CHEMISTRY LETTERS pp. 381-384, 1982. © The Chemical Society of Japan 1982

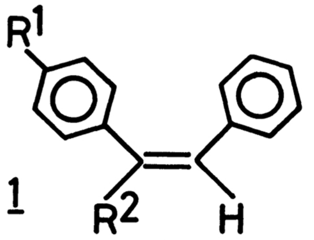
$Ru(bpy)_3{}^{2+}$ SENSITIZED PHOTOOXIDATION REACTION OF cis-STILBENES NOVEL PRODUCTS FORMATION

Shigeru FUTAMURA, Hiroyuki OHTA*, and Yoshio KAMIYA
Department of Reaction Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

$Ru(bpy)_3{}^{2+}$ sensitized photooxidation of cis-stilbenes in acetonitrile gave novel [2+6] cycloadducts. Product distribution changed remarkably depending on sensitizers.

Recently, there have been an increasing number of reports on the reactions of $^1O_2$ with vinyl aromatic compounds,[1-4] which may be categorized into two cases. The first of these involves [2+2] cycloaddition and the second type is [2+4] cycloaddition between singlet oxygen and olefin moieties. In the above reactions, product distribution is greatly affected by sensitizer, solvent, and temperature. However, factors determining the aspect of the reaction have still to be unraveled. We now report $Ru(bpy)_3{}^{2+}$ sensitized photooxidation reactions of cis-stilbenes(1), where novel [2+6] cycloadducts can be isolated. $Ru(bpy)_3{}^{2+}$ is well known as a stable triplet sensitizer[5] though there have been only a few reports where it is applied to sensitized photooxidation reactions.[6]

A solution of 1 (10^{-1}M) and $Ru(bpy)_3{}^{2+}$ (10^{-4}M) in 140ml of acetonitrile was irradiated with a 400-W high pressure mercury arc through a filter solution ($\lambda_{irrad.} > 410$nm)[7] in oxygen streams. The reaction vessel was kept below 10 °C, and the conversion of 1 was always kept no more than 30% to prevent secondary reactions and photolyses of the primary products. The products were separated and purified by column and thin-layer chromatography.



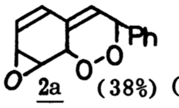
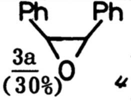
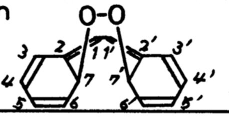
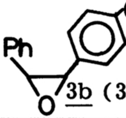
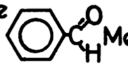
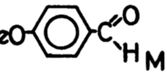
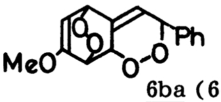
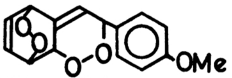
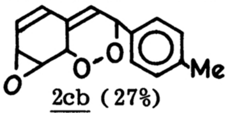
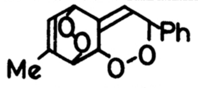
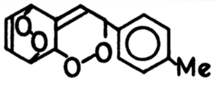
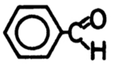
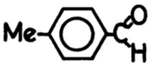
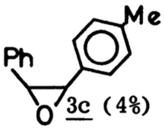
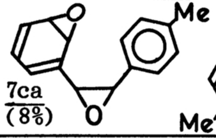
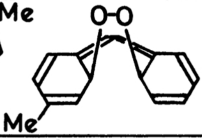
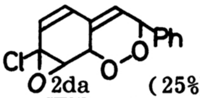
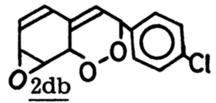
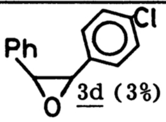
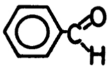
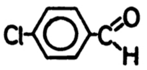
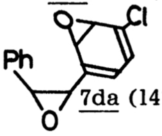
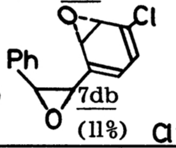
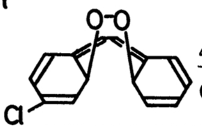
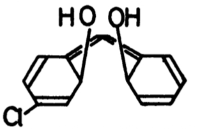
1

1a: R^1=H R^2=H
1b: R^1=MeO R^2=H
1c: R^1=Me R^2=H
1d: R^1=Cl R^2=H
1e: R^1=H R^2=CN

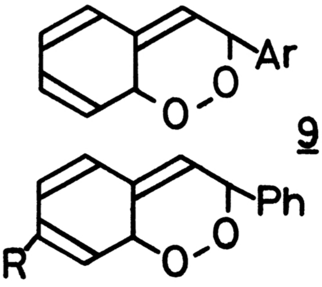
Irradiation of 1a gave an epoxy-1,4-endoperoxide(2a) (pale yellow oil), cis-stilbene oxide(3a), and a [2+6] cycloadduct(4a) (colorless granules, mp. 96.0-96.7 °C) as major products.[8,9] The structures were further confirmed by ^{13}C-NMR spectroscopy. It showed that they had no carbonyl carbon atom and that 4a had a symmetrical ring structure. Treatment of 4a (3.4×10^{-5}M) with the excess of triphenylphosphine at 25 °C in $CHCl_3$ gave 0.8 equivalent of triphenylphosphine oxide.[10]

Table 1 summarizes the effect of substituent R^1 on product distribution. Selectivities of benzaldehydes(5) are generally low though an electron-donating methoxy group increases the percentage of [2+2] cycloaddition. Our results make remarkable contrast to those by Rio and Berthelot, using methylene blue(MB) as sensitizer.[11] Quite recently, Foote and his coworkers assert that benzaldehyde(5a) is formed via trans-stilbene radical cation in its MB sensitized photooxidation

Table 1. $Ru(bpy)_3^{2+}$ sensitized photooxidation of 1 in acetonitrile

Substrate	Irrad.time	Conv.	Products(Selectivity)
1a	7h	27%	 2a (38%)  3a (30%)  4a (25%)
1b	2h	22%	 3b (3%)  5a (15%)  5b (16%)  6ba (64%)  6bb
1c	5h	31%	 2cb (27%)  6ca (28%)  6cb (18%)  5a (3%)  5c (3%)  3c (4%)  7ca (8%)  4c (8%)
1d	12.5h	27%	 2da (25%)  2db  3d (3%)  5a (4%)  5d (4%)  7da (14%)  7db (11%)  4d (23%)  8d (15%)

reaction.[12] In our systems, however, such an electron-transfer process as induced from 1 to the sensitizer can be excluded because 1a–e quenches $Ru(bpy)_3^{2+*}$ phosphorescence at nearly the same rate ($k \leq 10^7 M^{-1}s^{-1}$) in acetonitrile, much smaller than the diffusion controlled rate limit ($k_{diff.} = 1.8 \times 10^{10} M^{-1}s^{-1}$, in MeCN at 15 °C). Stereospecific formation of 3 further confirms this speculation. As Table 1 shows, only 3 was obtained and no trans-isomer was detected by ^{1}H-NMR, while the non-stereospecific epoxidation reaction in 9,10-dicyanoanthracene sensitized photooxidation of 1a could be explained in terms of isomerization of 1a radical cation into trans-isomer.[13] ^{1}H-NMR data suggest that epoxide protons of 2 and diepoxide(7) are cis to each other.[14] As to [2+4] cycloaddition products, 2 is formed in 1a, 1c, and 1d, and that two types of [2+4] cycloaddition products were obtained. There could be two secondary paths for 1,4-endoperoxide(9), which is a possible intermediate to yield 2 and 6. One proceeds further in a [2+4] fashion, and the other, to epoxidation. Formation of 2 and 3 is of interest, considering the facts that sterically hindered olefins are epoxidated in their oxidation reactions by $^1O_2$.[15-17] But the ruling factors determining the reaction mode of 9 and the mechanism of epoxidation remain to be seen. The selectivity of 4 increased as substituent R^1 gets more electron-withdrawing. Table 2 shows the change in the site-selectivity of 1 toward


9

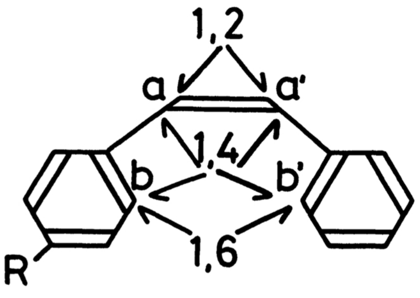


Fig.1

the active oxygen species. Replacement of R by electron-withdrawing group in Fig. 1 diminishes the electron density of carbon atom Ca, and relatively, that of Cb increases. Thus, [2+6] cycloaddition comes to predominate over [2+2] cycloaddition. The product distribution in the case of 1c offers the clear data for the preferable orientation in [2+4] cycloaddition. An electron-donating methyl group would make the electron densities of Ca and Cb' larger than those of Ca' and Cb, respectively. In fact, selectivity ratio (2cb+6cb)/(6ca) is 1.6, and it reflects that [2+4] cycloaddition at Ca-Cb' predominates actually.[18] As described above, the magnitude of electron density on the carbon atom controls the site-reactivity toward the active oxygen species.

Table 2. The site-reactivity of 1 in the system of $Ru(bpy)_3^{2+*}$-O_2

Substrate	[2+2] Cycloaddition	[2+4] Cycloaddition	[2+6] Cycloaddition	Epoxidation
1a	0	1	0.66	0.87
1b	0.25	1	0	0.05
1c	0.04	1	0.10	0.05
1d	0.10	1	0.97	0.36

Solvent=MeCN

The site-reactivity was given as a ratio of %(X)/%([2+4] Cycloaddition). 3 and 7db were counted as epoxidated products.

The sensitized photooxidation of 1a is affected by combination of sensitizer and solvent. Thus, product distribution drastically changes, using tetraphenylporphin(TPP) or MB as sensitizer in $CHCl_3$ under otherwise the same conditions. When TPP was used, the reaction was more complex, and only 6a was isolated in 7% yield. Formation of 5a was not detected by ^1H-NMR, while in MB sensitized photooxidation, the reaction was very clean and 5a was obtained in 29% yield as the sole product. In ZnTPP sensitization, the photooxidation proceeded too slow to detect products. Strikingly, no 4a was obtained in any case, but the elucidation of such sensitizer and solvent effect on product distribution awaits further investigation.[19]

The relative rates for $Ru(bpy)_3^{2+}$ sensitized photooxidation reactions of various olefins were also measured to probe the active oxygen species in the system. The results were as follows: 2,3-dimethyl-2-butene($k_{rel.}$=100), *trans*-anethole(2.7), α-methylstyrene(1.5), indene(1.3), β-methylstyrene(1.0), 1a(0.78), 1,1-diphenylethylene(0.69), styrene(0.38), ethyl cinnamate(0.027). Interestingly, the relative disappearance rate of 1 decreased in the order of 1b>1c>1a>1d>1e. These facts suggest the presence of an electrophilic active oxygen species.

Dabco(5.0×10^{-2}M) quenched the formation of all the photooxygenated products derived from 1a and the product distribution did not vary at all in the presence of 2,6-di-*t*-butyl-4-methylphenol (5.0×10^{-2}M). An oxidation reaction of 1a(2.3×10^{-2}M) was carried out in acetonitrile with equimolar amounts of KO_2 and 18-crown-6-ether, but the starting material was recovered quantitatively. Therefore, the involvement of $O_2^{\cdot -}$ can be excluded under the above reaction conditions. Moreover, the controlled experiments established that all of $Ru(bpy)_3^{2+}$, light, and oxygen were indispensable for product formation. All of these results support that $^1O_2$ is the active oxygen species in our systems.

In conclusion, we have shown that novel [2+6] cycloadducts were obtained in the $Ru(bpy)_3^{2+}$ sensitized photooxidation reaction of 1, but that they were not obtained when TPP or MB was used as sensitizer. Different aspects of sensitized photooxidation reactions of 1 should be further unraveled.

References

1) C. S. Foote, S. Mazur, P. A. Burns, and D. Lerdal, J. Am. Chem. Soc., 95, 586(1973).
2) M. Matsumoto and K. Kuroda, Tetrahedron Lett., 1607(1979), and references cited therein.
3) D. S. Steichen and C. S. Foote, ibid., 4363(1979).
4) J. D. Boyd and C. S. Foote, J. Am. Chem. Soc., 101, 6758(1979).
5) M. Wrighton and J. Markham, J. Phys. Chem., 77, 3042(1973).
6) J. N. Demas, D. Diemente, and E. W. Harris, J. Am. Chem. Soc., 95, 6864(1973).
7) 750g of $NaNO_2$ diluted with water to 1000ml.
8) Spectral data on 2a: ^1H-NMR($CDCl_3$), 7.19(s, 5H), 3.61(m, 2H), 4.68(m, 1H), 4.91(m, 1H), 5.81(m, 1H), 6.13(m, 1H), 6.61(m, 1H) (δ, in ppm); IR(nujol), 1269, 1169, 971, 892, 766, 745, 727 (cm^{-1}).
9) Spectral data on 4a: ^1H-NMR($CDCl_3$), 4.00(s, 2H), 7.05(m, 10H) (δ, in ppm); ^{13}C-NMR($CHCl_3$), 120.0(C_1, $C_{1'}$), 133.3(C_2, $C_{2'}$), 120.7(C_3, $C_{3'}$), 128.1(C_4, $C_{4'}$), 130.3(C_5, $C_{5'}$), 131.6 (C_6, $C_{6'}$), 75.3(C_7, $C_{7'}$) (δ, in ppm); IR(nujol), 1675, 1611, 1600, 1583, 1273, 1220, 1102, 1008, 881, 855 (cm^{-1}); UV(EtOH), λ_{max} at 248.9(ε = 8300), (278.8(ε = 2900)), 315.0(ε = 270) (nm); Elemental analysis; Found: C, 79.29; H, 5.30; Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.40.
10) The reduction products are complicated, but formation of epoxide and alcohol is suggested by ^1H-NMR; see also, W. Adam and M. Balci, J. Am. Chem. Soc., 101, 7542(1979).
11) G. Rio and J. Berthelot, Bull. Soc. Chim. Fr., 3609(1969).
12) L. E. Marning, J. Eriksen, and C. S. Foote, J. Am. Chem. Soc., 102, 4275(1980).
13) a) L. T. Spada and C. S. Foote, ibid., 102, 391(1980); b) J. Eriksen and C. S. Foote, ibid., 102, 6083(1980).
14) P. A. Burns, C. S. Foote, and S. Mazur, J. Org. Chem., 41, 899(1976).
15) A. P. Schaap and G. R. Faler, J. Am. Chem. Soc., 95, 3381(1973).
16) P. D. Bartlett and M. S. Ho, ibid., 96, 627(1974).
17) C. W. Jefford and A. F. Boschung, Helv. Chim. Acta, 57, 2257(1974).
18) Similar discussions could be made for 1b and 1d, but the isomeric mixtures of 6b and 2d have not been isolated yet.
19) Photooxidation of indenes also depends on sensitizers and solvents.

(Received September 3, 1981)