Photocatalytic Oxygenation of Selected Cycloalkenes in Aqueous Solutions Induced by Water-Soluble Metal Porphyrin Complexes

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Water-soluble manganese(III) as well as iron(III) porphyrinates are introduced as light-sensitive precursor compounds for the photocatalytic activation of dioxygen in aqueous solutions. It is shown that in the presence of *α*-pinene (**4**) and the further cycloalkenes **11**–**13** photocatalytic oxygenation reactions occur. The dependence of the selectivity of the oxygen transfer to the olefin on both the presence of water and the variation of the substrate-to-catalyst ratio is discussed. The catalyst may be conveniently separated from the substrates/products by using aqueous solvent systems.

The catalytic oxygenation of hydrocarbons with dioxygen in the presence of metal porphyrinates has attracted considerable attention in the chemical as well as biochemical literature particularly with respect to the biomimetic modeling of the function of natural monooxygenases containing iron porphyrin complexes as prosthetic group. This path of the direct activation of dioxygen under mild reaction conditions is of additional interest because of the selectivity and also variability of the oxygen transfer to organic substrates. A number of papers deal with the catalytic oxygenation of various substrates in the presence of metal porphyrinates. However, instead of a direct activation of O_2 monooxygen donors like iodosylbenzene or peracids are mostly used[1]. Oxygenation reactions using dioxygen require additional reductants like borohyride[2] or colloidal platinum in the presence of H_2 or Zn/acetic acid[3]. Oxometal(IV) porphyrin π cation radicals of the type $[(P^{+\bullet})M^{IV}{=}O]$ are found to be the catalytically reactive intermediates by using iron and manganese porphyrinates, respectively. The π cation radical $[(P^{+\bullet})Fe^{IV}{=}O]$ is also considered as the catalytically active species of cytochrome P-450 or appropriate metalloenzymes in biological oxygenation cycles, as detailed mechanistic investigations have shown[4]. However, in contrast to their natural prototypes most of the hitherto described artificial oxygenation reactions have been performed in organic solvents (e.g., benzonitrile, acetonitrile, and dichloromethane).

Within the frame of our general investigations of photocatalytic systems based on light-sensitive transition-metal complexes and organometallic compounds, respectively[5], we were able to show very recently that the photocatalytic activation of molecular oxygen may be considered as an interesting alternative to the well-known catalytic thermal oxygenation reactions[6]. Here, in modeling of enzymatic oxygen transfer reactions induced by P-450 cytochromes or other metalloenzymes, we report on photocatalytic oxygenation reactions of selected cycloalkenes (selective epoxidations and hydroxylations; e.g. selective syntheses of natural products like *trans*-verbenol (**6**) from *α*-pinene (**4**), in aqueous solvent systems (water/acetone mixtures) instead of using aprotic organic solutions.

Besides the avoidance of mostly toxic aprotic organic solvents (usually benzene or toluene) the use of aqueous solvent systems allows a convenient separation of catalyst and product. However, aqueous solvent systems require water-soluble metal porphyrinates and solvent mediators like acetone with respect to the solubility of the organic substrates to be oxygenated. Water-soluble metal porphyrinates are insoluble in both the organic substrates [here *α*-pinene (**4**) and other cycloalkenes (**11**)–(**14**)] and acetone. This is of some importance with regard to the continuous replacement of photolytically destroyed catalyst by fresh metal porphyrins without interrupting the oxygenation cycle.

Results and Discussion

Cationically and anionically substituted metal 5,10,15,20-tetraphenylporphyrins (H_2TPP) have been used as water-soluble catalyst and catalyst precursors, respectively. Ionically substituted H_2TPP was obtained by introduction of alkylammonium [$H_2TEAP(SO_4)_2$, **1**], pyridinium (H_2-TM4PyPCl_4, **2**) as well as sulfonium groups ($H_2TPPSNa_4 \cdot 2\ H_2O$, **3**) into the phenyl residues of H_2TPP. The corresponding water-soluble iron(III) **1a**, **2a**, **3a** or manganese(III) complexes **1b**, **2b**, **3b** were isolated as described in the literature[7].

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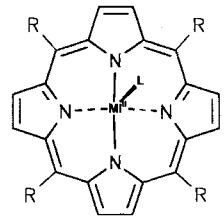
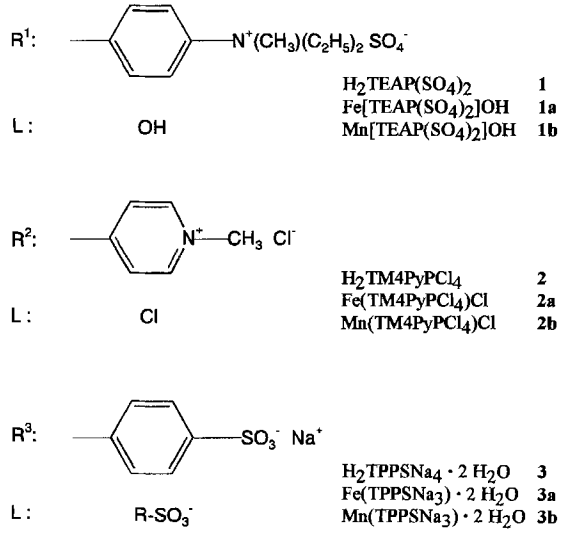
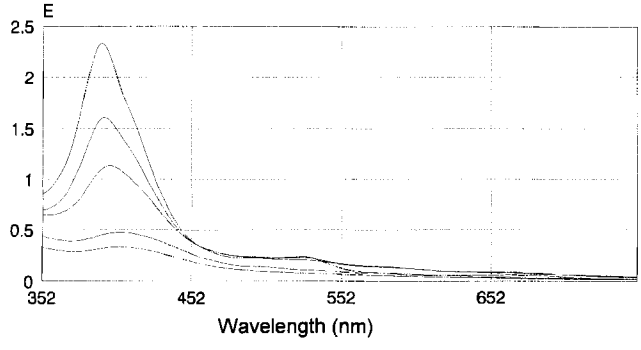




However, besides the water solubility of the complexes **1a**, **2a**, **3a** as well as **1b**, **2b**, **3b** their photochemical stability is of considerable importance with respect to large number of catalytic cycles. As already known[8], the photochemical stability of manganese porphyrinates is much more higher compared with that of analogous iron complexes. We were able to show that in aqueous solutions the porphyrin ligand of the manganese complex **1b** is very stable toward photooxidative destruction during more than 16 h of polychromatic irradiation under anaerobic conditions, whereas the corresponding iron complex **1a** was destroyed under the same conditions already after 8 h (Figure 1).

Figure 1. UV/Vis spectrum of **1a** before and after 90, 180, 300, and 480 min of polychromatic irradiation



Therefore, in consideration of the high photostability of the porphyrin complex fragment, exclusively the manganese(III) porphyrinates **1b** and **2b** were used. The complex compounds **3a** and **3b** have proven as to be photocatalytically inactive under the experimental conditions used. This inactivity is due to the formation of associates in aqueous solutions as already mentioned in the literature[9].

The primary photoreactions of the manganese(III) porphyrinates **1b** or **2b** induces upon irradiation into the spectral region of the Soret bands (λ^{max} = 460–470 nm) redox reactions resulting in the formation of the coordinatively unsaturated and catalytically reactive manganese(II) porphyrinates on the one hand and hydroxyl radicals (in the case of **1b**) or chlorine atoms (in the case of **2b**) on the other hand as shown by eq. (1). The primary quantum yields (Φ^{466}) of these photoredox reactions (eq. 1) are in the order of $0.5 \cdot 10^{-3}$. The manganese(II) porphyrinates generated photochemically react stepwise with O_2 with formation of the oxygen-transfer species $[(P)Mn^{IV}=O]$ as illustrated by eqs. (2)–(5). This intermediate contains one more electron compared with the reactive species of P-450 enzymes, the corresponding π cation radical complex $[(P^{+\bullet})Fe^{IV}=O]$.

$$(P)Mn^{III}Cl \overset{h\nu}{\rightleftharpoons} (P)Mn^{II} + Cl^{\bullet} \quad (1)$$

$$(P)Mn^{II} + O_2 \rightleftharpoons (P)MnO_2 \rightleftharpoons (P)Mn^{III}-O-O^{\bullet} \quad (2)$$

$$(P)MnO_2 + (P)Mn^{II} \rightarrow (P)Mn^{III}-O-O-Mn^{III}(P) \quad (3)$$

$$(P)Mn^{III}-O-O-Mn^{III}(P) \rightarrow (P)Mn^{III}-O-Mn^{V}O(P) \quad (4)$$

$$(P)Mn^{III}-O-Mn^{V}O(P) \xrightarrow{h\nu} 2\,[(P)Mn^{IV}=O] \quad (5)$$

The $[(P)Mn^{IV}=O]$ intermediates behave as very efficient oxygen transfer reagents which react with the concomitant regeneration of the catalyst $[(P)Mn^{II}]$. The different pathways of reaction of the $[(P)Mn^{IV}=O]$ intermediates with cycloolefins are summarized in Scheme 1. Particularly *α*-pinene (**4**) was used as substrate because the mechanisms of thermal and other photochemical oxygenation processes are well investigated. The course of the oxygenation of **4** known from other oxidation systems provides an ideal basis regarding the mechanistic interpretation of the interaction of the $[(P)Mn^{IV}=O]$ intermediates with respect to the product distribution obtained under the conditions of the photocatalytic oxygenation in aqueous solutions (see paths A, B, and C, in Scheme 1). Furthermore, the selective epoxidation of **4** to *α*-pinene oxide (**5**) or its hydroxylation to *trans*-verbenol (**6**), the pheromone of the bark beetle (*ips typographicus*), is still of considerable synthetic interest. In aprotic organic solvents like benzene in the presence of **4** we observed selective formation of **6** and **7**. This result is contrary to that of thermal oxygenation reactions and indicates the intermediate formation of the catalytically reactive species $[(P)Mn^{IV}=O]$. Very recently, we have reported on the formation of the corresponding $[(P)Fe^{IV}=O]$ species upon photochemical excitation of appropriate iron(III) porphy-

rinates and its selectivity depending on the reaction conditions[6a].

Scheme 1. Photocatalytic oxygenation of alkenes in the presence of metal porphyrinates [A: autoxidation; B: "oxygen rebound" mechanism; C: direct oxygen transfer; the dashed arrow corresponds to the processes described by eqs. (2)–(5)]

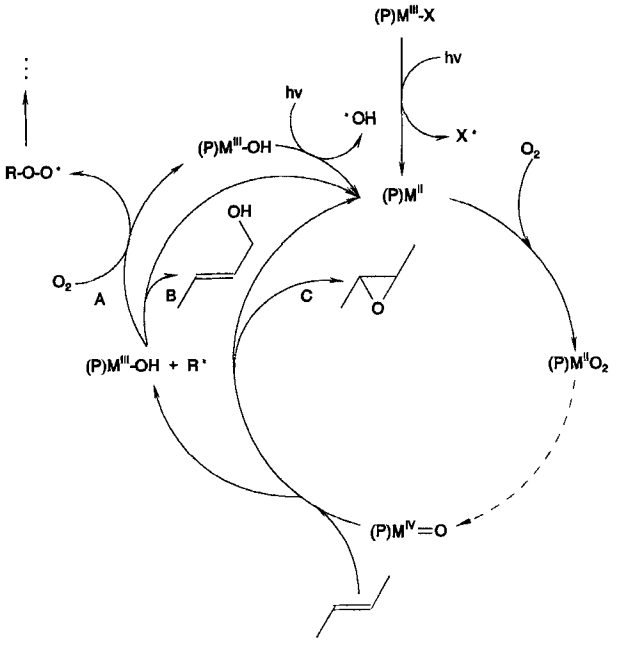


Table 1 compiles the results of the photocatalytic oxygenation of **4**. All experiments under discussion were performed in acetone/water mixtures. A thermostated photoreactor (50 ml, 55-W tungsten halogen immersion lamp, polychromatic irradiation) was used for estimation of the selectivity, product distribution, and yields, whereas a thin-film photoreactor (500 ml) with the same irradiation equipment was applied for preparative purposes. During the irradiation experiments the light-sensitive complexes **1b** or **2b** (dissolved in water) and the substrates (dissolved in acetone) were mixed with continuous stirring in the photoreactor and aerial oxygen was bubbled through the solution during the whole reaction time. These experimental conditions allow a sufficient interaction between the photochemically generated catalyst [(P)Mn^{II}] or [(P)Mn^{IV}=O] with both dioxygen and the organic substrate. After termination of the irradiation the organic and aqueous phases were separated and the product analysis was performed in the organic phase exclusively. An eventual degradation of the porphyrin complexes was estimated in the aqueous phase by means of UV/Vis spectroscopy. The results of these investigations led within the limit of error of the analytical methods used to the conclusion that the presence of substrate and product in the aqueous phase or of porphyrin complexes in the organic phase can be neglected. Furthermore, these results confirm the advantageous separation of the catalyst or its decomposition products from the substrates and products, respectively.

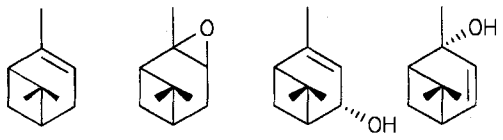
As it was already shown for **1b** or **2b** in purely organic solvents[6], both the product yield and the selectivity of the photocatalytic oxygenation of *a*-pinene (**4**) strongly depend on the substrate-to-catalyst ratio (S/C), even in water/acetone mixtures (1:1): At a ratio of S/C = 5000 favorable product yields (ca. 10%) were obtained when a micro-photoreactor not optimized with respect to high synthetic yields was used. The product distribution obtained under these conditions is in agreement with the result of a typical autoxidation reaction (see path A, Scheme 1). With a further increase of the ratio S/C > 10000 no influence on the product yields was found. However, it is noteworthy that a decrease of the substrate concentration results in an enhancement of the selectivity with respect to the formation of *a*-pinene oxide **5** due to the preference of the path C (Scheme 1). In the case of **2b** the direct transfer of oxygen to the substrate was exclusively observed by using a ratio of S/C = 500 as shown by the selective formation of **5** (product yield ca. 11%). On the other hand, application of **1b** at the same S/C ratio led again to an increase of the yield of **5**, but besides additional oxygenation products, like *trans*-verbenol (**6**), *trans*-pin-3-en-2-ol (**7**), *trans*-pinocarveol (**8**), verbenone (**9**), and pinocarvone (**10**) were generated.

The decreased selectivity observed in the photooxygenation with **1b** is assumed to be due to the formation of hydroxyl radicals upon irradiation of the catalyst precursor Mn[TEAP(SO$_4$)$_2$]OH. These radicals may react independently on the photochemically formed manganese(II) porphyrinates with the substrate with formation of the corresponding allylic radicals which give rise to competitive au-

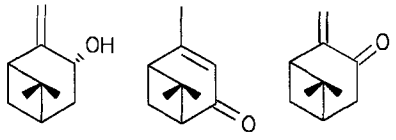
Table 1. Product distribution of the photocatalytic oxygenation of *a*-pinene (**4**) with O_2 in the presence of **1b**, **2b**, and **3b** in water/acetone mixtures

Metal compl.	S / C[a]	TO[b]	Product ratio (mol%) 5	6	7	8	9	10	Exp.
1b	10 000	486·10^3	51	15	9	3	16	6	A
1b	5 000	542·10^3	43	18	13	15	11	-	B
1b	1 000	127·10^3	67	13	11	4	5	-	C
1b[c]	1 000	74·10^3	73	8	7	5	3	4	D
1b	500	71·10^3	78	6	5	3	5	3	E
1b[c]	500	24·10^3	100	-	-	-	-	-	F
1b[e]	500	126·10^3	42	7(9)[b]	14(11)[b]	-	11	6	G
1b[f]	500	311·10^3	100	-	-	-	-	-	H
1b	100	34·10^3	91	6	3	-	-	-	I
1b[d] 1-MeIm / 1	5 000	247·10^3	7	14	55	11	9	4	K
1b[d] 1-MeIm /5	5 000	191·10^3	24	19	37	12	5	3	L
1b[d] 1-MeIm / 10	5 000	118·10^3	21	14	32	10	13	10	M
2b	5 000	311·10^3	57	17	9	2	10	5	N
2b	1 000	79·10^3	71	12	10	7	-	-	O
2b	500	54·10^3	100	-	-	-	-	-	P
2b[e]	500	101·10^3	33	7(9)[b]	22(4)[b]	11(3)[b]	2	9	Q
2b[f]	500	274·10^3	100	-	-	-	-	-	R
3b	5 000	0	-	-	-	-	-	-	S

[a] Ratio of **4** to **1b**, **2b**, and **3b**, respectively (constant complex concentration of 10^{-5} mol). – [b] Turnover: Product generated in mol versus concentration of catalysts in mol. The factor 10^3 refers to the complex concentration divided by Φ. Values in brackets refer to the portions of the corresponding hydroperoxides analyzed by means of ^{13}C-NMR spectroscopy. – [c] Addition of 5 ml of a solution of 0.1 M potassium formate as radical scavenger. – [d] Addition of 1-methylimidazole in a 1:1, 1:5, and 1:10 ratio with respect to the concentration of the porphyrin complex. – [e] Addition of 10^{-4} mol of hydrogen peroxide. – [f] Oxygenation under thermal reaction conditions performed with hydrogen peroxide and 10^{-5} mol of benzoic acid.



4 5 6 7



8 9 10

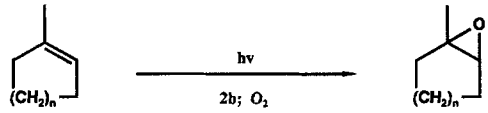
toxidation processes (see path A, Scheme 1). The hydroxyl radicals can be trapped by the addition of appropriate radical scavengers: At low S/C ratios (ca. 500) **5** was formed selectively even by use of **1b** if sodium formate was added as a scavenger. However, a decrease of the product yield was observed in the presence of this radical scavenger. On the other hand, addition of hydrogen peroxide in a tenfold excess led to a product distribution comparable with that observed when **1b** was used only; however, a considerable enhancement of the product yield (ca. 25%) was obtained. This result further confirms involvement of an additional hydroxyl radical-induced reaction step if **1b** is used as a light-sensitive precatalyst. Also in the case of **2b**, addition of hydrogen peroxide led to a doubling of the photocatalytic product yield (ca. 20%), however, at the expense of a reduced selectivity (product distribution according to path A, Scheme 1). The chlorine atoms generated photochemically by using **2b** were proven to be without any detectable influence on both selectivity and product yields. Products resulting from reaction with chlorine atoms have not been identified till now. However, we were able to show that chlorine atoms generated by independent procedures exert no influence on the selectivity of the product formation.

In contrast to organic solvent systems our preliminary results obtained by tuning of the reactivity of the water-soluble metal porphyrinates achieved by variation of the neutral axial ligands show no significant effect in aqueous solutions. Thus, the addition of 1-methylimidazole (1-MeIm) to a solution of the porphyrin complexes **1b** and **2b** in a 1:1 ratio has no effect on both selectivity and turnover. Application of higher concentrations of 1-methylimidazole led to a slow decrease of product generation due to the increased formation of a twofold axially coordinated complex $[(1\text{-MeIm})_2Mn^{II}(TM4PyPCl_4)]$. This complex behaves catalytically inert.

With respect to a better comparability with earlier investigations[6] performed in benzene solutions all turnovers (TO) and product yields shown in this paper are related to an irradiation time of 8 hours. Prolonged irradiation time of the reaction solutions (S/C = 500, in analogy to experiment P) up to 36 hours led to the degradation of **2b** up to 80%. The product yield of **5** obtained under these conditions amounts to nearly 40% (TO = $191 \cdot 10^3$). The continuous addition of further precatalyst complex in accordance with the bleaching of the metal porphyrinates estimated by means of UV/Vis spectroscopy allow the product yields to be increased up to 80%. Thus, the use of preparative photoreactors (500 ml thin-film reactors, e.g.) may make the photoinduced catalytic oxygenation of olefins in the presence of metal porphyrinates a synthetically interesting preparative method in organic chemistry.

The product yields (expressed as turnover numbers TO) discussed in this paper (Tables 1 and 2) are related to the ratio of the amount of the $[(P)Mn^{III}X]$ complex **1b** or **2b** to the quantum yield Φ. Thus, the complexes **1b** and **2b** are viewed as catalyst precursors which are converted photochemically with quantum yields $\Phi^{466} \approx 10^{-3}$ into the true catalysts $[(P)Mn^{IV}{=}O]$ and $[(P)Mn^{II}]$, respectively, as shown by eqs. (1)–(5). The TO values compiled in Tables 1 and 2 have therefore to be reduced by a factor of 10^{-3} if the weighing-in of the precatalyst **1b** or **2b** is of interest.

The most interesting result of the transfer of the described photocatalytic reactions to aqueous solutions is based on the fact that oxygenations of organic substrates may conveniently be performed even under these solvent conditions. However, at low substrate-to-catalyst ratio (S/C = 500) selective epoxidation of **4** to *α*-pinene oxide **5** occured in aqueous solutions by using **2b** and dioxygen, whereas in aprotic organic solvents like benzene or toluene a different control of selectivity was observed, leading to allylic hydroxylation products (path B, Scheme 1) like *trans*-verbenol (**6**) under the same experimental conditions.

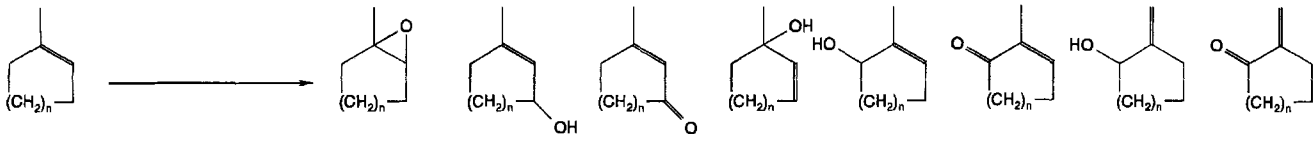


11: n = 2 **14**
12: n = 3 **22**
13: n = 4 **30**

This result was also confirmed by the photocatalytic oxygenation of further 1-methylcycloalkenes for which in aprotic organic solvents (S/C = 10000) the formation of different oxygenation products depending on their ring strain was observed[10]. However, in aqueous solutions, using **2b**, we observed exclusively selective formation of the corresponding epoxides **14**, **22**, and **30** in the presence of 1-methylcyclohexene (**11**), -heptene (**12**), and -octene (**13**), respectively, as illustrated in Scheme 2. The use of **1b** as a catalyst precursor led to the generation of small amounts of ketones or allylic alcohols in the photocatalytic oxygenation of **11** and **12** (Table 2).

The product distribution obtained by use of **1b** confirms the tendency that the amount of epoxides formed photocatalytically increases with increasing ring size of the cycloalkenes and growing ring strain. The product yields obtained with **1b** are comparable with that observed in benzene solutions, whereas the selectivity of the oxygenation of **11** and **12** is somewhat decreased.

Table 2. Distribution of the products obtained by photocatalytic oxygenation of 1-methylcycloalkenes **11**, **12**, **13** by using the water-soluble metal porphyrinate **1b** in water/acetone mixtures in the presence of dioxygen

Substrate[a]	TO[b]	Product ratio (mol%)[c]							
									
11		**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
12		**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**
13		**30**	**31**	**32**	**33**	**34**	**35**	**36**	**37**
1-Methylcyclohexene (**11**) (n = 2; experiment T)	$1224 \cdot 10^3$	21	19	13	24	11	6	4	2
1-Methylcycloheptene (**12**) (n = 3; experiment U)	$887 \cdot 10^3$	64	6	12	4	-	6	3	5
1-Methylcyclooctene (**13**) (n = 4; experiment V)	$41 \cdot 10^3$	100	-	-	-	-	-	-	-

[a] Concentration of the complex: 10^{-5} mol; substrate-to-catalyst ratio: 5000. – [b] Turnover: $c_{product}/c_{catalyst}$ (the factor 10^3 refers to the ratio of $c_{complex}/\Phi$). – [c] The analysis of the products obtained was performed by means of quantitative capillary gas chromatography (Hewlett-Packard 5890 II); *n*-decane was used as internal standard.

The photocatalytic activation of dioxygen in aqueous solutions furnishes at low S/C ratios epoxides with high selectivity, due to the "direct oxygen transfer" illustrated in Scheme 1 (path C). Parallel reactions observed at higher S/C ratios apply to the generation of allylic alcohols due to the "oxygen rebound" within the radical cage (path B) and/or to the formation of typical autoxidation products (path A) caused by the escape of allylic radicals from the cage, subsequently reacting directly with O_2.

Summarizing the results of our investigations, we can state that photocatalytic oxygenation reactions of alkenes may be performed advantageously even in aqueous solvent systems. The main advantage of such solvent conditions consists besides the avoidance of using toxic organic solvents particularly in the easy and nearly complete recovery of the catalysts which can mostly be achieved under homolytic reaction conditions only with difficulty. Furthermore, the use of aqueous solvents leads in comparison with aprotic organic solvent systems to a change in the control of selectivity. Thus, we were able to show the preferential generation of epoxides in aqueous solutions due to the direct oxygen transfer to the appropriate alkenes. The preferred epoxidation of cyclic alkenes by use of porphyrin ligands supported by π-electron-deficient substituents (here: **2b**), well-known to occur under thermal reaction conditions, was also observed for the photocatalytic processes.

Furthermore, we were able to show that the introduction of chiral groups allows an enrichment of enantiomers even in aqueous solutions. The results of these investigations will be discussed in a forthcoming paper.

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Experimental

Synthesis and Photochemistry of the Metal Porphyrinates: The water-soluble porphyrin ligands and their metal complexes were synthesized according to literature procedures[7]. – The primary quantum yields referring to the decrease of the concentration of the appropriate metal porphyrinates were estimated in acetone/water mixtures (50/50) by means of ferrioxalate actinometry[11]. Under anaerobic conditions the irradiation was performed at the following wavelengths: **1b**: 466 nm, **2b**: 460 nm, and **3b**: 469 nm. – The UV/Vis spectra were recorded with a Varian Cary 3 spectrometer.

Substrates: α-Pinene (**4**) (98%, Aldrich), and 1-methylcyclohexene (**11**) (96%, Aldrich) were passed through a column filled with neutral Al_2O_3 before use to remove oxygenated impurities. 1-Methylcycloheptene (**12**) and 1-methylcyclooctene (**13**) were synthesized from the corresponding cycloalkanones by standard procedures.

Photocatalytic Oxygenation of the Cycloalkenes: A solution of 40 ml of the cycloalkene (**4**, **11**, **12**, **13**) and the manganese(III) porphyrinate **1b** or **2b** in acetone/water (50:50) was irradiated with vigorous stirring with a 55-W tungsten halogen immersion lamp in a thermostated 50-ml photoreactor. A stream of air (5 l h^{-1}) was passed through the solution at 40°C during 8 h. The solutions contained 10^{-5} mol of **1b** or **2b**, and the corresponding cycloalkene and additives (e.g. axial ligands, radical scavenger, and hydroperoxide) (Tables 1 and 2). The following concentrations conditions were, for example, used in experiment A: S/C = 10000, **1b** = 10^{-5} mol, **4** = 0.1 mol (13.6 g). The details of the experiments B–V are summarized in Tables 1 and 2. – After termination of the photolysis acetone was removed by vacuum distillation. The remaining two phases were separated by standard methods. The water-insoluble oxygenation products remained in the organic phase together with unchanged substrate. The amount of oxygenation products in the aqueous phase was estimated to be lower than 0.1%. – A 500-ml Normag thin-film photoreactor was used for preparative purposes particularly with respect to the selective epoxidation of **4** to α-pi-

nene oxide (**5**). The experimental conditions were the same as used in the case of the micro-photoreactor. 10^{-3} mol of **2b** was dissolved in 150 ml of distilled water and the solution was thoroughly mixed with a solution of 0.5 mol of **4** in 250 ml of acetone. The photochemical decomposition of **2b** was controlled by means of UV/Vis spectroscopy and the portion of decomposed **2b** was replaeced by the addition of a new complex. After an irradiation time of 36 h the organic phase containing both α-pinene oxide (**5**) and uncomsumed substrate **4** was separated by standard distillation procedures and 78% of **5** was obtained.

Analysis of the Oxygenation Products: Analysis was performed by quantitative ^{13}C-NMR spectroscopy and computer analysis of the results obtained and quantitative capillary GC. ^{13}C-NMR spectra of the samples containing chromium(III) acetylacetonate were recorded with a Varian Unity 400 spectrometer as described recently[6]. Samples were analyzed in parallel by capillary GC (Hewlett-Packard 5890 II) by using *n*-decane as internal standard.

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[261/94]