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Efficient Oxygenation of Alkene through Reductive Quenching of Excited Sb(V)tetraphenylporphyrin by Triphenylphosphine

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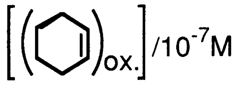
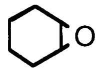
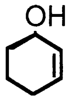
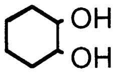
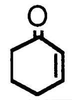
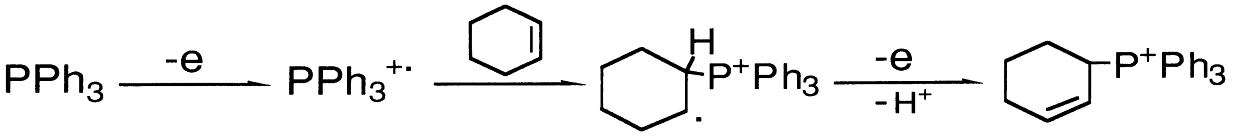
Novel efficient oxygenation route of cyclohexene into 2-cyclohexen-1-one (Φ =0.14) upon visible light irradiation to tetraphenylporphyrinatoantimony(V) through reductive quenching of the excited triplet porphyrins by triphenylphosphine in aqueous acetonitrile has been found.

Many intensive studies on photoredox reaction aiming at an artificial photosynthesis have been made and rather efficient hydrogen evolution has been found,1) while practical solar energy conversion system is still in distrustful situation.2) Attention would be thus shifted to the point of how actually useful oxidative reaction and a water molecule as an ideal electron donor could be coupled in the oxidation terminal end of the photoredox system from both synthetic and energetic-viewpoints.3) Recently we have found a photochemical epoxidation of alkene sensitized by high-valent metalloporphyrins such as Sb(V)-, P(V)-, Sn(IV)-, and Ge(IV)-tetraphenylporphyrin in a redox system involving water both as electron and oxygen donors.4) The epoxidation has been revealed to be induced by oxidative quenching of the porphyrin triplet by electron acceptor methylviologen to produce metal oxo-porphyrin as a key intermediate for oxygen transfer to alkene and simultaneous reductive quenching by hydroxide ion in the reaction system exerts only negative effect of suppressing the epoxidation to be in rather low reactivity ($\Phi=10^{-3}$).5) Extensive studies of additive effects on the epoxidation for improvement of the reactivity have led to finding of another novel oxygenation route through reductive quenching by triphenylphosphine(PPh_3). When a reaction mixture of $[Sb(V)TPP(OH)_2](OH)$ (**1**) as a sensitizer (2×10^{-6}M), methylviologen (MV^{2+}: 8×10^{-3}M), cyclohexene (10^{-1}M), and potassium hydroxide(1×10^{-4}M) in 95:5 acetonitrile-water was irradiated by visible light of λ = 420 nm under the degassed conditions, the main oxidation reaction was the epoxidation of cyclohexene with a rather low quantum yield of 10^{-3}. Among the examined various kinds of additive to the above reaction system, PPh_3 induced unique and enormous effect on the oxidation (Table 1); the main oxidation product was revealed to be changed into 2-cyclohexen-1-one (**2**) with a high quantum yield of 0.14, while the epoxidation was also enhanced by a factor of several times. The oxygen atom of water in the reaction system was confirmed to be incorporated in the oxidation product **2** by an experiment using $H_2{}^{18}O$; the yield of ^{18}O incorporation in **2** was 13% when $H_2{}^{18}O/(H_2{}^{16}O+H_2{}^{18}O)$ =0.09. Since **2** is a four electron oxidized product from cyclohexene and 2-cyclohexen-1-ol(**3**) is a two electron oxidized one, the compound **2** could be easily speculated to be produced by the further oxidation of **3** once generated in the reaction system upon light irradiation. Time profile of the production of **2** and **3** clearly excluded the postulate. The compounds **2** and **3** were both monotonically produced with the light irradiation without showing any induction period, suggesting that **2** was directly produced from cyclohexene. When only **1** and $PPh_3(1\times10^{-3}M)$ in 95:5 $MeCN-H_2O$ were irradiated by the light of λ = 420 nm, efficient production of the radical anion of **1** was observed (Φ= 0.51), while the cation radical of MV^{2+}($MV^{+\cdot}$) was effectively produced without any formation of the radical anion of **1** in the presence of MV^{2+} under the same conditions of the light irradiation. Since fluorescence of **1** was not affected by PPh_3, the excited state responsible for the photoreduction should be the triplet state of the porphyrin. This strongly suggests that the cation radical of PPh_3 is obviously produced by reductive quenching of an electron transfer to the excited porphyrin triplet and participates in the oxidation of the alkene. Since the cation radical of PPh_3 has been reported to produce an adduct with alkene,$^{6)}$ a possible formation of **2** from the adduct was further examined. Oxidative voltammetric electrolysis of methylene chloride solution involving PPh_3 and cyclohexene afforded (2-cyclohexen-1-yl)triphenylphosphonium ion (**4**) which could be derived from reaction between the cation radical of PPh_3 and cyclohexene (Scheme 1).$^{6,7)}$

Table 1. Additive Effect on Photosensitized Oxidation of Cyclohexene $^{a)}$

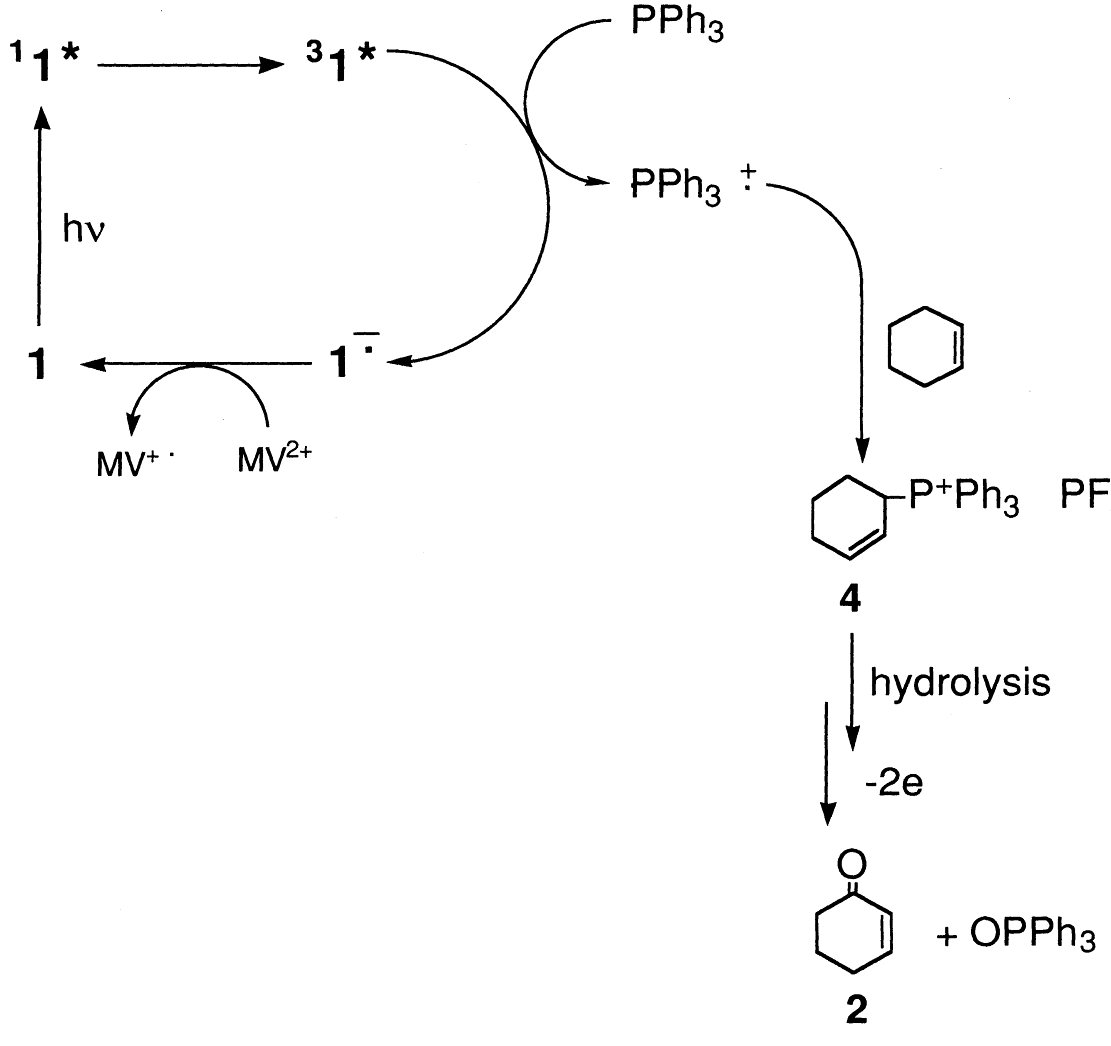
Additive				
				
None$^{b)}$	10.1	0	0	0
Triethylamine	2.2	0	0	4
Diisopropylamine	3.0	0	0	14
N-Methylimidazol	0.8	8	0	0
Imidazol	0.8	2	0	0
Tribenzylamine	3.0	2	0	3
Lithium bromide$^{c)}$	0.0	110	0	—
Triethyl phosphite	6.5	21	0	48
Trimethyl phosphite	0.0	0	0	52
Triphenylphosphine$^{c)}$	25.7	402	50	1666
Triethyl phosphate	2.9	2	0	0
Triphenylphosphine oxide$^{d)}$	6.8	0	0	11

a) [[Sb(V)TPP$(OH)_2$](OH) (**1**)]=1.7×10^{-6} M, [MV^{2+}]=8.3×10^{-3}M, []=0.1 M, [Additive]=1.0×10^{-2} M, in degassed CH_3CN/H_2O (95/5), 420 nm irrdn. for 60 min.
b) [KOH]=1×10^{-4} M, c) [KOH]=2×10^{-4} M, d) [$OPPh_3$]=2×10^{-3} M, [KOH]=2×10^{-4} M .



Scheme 1. **4**

The adduct **4** was revealed to produce **2** in the dark within one hour at ambient temperature (yield = 53.2%) under the conditions in alkaline aqueous acetonitrile ($[OH^-] = 1 \times 10^{-2}$M in 95:5 MeCN-$H_2O$). ^{18}O atom was also confirmed to be incorporated in **2** when $H_2{}^{18}O$ was used in the hydrolysis of **4** ; the yield of ^{18}O incorporation in 2 was 69 % when $H_2{}^{18}O/(H_2{}^{16}O+H_2{}^{18}O) = 0.56$. The adduct **4** was actually detected in the irradiated reaction mixture by GPC analysis,8) indicating the adduct formation in the photochemical reaction system. The production of **2** from the adduct **4** in the dark requires further oxidation of two electrons. Though the detailed reaction mechanism is not yet clear, the ^{18}O incorporation of $H_2{}^{18}O$ into **2** strongly suggests that hydrolysis of the adduct **4** should be involved in the production route of **2**. Since MV^{2+} is known to be rather efficient oxidizing agent, it may participate in the subsequent oxidation processes. The obtained results clearly indicate that the efficient photochemical oxygenation of cyclohexene sensitized by **1** proceeds through the reductive quenching of the excited porphyrin triplet by PPh_3 and the resultant $PPh_3{}^{+\cdot}$ reacts with cyclohexene to afford the adduct **4** which suffers effective hydrolysis to produce **2** (Scheme 2) .



Scheme 2.

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7) The electrolysis was carried out according to the literature,6) though the structure of the obtained adduct was revealed to be different from that reported; **4** yield 51% in the electrolysis. ^{1}H-NMR ($CDCl_3$) 1.5-2.4(6H,m), 4.6(1H,m), 5.6(1H,m), 6.1(1H,m), and 7.6-7.9(15H,m) ppm. ^{13}C-NMR ($CDCl_3$) 20.3(d,J_{CP}=11 Hz), 22.9(s), 24.1(s), 31.1(d,J_{CP}=50 Hz), 117.2(d,J_{CP}=83 Hz), 117.7(d,J_{CP}=6 Hz), 130.6(d,J_{CP}=11 Hz), 133.9(d,J_{CP}=9 Hz), 135.2(d,J_{CP}=4 Hz), and 136.6(d,J_{CP}=11 Hz) ppm. ^{31}P-NMR ($CDCl_3$) 24.6(s) ppm (H_3PO_4 as a standard). IR (KBr) 1430, 1100, and 1000 cm^{-1}. FAB-MS 343 ($(M-BF_4)^+$). The structure of **4** was further confirmed by comparison with the authentic sample obtained in the reaction of 3-bromocyclohexene with PPh_3. (J. M. McIntosh and R. S. Steevensz, Can. J. Chem., 55, 2442(1977)).

8) The adduct **4** isolated from the irradiated reaction mixture by GPC (Column; K-2001 Shodex, 20 mm ϕ x600 mm, eluent; $CHCl_3$) had the same λmax's (275, 268, 262 nm) with those of **4** obtained in the electrolysis.

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