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SENSITIZED PHOTOOXIDATION REACTIONS OF *cis*-α,α'-DIMETHYLSTILBENE. SENSITIZER, TEMPERATURE, AND SOLVENT EFFECTS ON PRODUCT DISTRIBUTION.

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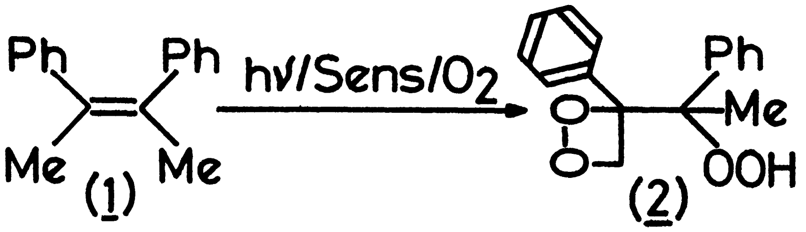
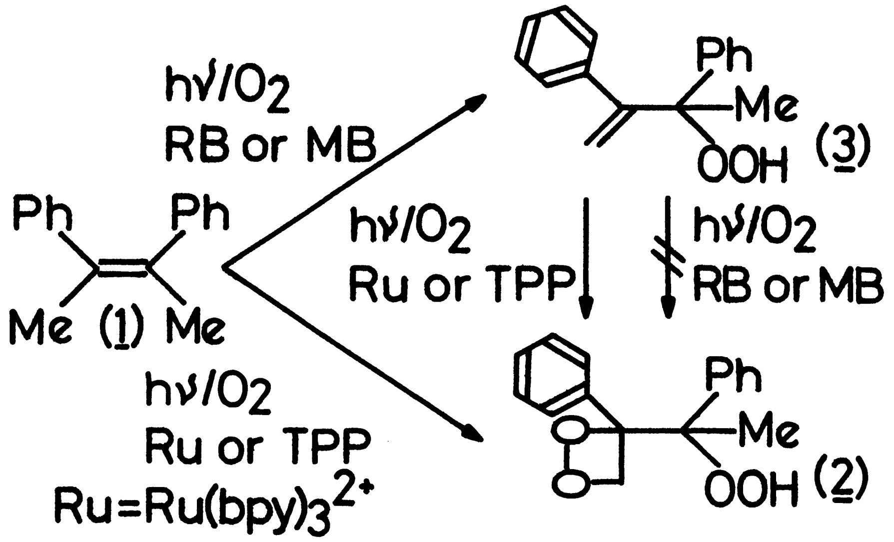
Sensitized photooxidation of *cis*-α,α'-dimethylstilbene(1) depends on sensitizer, solvent, and temperature. At room temperature, $Ru(bpy)_3^{2+}$- or TPP- sensitized photooxidation reaction of 1 affords a dioxetane hydroperoxide(2), while only an allylic hydroperoxide(3) is obtained when RB or MB is used as sensitizer. At low temperature, 2 comes to be formed independent of the sensitizer used.

We have already found that the photooxidation of *cis*-stilbenes sensitized by $Ru(bpy)_3^{2+}$ is different from the other sensitized photooxidation reactions.$^{1)}$ Interestingly, hitherto accumulated papers show that the reactions of $^1O_2$ with certain organic substrates such as stilbenes,$^{1-3)}$ indenes,$^{4)}$ tryptophan,$^{5)}$ tetramethylethylene,$^{6)}$ and sulphides,$^{7)}$ are greatly affected by combination of sensitizer, solvent, and temperature. Thus, as the extension of our previous work,$^{1)}$ we have investigated the effects of sensitizer, solvent, and temperature on sensitized photooxidation reactions of *cis*-α,α'-dimethylstilbene(1), which is known to yield an allylic hydroperoxide(3).$^{2)}$ We report here that the sensitized photooxidation reaction of 1 gives a dioxetane hydroperoxide(2), depending on sensitizer and temperature.

2 was obtained quantitatively on irradiation of a solution of 1 (10^{-2}M) and $Ru(bpy)_3^{2+}$ (10^{-4}M) in acetonitrile under bubbling of oxygen at room temperature with a 200-W super high pressure mercury arc through a UV cutoff glass filter ($\lambda_{irrad.} \geq 430$nm) for 20 min.$^{8)}$ The reaction was retarded by changing solvent from acetonitrile to methanol, but no product other than 2 was obtained. 2 was also afforded when tetraphenylporphin(TPP) was used as sensitizer in chloroform. On the other hand, only the "ene" product 3 was obtained in methylene blue(MB)- or rose bengal(RB)-sensitized photooxidation reaction of 1 in methanol.$^{9)}$ In MB-sensitization, 1 reacted three times faster in $CDCl_3$ than in $CHCl_3$, which parallels solvent deuterium isotope effect on $^1O_2$ lifetime.$^{10)}$ The single product obtained, however, was 3 in either case. Thus lengthening of $^1O_2$ lifetime does not affect the product distribution in the MB-sensitized photooxidation of 1. Since 3 was presumed to be a likely precursor of 2, independently isolated 3 was photooxidized in the presence of different sensitizers. When TPP or $Ru(bpy)_3^{2+}$ was used as sensitizer, 2 was afforded quantitatively in less than 30 min, but no reaction proceeded to 2 by using RB or MB as sensitizer. These results suggest that 3 can be the intermediate.



Sensitizer	Solvent
$Ru(bpy)_3^{2+}$	MeCN
$Ru(bpy)_3^{2+}$	MeOH
TPP	$CHCl_3$



The [2+2] cycloaddition of 3 with another singlet oxygen molecule to afford 2 is drastically affected by sensitizer.

In order to clarify the different reactivity of 1 toward $^1O_2$, the β value was measured in each system at room temperature. Table 1 shows that almost the same value of β is obtained in both cases ($Ru(bpy)_3^{2+}$-MeCN, TPP-$CHCl_3$) where only 2 is afforded. In methanol, the β value is of the same order (Runs 2-4) independent of the sensitizer used, but the product distribution changes. Although $^1O_2$ is the primary common active oxygen species in each system, the different product distribution cannot be interpreted in terms of β value difference. Actually, Runs 6 and 7 show the β values which are largely different from the reported ones[12]; β value for 2,5-dimethylfuran is 1×10^{-3}, and 6.7×10^{-1} for 1-methylcyclohexene. However, the products observed in Runs 6 and 7 are the same as those reported.[12]

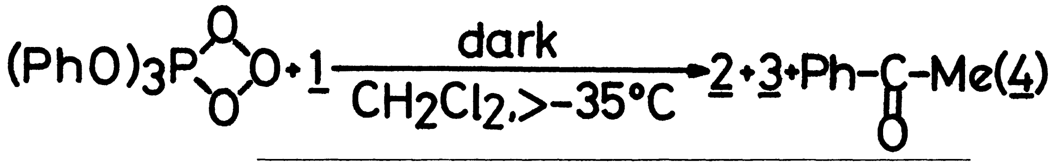
A possible speculation is that the difference in product distribution irrespective of the β value and solvent deuterium isotope effect is ascribable to some interaction among $^1O_2$, substrate, sensitizer, and solvent after generation of $^1O_2$.

Table 1. β Value

Run	1	2	3	4	5	6	7
Substrate	1	1	1	1	1	DMF	MCH
Sensitizer	$Ru(bpy)_3^{2+}$	$Ru(bpy)_3^{2+}$	RB	MB	TPP	$Ru(bpy)_3^{2+}$	$Ru(bpy)_3^{2+}$
Solvent	MeCN	MeOH	MeOH	MeOH	$CHCl_3$	MeCN	MeCN
β	0.089	0.42	0.27	0.20	0.085	0.030	0.053

DMF=2,5-Dimethylfuran, MCH=1-Methylcyclohexene.

The probable existence of a complex consisting of the sensitizer, $^1O_2$, solvent, and 1 (possibly 3) in the above reactions prompted us to carry out the oxidation reaction of 1 by chemically generated $^1O_2$.[6] As the below equation shows, 2 and 3 were obtained as major products along with small amounts of acetophenone(4) in the dark reaction, and the presence of $Ru(bpy)_3^{2+}$ (10^{-4}M) in the reaction solution increased the yields of 2 and 4 though slightly.[13] Moreover, it seemed necessary to lower temperature during the reaction of 1 with $^1O_2$ to obtain 2.



Additive	Conv. of 1	2	3	4	(2+4)/3
None	84%	27%	50%	3%	0.60
$Ru(bpy)_3^{2+}$	87%	30%	43%	5%	0.81

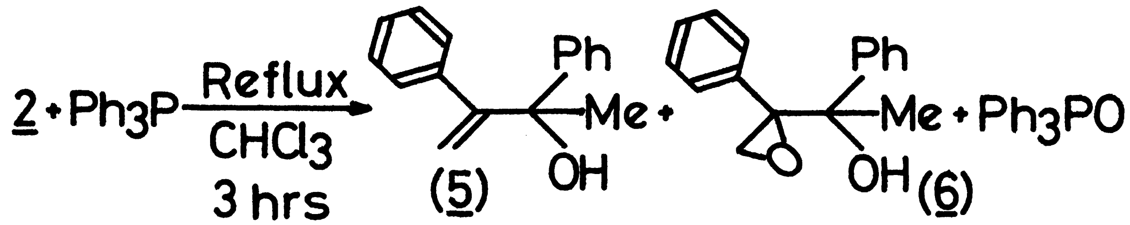
Thus, sensitized photooxidation reactions of 1 were carried out at -78 °C. The results are summarized in Table 2. In $Ru(bpy)_3^{2+}$-sensitization, no temperature dependency was observed. However, not only 3 but 2 was afforded when either MB or RB was used as sensitizer. Solvent effect is also observed that 2 is given in a better yield in butyronitrile than in methanol in the RB-sensitized photooxidation reaction of 1. These temperature effect and the sensitizer dependency on the product distribution might suggest the intermediacy of the forementioned ternary complex for formation of 2 from 3, but its verification awaits further kinetic studies.

Table 2. Temperature dependency of product formation

Sens.	Solvent	at r. t.	at -78 °C
Ru	MeCN	2	
Ru	MeOH	2	
RB	MeOH	3	2,3(1:9)*
RB	PrCN	3	2,3(1:1)*
MB	$CHCl_3$	3	
MB	MeOH	3	2,3(1:5)*

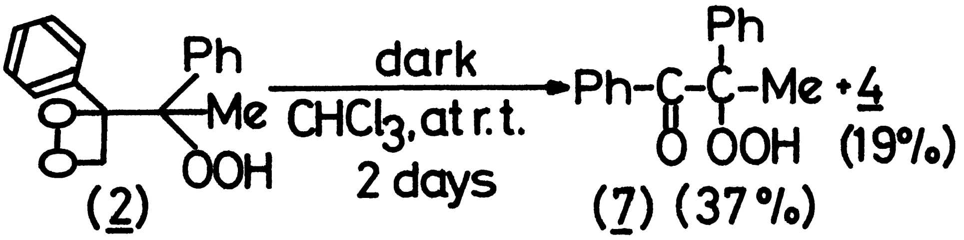
* Based on NMR.

Because of thermal instability of 2, deoxygenation reaction of 2 by triphenylphosphine was carried out to obtain the information on the structure of 2. 2 was refluxed in chloroform for 3 hours with the excess of triphenylphosphine to give an allylic alcohol(5)[14] and an epoxy alcohol(6)[15] in 90% and 7% yields, respectively. It is noteworthy that 2.4 equivalent of triphenylphosphine oxide was formed in this reaction. Under the same conditions, 3 was also deoxygenated to give 5 in 96% yield as a sole product, but only 0.8 equivalent of triphenylphosphine oxide was obtained in this case. These facts support that 2 has two O-O linkages.



Hydroperoxide	5	6	Ph_3PO
2	90%	7%	2.4 equiv.
3	96%	——	0.8 equiv.

Allowed to stand at room temperature in the dark, 2 gradually decomposes to form an α-keto hydroperoxide(7)[16] and 4. 7 is considered to be a decomposition product of 2. 4 is one of the decomposition products, but its unstable counterpart has not been isolated yet.



This communication has shown the new facts that the singlet oxygenation of 1 depends on the combination of sensitizer, solvent, and temperature. A reasonable interpretation to the above facts needs further investigation.

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8) Spectral data on 2: ^{1}H-NMR(CCl_4), 1.64(3H, s), 5.13(2H, dd, J=6.3 Hz), 6.47-7.01(11H, m) (δ, in ppm), IR(neat), 3480, 1623 (cm^{-1}), UV, 217, 236, 272 (nm, in EtOH).
9) Spectral data on 3: ^{1}H-NMR(CCl_4), 1.71(3H, s), 5.33(2H, dd, J=3.9 Hz), 7.03(11H, m) (δ, in ppm), IR(neat), 3480, 1651, 888 (cm^{-1}), UV, 209, 218, 231 (nm, in EtOH).
10) The ratio of the observed reaction rate is equivalent to that of $^1O_2$ lifetime, as given by $k_{rel,CDCl_3}/k_{rel,CHCl_3}=\tau_{CDCl_3}/\tau_{CHCl_3}$.[11a] Direct singlet oxygen luminescence measurements led to $k_{rel,CDCl_3}/k_{rel,CHCl_3}=3.4$.[11b] This is markedly close to our value for 1(3.0).
11) a) P. R. Ogilby and C. S. Foote, J. Am. Chem. Soc., 103, 1219 (1981); b) G. Peters and M. A. J. Rodgers, ibid., 103, 6759 (1981).
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13) The reaction was repeated twice and the reproducibility was confirmed. The values for 2, 3, and 4 were obtained by ^{1}H-NMR after ca. 2 hours of the reaction.
14) Spectral data on 5: ^{1}H-NMR(CCl_4), 1.55(3H, s), 1.91(1H, s), 5.00(1H, d), 6.61-7.27(10H, m) (δ, in ppm), IR(neat), 3580, 3460, 1491, 1447, 1067, 916 (cm^{-1}).
15) The IR and NMR spectra were superimposable on those of the authentic sample prepared in epoxidation of 3 by m-chloroperbenzoic acid in a basic biphase solution. Spectral data on 6 : ^{1}H-NMR(CCl_4), 1.92(3H, s), 4.15(2H, s), 7.40(1H, s), 7.48(10H, s) (δ, in ppm), IR(neat), 3380, 1601, 1026, 991, 916, 769, 707 (cm^{-1}).
16) Spectral data on 7: ^{1}H-NMR(CCl_4), 1.88(3H, s), 6.70-7.26(11H, m) (δ, in ppm), IR(neat), 3410, 1719, 1599, 1070, 1027, 916, 707 (cm^{-1}).

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