Photoinitiated Olefin Epoxidation with Molecular Oxygen, Sensitized by Free Base Porphyrins and Promoted by Hexacarbonylmolybdenum in Homogeneous Solution

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Keywords: Epoxidations / Molybdenum / Oxygen / Photooxidations / Porphyrinoids / Singlet oxygen

The photooxidation of various olefins in homogeneous solution under an oxygen atmosphere, by use of visible light, a dye sensitizer, and an oxygen-transfer catalyst, has been investigated. The oxygen transfer from molecular oxygen to olefin involves the following steps: i) photoinduced singlet-oxygen formation, ii) alkyl hydroperoxide formation through the ene reaction, iii) the intermediacy of a reactive molybdenum peroxide, and iv) olefin epoxidation of the remaining substrate or of a second olefin. Among the various sensitizers and catalysts tested, the electron-deficient free base porphyrin 5,10,15,20-tetrakis(2′,6′-dichlorophenyl)-β-octabromoporphyrin and hexacarbonylmolybdenum showed the best performances in terms of robustness and activity. Under suitable conditions, complete olefin conversion may be obtained by adoption of molar ratios of sensitizer/catalyst/substrate of 1:50:2000, with the formation of the corresponding epoxide in up to 38% yield, which corresponds to 77% of the theoretical maximum. Quite interestingly, olefins reluctant to undergo ene reactions may be epoxidized in the presence of a second sacrificial olefin, yielding the corresponding epoxides with up to 80% total selectivity.

Introduction

The oxidation of hydrocarbons still attracts great interest from both industrial and academic research areas, because oxygenated hydrocarbons − epoxides in particular − are among the most useful synthetic intermediates for a variety of products. For nearly a century, stoichiometric oxidation processes, such as the epoxidation of alkenes by peracids[1,2] and epoxide preparation by alkaline dehydrochlorination of chlorohydrins,[3] have found wide use. However, stoichiometric processes such as these present several disadvantages, the main ones being the high cost of the reagents and the formation of large amounts of by-products. More recently, it was found that some metal complexes, in particular those of Ti, V, Mo, and W, in their highest oxidation states, were able to catalyze oxidations by alkyl hydroperoxides effectively.[4−6] Today, several processes for the synthesis of epoxides based on alkyl hydroperoxides or hydrogen peroxide are in use for industrial productions. Typical examples are the Halcon process,[7] which employs a hydroperoxide as primary oxidant together with a Mo^{VI} derivative as catalyst, and the Shell process,[8,9] in which a hydroperoxide is used together with a silica-supported titanium complex. Even in these cases, however, the primary oxidant and the recovery of the by-products weigh heavily upon the operating cost of the overall process.

The obvious alternative, namely the utilization of molecular oxygen as a primary oxidant for selective oxidations, meets with significant obstacles because of the triplet nature of oxygen, which hampers reactions with organic compounds in singlet states. These difficulties can be overcome by following described procedures in which molecular oxygen reacts with aldehydes or alcohols in the presence of radical initiators, initially forming peracids or alkyl hydroperoxides, which may, in a second step, give rise to epoxide formation.[10−18] Clearly, though, a major drawback in these cases is related to the consumption of stoichiometric amounts of valuable chemicals such as aldehydes or alcohols. On the other hand, some scattered examples of alkene epoxidation have been performed with only oxygen and a catalyst in the absence of a reducing agent and radical initiators;[19,20] in these cases, however, either a limited turnover number is achieved[19] or severe experimental conditions are required ($T > 80$ °C, reaction times ≈ 500 hours).[20]

A potential alternative, effective for alkenes bearing allylic protons, is to produce in situ, through an ene reaction, an alkyl hydroperoxide that oxidizes the remaining substrate in a subsequent catalyzed step.[21] By these means, it should be possible, under appropriate kinetic conditions, to convert up to half of the starting alkene into epoxide and the other half into the corresponding allylic alcohol, according to Scheme 1.

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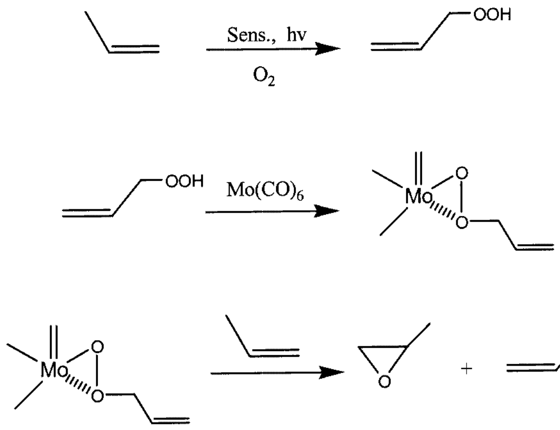

Scheme 1

In practice, since both the alkyl hydroperoxide and the allylic alcohol are still oxidizable substrates, the final yield of epoxide almost never reaches the theoretical (50%) maximum value relative to the starting material.

In this paper we present the results of a study of the oxidation of cyclooctene and a few other alkenes in the presence of oxygen (1 atm), visible light, a dye sensitizer, and an oxygen-transfer catalyst, in homogeneous solution. We report on a preliminary search for the most suitable and effective sensitizer and catalyst, and on the results obtained with the mediators of choice: namely a 5,10,15,20-tetrakis(phenyl)porphyrin derivative and hexacarbonylmolybdenum. Furthermore, we have verified the possibility of epoxidizing alkenes that do not easily undergo the ene reaction by exploiting the reactivity of a second sacrificial olefin towards singlet oxygen.

Results and Discussion

Preliminary experiments were carried out in order to check the efficiency and stability of some molecules that might potentially act as dye sensitizers on the photooxidation of cyclooctene, in 1,2-dichloroethane (DCE) as solvent. Cyclooctene was the substrate of choice, because its symmetry limits the number of potential products and its epoxide is stable under the experimental conditions adopted. On the other hand, DCE was employed as the first solvent, since it is known[22] that oxidations catalyzed by transition metals in high oxidation states usually proceed smoothly in low/medium-polarity solvents while the ene reaction does not depend much on the nature of the solvent,[23] while DCE also solubilizes a variety of high molecular weight substances such as porphyrins. The photooxidation reactions were carried out in a jacketed reactor maintained at the desired temperature by circulation of thermostatted water, with magnetic stirring and under an oxygen atmosphere achieved by continuous bubbling of pure oxygen into the reaction mixture; the reactor was irradiated with an external tungsten-halogen lamp for all the time required to reach a stationary concentration of reactant and products. The progress of the reaction was monitored by GLC analysis of organic solution samples taken at appropriate times to determine the concentrations of reactant and products. In particular, the concentrations of cyclooctene, cyclooctene epoxide, 2-cycloocten-1-ol, and 2-cycloocten-1-one were followed.

The Sensitizers

Preliminary experiments were carried out in the presence of various sensitizers but in the absence of an oxygen-transfer catalyst, in order to single out the proper dye for the occurrence of the ene reaction. The following sensitizers tested in the course of the work were:

9,10-dicyanoanthracene (9,10-DCA, **1**),
tris(2,2′-bipyridyl)dichlororuthenium(II) hexahydrate [Ru(bipy)$_3$, **2**],
5,10,15,20-tetrakis(phenyl)porphyrin (TPPH$_2$, **3**),
5,10,15,20-tetrakis(2′,6′-dichlorophenyl)porphyrin (TDCPPH$_2$, **4**),
5,10,15,20-tetrakis(2′,6′-dichlorophenyl)-β-octabromoporphyrin (Br$_8$TDCPPH$_2$, **5**), and
5,10,15,20-tetrakis(mesityl)porphyrin (TMPH$_2$, **6**).

The results obtained in the photooxidation of cyclooctene are shown in Table 1.

Table 1. Photooxidation of cyclooctene ($3.84 \cdot 10^{-2}$ M) in the presence of oxygen (1 atm), visible light, and a sensitizer, in DCE

Run	*T* [°C]	Sensitizer $\times 10^5$ M	Cyclooctene conversion (%)	Time [min]	Cyclooctene yield (%)
1	30	**1**, 10.5	13	420	0.8
2	40	**2**, 2.1[a]	0	60	0
3	30	**3**, 10.5	94	420	1.4
4	40	**3**, 2.1	53	540	12.0
5	40	**4**, 2.1	87	610	16.0
6	40	**5**, 2.1	93	480	6.7

[a] In the presence of 1% acetonitrile.

Typical chromophores usually employed as sensitizers in polar solvents, namely **1** and **2** (runs 1−2), show little or no effect on cyclooctene photooxidation in DCE. In fact, the olefin consumption is negligible or slight even after prolonged reaction times. Conversely, free base porphyrins **3−5** act as effective sensitizers, giving degrees of cyclooctene conversion greater than 87% after 7−10 hours of reaction time (runs 3−6). Among the products of cyclooctene photooxidation revealed by GLC analysis, the major products are 2-cycloocten-1-ol and 2-cycloocten-1-one, together with minor amounts of cyclooctene oxide. It should be pointed out that a variable amount (0−16%) of cyclooctene oxide is formed even in the absence of an oxygen-transfer catalyst, depending on dye and temperature. Comparison of runs 3 and 4 indicates that, in the case of **3**, temperature has a remarkable effect on the cyclooctene oxide yield, which increases from 1.4 to 12.0% on going from 30 to 40 °C in spite of a lower substrate conversion. Although the reaction times at comparable cyclooctene conversions indicate a roughly similar porphyrin activity, the stabilities of

3−5 appear to be strongly affected by the nature of the substituents on the porphyrin ring. In all the experiments in Table 1, the sensitizers were bleached when cyclooctene conversions reached the values reported and the sensitizer stability appears to follow the order: **5** > **4** > **3**.

The Catalysts

Table 2 shows the results of experiments aimed at finding an oxygen-transfer catalyst capable of interacting with the alkyl hydroperoxide formed in the course of the ene reaction and of performing a catalytic epoxidation of the remaining olefinic substrate.

Table 2. Photooxidation of cyclooctene ($3.84\cdot10^{-2}$ M) in the presence of oxygen (1 atm), TPPH$_2$ (**3**, $10.5\cdot10^{-5}$ M), and visible light, in DCE at 30 °C, in the presence of various oxygen-transfer catalysts

Run	Catalyst $\times 10^4$ M	Cyclooctene conversion (%)	Time [min]	Cyclooctene oxide yield (%)
7	**7**, 21.0[a]	88	420	1.5
8	**8**, 360	98	450	1.3
9	**9**, 1.5	84	420	1.5
10	**10**, 152	22	270	6.6
11	**10**, 1.5	89	300	13.8
12	**11**, 1.5	96	480	1.8
13	**12**, 1.5	96	480	0.8

[a] In the presence of 4*t*Bu-Py ($3.4\cdot10^{-2}$ M), acting as axial ligand of the catalyst.

In conjunction with the sensitizer of choice (TPPH$_2$, **3**) as the cheaper still effective porphyrin derivative (see below), the following potential catalysts were tested:

5,10,15,20-tetrakis(phenyl)porphyrinatemanganese [Mn(TPP)Cl, **7**],

hexafluoroacetone trihydrate [$(CF_3)_2CO\cdot3H_2O$, **8**],

hexacarbonyltungsten [$W(CO)_6$, **9**],

hexacarbonylmolybdenum [$Mo(CO)_6$, **10**],

oxodi(peroxo)(hexamethylphosphorotriammide)molybdenum (MoO_5HMPT, **11**), and

oxodi(peroxo)(picolinate-*N*-oxide)molybdenum (MoO_5PICO, **12**).

Comparison of run 3 in Table 1 with run 7 in Table 2, in which **7** was added to the reaction mixture in conjunction with 4-*tert*-butylpyridine, indicates that a manganese(III) porphyrin is not a suitable catalyst for epoxidation under the experimental conditions adopted. In fact, the epoxide yield does not increase significantly and the lower level of cyclooctene conversion observed in the presence of manganese porphyrin indicates that quenching of the excited state of the free base porphyrin **3** may occur. Similarly, **8**, an organic catalyst for alkene epoxidation with hydrogen peroxide, proved to be unreactive under these conditions (run 8) and this outcome could be related to the formation of alcoholic substrates such as the 2-cycloocten-1-ol, which may compete with the alkyl hydroperoxide for the catalyst. In contrast, $Mo(CO)_6$ (**10**), a well known catalyst for alkene epoxidation with alkyl hydroperoxide, exhibits a definite effect on the epoxidation reaction (runs 10 and 11). On examination of the effect of catalyst concentration on cyclooctene conversion and cyclooctene oxide yield, it can be seen that **10** is capable of association with the porphyrin ring. In fact, at the higher concentration of **10** employed (run 10), the cyclooctene conversion stops in correspondence with the disappearance of the starting porphyrin, and the simultaneous formation of a green porphyrin derivative is observed. Quite surprisingly, other molybdenum derivatives, either neutral such as **11** (run 12) or anionic such as **12** (run 13), proved to be just as unreactive as the tungsten derivative **9** (run 9).

As far as the nature of the actual epoxidizing agent is concerned, the results of runs 9, 12, and 13 seem to question the formation of an oxo-peroxo complex. In fact, previous investigations have shown that, in ethanol as solvent and in the presence of H_2O_2 as primary oxidant, an oxo-diperoxo complex is formed independently of the molybdenum species added.[24] A possible alternative is that hexacarbonylmolybdenum exercises its catalytic activity, interacting with a labile intermediate (perepoxide?) prior to the formation of the alkyl hydroperoxide. However, further work is needed in order to shed some light on this point.

Refinement of the System

Having chosen $Mo(CO)_6$ (**10**) as the effective catalyst for the epoxidation step and the porphyrin derivatives as the most efficient sensitizers, we examined the effect of the substituents present on the porphyrin ring and of other parameters on the yields of cyclooctene epoxide, 2-cycloocten-1-ol, and 2-cycloocten-1-one. Pertinent results are shown in Table 3.

An electron-rich porphyrin such 5,10,15,20-tetrakis(mesityl)porphyrin (TMPH$_2$, **6**, run 15) exhibits the same activity as TPPH$_2$ (**3**, similar alkene conversion and epoxide formation) under identical conditions (run 14). Conversely, an electron-deficient porphyrin such as **4** almost doubles the cyclooctene oxide yield (run 16). The effect of sensitizer concentration on the cyclooctene oxide yield is minimal in the 23.4% to 27.7% range (Runs 16−19). At higher sensitizer concentrations, however (runs 16 and 17), a lower level of olefin conversion is observed. This outcome is probably related to the formation of dimers and higher aggregates, which favor a bimolecular autoquenching of the sensitizer excited state. The level of olefin conversion diminishes even at the lower concentration of sensitizer employed (run 19), probably because of porphyrin bleaching. On the other hand, the cyclooctene oxide yield increases slightly with increasing temperature (runs 19−21). A further improvement is obtained by increasing the concentration of the oxygen-transfer catalyst (runs 21−24). This outcome indicates that the insertion of molybdenum into the porphyrin ring of **4** is a much harder task than the metallation of **3**. As pointed out above, a 37.2% cyclooctene epoxide yield represents 74.4% of the theoretical maximum epoxide yield (50%), achievable in this process only if the epoxidation of the remaining olefin is faster than alkyl hydroperoxide formation and if the latter oxidizes only the olefin.

Table 3. Photooxidation of cyclooctene ($3.84 \cdot 10^{-2}$ M) in the presence of oxygen (1 atm), various porphyrins as sensitizers, and visible light, in DCE, in the presence of $Mo(CO)_6$ (**10**) as catalyst

Run	*T* [°C]	Sensitizer × 10^5 M	**10** × 10^4 M	Cyclooctene conversion (%)	*t* [min]	Cy.oct. oxide yield (%)	2-Cy.oct.-1-ol yield (%)	2-Cy.oct.-1-one yield (%)
14	30	**3**, 10.5	1.5	89	300	13.8	12.5	12.8
15	30	**6**, 10.5	1.5	95	420	13.3	8.0	14.6
16	30	**4**, 10.5	1.5	92	540	23.6	8.7	11.9
17	30	**4**, 21.0	1.5	72	540	24.9	15.0	5.5
18	30	**4**, 5.2	1.5	96	615	27.7	5.8	8.6
19	30	**4**, 2.1	1.5	84	480	23.4	11.3	7.7
20	25	**4**, 2.1	1.5	85	480	23.5	10.2	6.3
21	40	**4**, 2.1	1.5	91	540	26.0	6.3	6.4
22	40	**4**, 2.1	3.0	97	600	32.8	3.3	4.8
23	40	**4**, 2.1	6.0	98	600	35.2	3.2	2.6
24	40	**4**, 2.1	12.0	95	540	37.7	6.5	2.8
25	40	0	12.0	0	360	0	0	0
26	40	**5**, 2.1	12.0	97	420	38.3	1.8	3.5
27[a]	40	**5**, 2.1	12.0	100	480	10.8	11.8	37.4
28[b]	40	**5**, 2.1	12.0	0	120	0	0	0

[a] In CH_3CN as solvent. [b] In isooctane as solvent.

In the absence of sensitizer, no olefin conversion is observed, even in the presence of catalyst and light (run 25). This outcome corroborates the hypothesis that the epoxidation step is carried out by an intermediate formed between the molybdenum derivative and an oxygenated species derived from alkene photooxidation (hydroperoxide or perepoxide).

The results in Table 1 (run 6) indicate that $Br_8TDCPPH_2$ (**5**) is the most active free porphyrin in promoting the ene reaction during cyclooctene photooxidation, even if the amount of cyclooctene oxide formed in this step is lower than those found in the presence of **3** and **4** under identical conditions (runs 4−5). Since **5** is by far the most expensive sensitizer among those tested, most of the experiments were carried out first with **3** and then with **4**. However, once the best conditions for **4** had been selected, the performance of **5** was also tested.

Three solvents of different polarity were employed in order to examine the influence of this parameter, mainly on the molybdenum-catalyzed epoxidation step (runs 26−28). The epoxide yields with respect to the theoretical maximum yield achievable by this procedure (corresponding to 50% of the starting alkene) are: 38.3% (76.6% of the theoretical maximum) in DCE (run 26) and 10.8% (21.6% of the maximum) in CH_3CN (run 27). DCE is characterized by a Reichardt−Dimroth polarity factor (R_t) of 41.9, while the R_t value of CH_3CN is 46.0. This result fits with the well known reactivity of peroxidic species towards nucleophilic substrates, which is enhanced in non-polar solvents.[22] This solvent effect reactivity is ascribed to better stabilization of reagents relative to the transition state in polar solvents. On the other hand, the olefin conversion rate in CH_3CN is similar to that found in DCE, thus suggesting that the first step of the process, namely the ene reaction, is scarcely influenced by the solvent. We also explored the effect of isooctane (run 28), a solvent of very low polarity ($R_t = 31$), and the epoxide yield drops to near zero. In this case, however, the very low cyclooctene conversion is probably due to the precipitation of the sensitizer as a molybdenum derivative. As a matter of fact, the porphyrin ring appears to be much more susceptible to the metallation in nonpolar solvents, thus precluding simultaneous utilization of free base porphyrins and hexacarbonylmolybdenum.

In all these experiments, variable amounts of 2-cycloocten-1-ol and 2-cycloocten-1-one were formed along with cyclooctene oxide (runs 14−28). Since both compounds are susceptible to further oxidation by singlet oxygen, their yields do not reflect the efficiency of the catalyzed epoxidation step. However, it may be noted that when the epoxidation step reaches its highest efficiency (runs 22, 23, 24, and 26), the yields of 2-cycloocten-1-ol and 2-cycloocten-1-one assume their lowest values. In the light of these results, the hypothesis of the formation of an intermediate molybdenum perepoxide appears more likely then that of an intermediate molybdenum hydroperoxide. In the latter case in fact, a relevant degree of formation of 2-cycloocten-1-ol should be observed as a result of the peroxidic intermediate reduction.

Catalytic Oxidations in the Presence of Sacrificial Olefins

On the basis of the results obtained with cyclooctene, we examined a few other alkenes under the same conditions, namely in the presence both of dye sensitizer and of oxygen-transfer catalyst. The results are shown in Table 4.

Both cyclohexene and 1-octene (runs 29 and 30) are fairly unreactive under these conditions, as far as epoxide formation is concerned. However, cyclohexene reacts with singlet oxygen, as shown by the formation of 2-cyclohexen-1-ol and 2-cyclohexen-1-one; apparently the hydroperoxide (or the perepoxide) formed in the course of the ene reaction does not interact efficiently with the molybdenum derivative to carry out the epoxidation step.

In contrast, a tetrasubstituted olefin such as 2,3-dimethyl-2-butene reacts about ten times more rapidly than

Table 4. Photooxidation of various alkenes in the presence of oxygen (1 atm), $Br_8TDCPPH_2$ (**5**, $2.1 \cdot 10^{-5}$ м) as sensitizer, and of $Mo(CO)_6$ (**10**, $1.2 \cdot 10^{-3}$ м) as oxygen-transfer catalyst, in DCE at 40 °C

Run	Substrate × 10^2 м	Substrate[a] conversion (%)	Time [min]	Epoxide[a] yield (%)	Allylic-OH[a] yield (%)	Allylic-CO[a] yield (%)
29	cyclohexene, 4.9	n.d.[b]	240	1.5	12.0	6.8
30	1-octene, 3.2	9.1	420	0	0	0
31	2,3-dimethyl-2-butene, 4.2	100[c]	45	24.2	33.0	–
32	cyclooctene, 3.84	94	480	cyclooctene oxide, 14.8	5.2	6.5
	+ cyclohexene, 24.7			+ cyclohexene oxide, 61.7	54.2	27.8
33	2,3-dimethyl-2-butene, 4.2	n.d[b]	540	2,3-dimethyl-2-butene oxide, n.d.[c]	n.d.[b]	–
	+ cyclohexene, 24.7			+ cyclohexene oxide, 53.8	58.6	21.6
34	cyclooctene, 3.84	93	420	cyclooctene oxide, 30.0	11.0	6.9
	+ 1-octene, 16.0			+ 1,2-octene oxide, 7.1	0	0

[a] When two substrates are present, conversion and yields refer to the one in lower amount. [b] Gas chromatographic determination was not feasible in DCE due to peak overlaps. [c] In CH_2Cl_2 at 30 °C.

cyclooctene (run 31) at a temperature 10 °C lower: complete olefin conversion is in fact obtained in about 45 minutes and 24.2% of 2,3-dimethyl-2-butene oxide is detected together with 33% of 2,3-dimethylbut-3-en-1-ol.

A control experiment carried out in the absence of $Mo(CO)_6$ found that only 3.8% of epoxide was formed along with 5% of allylic alcohol, the major product being 2,3-dimethylbut-3-enyl hydroperoxide (79% yield). By the way, it may be noticed that the allylic alcohol/epoxide ratio measured in the control experiment is essentially the same as found in the molybdenum-catalyzed experiment, thus suggesting that epoxide formation is in this case entirely due to intermolecular oxidation carried out by the alkyl hydroperoxide.

Photooxidation of cyclooctene in the presence of an excess of cyclohexene (run 32) indicates that cyclohexene easily undergoes the molybdenum-catalyzed oxidation step when a suitable peroxidic intermediate is formed in solution. In fact, cyclohexene oxide is formed along with cyclooctene oxide. On the assumption that only cyclooctene gives the corresponding alkyl hydroperoxide in the course of the ene reaction, the total epoxide selectivity measured in run 32 is 81%. The cyclohexene oxide/cyclooctene oxide ratio found is 4.2, roughly similar to the initial olefin concentrations (5.9). This outcome suggests a similar reactivity of the two olefins towards the actual oxidant formed in solution. Run 33 shows the possibility of employing sacrificial substrates other than cyclooctene in order to epoxidize an olefin reluctant to undergo the ene reaction. For example, cyclooctene can be replaced by 2,3-dimethyl-2-butene in cyclohexene oxidation. In this case the yield of cyclohexene oxide is 53.8%, compared with 61.7% obtained with cyclooctene. This is probably due to a larger amount of 2,3-dimethyl-2-butene oxide formed, according to the higher reactivity of tetrasubstituted olefins towards epoxidation.

Furthermore, run 34 indicates the possibility of oxidizing a substrate reluctant to undergo both the ene reaction and the molybdenum-catalyzed oxygen transfer. This is the case for 1-octene when photooxidized in the presence of cyclooctene: 1-octene oxide is formed, although in low yield (7.1%), along with cyclooctene oxide (30%).

Conclusion

In conclusion, we have demonstrated the feasibility of a catalytic process for alkene epoxidation by exploiting molecular oxygen, visible light, a sensitizer, and an oxygen-transfer catalyst, in homogeneous solution. The catalytic procedure optimized here is not limited to the oxidation of alkenes prone to undergo the ene reaction. In fact, by employing a low-cost sacrificial alkene, it is possible to achieve the epoxidation of alkenes without allylic protons, and also of olefins that are reluctant to react with singlet oxygen under mild conditions. The sensitizer plays the most crucial role in the entire process. In fact, sensitizer decomposition is a damaging side reaction that takes place with poorly reactive substrates and also when the level of substrate conversion reaches high values. This study indicates that highly electron-deficient free base porphyrins appear to be the most promising dye sensitizers: about 2000 mol of alkenes per mol of sensitizer can be converted into the corresponding alkyl hydroperoxide. We are currently studying how to improve the sensitizer stability.

Experimental Section

Materials: 5,10,15,20-Tetrakis(phenyl)porphyrin ($TPPH_2$, **3**), 5,10,15,20-tetrakis(mesityl) porphyrin ($TMPH_2$, **6**), and 5,10,15,20-tetrakis(2′,6′-dichlorophenyl)porphyrin ($TDCPPH_2$, **4**) were synthesized by a slightly modified Lindsay−Smith method.[25,26] 5,10,15,20-Tetrakis(2′,6′-dichlorophenyl)-β-octabromoporphyrin ($Br_8TDCPPH_2$, **5**) was obtained by NBS (*N*-bromosuccinimide) bromination of the pyrrole β-positions of $TDCPPH_2$.[27] The metallation of free base ligand porphyrin $TPPH_2$ with $Mn^{II}(OAc)_2$ was performed by conventional methods.[28,29] Oxodi(peroxo)(hexamethylphosphorotriamide) molybdenum complex (MoO_5HMPT, **11**)[30] and oxodi(peroxo)(picolinate-*N*-oxide) molybdenum complex (MoO_5PICO, **12**)[31] were synthesized by literature procedures. *n*-Decane (GLC internal standard), 4-*tert*-butylpyridine (axial ligand of manganese porphyrin, **3**), hexacarbonyltungsten (**9**), hexacarbonylmolybdenum (**10**), 9,10-dicyanoanthracene (9,10-DCA, **1**), tris(2,2′-bipyridyl)dichlororuthenium(II) hexahydrate [$Ru(bipy)_3$, **2**], hexafluoroacetone trihydrate (**8**), cyclooctene, cyclohexene, 1-

octene, and 2,3-dimethyl-2-butene were all commercially available, high purity products (Aldrich) used as received.

Photoinitiated Oxidation Procedure: Photooxidation experiments were carried out in a 15 mL jacketed reactor maintained at the desired temperature by circulation of thermostatted water (HAAKE-L thermostatic bath controlled by an HAAKE D8 head). The reactor contained a magnetically stirred DCE solution (10 mL) of olefinic substrate ($3.8-24.7 \times 10^{-4}$ mol), *n*-decane as G.C. internal standard ($2.6 \cdot 10^{-4}$ mol), the sensitizer ($2.1-21.0 \times 10^{-7}$ mol), and the oxygen-transfer catalyst ($1.5-2.0 \times 10^{-6}$ mol). Gaseous gas-chromatographic purity grade oxygen (ALPHAGAZ, C, purity ≥ 99.9%) was continuously bubbled into the organic solution through a glass-sintered septum. After a few minutes of oxygen flow, the reaction was started by turning on the tungsten-halogen lamp (Qartzline, K9, 230 V, Q300, 100 W), positioned ≈ 10 cm from the jacketed reactor. At various time intervals, the stirring was suspended and 1 μL of the organic solution was withdrawn and analyzed by GL chromatography on a HP-5 capillary column (crosslinked 5% PH ME Siloxane, 30 m × 0.32 mm, 0.25 μm). The concentrations of the oxygenated products were measured on the basis of previously determined response factors. The identification of the reaction products was accomplished by comparison of the GLC data with those of authentic samples and by GC-MS analysis carried out with an Agilent 6850 gas chromatograph, connected with an Agilent 5973 mass selective detector, with a 15 m HP-5 capillary column.

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Received June 5, 2002
[O02306]