

## The Methylene Blue-Sensitized Photooxidation of Quadricyclane, Reinvestigated

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Photooxygenation of quadricyclane(**1**) was shown to proceed via the electron transfer mechanism on the basis of the structure revision of a methoxy alcohol. Photoisomerization of **1** to norbornadiene occurred during the irradiation.

Photooxidation of quadricyclane(**1**) sensitized by Methylene Blue(MB) in MeOH was studied by Itô et al. in 1975.<sup>1)</sup> Three methoxy alcohols(**2-4**) were isolated after reduction, and they were interpreted by the solvent attack to the polar intermediate formed in the reaction of **1** with singlet oxygen( $^1\text{O}_2$ ). Since then, this has been regarded as an evidence supporting the polar mechanism of the  $^1\text{O}_2$ -oxygenation.

However, it is true that this reaction suffers a severe bleaching of the dye, and the possibility of the photo-electron transfer from **1** to the excited state of MB should not be disregarded.<sup>2-4)</sup> These prompted us to re-examine the photo-oxidation of **1** to confirm the mechanism.

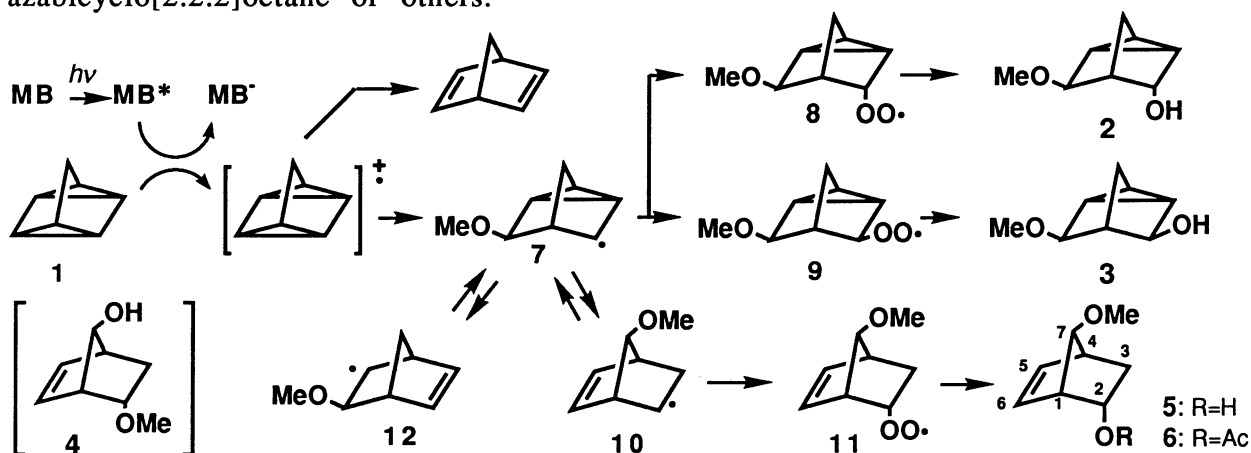
An MeOH solution (20 cm<sup>3</sup>) of **1** (1.00 g) and MB (20 mg) was irradiated by means of a 500-W halogen lamp for 12 h with O<sub>2</sub>-bubbling, while cooled with running water. The dye was bleached quite rapidly,<sup>5)</sup> and the occasional additions of MB reached to ca. 120 mg. After the reaction, aq Na<sub>2</sub>SO<sub>3</sub> solution was added, stirred for overnight, and extracted with ether. The GC-analysis of the products showed a disappearance of **1** and a formation of norbornadiene. After the evaporation of the solvent, oily mixture (238 mg) was separated by silica-gel chromatography to give three methoxy alcohols(**2**, **3**, and **5**). The first two, which had been characterized as a mixture by Itô et al.,<sup>1)</sup> were identified to be the isomeric 5-methoxy-3-nortricyclanols from the NMR spectra (**2**(30% of the products):  $\delta(^1\text{H})=1.31(\text{tm}, J=5 \text{ Hz}), 1.36(\text{br d}, J=11 \text{ Hz}), 1.47(2\text{H}, \text{br d}, J=5.5 \text{ Hz}), 1.74(\text{br s}, \text{OH}), 1.77(\text{d}, J=11 \text{ Hz}), 1.98(\text{br s}), 3.34(3\text{H}, \text{s}), 4.02(\text{t}, J=2 \text{ Hz}), \text{ and } 4.09(\text{br s}); \delta(^{13}\text{C})=14.9, 15.1, 19.3, 27.7, 38.5, 56.8, 77.4, \text{ and } 83.8$ . **3**(30%):  $\delta(^1\text{H})=1.35\text{--}1.50(3\text{H}, \text{m}), 1.73(\text{dt}, J=11, 1.3 \text{ Hz}), 1.78(\text{dt}, J=11, 1.3 \text{ Hz}), 2.06(\text{s}, \text{OH}), 2.12(\text{m}), 3.27(3\text{H}, \text{s}), 3.37(\text{t}, J=1.7 \text{ Hz}), \text{ and } 3.81(\text{t}, J=1.7 \text{ Hz}); \delta(^{13}\text{C})=11.9, 18.6, 20.2, 26.1, 38.8, 56.3, 73.3, \text{ and } 81.5$ ). Their configurations were deduced from the chemical shift data and the NOE study with **3**.

The  $^1\text{H}$  NMR spectrum of **5**(15%) showed a coincidence with that reported for **4**.

However, its  $^{13}\text{C}$ -NMR ( $\delta=34.5(\text{C}_3)$ ,  $44.0(\text{C}_4)$ ,  $49.7(\text{C}_1)$ ,  $56.1(\text{MeO})$ ,  $71.7(\text{C}_2)$ ,  $93.5(\text{C}_7)$ ,  $129.9(\text{C}_6)$ ,  $138.3(\text{C}_5)$ ) revealed a very deshielded 7-methine carbon in comparison with those of 7-norbornenols ( $\delta=86.9$  for *syn*-;  $\delta=82.0$  for *anti*-).<sup>6)</sup> So, **5** was converted to its acetate **6**, whose 7-methine proton did not show a low field shift, but the 2-*exo*-methine proton did to  $\delta=5.36$ . The other NMR data were also consistent with **6**, i.e.,  $\delta(^1\text{H})=1.04(\text{ddd}, J=12.5, 2.5, 1.8 \text{ Hz}; \text{H}_{3\text{endo}})$ ,  $1.98(3\text{H}, \text{s}; \text{Ac})$ ,  $2.34(\text{ddd}, J=12.5, 7.7, 4 \text{ Hz}; \text{H}_{3\text{exo}})$ ,  $2.75(\text{m}, \text{H}_4)$ ,  $3.12(\text{m}; \text{H}_4)$ ,  $3.25(3\text{H}, \text{s}; \text{MeO})$ ,  $3.30(\text{q}, J=1.8 \text{ Hz}; \text{H}_7)$ ,  $5.36(\text{ddd}, J=7.7, 3.5, 2.5 \text{ Hz}; \text{H}_2)$ ,  $5.90(\text{dd}, J=6, 3.5 \text{ Hz}; \text{H}_6)$ , and  $6.27(\text{ddd}, J=6, 3.7, 1.7 \text{ Hz}; \text{H}_5)$ .

As a result, **5** was not *endo*-5-methoxy-2-norbornen-7-ol, but *syn*-7-methoxy-5-norbornen-*endo*-2-ol. This suggests that the initial attack to **1** was by an  $\text{MeO}^\cdot$  group, but not by  $^1\text{O}_2$ . So, the mechanism of this photooxidation must be shown in the scheme depicted below. The electron transfer from **1** to the excited MB and subsequent addition of MeOH to the cation radical of **1** should form a nortricycyl radical (**7**), which reacted with  $\text{O}_2$  to afford a pair of peroxy radicals (**8** and **9**). The formation of **5** can be explained in terms of the rearrangement of the **7** to 7-methoxy-5-norbornen-2-yl radical (**10**), which in turn gives **11**. No products derived from 3-methoxy-5-norbornen-2-yl radical (**12**) were detected.

In conclusion, the MB-sensitized photooxidation of **1** is not caused by  $^1\text{O}_2$ , but goes through the photo-electron transfer mechanism. It should be noted that the participation of  $^1\text{O}_2$  is not always secured by the quenching experiment with 1,4-diazabicyclo[2.2.2]octane or others.



#### References

- 1) T. Kobayashi, M. Kodama, and S. Itô, *Tetrahedron Lett.*, **1975**, 655.
- 2) L. E. Manring, J. Eriksen, and C. S. Foote, *J. Am. Chem. Soc.*, **102**, 4275(1980).
- 3) T. Akasaka and W. Ando, *J. Am. Chem. Soc.*, **109**, 1260(1987).
- 4) The oxidation potential of **1** is low enough;  $E(\text{D}/\text{D}^+)=0.91 \text{ V}$ .<sup>7)</sup> For MB,  $E(\text{A}^\cdot/\text{A})=-0.25 \text{ V}$  and  $E_{00}=177 \text{ kJ.mol}^{-1}$ .<sup>2)</sup> Therefore,  $\Delta G$  was estimated to be  $-65 \text{ kJ mol}^{-1}$ .
- 5) Without oxygen, the dye was bleached very rapidly, with no isomerization of **1**.
- 6) J. B. Stothers and C. T. Tan, *Can. J. Chem.*, **55**, 841(1977).
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