neighboring ester groups. The resulting crude tertiary amine, which could be isolated as the borane complex **17**, was simply heated with dilute hydrochloric acid to effect both hydrolysis and decarboxylation of the geminal diester moiety. (±)-Matrine was obtained as the hydrochloride salt in 85% overall yield. The ^{1}H and ^{13}C spectra (400 MHz) of the free base in deuterated benzene was identical to those described by Chen et al.[2a]

The short, convergent approach to matrine we implemented here highlights the utility of several radical processess, especially the cascade reaction mediated by the xanthate group. In principle, the *tert*-butyl ester group can be replaced by a bulkier group to improve selectivity or, perhaps even better, by a chiral amide unit, which would allow an asymmetric synthesis of matrine and its congeners.[12]

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Micelle-Bound Metalloporphyrins as Highly Selective Catalysts for the Epoxidation of Alkenes**

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The synthesis and the study of metalloporphyrins as catalysts for the oxidation of organic substrates is an active area of research.[1] Much effort has been devoted to the construction of systems able to mimic the activity of metalloenzymes such as the family of cytochrome P_{450} dependent monooxygenases. Their reactivity, in terms of turnover number, and regio- and stereoselectivity, can be finely modulated by the presence of substituents on the macrocycle. Encouraging results were obtained when the reactions were performed in the ordered microenvironment offered by vesicles, liposomes, and monolayers,[2] and when dendritic polymers were introduced along the periphery of the pyrrolic macrocycle.[3] Guilard et al. reported recently on the synthesis and the spectroscopic characterization of some metalloporphyrin derivatives that are able to form micellar aggregates.[4] The use of an organized medium[5] is known to strongly affect the rate and the selectivity of many organic reactions[6] as well as some metal-catalyzed reactions.[7] With this aim we began a study on the synthesis and the reactivity of porphyrin derivatives bearing a suitable, appended functionality making them soluble in the micellar phase.[8] We report here the results obtained in the application of these porphyrins as catalysts for the epoxidation of selected alkenes carried out in the presence of surfactants.

Porphyrin **1a** was synthesized and demethylated according to literature methods (Scheme 1).[9] Williamson coupling of the intermediate 5-(*p*-hydroxyphenyl)-10,15,20-triphenylporphyrin with triethyleneglycol monochloride and 1-bromopropyl-3-trimethylammonium bromide gave the porphyrins **2a** and **3a**, respectively, in good yield. The metalloporphyrins **1b**, **2b**, and **3b** were obtained by standard procedures,[10] purified by column chromatography and crystallization, and characterized (^{1}H NMR, UV/Vis, and FAB-MS). Detailed experimental procedures along with the spectroscopic and analytical data will be reported elsewhere. The metalated porphyrins **2b** and **3b** are fairly soluble in aqueous media.

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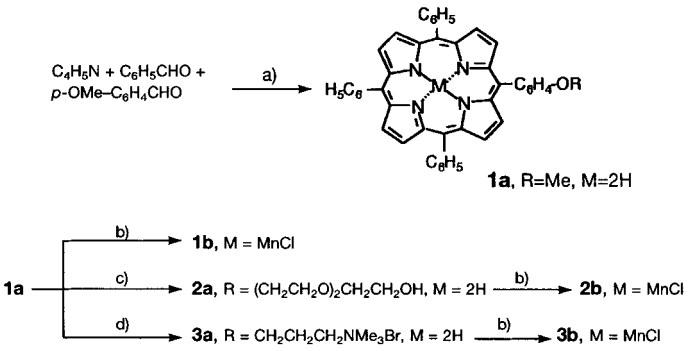

Scheme 1. Synthesis of porphyrins **1a**–**3a** and **1b**–**3b**. a) CH_3CO_2H, △, 6 h, 15 %; b) $MnCl_2 \cdot 4H_2O$, DMF, 80 °C, 3 h, 87 %; c) BBr_3, CH_2Cl_2, 0 °C, 12 h, 85 %; $ClCH_2CH_2(OCH_2CH_2)_2OH$ (2.5 equiv), KOH, DMF, 80 °C, 12 h; dilute HCl, 65 %; d) BBr_3, CH_2Cl_2, 0 °C, 12 h, 85 %; $BrCH_2CH_2CH_2NMe_3Br$ (3 equiv), K_2CO_3, THF/MeCN 1:1, 20 °C, 5 d; dilute HCl, 70 %.

Micellar phase solutions of the porphyrin derivatives were prepared by injection with 1,4-dioxane and sonication.[2b] The incorporation of the macrocycles into the micellar phase upon dissolution was followed by ^{1}H NMR and UV/Vis spectroscopy. The inclusion of the porphyrins **1a**, **2a**, and **3a** in D_2O/surfactant solutions (Brij 35 and CTAB) causes, as expected, broadening of the proton signals.[11] Typical changes in the UV/Vis spectra of the porphyrins in the presence of surfactants were also observed, confirming the inclusion of the macrocycles into the micellar phase. Coordination of an additional axial ligand (e.g. imidazole) to the metallomacrocycle embedded inside the micellar assemblies was ascertained by monitoring the UV/Vis spectrum (Table 1).[12]

Table 1. Spectroscopic data of porphyrins incorporated in aqueous micellar phase.

Porphyrin	Absorptions[a] λ_{max} [nm]					
1b[b]	380	400	422	468 (Soret)	567	601
1b[c]	383	400	423	470 (Soret)	571	603
1b[d]		402		472 (Soret)		635
1b[e]	386	407		472 (Soret)		635
1b[f]	394			472 (Soret)		635
2b[g]	381	401	420	469 (Soret)	568	601
2b[c]	384	404		468 (Soret)	571	605
2b[d]	376	403		471 (Soret)	578	616
3b[g]	382	403	422	470 (Soret)	568	602
3b[e]	385	403	419	471 (Soret)	571	604
3b[f]	381	406		472 (Soret)	585	622

[a] [Porphyrin] = 1×10^{-5} M. [b] In methanol. [c] 1×10^{-2} M Brij 35. [d] 1×10^{-2} M Brij 35, 5×10^{-3} M imidazole. [e] 1×10^{-2} M CTAB. [f] 1×10^{-2} M CTAB, 5×10^{-3} M imidazole. [g] In water.

Epoxidation of olefins such as cyclooctene, cyclohexene, and 1-octene in the presence of NaClO and an excess of imidazole (the axial ligand) proceeded smoothly at room temperature to give the corresponding epoxides. Blank experiments carried out without catalysts yielded the chlorohydrin derivatives as major products (Table 2). When the reaction is conducted in the presence of the surfactant, conversion is much higher than when the reaction is performed in water/ethanol and water/dioxane, media that reproduce the polarity of the aqueous interface of CTAB and Brij 35, respectively. Another striking feature of the reaction is the large influence exerted by the nature of the micellar phase on the chemoselectivity of the epoxidation. With catalyst **3b** in the presence of CTAB, for example, the epoxidation of cyclohexene is nearly quantitative, whereas the yield of the epoxide dramatically drops in the case of cyclooctene. An opposite trend is evident in the case of the system **2b**/Brij 35, which converts cyclooctene efficiently but cyclohexene only modestly. This could be ascribed to the different location of the substrate in the micelles. The less hydrophobic cyclohexene, which is located close to the aqueous interface, can better interact with the cationic porphyrin **3b** located in the same region.[13] In the case of the neutral amphiphilic porphyrin **2b**, which is located in a more hydrophobic region of Brij 35 aggregates, optimal interaction is possible only with the more hydrophobic eight-membered ring. The same explanation holds for the results obtained with 1-octene. These results are in agreement with earlier studies which pointed out the crucial role played by olefin hydrophobicity in electrophilic halogenation reactions.[14] In experiments with "crossed systems" (**2b**/CTAB and **3b**/Brij 35) and with the nonspecifically reacting **1b** low yields of epoxides were observed which were similar to those obtained in the absence of surfactant. This is possibly due to the less than optimal interaction between the catalyst and the surfactant, since the two have polar heads of different nature. The solubilities of porphyrins **2b** and **3b** in the neutral and the cationic surfactants could also play a role. Further experi-

Table 2. Epoxidation of alkenes with NaOCl in micellar phase.[a]

Entry	Catalyst	Medium	Substrate	Yield [%]
1	**1b**	Brij 35	cyclooctene	26
2	**1b**	CTAB	cyclohexene	< 5
3	**1b**	Brij 35	1-octene	25
4	**2b**	CTAB	cyclooctene	24
5	**2b**	Brij 35		85
6	**2b**	[b]		25
7	**2b**	Brij 35	cyclohexene	10
8	**2b**	CTAB		5
9	**2b**	Brij 35	1-octene	48
10	**3b**	CTAB	cyclooctene	8
11	**3b**	Brij 35		25
12	**3b**	[c]		23
13	**3b**	CTAB	cyclohexene	96
14	**3b**	Brij 35		15
15	**3b**	[c]		< 5
16	**3b**	CTAB	1-octene	< 5
17	–	Brij 35	cyclooctene	0[d]
18	–	CTAB	cyclohexene	0[d]
19	–	Brij 35	1-octene	0[d]

[a] In a typical reaction NaClO solution (100 μL of a 1 M solution; 100 μmol), which was buffered to roughly pH 10.5 by addition of solid $NaHCO_3$, was added in 10 μL aliquots over 2 h to 2 mL surfactant solution ($1-3 \times 10^{-2}$ M) containing the porphyrin catalyst (1 μmol), imidazole (20 μmol), and olefin (10 μmol). An internal standard (*n*-decane or *n*-dodecane) was added, and an aliquot of the reaction mixture (100 μL) was removed, quenched with methanol (200 μL) to disrupt the micellar aggregates, filtered from the precipitated salts, and analyzed by GC and GC-MS. Runs were duplicated and were reproducible within 5 %. [b] 1,4-dioxane/water 1/1 v/v. [c] EtOH/water 1/1 v/v. [d] Chlorohydrin is formed along with some 1,2-diol.

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ments are needed to fully understand the intimate nature of the interactions involved. Moreover, the relevance of the result obtained with 1-octene in Brij 35—epoxidation in up to 48% yield—must be pointed out. These results compare very well with those reported for reactions carried out with simple porphyrins,[15] which underlines the value of our system. Olefins such as 1-octene, cyclooctene, and cyclohexene could be oxidized with NaClO in homogeneous medium to give good yields of the epoxides only in the presence of polyhalogenated or tailor-made metalloporphyryns.

Finally, in the presence of micellar aggregates the catalysts showed remarkable stability toward the degradative action of NaClO. In fact, under the conditions used for the epoxidation less than 5% degradation had occurred (UV/Vis) even after a reaction time of two days.[16]

The catalytic system reported here may be a good mimic for the enzyme-catalyzed oxidation reaction, owing to its high stability and its high degree of selectivity with regard both to the substrate and the formation of epoxides. Further studies aimed at the construction of more robust macrocycles suitable for use with stronger oxidants on a wider range of substrates are underway.

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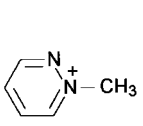
A New Tetracycle from Dimerization of the *N*-Methylpyridazinium Ion in Aqueous Solution**

Charles R. Clark,* Allan G. Blackman,* Akbar Mobinikhaledi, Wayne A. Redmond, and Rex T. Weavers*

Dedicated to Professor David A. Buckingham on the occasion of his 60th birthday

During an investigation into OD^--catalyzed H–D exchange in the *N*-methylpyridazinium ion (**1**), we observed that in aqueous alkaline solution this species stereospecifically forms the tetraazafluorene **2**.[1] Despite an extensive literature



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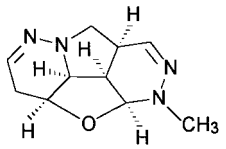

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