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9-Mesityl-10-methylacridinium: An Efficient Type II and Electron-Transfer Photooxygenation Catalyst

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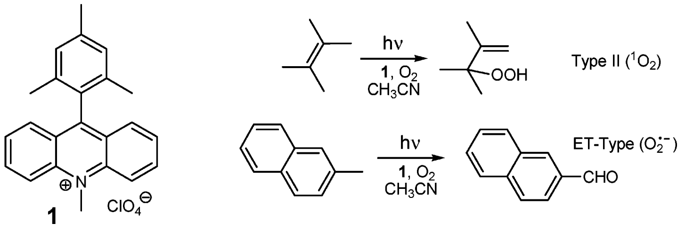
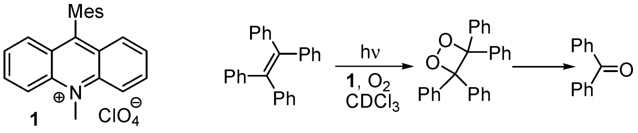
ABSTRACT



The visible-light irradiation of 9-mesityl-10-methylacridinium perchlorate 1 in the presence of monoalkenes and molecular oxygen leads to typical products of singlet oxygen addition (type II photooxygenation). The molecular probes 1-methylcyclohexene and limonene, respectively, result in hydroperoxide mixtures with a characteristic product pattern. A switch in the oxidative mechanism (electron-transfer photooxygenation) is observed for naphthalene derivatives as electron-rich acceptor molecules, revealing that the 9-mesityl-10-methylacridinium cation serves as a dual sensitizer with the capacity of efficient singlet oxygen formation and electron-transfer reaction.

Numerous visible-light absorbing molecules are known that can serve as sensitizers in photooxygenation reactions and transfer either energy (generating singlet oxygen $^1\Delta_g$-O_2) or an electron (generating the superoxide radical anion $O_2^{-\bullet}$) to oxygen. The latter process is often transmitted in an indirect manner via primary oxidation of an organic substrate resulting in the anion radical of the sensitizer and subsequent electron donation to oxygen. These reactions, if terminated by the oxidation of the organic substrate, are termed type II and electron-transfer (ET) (type I) photooxygenations.[1] Not many examples are known where sensitizers are capable of catalyzing both processes.[2] The N-alkylated 9-mesityl acridinium salts **1** have recently been described as compounds possessing charge-transfer states with remarkable long lifetimes.[3] As such, they appear to be suitable catalysts for electron-transfer-initiated processes in organic synthesis. The application of **1** as catalyst in the photooxygenation of tetraphenylethylene has been discussed as a type I process (Scheme 1).[4] The intermediary 1,2-dioxetane has also been observed and isolated for this process. An analogous reaction involving tetramethyl-dioxetane as the intermediate was described for 2,3-dimethyl-2-butene **4**, an excellent substrate also for singlet oxygen.[5] Singlet oxygen, as expected from an energy transfer process involving a triplet excited state of the sensitizer, was not detected in the reaction of **4**.

Scheme 1



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[1] The term type I for electron-transfer-induced oxygenation has been suggested by C. S. Foote as an extension of the historical type I and II definitions: Foote, C. S. *Photochem. Photobiol.* **1991**, *54*, 659.

[2] 9,10-Dicyanoanthracene (DCA), e.g.: Santamaria, J.; Gabillet, P.; Bokobza, L. *Tetrahedron Lett.* **1984**, *25*, 2139.

[3] Fukuzumi, S.; Kotani, H.; Ohkubo, K.; Ogo, S.; Tkachenko, N. V.; Lemmetyinen, H. *J. Am. Chem. Soc.* **2004**, *126*, 1600.

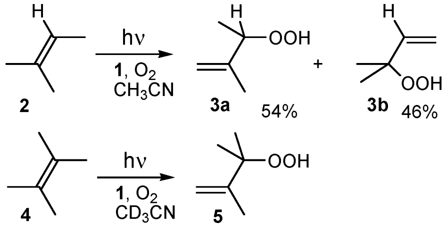
[4] Ohkubo, K.; Nanjo, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **2005**, *7*, 4265.

[5] Kotani, H.; Ohkubo, K.; Fukuzumi, S. *J. Am. Chem. Soc.* **2004**, *126*, 15999.

10.1021/ol0628661 CCC: $37.00

To further evaluate the possibility of type II processes catalyzed by **1**, we examined a series of indicative substrates. We applied three features which are typical for $^1O_2$ reactions: *chemo*selectivity (methylated alkenes tend to favor ene reactions with $^1O_2$ instead of oxidative cleavage), *regio*selectivity (low selectivity in the ene reaction of trialkylated olefins), and *diastereo*selectivity.[6] A further requirement for ET activation is the oxidation potential of the substrate, which, to match the reduction potential of a charge-transfer (CT) state of **1**, should be lower than 1.88 V. As the first substrate, 2-methyl-2-butene (**2**) was applied: when irradiated (λ > 350 nm) as a 10^{-2} M solution in CH_3CN (10^{-4} M in **1**) under an oxygen atmosphere, rapid oxygen uptake was observed and a 54:46 (by NMR) mixture of allylic hydroperoxides **3a** and **3b** was obtained (Scheme 2). The regioselectivity is identical when **2** is reacted with $^1O_2$ in polar aprotic solvents using classical type II photocatalysts such as rose bengal (RB). Next, the tetrasubstituted alkene **4** was investigated: to detect also initial products such as the dioxetane or cleavage products thereof, the reaction was performed in CD_3CN and investigated by NMR directly. The NMR spectra after 50% conversion clearly indicated the formation of the allylic hydroperoxide **5** as the major product beside minor amounts of another product which, by comparison with literature data, is possibly the dioxetane. Less than 10% of this compound appears in the spectra, and after complete conversion, 75% of product **5** was isolated (preparative photooxygenation). From the oxygen uptake curve (**1**/CH_3CN) and the comparison with a typical type II model system (RB/CH_3CN), a reactivity difference of approximately 3.5 was determined (Figure 1).

Scheme 2



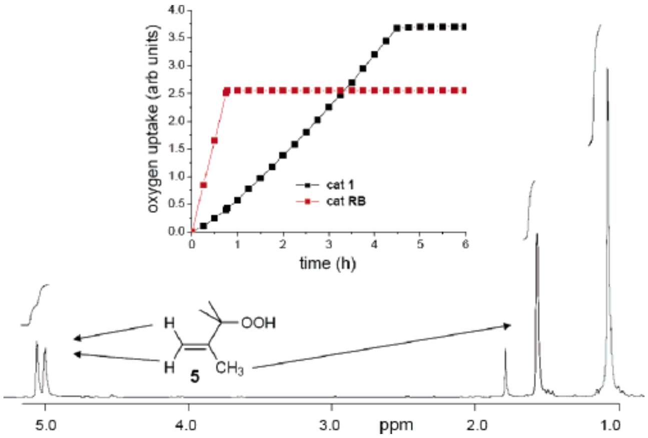
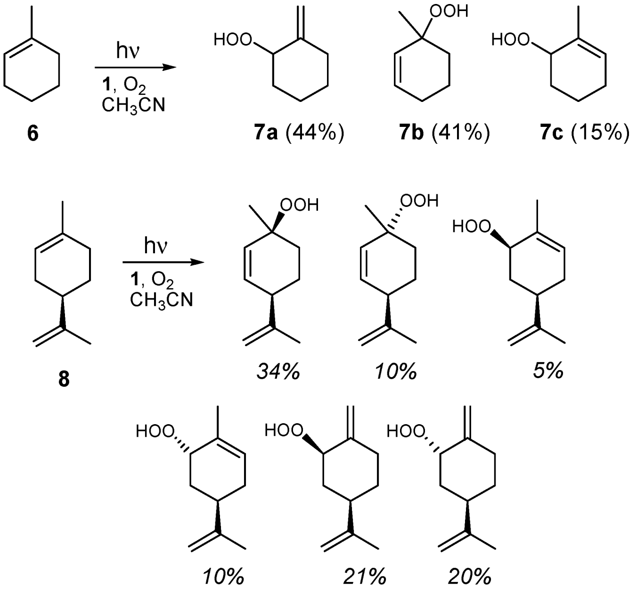


Figure 1. Oxygen uptake curve and product ^1H NMR from the photooxygenation of **4** with 1 mol % of **1** in CH_3CN.

The third substrate was 1-methylcyclohexene (**6**), which gave the typical three regioisomeric ene products **7a**−**c**[7] when irradiated under oxygen in the presence of 1 mol % of **1**. With respect to the regioisomer composition, the results for 1-methylcyclohexene (**6**) are clearly different compared with the 9,10-dicyanoanthracene (DCA) experiments reported by Foote and co-workers.[8] Even more indicative is (*R*)-limonene (**8**), a product-based $^1O_2$ probe:[9] six products can be obtained from the ene reaction of $^1O_2$ with **8**, whereas additional products are reported from radical- or electron-transfer-initiated oxygenations (Scheme 3, numbers given in italics correspond to the average composition under standard $^1O_2$ conditions).[10]

Scheme 3



The comparison of the ^1H and ^{13}C NMR spectra of the crude reaction mixtures (see Supporting Information) obtained under typical singlet oxygen conditions with the ones obtained from the irradiation under oxygen in the presence of catalytic amounts of **1** showed excellent agreement.

Another series of substrates, which are useful as probes for singlet oxygen and ET oxygenation, respectively, are methylated naphthalenes. We investigated two compounds,

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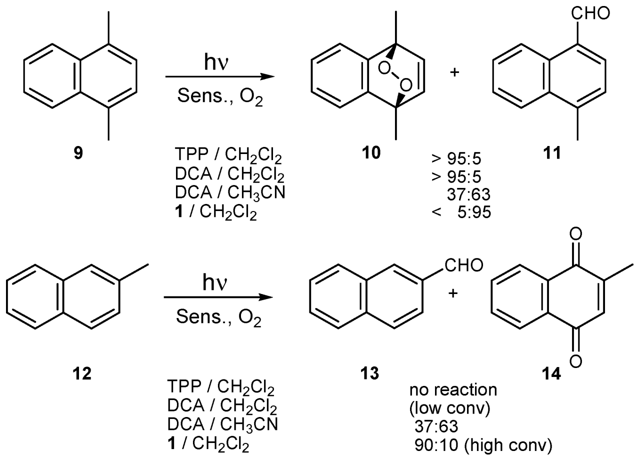
(10) Schenck, G. O.; Gollnick, K.; Buchwald, K.; Schroeter, S.; Ohloff, G. *Liebigs Ann. Chem.* **1964**, *674*, 93.

1,4-dimethylnaphthalene (**9**) and 2-methylnaphthalene (**12**). The former is known to add singlet oxygen in a [4+2] cycloaddition to give the endoperoxide **10**. Under electron-transfer conditions (e.g., DCA in CH_3CN), the naphthalene aldehyde **11** is formed as result of arene oxidation, deprotonation from the methyl group, and oxygen addition (type I mechanism).[2] In the less polar solvent methylene chloride, however, predominately the type II product **10** was observed. With **1** in CH_2Cl_2, the aldehyde **11** was the major product (Scheme 4). More significant were the results from 2-methylnaphthalene (**12**), a substrate that does not react with singlet oxygen (i.e., no conversion under irradiation conditions in the presence of TPP). Both DCA and **1** gave the aldehyde **13** and naphthoquinone **14** as major oxidation products. The efficiency of these two catalysts, however, was clearly different: whereas the DCA photolyses always resulted in relatively low conversions, the reactions with **1** as a photocatalyst were complete after standard reaction times. The solvent effect for the acridinium catalyst **1** was reversed compared with DCA: efficient oxygenation was only observed in methylene chloride, whereas the reaction in acetonitrile was strongly retarded—a phenomenon also described for the photooxygenation of 4,4′-dimethylbiphenyl.[11]

Scheme 4



There is a lively scientific dispute on whether the remarkably long-lived photocatalytically reactive state of **1** is a charge-transfer state with approximately 2.4 eV pair energy[3] or the 2 eV acridinium triplet state.[12] Verhoeven and co-workers have detected singlet oxygen by time-resolved luminescence and report a quantum yield of 42% in acetonitrile, a fact accounting for an energy-transfer active triplet acridinium state.[13] Fukuzumi and co-workers did not detect singlet oxygen emission during the photolysis of **1** in acetonitrile in the presence of 9,10-dimethylanthracene and thus excluded a singlet oxygen (type II) path for the formation of the 9,10-dimethylanthracene endoperoxide.[5]

Under the various reaction conditions used by us for the chemical detection of singlet oxygen, all substrates with high oxidation potentials such as 2-methyl-2-butene (**2**) with an E_{ox} of 1.81 V (vs SCE)[14] as well as the regioselectivity probes 1-methylcyclohexene (**6**, E_{ox} = 1.88 V vs SCE)[14] and limonene (**8**) did result solely in ene products typical for type II photooxygenation. The stereochemistry probe limonene **8** showed a product composition that was nearly congruent with results obtained with typical singlet oxygen sensitizers (such as tetraphenylporphyrin, TPP, in nonpolar solvents, and rose bengale, RB, in polar solvents). This probe is highly sensitive for electron-transfer or radical-induced oxygenation, leading to a different regio- and diastereoisomeric product composition.[10] Concerning the photocatalytic activity of **1**, turnover numbers (TON) of 100 were easily achieved, accounting for efficient energy transfer sensitizing. This result is in excellent agreement with the results of the singlet oxygen detection described by Benniston et al.[12] The tetrasubstituted alkene **4** with an E_{ox} of 1.50 V showed only traces of an additional product which might originate from an electron-transfer-induced oxygenation. These traces were, however, also detected with RB in acetonitrile and thus might arise from a radical-type background reaction. Substrates with oxidation potentials lower than 1.5 V do, however, show a divergent oxygenation pattern; i.e., they reveal type II as well as electron-transfer reactivity. The naphthalene derivatives **9** and **12**, respectively, have oxidation potentials of 1.05[15] and 1.22 V[16] (vs SCE). These results indicate that the photocatalytic reactive state of **1** is also capable of oxidizing substrates with moderate to low oxidation potentials in competition with singlet oxygen generation.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of the photooxygenation experiments with **2**, **4**, **6**, **8**, **9**, and **11** under singlet oxygen conditions (RB/CH_3CN or TPP/CH_2Cl_2) and with 9-mesityl-10-methylacridinium perchlorate **1** as the photocatalyst. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) For **12**, 1.63 V has been reported recently: Sakamoto, M.; Cai, X.; Hara, M.; Fujitsuka, M.; Majima, T. *J. Am. Chem. Soc.* **2004**, *126*, 9709.