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# SENSITIZED PHOTOOXIDATION OF QUADRICYCLANE AND NORBORNADIENE

## NEW TYPES OF REACTION OF $^1O_2$

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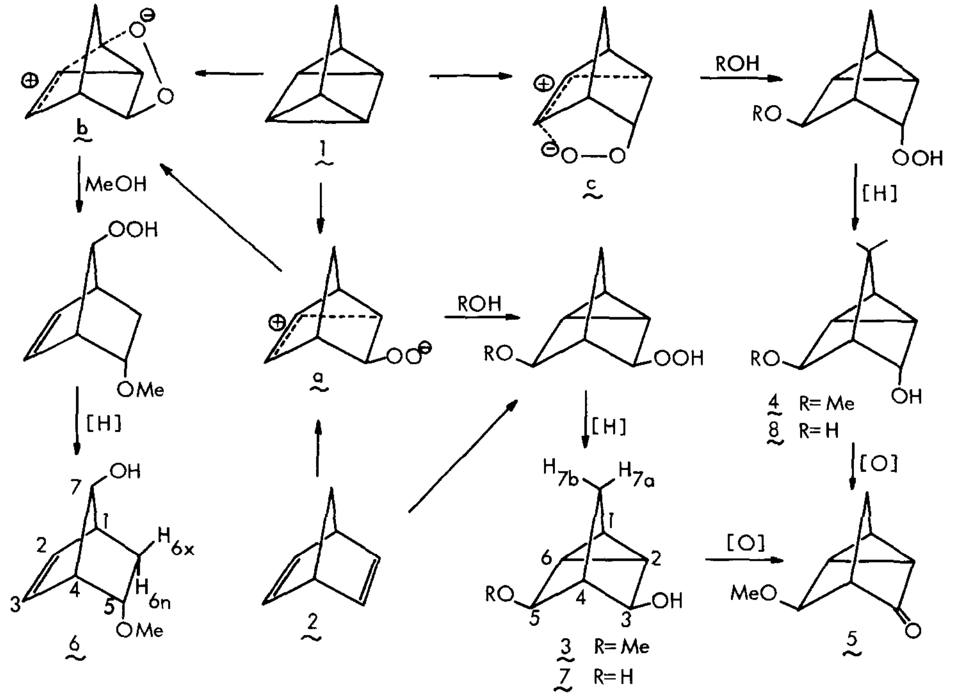
As singlet oxygen is well known (1) to react with cisoid 1,3-dienes to give Diels-Alder type of adducts, we are intrigued into its behavior toward quadricyclane 1 and norbornadiene 2, both of which are known to undergo [2+2+2] cycloaddition reactions (2,3)  We wish to describe the result which revealed novel reaction for singlet oxygen

Quadricyclane 1 in methanol was irradiated by 300 W tungsten lamp in the presence of methylene blue under stream of oxygen at room temperature  Dye-bleaching occurred rather rapidly and the slow formation of peroxide was observed  The reaction mixture was reduced with aqueous sodium bisulfite after 50 hrs  The product obtained in ca  32% yield was a mixture of at least four compounds as analysed by glc (DEGS column, 150°)

Although the major product (colorless oil, 67% of the products) was chromatographycally pure (glc and tlc), it was apparently an inseparable mixture of almost equal amount of two methoxy alcohols 3 and 4  $M^+$ 140 (trimethylsilyl ether, $M^+$ 212), ν ($CCl_4$) 3580, 3540 $cm^{-1}$ (OH), δ ($CDCl_3$) 3 06 (OMe), 3 39 (OMe), 3 40 (t, J=2), 3 81 (t, J=2), 4 02 (t, J=2) and 4 11 (br s) (intensity ratio, 3 3 1 1 1 1) By the application of $Eu(fod)_3$ shift reagent, the NMR spectrum was analysed to lead nortricyclyl structures 3 and 4 for these products  δ ($CDCl_3$ + $Eu(fod)_3$), 3, 2 15 (t, J=5, $H_1$), 2 24 (t, J=5, $H_6$), 2 95 (d, J=11, $H_{7b}$), 3 36 (t, J=5, $H_2$), 3 59 (s, OMe), 3 83 (br s, $H_4$), 4 09 (d, J=11, $H_{7a}$), 4 19 (t, J=2, $H_5$), 7 30 (t, J=2, $H_3$), 4, 1 89 (d, J=11, $H_{7b}$), 1 95 (t, J=5, $H_1$), 2 26 (t, J=5, $H_6$), 2 30 (d, J=11, $H_{7a}$), 2 54 (t, J=5, $H_2$), 3 12 (br s, $H_4$), 3.70 (s, OMe), 5 63 (t, J=2, $H_5$), 6 16 (t, J=2, $H_3$)



Relative configuration of the hydroxyl group was determined by the magnitude of down-field shift upon the addition of Eu(fod)$_3$ The signal due to $H_{7a}$ showed larger down-field shift than that of $H_5$ in the case of 3, while the reverse is true for 4 Epimeric relation of the hydroxyl groups in 3 and 4 was further confirmed by the $CrO_3$ oxidation of the mixture to give a single ketone 5, $M^+$ 138, ν ($CCl_4$), 1750 cm$^{-1}$, 2,4-DNP, m p 160 5-161° (4), which was identical with one of the products obtained in 3% yield in the sensitized oxidation

The another product 6 (colorless oil, 17% of the products, $M^+$ 140) contains hydroxyl (ν 3350 cm$^{-1}$) and methoxyl groups (δ 3 22 ppm) From the extensive decoupling experiments the norbornene type structure was deduced unequivocally δ ($CDCl_3$) 0 89 (ddd, J=12, 2 5, 2, $H_{6n}$), 1 96 (OH), 2 29 (ddd, J=12, 8, 4, $H_{6x}$), 2 73 (ddd, J=4, 3 5, 1, $H_1$), 2 97 (ddd, J=4, 3 5, 1, $H_4$), 3 22 (s, OMe), 3 30 (d, J=2, $H_7$), 4 57 (ddd, J=8, 4, 2 5, $H_5$), 5 98 (ddd, J=6 5, 3 5, 1, $H_3$), 6 37 (ddd, J=6 5, 3 5, 1, $H_2$) Couplings between $H_4$ and $H_5$ (J=4) and $H_{6n}$ and $H_7$ (J=2) revealed the configuration of the hydroxyl and methoxyl groups

As the minor products, two diols 7 (ν 3300 cm$^{-1}$) and 8 (ν 3300 cm$^{-1}$) were obtained up to 5% of the mixture δ ($CDCl_3$ + $Eu(fod)_3$), 7, 2 20 (t, J=5, $H_2$), 2 46 (t, J=5, $H_1$), 2 93 (d, J=11, $H_7$), 2 98 (t, J=5, $H_6$), 3 54 (br s, $H_4$), 3 80 (d, J=11, $H_7$), 4 49 (br s, $H_3$), 6 79 (br s, $H_5$), 8, 2 20 (d, J=11, $H_{7a}$), 2 24 ( t, J=5, $H_1$), 2 59 (t, J=5, $H_2$), 2 65 (d, J=11, $H_{7b}$), 3 06 (t, J=5, $H_6$), 3 54 (br s, $H_4$), 6 67 (br s, $H_3$), 7 27 (br s, $H_5$) Although a few more minor products are present in the reaction mixture, none was obtained pure to allow structural assignment

Involvement of singlet oxygen in the reaction was secured by i) complete inhibition of the reaction in the absence of sensitizer ii) appreciable slow-down (5) by the addition of 1,4-diazabicyclo[2 2 2]-octane, without changing the product ratio

Sensitized photooxidation of norbornadiene 2 was carried out in the same condition described above In this case, however, the reaction was extremely slow (6) and after 10 days of irradiation oxidation product was obtained only in 4% yield The product was a mixture of 3 (72%) and 6 (8%) and some unknown compounds

The entire reaction sequence can be depicted as shown in the chart The general course of the reaction is remniscent of those with electrophiles for both compounds The initial attack of electrophilic singlet oxygen on 2 would produce the nonclassical ion a, either directly or through the corresponding "perepoxide" and the ion a would in turn be attacked by a nucleophile The ion should be assymmetrically perturbed to rationalize the stereospecific "exo" attack (7) to compound 3 Alternatively, the pathway from 2 to 3 may well be a concerted process The formation of a small amount of 6 is a "leak" from the concerted or stereospecific process and involves the ion b which can be stabilized by the intramolecular ion pairing $S_N2$ type of the attack of methanol on the ion b yields 6 stereospecifically For the reaction of 1, a new reaction sequence was observed in addition to the common pathways to 3 and 7 in this case, and to 6 The new type of the reaction is that utilizing the bonding lobe of cyclopropane unlike in the reactions of common electrophiles (8) Although "edge" type cleavage of cyclopropane rings has precedences (9), this is, as far as we are aware, the first instance for 1 to undergo such a cleavage The resulted ion c would be stabilized by the ion pairing and eventually yield 4 stereospecifically Furthermore, even in the formation of a and b large quantitative difference was noted While the formation ratio of 3 to 6 is 9 in the reaction of 2, it is only 2 for 1 This could only be explained by the direct formation of b from 1 besides through the ion a In any event, these reactions revealed interesting pathway of singlet oxygen toward **1** and **2**

The reactions of singlet oxygen with other strained systems are in progress

## References and Footnotes

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5) About 30% slow-down of the reaction was observed when the equimolar base was added [see, C Ouannes and T Wilson, *J Am Chem Soc*, **90**, 6527 (1968)] Taking account of no change in product ratio, the possibility of any radical processes involved can be excluded

6) Matsuura, *et al*, have reported the relative rate of the sensitized oxidation of norbornadiene However, none of the products has been described T Matsuura, A Horinaka and R. Nakashima, *Chem Letters*, 887 (1973)

7) Completely delocalized ion or totally localized ion would suffer an attack of nucleophile at C-6 from both sides

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