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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.[1] 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($^1O_2$). Since then, this has been regarded as an evidence supporting the polar mechanism of the $^1O_2$-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.[2-4] These prompted us to re-examine the photo-oxidation of **1** to confirm the mechanism.

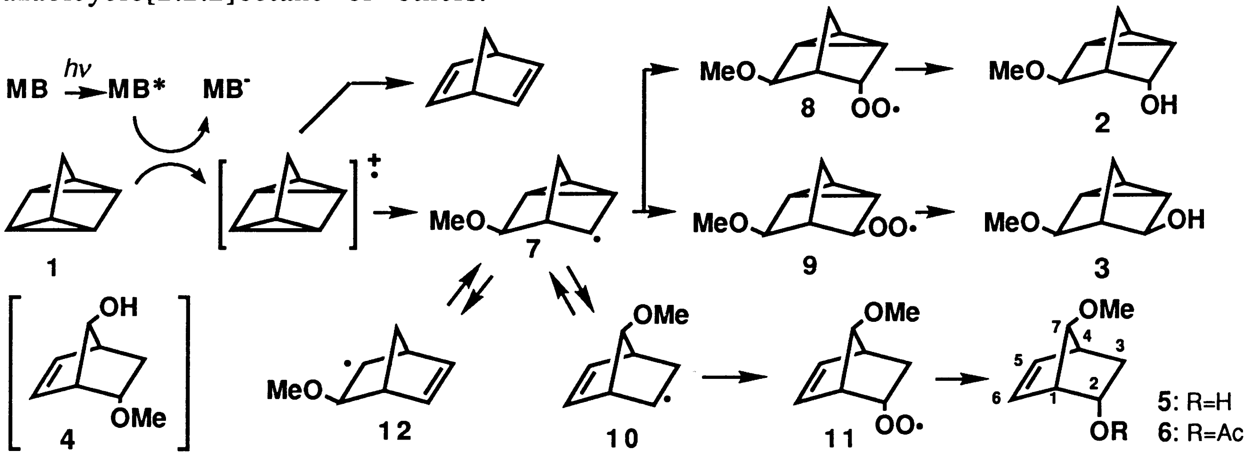
An MeOH solution (20 cm^3) of **1** (1.00 g) and MB (20 mg) was irradiated by means of a 500-W halogen lamp for 12 h with O_2-bubbling, while cooled with running water. The dye was bleached quite rapidly,[5] and the occasional additions of MB reached to ca. 120 mg. After the reaction, aq Na_2SO_3 solution 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.,[1] were identified to be the isomeric 5-methoxy-3-nortricyclanols from the NMR spectra (**2**(30% of the products): $\delta(^1H)$=1.31(tm, $J\cong5$ Hz), 1.36(br d, J=11 Hz), 1.47(2H, br d, J=5.5 Hz), 1.74 (br s, $\underline{OH}$), 1.77(d, J=11 Hz), 1.98 (br s), 3.34(3H, s), 4.02(t, J=2 Hz), and 4.09(br s); $\delta(^{13}C)$=14.9, 15.1, 19.3, 27.7, 38.5, 56.8, 77.4, and 83.8. **3**(30%): $\delta(^1H)$=1.35-1.50(3H, m), 1.73(dt, J=11, 1.3 Hz), 1.78(dt, J=11, 1.3 Hz), 2.06(s, $\underline{OH}$), 2.12(m), 3.27(3H, s), 3.37(t, J=1.7 Hz), and 3.81(t, J=1.7 Hz); $\delta(^{13}C)$=11.9, 18.6, 20.2, 26.1,. 38.8, 56.3, 73.3, and 81.5). Their configurations were deduced from the chemical shift data and the NOE study with **3**.

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

However, its ^{13}C-NMR(δ=34.5(C_3), 44.0(C_4), 49.7(C_1), 56.1(MeO), 71.7(C_2), 93.5(C_7), 129.9(C_6), 138.3(C_5)) revealed a very deshielded 7-methine carbon in comparison with those of 7-norbornenols (δ=86.9 for *syn-* ; δ=82.0 for *anti-*).[6] 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 δ=5.36. The other NMR data were also consistent with **6**, i.e., δ(^{1}H)=1.04(ddd, J=12.5, 2.5. 1.8 Hz; H_{3endo}), 1.98(3H, s; Ac), 2.34(ddd, J=12.5, 7.7, 4 Hz; H_{3exo}), 2.75(m, H_4), 3.12(m; H_4), 3.25(3H, s; MeO), 3.30(q, J=1.8 Hz; H_7), 5.36(ddd, J=7.7, 3.5, 2.5 Hz; H_2), 5.90 (dd, J=6, 3.5 Hz; H_6), and 6.27(ddd, J=6, 3.7, 1.7 Hz; 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 MeO$^-$ group, but not by $^1O_2$. 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 nortricyclyl radical (**7**), which reacted with 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 $^1O_2$, but goes through the photo-electron transfer mechanism. It should be noted that the participation of $^1O_2$ is not always secured by the quenching experiment with 1,4-diazabicyclo[2.2.2]octane or others.



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4) The oxidation potential of **1** is low enough; $E(D/D^+)$=0.91 V.[7] For MB, $E(A^-/A)$= −0.25 V and E_{00}=177 kJ.mol.[2] Therefore, ΔG was estimated to be −65 kJ mol^{-1}.
5) Without oxygen, the dye was bleached very rapidly, with no isomerization of **1**.
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