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Rose-Bengal-Sensitized Photooxidation of Quadricyclane. A [$2\sigma+2\sigma+2\pi$] Cycloaddition of Singlet Oxygen

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Quadricyclane was photooxygenated with singlet oxygen generated under Rose-Bengal-sensitized conditions to a dioxetane, which in turn gave 2-cyclopentene-1,4-dicarbaldehyde and 5-norbornene-*cis*-2,3-*exo*-diol. For the mechanism to form the dioxetane, an involvement of a [$2\sigma+2\sigma+2\pi$] electrocyclic process is proposed.

Recently, we have re-examined$^{1)}$ a Methylene Blue (MB)-sensitized photooxidation of quadricyclane (**1**),$^{2)}$ and observed a photo-electron transfer from **1** to the excited state of the dye, MB*. The radical cation, $\mathbf{1}^{\cdot+}$, thus formed, suffered an attack of solvent nucleophile to form methoxynorbornenyl and methoxynortricyclyl radical which then coupled with ground state oxygen ($^3O_2$) to result in the formation of methoxynortricyclanols and methoxynorbornenols. The participation of singlet oxygen ($^1O_2$) was not observed in that case.

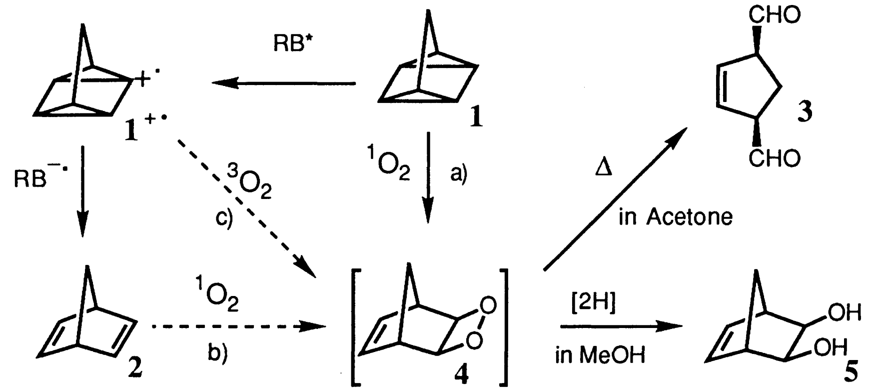
So is remaining the interest in the $^1O_2$ reactivity toward **1**, and now the Rose Bengal (RB)-sensitized photooxidation of **1** was investigated to compare with the MB-sensitized reaction.

An acetone solution of **1** (500 mg/10 dm^3) and RB (20 mg), cooled in ice-water bath, was irradiated by means of a 500-W halogen lamp with bubbling oxygen. In a period of 2 h-irradiation, more than 70% of **1** was isomerized to norbornadiene (**2**). After removing the volatile **1** and **2** in vacuo, the mixture afforded a dialdehyde (**3**, 70% of the residue) [^{1}H NMR$^{3)}$ δ=2.29(1H, dt, *J*=14.3, 9.3 Hz), 2.55(1H, dt, *J*=14.3, 5.2 Hz), 3.65(2H, dddd, *J*=9.3, 5.2, 1.5, 0.7 Hz), 5.99(2H, s), and 9.60(2H, dd, *J*=1.5, 0.7 Hz). ^{13}C NMR δ=23.0, 58.6(2C), 130.8(2C), and 200.1(2C)], a cleavage product of dioxetane (**4**).

When the reaction was carried out in MeOH for 2 h, alternatively obtained was 5-norbornene-*cis*-2,3-*exo*-diol (**5**) [colorless crystals, mp 115 °C (lit.$^{4)}$ 118 °C) ^{1}H NMR δ=1.63(1H, dt, *J*=9.2, 1.6 Hz), 1.88(1H, d, *J*=9.2 Hz), 1.70(2H, t, *J*=1.6 Hz), 3.69(2H, d, *J*=1.6 Hz), and 6.04(2H, t, *J*=1.6 Hz). ^{13}C NMR δ=42.2, 47.9 (2C), 68.8(2C), and 136.3(2C)] in 70% yield as shown in Scheme 1. The brief irradiation (30 min) in CD_3OD revealed that only **5** was an oxygenated product by the NMR spectroscopy (**1**:**2**:**5**=80:20:1).

The selective formation of **3** and **5** in different conditions can be explained as a result of the secondary reactions taken place with a common precursor, which must be the dioxetane, **4**; the photoreduction of dioxetanes to *cis*-1,2-diols under RB-sensitization conditions has been recorded.$^{5)}$

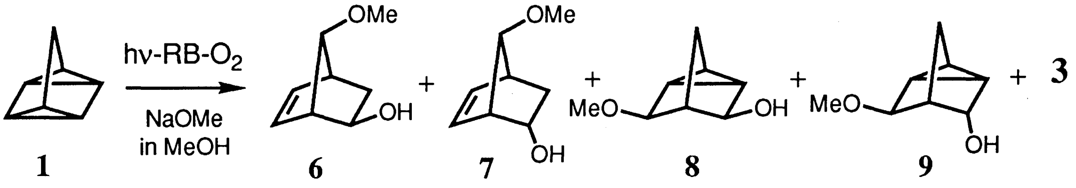
For the mechanisms leading to **4** from **1**, one has to consider three possibilities; i.e., the route a) the [$2\sigma+2\sigma+2\pi$] cycloaddition of $^1O_2$ with **1**, the route b) the photoisomerization of **1** to **2** and subsequent [2+2] cycloaddition with $^1O_2$, and the route c), the reaction of the radical cation $\mathbf{1}^{\cdot+}$, an intermediate in the isomerization of **1** to **2**, with $^3O_2$. Although, the major process of the reaction is an isomerization of **1** to **2**, the route b) is ruled out from the established inertness of **2** toward $^1O_2$-oxygenation.$^{1,2)}$ As the isomerization of **1** to **2** is suggested to be caused via a charge transfer complex of **1** and RB or via an electron transfer to RB from **1**,6) There still remain two possibilities, the routes a) and c), although the fact that we could not find **4** or the secondary product, **3**, in the MB-sensitized photooxidation1) disfavors the latter.



Scheme 1.

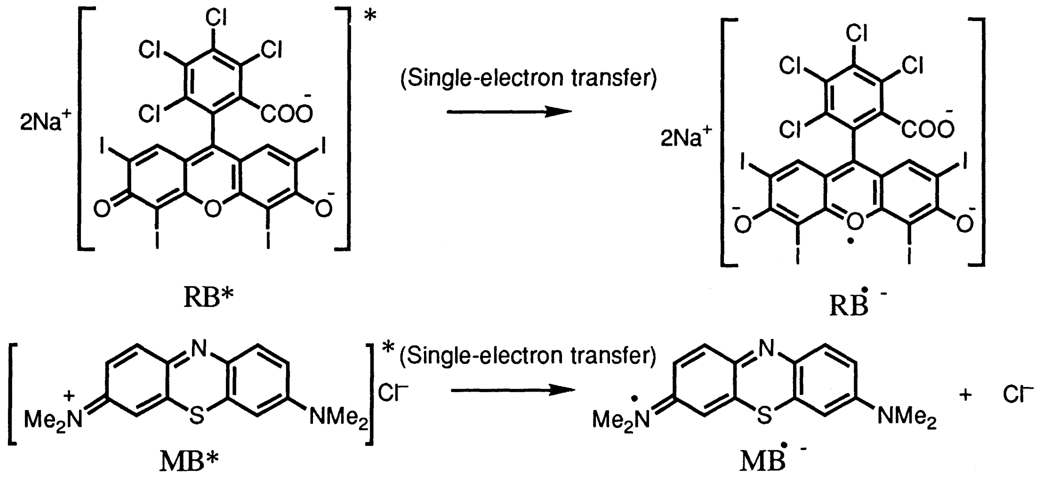
First of all, the absence of solvent-incorporated oxidation products in the RB-sensitized photooxidation should be mentioned. In the case of MB-sensitized photooxidation of **1**, the resultant **1**$^{\cdot+}$ consumes chloride ion to make the medium basic.7) As the result, methoxide ion was accumulated in the solution. Namely, the results indicate that **1**$^{\cdot+}$ is reactive with not MeOH, but methoxide ion.8)

This was verified when the MeOH solution of **1** and RB was irradiated for 30 min in the presence of NaOMe under O_2 stream, the yields of oxygenation products were doubled when compared with those without NaOMe; i.e., epimeric pairs of methoxynorbornenols (**6** and **7**) and methoxynortricyclanols (**8** and **9**)1,9) were obtained together with **3** (Scheme 2). It was noticed that the rate of formation of **3** was almost same in these two conditions, with or without NaOMe. Therefore, generated radical cation **1**$^{\cdot+}$ resulted in the formation of not **4**, but methoxylated products, and the route c) is ruled out.



Scheme 2.

Moreover, there is another point worth to note; **1**$^{\cdot+}$ formed from the RB-sensitization was reluctant toward reaction with MeOH; the organic moiety of the semiquinone radical of MB (MB·–) formed by the single-electron transfer is a neutral radical, but that of RB (RB·–) is an anion radical (Scheme 3). Accordingly, **1**$^{\cdot+}$ in the RB-sensitization environment may suffer a facile reverse electron transfer process, while **1**$^{\cdot+}$ from MB-sensitization may has longer mean life to enable to react with solvent residue and with $^3O_2$10) as there is no Coulomb attractive interaction between **1**$^{\cdot+}$ and MB·–; indeed, **1**$^{\cdot+}$ from MB-sensitization reacted with chloride ion, the counter ion of the dye.7) As the results, MB-sensitized photooxidation reaction yielded the methoxylated products.



Scheme 3.

The electron-transfer process of RB- and MB-sensitized photooxidations are different in view of an important aspect; i.e., the process is still fast from **1** to ^{3}MB as diffusion control, but not to ^{3}RB as could be predicted from the thermodynamic parameters.[6,11] Consequently, as the lowest triplet state of dyes has much longer life time than the singlet excited state, the most of $\mathbf{1}^{\cdot +}$ in the MB-sensitization should be produced from ^{3}MB, but in the RB-sensitization, $\mathbf{1}^{\cdot +}$ could be produced only from ^{1}RB.[12] This is the explanation for the exclusive formation of **4** in the RB-sensitized photooxidation. In other words, prior to form $^1O_2$, ^{3}MB was quenched by **1**, but ^{3}RB was not.[13]

$$\text{Dye} \xrightarrow{h\nu} {}^1\text{Dye} \longrightarrow {}^3\text{Dye} \xrightarrow{O_2} {}^1O_2 + \text{Dye}$$

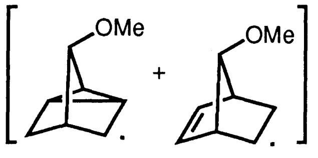
$$^1\text{Dye} + \mathbf{1} \longrightarrow \text{Dye}^{\cdot -} + \mathbf{1}^{\cdot +}$$

$$^3\text{Dye} + \mathbf{1} \longrightarrow \text{Dye}^{\cdot -} + \mathbf{1}^{\cdot +} \quad \left\{ \begin{array}{l} ^3\text{MB} + \mathbf{1} \longrightarrow \text{MB}^{\cdot -} + \mathbf{1}^{\cdot +} \\ ^3\text{RB} + \mathbf{1} \not\longrightarrow \text{RB}^{\cdot -} + \mathbf{1}^{\cdot +} \end{array} \right\}$$

$$^1O_2 + \mathbf{1} \longrightarrow \mathbf{4}$$

$$\mathbf{1}^{\cdot +} + \text{MeOH} \xrightarrow[\text{slow}]{}$$

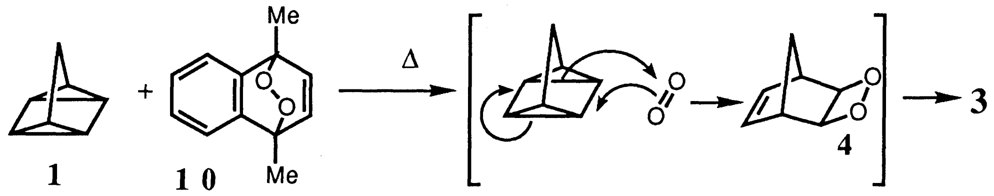
$$\mathbf{1}^{\cdot +} + \text{MeO}^- \xrightarrow[\text{fast}]{}$$



$$\xrightarrow{\text{1. } O_2 \quad \text{2. } NaHSO_3} \mathbf{6}-\mathbf{9}$$

(Methoxyalcohols)

The positive role of $^1O_2$ in the formation of **3** was verified independently. When a CH_2Cl_2 solution of **1** was heated at 40 °C for 6 h with an endoperoxide **10**, which is known to liberate $^1O_2$,[14] **3** was formed in 3% yield together with 1,4-dimethylnaphthalene (Scheme 4).



Scheme 4.

In conclusion, it is interesting to note that the dye-sensitized photooxygenation of **1** is sensitizer-dependent. With MB, **1** gives various solvent-incorporated products via a nucleophilic attack to the intermediate radical cation, $\mathbf{1}^{\cdot+}$,1) while with RB, it furnishes dioxetane **4** as the sole primary product, although an occurrence of $\mathbf{1}^{\cdot+}$ in those conditions was confirmed as it gave methoxylated products in the presence of added NaOMe. Highly efficient reduction of **4** to **5** under RB-sensitized conditions in MeOH is also worth to mention; the photoreduction of dioxetanes was initially discovered in the RB-sensitized photooxidation of vinylcyclopropanes as a competitive process to the ordinary dicarbonyl fragmentation.5)

References

1) T. Hatsui and H. Takeshita, *J. Photochem. Photobiol. A: Chem.*, **57**, 257 (1991).
2) T. Kobayashi, M. Kodama, and S. Itô, *Tetrahedron Lett.*, **16**, 655 (1975).
3) The NMR spectra were measured by means of a JEOL GSX 270H Model spectrometers in $CDCl_3$.
4) Y. F. Shealy and J. D. Clayton, *J. Am. Chem. Soc.*, **91**, 3075 (1969).
5) H. Takeshita and T. Hatsui, *J. Org. Chem.*, **43**, 3080 (1978); T. Hatsui and H. Takeshita, *Bull. Chem. Soc. Jpn.*, **53**, 2655 (1980); H. Takeshita and T. Hatsui, *ibid.*, **54**, 3609 (1981).
6) The electron transfer from **1** to ^{1}RB is an exothermic, but that to ^{3}RB is an endothermic: $E_{ox}(\mathbf{1}) = 0.91$ V.15) E_S(0-0) for RB = 48.2 kcal/mol, E_T(0-0) for RB = 39.4 kcal/mol, E_{red}(RB) = -1.10 V.16) Then, ΔG for ^{1}RB = -8.1 kJ/mol, and ΔG for ^{3}RB = +28.9 kJ/mol.
7) In the MB-sensitized reaction, chloronortricyclanol and chloronorbornenol were isolated. In the first stage occurred the bleaching by quick precipitation of the dye which slowly dissolved to give a solution with slightly greenish blue in color.
8) Indeed, when an MeOH solution of **1** was irradiated in the presence of RB under N_2 atmosphere, the isomerization occurred, but no MeOH-incorporated compounds could be detected.
9) Three isomers (**7**, **8**, and **9**) were isolated in nearly equal amounts, except for **6**, which is quite volatile.
10) It is already known, in the MB-sensitized photooxidation, that the reaction of $\mathbf{1}^{\cdot+}$ with $^3O_2$ via radical coupling process was slower than the nucleophilic attack of MeOH.1)
11) D. Rehm and A. Weller, *Israel J. Chem.*, **8**, 259 (1970).
12) Responsibility of short-lived ^{1}RB for electron transfer process has been reported. See D. C. Neckers, *J. Photochem. Photobiol. A: Chem.*, **47**, 1 (1989).
13) E_S(0-0) for MB = 1.84 eV, $E_{red}(MB^+/MB^\cdot) = -0.25$ V.17) E_T(0-0) for MB = 11640 cm^{-1} = 139.2 kJ/mol.18) Then, ΔG for ^{1}MB = -65.6 kJ/mol, and ΔG for ^{3}MB = -27.3 kJ/mol.
14) H. H. Wasserman and D. L. Larsen, *J. Chem. Soc., Chem. Commun.*, **1972**, 253; N. Turro, M. -F. Chow, and J. Rigandy, *J. Am. Chem. Soc.*, **103**, 7218 (1981).
15) P. G. Gassman and R. Yamaguchi, *Tetrahedron*, **38**, 1113 (1982).
16) S. N. Linden and D. C. Neckers, *Photochem. Photobiol.*, **47**, 543 (1988).
17) L. E. Manring, J. Ericksen, and C. S. Foote, *J. Am. Chem. Soc.*, **102**, 4277 (1980).
18) T. Ohno and N. N. Lichtin, *J. Phys. Chem.*, **86**, 354 (1982).

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