
$$-\overset{|}{C}=\overset{|}{C}-\underset{H}{\underset{|}{\overset{|}{C}}}- \xrightarrow{^1O_2} -\underset{OOH}{\underset{|}{\overset{|}{C}}}-\overset{|}{C}=\overset{|}{C}- \qquad (1)$$



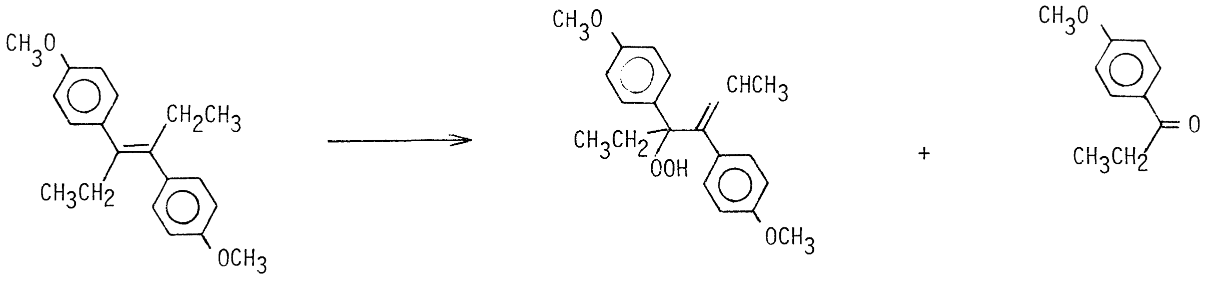
$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow{^1O_2} -\underset{O-O}{\underset{|\quad|}{\overset{|}{C}-\overset{|}{C}}}- \xrightarrow{\Delta} -\underset{O}{\underset{\|}{C}} + \underset{O}{\underset{\|}{C}}- \qquad (2)$$

Since stilbene is known to undergo cleavage to carbonyl fragments by singlet oxygen,[5a,6)] we selected substituted stilbenes in order to know the influence of α,α'-dialkyl substituents (introducing allylic hydrogen) and of p-methoxy groups (electron-donating ability) on singlet oxygen reaction.

Rose bengal-sensitized photooxygenation of cis- (**1**) and trans- (**2a**) α,α'-dimethylstilbenes in methanol at room temperature under irradiating with a tungsten-bromine lamp yielded a hydroperoxide **3a** in almost quantitative yield,[7] but no acetophenone (**5a**) was detected in both case.[8] On the other hand, photooxygenation of trans-p,p'-dimethoxy-α,α'-dimethylstilbene (**2b**) in methanol under similar conditions gave a hydroperoxide **3b** (80%) and p-methoxyacetophenone (**5b**; 7%), but in acetone gave only **3b** (95%). Hydroperoxides **3a** and **3b** were reduced by sodium borohydride to give allylic alcohols **4a** and **4b**, respectively.[9]



Dye-sensitized photooxygenation of the dimethyl ether **6** of stilbestrol was carried out in several solvent systems. The products were found to be a hydroperoxide **7**[10] and p-methoxypropiophenone (**8**). As shown in Table, the product ratio was affected more or less by solvent. In particular, the cleavage reaction was predominant in the methlylene blue-methylene chloride system.



6 7 8

Table*

solvent	sensitizer	Product (%) 7	Product (%) 8
MeOH	rose bengal	10	13
Acetone	rose bengal	54	2
MeOH-Pyridine (50 : 1)	rose bengal	73	5
CH_2Cl_2	methylene blue	5	60

* The reactions were carried out at room temperature. Yields of products were determined by NMR analysis.

In order to check whether or not 8 is formed through a dioxetane which may be a rearranged product of hydroperoxide 7,[2b)] 6 was photooxygenated in CH_3OD under similar conditions. No deuterium incorporation was observed in p-methoxypropiophenone 8 obtained. Furthermore, 7, on refluxing in methanol or methylene chloride, gave a complex mixture of products from which only a trace of 8 was detected. These facts indicate that 7 may not be the precursor of 8 in this reaction.

There have been two reports on the solvent dependence on a competition between "ene" reaction and cleavage to carbonyl fragments in the singlet oxygen reaction of electron-rich olefins having allylic hydrogen: in nonpolar solvent 1,2-diphenylcyclobutene undergoes predominantly cleavage,[5c)] while dihydropyran does "ene" reaction.[11)] Our result with 6 is consistent with that with 1,2-diphenylcyclobutene. The solvent dependence should await further examination.

Since it is known that reactivities of olefins toward singlet oxygen are correlated to their π-ionization potentials[12)] which are parallel to their $\nu_{\max.}^{c.t.}$ with tetracyanoethylene,[13)] the $\nu_{\max.}^{c.t.}$ values of the stilbene derivatives were determined in methylene chloride: $\nu_{\max.}^{c.t.}$ 515 nm (2a), 570 nm (2b) and 568 nm (6). The result indicates that both the "ene" and cleavage reactions occurs with lowering of the π-ionization potential of the substrate, whereas only "ene" reaction is observed with 2a having a higher π-ionization potential.

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7) Similar results were obtained by methylene blue-sensitized photooxygenation in methylene chloride.

8) Hydroperoxide **3a**, on refluxing in methanol, gave no acetophenone (**5a**) but a complex mixture.

9) Alcohols **4a** and **4b** exhibit following spectral properties which are in accord with structure **4a** and **4b**, respectively. Satisfactory elemental analyses were obtained for all new compounds.

4a: τ ($CDCl_3$) 2.20-3.30m (10H), 4.45d (1H, J=1.0 Hz), 4.70d (1H, J=1.0 Hz), 8.10s (1H, hydroxyl), and 8.30s (3H).

4b: τ ($CDCl_3$) 2.50-3.40m (8H), 4.60s (3H), 6.21s (3H), 6.30s (3H), and 8.20s (3H).

10) This product was characterized by NMR analysis: τ ($CDCl_3$) 2.60-3.40m (8H), 6.05q (1H, J=6Hz), 6.15s (3H), 6.23s (3H), 7.90q (2H, J=7 Hz), 8.45d (3H, J=6 Hz), and 9.18t (3H, J=7 Hz).

11) P. D. Bartlett, G. D. Mendenhall, and A. P. Schaap, Ann. N. Y. Acad. Sci., 171, 79 (1970).

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