Sodium Hypochlorite: A Convenient Oxygen Source for Olefin Epoxidation Catalyzed by (Porphyrinato)manganese Complexes

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Abstract: A new catalytic route is reported for the epoxidation of simple olefins with NaOCl as oxygen source and manganese porphyrin complexes as catalyst. Reaction rate, chemoselectivity, and stereoselectivity are largely increased by the presence of pyridine which behaves as an axial ligand of the metalloporphyrin. Thus modified, the catalytic system is highly efficient for the epoxidation of di-, tri-, and tetrasubstituted olefins (yields, 60–95%). Aliphatic olefins are stereospecifically epoxidized (syn addition of the oxygen atom), while *cis*-stilbene gives a mixture of *cis*- and *trans*-epoxides. In the latter case, an increase of stereoselectivity up to 94% is observed in the presence of pyridine. The reactivity modification observed with the system NaOCl/Mn(TPP)OAc/pyridine makes it a suitable model for understanding the role of the axial ligand in cytochrome P-450 and peroxidase enzymes.

While the epoxidation of unsaturated hydrocarbons with molecular oxygen is efficiently solved by monooxygenases such as P-450 enzymes (one oxygen atom of dioxygen is incorporated into the substrate while the second is reduced to water[1]), this epoxidation route is still a fascinating goal among chemists. The chemical catalytic epoxidation with dioxygen requires the presence of a coreductant in large excess (hydride,[2] H_2/Pt,[3] ascorbic acid[4]). The activation of dioxygen by two molecules of nitrosyl complexes[5] avoids the use of a coreductant partner, but on the other hand the slow transfer of the oxygen atom from the resulting nitro ligand limits this method to reactive olefins[5a,b] or requires olefin activation.[5c]

So far, the most efficient catalytic methods for olefin epoxidation have been obtained with "single-oxygen donors", such as hydrogen peroxide or alkyl hydroperoxides,[6] but with these reagents, the most selective reactions are observed when run in anhydrous conditions.[7] Furthermore, concentrated solutions of these oxidants are sensitive to radical-chain decomposition and may lead to potentially hazardous conditions, especially in the case of hydrogen peroxide.[8] Presently, we wish to focus the attention on *diluted solutions of NaOCl as an easy-to-handle oxygen source in the catalytic epoxidation of olefins*. Sodium hypochlorite is a cheap and readily available representative of the family of single-oxygen donors. NaOCl is known as a strong oxidant in basic medium (for a review, see ref 9). More recently, various reactions under phase-transfer conditions have been described, such as the oxidation of alcohols to ketones,[10] primary amines to nitriles,[11] secondary amines to ketones,[11] and hydroquinones and catechols to quinones[12] and the epoxidation of aromatic hydrocarbons.[13,14] The other non-metal-catalyzed epoxidation reactions described with NaOCl involve activated olefins like α,β-unsaturated ketones.[15]

Very few catalytic reactions have been described with NaOCl: (i) oxidation of aromatic rings, ethers, and alcohols with ruthenium salts[9,16] (via the generation of a strong oxidant, RuO_4), (ii) benzylic alcohol in benzaldehyde with K_2FeO_4[17] or manganese porphyrin complexes.[18]

We wish to report our results on the catalytic epoxidation of simple olefins by NaOCl in the presence of manganese porphyrin complexes.[19] These results bare a close relation to those described with analogous Fe, Mn, or Cr complexes and a rather uncommon reagent PhIO[20] (this system provides a good chemical model of P-450 enzymes[20]).

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(14) The reaction occurs with a good yield at pH 8–9 and can be attributed to the reactivity of HOCl which is present at 20–30% at these pH values (see ref 9 for the percentage of chlorine present as HOCl in hypochlorite solution at different pH's). The authors mentioned[15] that the reaction works with nonactivated olefins. However, at pH 12–13, we have checked that no epoxidation occurs with NaOCl and olefins.

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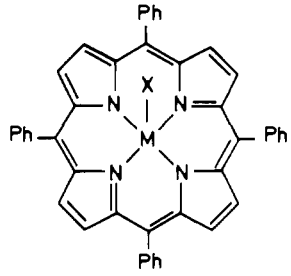
Chart I. Structure of Macrocyclic Metal(III) Complexes[a]



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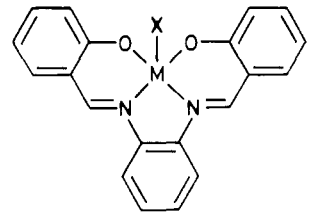

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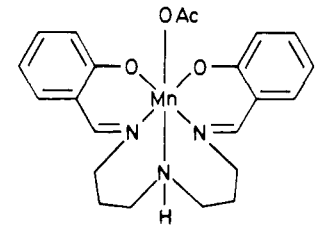

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[a] 1-4: *meso*-tetraphenylporphyrinato metal(III) complexes, M(TPP)X: Mn(TPP)OAc (1a), Mn(TPP)Cl (1b). 5: *N,N'*-(4-azaheptylene)-bis(salicylidiniminato)manganese(III) acetate, Mn(Salpr)OAc. 6-8: *N,N'*-(*o*-phenylene)bis(salicylidiniminato)metal(III) complexes, M(Salphen)X.

Table I. Oxidation of Styrene with NaOCl in the Presence of Various Transition-Metal Complexes[a]

complex	conversion, %[b]	yield in styrene oxide,[b] %
Cr(TPP)Cl (**2**)	24 (18)	8 (6)
Mn(TPP)OAc (**1a**)	80[c] (68)	36[c] (28)
Mn(TPP)Cl (**1b**)	75 (62)	35 (24)
Fe(TPP)Cl (**3**)	33 (18)	2 (2)
Co(TPP)Br (**4**)	53 (42)	6 (6)
Mn(Salpr)OAc (**5**)	22 (5)	0 (0)
Mn(Salphen)OAc (**6**)	17 (8)	4 (2)
Mn(Salphen)Br (**7**)	28 (20)	6 (4)
Co(Salphen)(O_2) (**8**)	38 (18)	8 (4)
$VO(Acac)_2$	3-4	0
$Mn(OAc)_3$	3-4	0
none	3-4	0

[a] Reactions are carried out in air at room temperatures as described in the Experimental Section. [b] Conversion and yield are determined after a reaction time of 3 h. Results corresponding to 1 h are indicated in parentheses. [c] The same reaction run under inert atmosphere (nitrogen) gives 76% of conversion after 3 h and 40% yield.

Results and Discussion

(A) Oxidation of Styrene with Different Transition-Metal Complexes. In a preliminary approach of the hypochlorite anion activation by transition-metal complexes, we decided to investigate the activity of complexes having a planar tetradentate ligand and an axial substituent, expecting this to favor a possible coordination of ^-OCl in the axial position after axial ligand substitution. As a hypothesis, we assumed that the phase-transfer conditions (H_2O, CH_2Cl_2, $R_4N^+Cl^-$) may help to increase the concentration of ^-OCl in the organic phase and that this anion would then act as a nucleophile and coordinate to the metal. Thus, the overall catalytic epoxidation reaction for styrene is expected to be

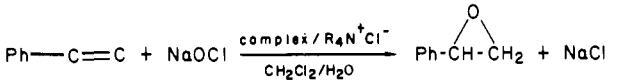

Table I summarizes our trials on the catalytic epoxidation of styrene with NaOCl in the presence of various macrocyclic complexes (Chart I). First of all, one should note that the styrene oxide is stable for several hours under the reaction conditions. The epoxide is quantitatively recovered after 6 h at room temperature. The same stability is observed for all the epoxides described in the present paper. The only significant styrene conversions[21] described in Table I are obtained with the planar tetradentate complexes (see Chart I for complex structures). However, $VO(Acac)_2$, the well-known complex for the catalytic epoxidation of allylic alcohol[8] with *t*-BuOOH, is ineffective under these conditions. This is also the case for $Mn(OAc)_3$, whereas the other macrocyclic manganese complexes are active. Among the complexes with a planar tetradentate ligand, the Schiff-base complexes are less effective compared to their porphyrin analogues. Usually, the olefin conversion ends after 2-3 h with a concurrent bleaching of the organic phase. The order of stability of the macrocyclic complexes found in this reaction is conventionally the same as the one observed with other strong oxidant mixtures: Schiff-base complexes < porphyrin complexes < phthallocyanine complexes. In the case of Schiff-base compounds, the bleaching of the catalyst occurs before the end of olefin conversion. For porphyrin compounds, the same phenomenon is usually observed close to the end of olefin conversion, whereas phthallocyanine complexes are stable for 10-20 h although the olefin is not transformed. In the case of Schiff-base and porphyrin complexes, it should be noted that in the absence of the olefin, the organic phase becomes colorless within a few minutes.

The nature of the metal has an important influence on the catalytic properties of porphyrin complexes. Chromium, iron, and cobalt complexes give a small amount of epoxide in the oxidation of styrene. Only the manganese(III) complex, Mn(TPP)OAc, leads to a significant amount of styrene oxide after 3 h (36%). The reaction is not affected if it is performed under nitrogen, indicating that the epoxide does not result from the interaction of a radical with molecular oxygen. The autooxidation of styrene usually leads to a small amount of epoxide and the major product is benzaldehyde.[22] In our case, less than 1% benzaldehyde is detected despite the stability of this compound under the catalytic conditions.[18] For reactions with a low epoxide selectivity phenylacetaldehyde is detected as a minor product in the organic phase. The same terminal aldehyde has been identified in the epoxide of 2-vinylnaphthalene. Even in the case of low-selective oxidation reactions, these products are the only ones detected in the organic phase, suggesting that all the other substrate oxidation compounds are water soluble and may consequently undergo further oxidations directly by NaOCl.

After these preliminary data, we wish to describe the main characteristics of this new epoxidation route with NaOCl and Mn(TPP)OAc as catalyst.

(1) Influence of Olefin Concentration on the Selectivity of the Reaction. Under the experimental conditions used for the data of Table I, the selectivity[21] of the styrene epoxidation is 45% in the case of Mn(TPP)OAc. We found that the selectivity of this reaction is highly dependent of the initial concentration of styrene where the ratio catalyst/olefin is kept constant (Figure 1). For instance, for a Mn complex/styrene ratio of 0.6%, the selectivity increases from 35% to 90% by changing the olefin concentration from 0.025 to 0.8 M (Table II). At 0.8 M, the conversion is nearly complete within 4 h and the yield in styrene oxide reaches 90%. So the increase in olefin concentration leads to an efficient catalytic epoxidation of styrene. To our knowledge, this is probably the first catalytic epoxidation reaction reported in the literature with NaOCl as oxygen source. The epoxide is easily recovered at the end of the reaction after the porphyrin residue is removed by silica gel or Florisil column chromatography.

(21) The terms of conversion, selectivity, and yield correspond to the percentage of transformed olefin in mole with respect to the starting material, the ratio of epoxide vs. converted olefin or vs. starting olefin, respectively.

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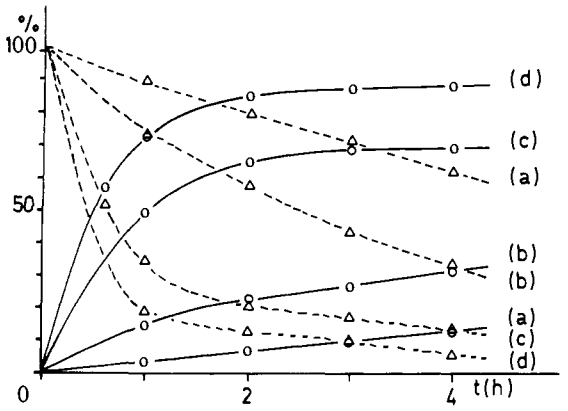

Figure 1. Styrene epoxidation at different initiation concentrations: $[styrene]_0$ = 0.025 (a), 0.1 (b), 0.4 (c), 0.8 M (d). (Δ) Styrene conversion, (O) epoxide formation.

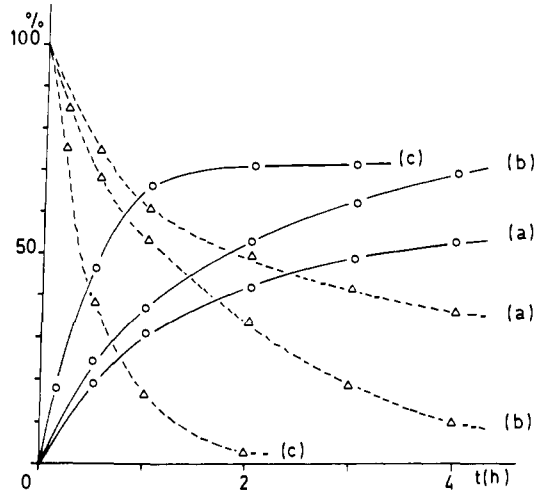

Figure 2. Influence of the catalyst concentration on styrene epoxidation Mn(TPP)OAc/olefin = 0.25% (a), 0.6% (b), 2.5% (c). Initial styrene concentration = 0.4 M. (Δ) Styrene conversion, (O) epoxide formation.

This reaction may also be performed when styrene is used as solvent. The neat olefin is converted to epoxide with 95% yield within 1 h with 0.15% Mn(TPP)OAc/styrene. The increased reaction temperature is controlled by an ice bath.

(2) Influence of Catalyst Concentration. The influence of catalyst concentration has been studied in the epoxidation of 0.4 M styrene solution in the presence of Mn(TPP)OAc. Figure 2 shows the conversion of styrene and the epoxide formation for three different catalyst/olefin ratios: 0.025%, 0.6%, and 2.5%. The epoxide selectivity is nearly the same in all cases (75–80%). The main effect observed with an increase in catalyst/olefin ratio is the increase of the reaction rate. For small amounts of Mn–porphyrin complex (less than 0.5% styrene), the conversion is not complete, most likely the result of bleaching of the catalyst after 6–8 h.

(3) Influence of the Phase-Transfer Agent. The phase-transfer agent (PTA) has an essential role in this reaction. Without the ammonium salt, less than 5% styrene is converted and no epoxide is detected (Figure 3). A small amount of the phase-transfer agent is required, but an increase of the PTA/olefin ratio from 0.125% to 0.5% does not affect the epoxidation reaction (Figure 3). This suggests that a minimum amount of PTA is needed to transfer the hypochlorite anion from the aqueous to the organic phase. After 0.125% PTA this transfer is not the rate-determining step of the epoxide reaction. Similarly, the stirring rate does not influence the reaction.

(4) Origin of the Oxygen Atom of Epoxides. As mentioned above, the catalytic reaction may be run under air or nitrogen without significant changes on the epoxide formation, suggesting that the oxygen atom of epoxide does not arise from molecular oxygen. To confirm that the source of oxygen for epoxide is the hypochlorite solution, we performed the epoxidation of *p*-methoxystyrene with powdered lithium hypochlorite dissolved in $H_2{}^{18}O$ (isotopic purity >98%). Complete conversion is obtained within 15 min, and after extraction and purification of *p*-methoxystyrene oxide on a Florisil column, the purified epoxide did not exhibit any significant incorporation of ^{18}O as shown by mass spectroscopy (from the relative intensity for peaks 150 and 152 the incorporation is less than 5%). This suggests that the oxygen exchange of the hypochlorite anions with water is slower than the catalytic transfer of the oxygen atom to olefins. These results confirm that the origin of epoxide oxygen is certainly the hypochlorite itself.

Table II. Influence of Styrene Concentration on the Epoxidation Selectivity[a]

$[styrene]_0$, M	selectivity, %	conversion, %	yield, %
0.025	39	38	15
0.1	49	67	33
0.4	84	85	72
0.8	95	94	90

[a] The data indicated here are those obtained after 4 h of reaction time.

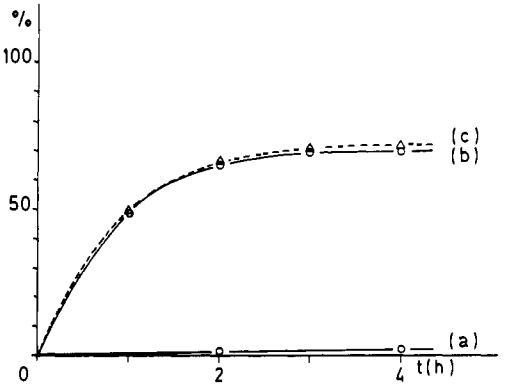

Figure 3. Influence of the phase-transfer agent on styrene oxide formation, (a) without PTA, (b) 0.125%/styrene, (c) 0.5%/styrene.

(5) Complementary Remarks on the Catalytic Epoxidation with NaOCl. All the reactions are run with regular hypochlorite solutions which are highly basic (pH ca. 13). At this pH value, the hypochlorite anion is the main species of bleach solutions:

$$2NaOH + Cl_2 \rightleftharpoons NaOCl + NaCl + H_2O$$

The equilibrium constant of the hypochlorite formation is 7.5×10^5 (see ref 9). By decreasing the pH value of hypochlorite solution, the hypochlorous acid, HOCl, gradually becomes the main species[9] and is usually a source of positive chlorine. So the pH values of hypochlorite solution largely influence its chemical properties. For instance, the epoxidation of aromatic hydrocarbon with NaOCl only occurs in the pH range 7–8.[13] We have studied the influence of the pH value of the aqueous phase on this catalytic reaction with NaOCl. Under the experimental conditions described in Table II and with a 0.4 M initial styrene concentration, the reaction has been performed with a hypochlorite solution lowered to pH 7.8 by addition of HCl (1 N). The organic phase becomes colorless within a few minutes, and olefin conversion is stopped at 30% after 30 min. Less than 5% of styrene oxide is detected.

The same evolution of the reaction is observed without Mn(TPP)OAc, indicating that this complex does not behave as a catalyst under these pH conditions. In fact, at low pH values, hypochlorite solutions are known to lead to chlorhydrin formation or allylic chlorination.[23,24]

Hydrogen peroxide and alkyl hydroperoxides have also been used as oxygen donors with metalloporphyrin catalysts.[25,26] Under

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Table III. Epoxidation of Styrene in the Presence of Pyridine (0.15 equiv/Styrene)

$[styrene]_0$, M		conversion, %	selectivity, %	epoxide yield, %
0.1 M	without pyridine	75 (5 h)	55	38
	with pyridine	100 (2 h)	70	70
0.4 M	without pyridine	95 (5 h)	78	74
	with pyridine	100 (30 min)	80	80

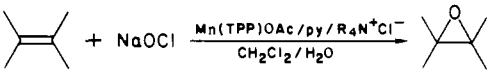
the same reaction conditions as used for NaOCl epoxidations (i.e., phase-transfer agent, pH 13), less than 10% styrene conversion is obtained after 3 h with H_2O_2 or *t*-BuOOH and only traces of epoxide (<2%) are observed. As mentioned in the introduction, dilute aqueous solutions of these oxidants do not seem to be suitable for catalytic oxygenation reactions.

Concerning the possibility of using hypochlorite sources different from sodium hypochlorite, we further studied lithium and calcium hypochlorites. They behave similarly to NaOCl in the styrene epoxidation.

(B) Improvement of This Epoxidation Route by Addition of an Axial Base on the Manganese Porphyrin Catalyst. As described above, the epoxidizing system "NaOCl/Mn(TPP)OAc" is efficient in the case of styrene, which can be converted to the corresponding epoxide with turnover rates of 30–40 cycles/h with 70–80% yield. For olefins that can be easily oxidized in the allylic position, this catalytic epoxidation method cannot be applied with the same success. They usually give poorer conversion and epoxide yield than styrene. For instance, with cyclohexene (0.4 M) the conversion is stopped at 72% after 6 h and the selectivity and epoxide yields are respectively 44% and 32%. With this olefin too, selectivity decreases just as olefin concentration does; e.g., at 0.1 M, cyclohexene oxide selectivity is only 13%.

So, in the experimental conditions used for styrene, this new epoxidation process is not applicable to large series of nonactivated olefins. However, it has been possible to improve this reaction and make it applicable to various olefins by addition of an extra ligand to the metalloporphyrins in the catalytic system.

In biology, it is well-known that heme enzyme reactivity is greatly influenced by the nature of the sixth ligand trans to the catalytic site of the metalloenzyme. For instance, this ligand is a sulfur atom from a cysteine residue in the case of P-450 monooxygenases,[27] a nitrogen from histidine in peroxidase,[28] and an oxygen from tyrosine in catalase.[29] For all these three enzymes with the same prosthetic group (iron protoporphyrin IX), the reactivity cycle is highly dependent on the nature of the sixth ligand. We will see now how the presence of pyridine as sixth ligand in the system NaOCl/Mn(TPP)OAc contributes to modify largely the characteristics of the catalytic reaction in terms of epoxidation rate, chemoselectivity, and stereoselectivity.



(py = pyridine)

We describe first the improvements brought on by the addition of pyridine in the case of styrene and second the results obtained with various substituted olefins.

(1) Modification of Styrene Epoxidation. One important aspect of this reaction is the modification of the epoxidation rate by addition of a small amount of pyridine (0.15 equiv/olefin; 20 equiv/catalyst) to the reaction mixture. The corresponding results are reported in Table III. *In the presence of pyridine, the epoxidation rate is highly accelerated.* For instance, with a 0.4 M initial olefin concentration, the reaction is complete within 30 min instead of 5 h without amine. At lower styrene concentration (0.1 M), the epoxidation is not the only modified parameter: the epoxide selectivity (or chemoselectivity) is also increased from 55% to 70%.

Table IV. Epoxidation of Styrene in the Presence of Various Substituted Pyridines

run	amine	pK_a	conversion, g	epoxide yield, %	reaction time[a]
1	no amine		95	74	5 h
2	pyridine	5.27[b]	100	80	30 min
3	2,6-dimethylpyridine	6.60[b]	100	75	2 h
4	2,6-di-*tert*-butylpyridine	3.58[c]	96	77	5 h
5	3,5-dimethylpyridine	6.15[b]	100	80	30 min
6	4-methylpyridine	6.00[b]	100	80	20 min
7	4-cyanopyridine	1.86[b]	95	75	2 h
8	triethylamine		55	43	5 h

[a] Time when olefin conversion is stopped. [b] Data from: Perrin, D. D. "Dissociation constants of organic bases in aqueous solution" Butterworths: London, 1965. [c] From: Brown, H. C.; Kanner, K. *J. Am. Chem. Soc.* **1966**, *88*, 986. Note: in the same experimental conditions, the determined pK_a value for pyridine is 4.38.

Such an influence of pyridine may have a priori two different interpretations: (i) the in situ oxidation of pyridine into the corresponding *N*-oxide which could be used afterward as a most efficient oxygen source or (ii) the effect of pyridine coordination on the manganese porphyrin during the catalytic reaction. The absence of olefin conversion when sodium hypochlorite is changed for pyridine *N*-oxide allowed us to reject the first hypothesis. Thus, in the present catalytic conditions, pyridine *N*-oxide does not seem to be a good oxygen donor. The absence of reactivity of pyridine *N*-oxide has also been observed by Sharpless in the ruthenium-catalyzed oxidation of alcohols,[30] whereas alkylamine *N*-oxides like *N*-methylmorpholine *N*-oxide in the osmium tetraoxide cis hydroxylation of olefins[31] or *p*-cyano-*N*,*N*-dimethylaniline in the N-dealkylation of tertiary amines with (porphyrinato)iron complexes are good oxygen donors.[32] It should be noted that if pyridine *N*-oxide is used instead of pyridine under the same conditions as in Table IV, the reaction is slower (2 h for complete olefin conversion), and the epoxide selectivity is only 60%. Pyridine *N*-oxide is a good ligand, especially for copper.

The second hypothesis in which the pyridine is coordinated to manganese is supported by the results shown in Table IV (runs 3 to 7) (see also ref 19b). The epoxidation rate of styrene is reduced when large substituents are in position 2 and 6 of the pyridine ring (runs 3 and 4). With 2,6-di-*tert*-butylpyridine the reaction rate observed is nearly the same as without amine. When the steric groups are moved away from nitrogen, in position 3 and 5, the reaction is reaccelerated (run 5 compared to 3). The reaction is also influenced by electronic effects on the pyridine ring. An electron-donating group (methyl) attached in the para position increases the rate (run 6) and the opposite effect is obtained with an electron-withdrawing group like cyano (run 7).

The different pK_a values of substituted pyridines are also indicated in Table IV in order to discuss a possible acid–base effect of pyridine on the reaction.

Three substituted pyridines are more basic than pyridine itself, namely, 2,6-dimethylpyridine, 3,5-dimethylpyridine, and 4-methylpyridine, but they do not behave similarly. For instance, the former is less active than pyridine, whereas the latter is more efficient. The main effect of pyridines on this epoxidation reaction does not seem to be directly related to a simple acid–base effect in the organic phase.

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Table V. Epoxidation of Cyclohexene with Different 4-Substituted Pyridines after a Reaction time of 4 h

4-X-pyridines	conversion, %	epoxide yield, %	selectivity, %
X = Me	95	80	85
X = H	85	72	85
X = CN	64	41	64
no pyridine	59	22	37

Table VI. Epoxidation of Various Olefins by NaOCl in the Presence of Pyridine[a]

olefin	conversion, %	epoxide yield, %	selectivity,[b] %	time,[c] h
styrene	100 (95)	80 (74)	80 (78)	0.5 (5)
α-methylstyrene	95 (83)	95 (59)	100 (72)	2 (4)
cyclohexene	85 (72)	72 (32)	85 (44)	4 (7)
1-methylcyclohexene	98 (60)	70 (11)	72 (19)	4 (7)
cyclooctene	95 (64)	86 (40)	91 (63)	2 (4)
2-methyl-2-heptene	95 (73)	60 (22)	63 (30)	3 (7)
2-methyl-1-heptene	51 (45)	42 (18)	82 (40)	3.5 (4)
1-octene	5	1		4

[a] Results without amine are indicated in parentheses. Standard reaction conditions: in 10 mL of CH_2Cl_2 are successively introduced Mn(TPP)OAc (0.025 mmol), benzyldimethyltetradecylammonium chloride (0.05 mmol), pyridine (0.62 mmol), olefin 4 mmol, after filtration through alumina to remove the peroxides), and then 20 mL of 0.35 M NaOCl (7 mmol). [b] The selectivity is defined as the ratio of epoxide to the converted olefin. [c] The indicated time is the end of conversion.

The behavior of these substituted pyridines in the catalytic reaction is best correlated with the electronic and steric effects of formation constants for axial ligation to manganese porphyrin complexes.[33] Furthermore, the stabilization of ferryl complexes with nitrogen bases has been described,[34] and the X-ray structure of the six-coordinated pyridine complex Mn(TPP)(py)Cl is known.[35]

Consequently, all the effects observed for the various pyridines on styrene epoxidation strongly suggest that pyridine acts as a ligand on metalloporphyrin during the catalytic cycle. A similar role of pyridine has been mentioned in the osmium tetraoxide catalyzed hydroxylation of hindered olefins, where the reactivity of OsO_4 is enhanced by the coordination of two pyridine molecules per osmium atom.[36]

We also studied the behavior of trialkylamines on the catalytic epoxidation of styrene. With Et_3N, for instance, the reaction is first accelerated and then stopped at a 55% conversion yield after 4 h (Table IV, run 8). The same phenomenon is observed with imidazole itself or *N*-methylimidazole, but not with *N*-arylimidazoles.[37] Oxidation of the alkyl chains or the nitrogen may occur under these drastic oxidant conditions. Such amine oxidations have been studied with NaOCl in phase-transfer reactions.[38] In the case of *N*-arylimidazole, conversion and epoxidation rates are more enhanced than with pyridine derivatives.[37]

(2) Case of Cyclohexene. As we mentioned above, the nonmodified NaOCl/Mn(TPP)OAc system does not give acceptable yields of epoxide for cyclohexene and other olefins susceptible to allylic oxidation. In the case of cyclohexene, however, addition of pyridine dramatically improves the reaction rate and the chemoselectivity for such substrates, as indicated in Table V. With 4-methylpyridine, conversion is nearly complete within 4 h (without pyridine, conversion usually stops after 6 or 7 h at 70% conversion) and chemoselectivity increases up to 85%. A fairly good yield of 80% is obtained, making this catalytic epoxidation suitable for cyclohexene.

Similar to the case of styrene, the rate and the selectivity depend on electronic effects on pyridine (Table V): 4-methylpyridine > pyridine > 4-cyanopyridine.

(3) Epoxidation of Various Olefins. The pyridine-modified epoxidizing system, NaOCl/Mn(TPP)OAc, can be applied to a large range of substituted olefins (Table VI). Most of the di- and trisubstituted olefins are epoxidized in fairly good yields (60–95%), e.g. tetramethylethylene, 1-methylcyclohexene, cyclooctene, and α-methylstyrene, the epoxide of which is highly susceptible to acid-catalyzed ring opening. A lower yield is obtained with 2,2-disubstituted olefins (2-methyl-1-heptene). Terminal olefins with a long alkyl chain are nearly inert (see 1-octene). In the latter case, the catalyst is decomposed after 4 h and the olefin conversion is only 5% at this point.[39] The order of olefin reactivity observed in this catalytic epoxidation is different than that in electrophilic epoxidation with peracids:[40] styrene (2.36) > tetramethylethylene (1.55) > 1-methylcyclohexene (1.15) > 2-methyl-1-heptene (1.09) > cyclohexene (1.0), (the relative rate $k_{olefin}/k_{cyclohexene}$ indicated in parentheses is determined from independent reactions).

The results concerning the relative reactivity of cis–trans olefins are presented below (cf. paragraph on stereochemical studies). Two main differences with peracid epoxidation should be noted: (i) the olefin reactivity slightly increases with the number of aliphatic substituents on the double bond, but the order of magnitude is considerably less than that observed in peracid epoxidation.[40b] With these peroxy acids, the relative rate for trisubstituted olefins vs. disubstituted ones is usually 8 to 10, and in the present case, the value is less than 1.2. (ii) Moreover, styrene is less reactive than cyclohexene in peracid epoxidation[40a] ($k_{sty}/k_{cyclohexene}$ ca. 0.3). With the NaOCl/Mn(porphyrin)X system, the reverse order of reactivity is observed ($k_{sty}/k_{cyclohexene}$ = 2.36), suggesting that the mechanism of oxygen transfer does not correspond to that of a classical electrophilic oxygen atom transfer. But this high reactivity of styrene is similar to that observed in chromyl complex epoxidation where a metal–oxo is also involved.[41] Furthermore, 2,2-disubstituted olefins present the same initial epoxidation rate as cyclohexene. However, the conversion is not complete indicating that, as observed by Groves[20o] with PhIO/Mn(TPP)Cl, steric effects are more important in the transfer of the electrophilic oxygen atom from the active manganese complex to the olefin than in the case of peracid reagents.

The rate of this pyridine-assisted epoxidation depends on the ratio pyridine/manganese complex as shown in Figure 4. For instance, the cyclooctene conversion is complete within 1 h with a 50/1 pyridine/Mn ratio, vs. 3 h with a 25/1 ratio. Without pyridine, the conversion is not achieved after 7 h. With a 50/1 pyridine/Mn ratio, it should be pointed out that the cyclooctene oxide yield is 85% within 1 h (ca. 135 cycles per h).

(4) Epoxidation Stereochemistry. As observed with peracids, aliphatic olefins are stereospecifically epoxidized: *cis*-2-hexene only gives the *cis*-epoxide and *trans*-2-hexene gives more slowly the *trans*-epoxide (k_{cis}/k_{trans} = 5.0, determined from competitive reaction). This value is larger than that obtained with peracids (k_{cis}/k_{trans}) = 1.2–2.2) and similar to that observed with the PhIO/Fe(TPP)Cl system[20o] (k_{cis}/k_{trans} = 5.8), indicating that the oxidant may interfer in the transition state of the oxygen transfer from the manganese complex to the olefin.

The retention of configuration is again in favor of the addition of an electrophilic oxygen atom in these catalyzed epoxidations.

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(39) The *meso*-tetraphenylporphyrin ligand is highly sensitive to the olefin geometry (cis olefins are more reactive than trans ones). For a terminal olefin with a shorter alkyl chain than 1-octene (e.g., 1-propene), a slow epoxidation is observed. Guilmet, E.; Meunier, B.; Brigandat, Y.; Schirmann, J. P., unpublished results.

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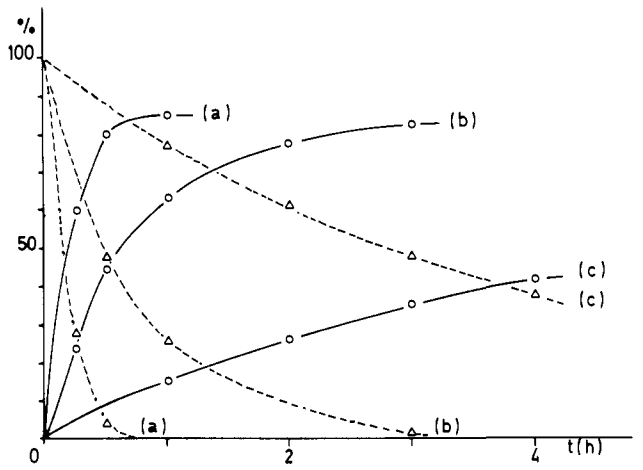
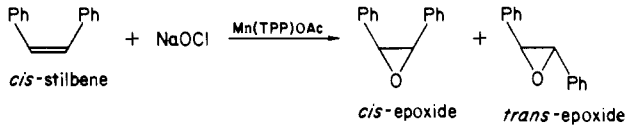


Figure 4. Pyridine influence on cyclooctene epoxidation: pyridine:catalyst = 50:1 (a), 25:1 (b), without pyridine (c). (△) Cyclooctene, (○) cyclooctene oxide.

However, this stereospecificity is not always observed. For instance, with a nonaliphatic olefin like *cis*-stilbene, the epoxidation gives a mixture of *cis*- and *trans*-epoxides, but the stereoselectivity is highly modified by the addition of pyridine in the reaction mixture (Table VII).



In the absence of pyridine, the *trans*-stilbene oxide is the major isomer obtained from *cis*-stilbene epoxidation (*cis*-/*trans*-epoxide ratio, 35:65) whereas addition of a small amount of pyridine (3 %/mol olefin) is able to reverse the isomer ratio and to give predominantly the *cis*-epoxide (cis/trans ratio, 70:30). The *cis*-epoxide ratio can reach 94% by increasing the pyridine concentration. *cis*- and *trans*-epoxides are stable in the catalytic conditions, and further the starting olefins are not isomerized during the reaction. Thus, the observed modifications of epoxidation stereoselectivity are due to the influence of pyridine on the catalytic oxygen transfer and not to the isomerization of the epoxide mixture in the reaction conditions. As previously observed with substituted pyridines, the stereoselectivity increase is related to the ability of these pyridines to act as manganese ligands. Better selectivities are obtained with pyridine and 4-methylpyridine and poorer ones with 2,6-disubstituted pyridines or 4-cyanopyridine.

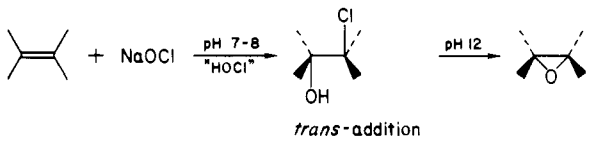
Similarly to styrene, the *cis*-stilbene epoxidation rate is accelerated by addition of pyridine. Without pyridine, the olefin conversion is complete after 7 h with overall yield of 70–80%, whereas with pyridine, the olefin disappears after 2–3 h (yield 80–85%). The trans isomer of stilbene is epoxidized more slowly than the cis, even in the presence of pyridine (15–20% yield after 5 h). In both cases, the *trans*-epoxide is the only product.

All these effects, namely, increased rate and considerable change in stereoselectivity, can be considered as direct consequences of pyridine coordination on the manganese porphyrin during the catalytic cycle. A similar influence of the ligand is further observed in Groves' system, where PhIO is the oxygen donor in a one-phase organic solution. The epoxidation of *cis*-stilbene with PhIO/Mn(TPP)Cl leads to nearly the same *cis*-/trans-epoxide ratio[20d] as that obtained with NaOCl/Mn(TPP)OAc (38/62 for PhIO/Mn and 35/65 for NaOCl/Mn). Assuming that the reactivity of the manganese–oxo species is somehow generated by pyridine as the sixth ligand trans to the metal–oxygen bond, we performed the epoxidation of *cis*-stilbene with Groves' system in the presence of pyridine (0.15 equiv/olefin). In this case again, the stereoselectivity changed and the cis/trans ratio increased up to 57/43. Thus, with a different source for the oxygen atom, the presence of a pyridine ligand on the manganese complex contributes to modify the stereoselectivity of these metalloporphyrin-catalyzed epoxidations. The similar stereochemical behavior of *cis*-stilbene in these two catalytic epoxidation reactions, using different oxidants, clearly suggests that similar manganese–oxo intermediates are involved in the reactions. Furthermore, in both cases, the lack of stereospecificity in aromatic olefin epoxidation might be due to the radical character of the manganese–oxo complex leading to long-life intermediate in the case of olefins bearing aromatic substituents on sp^2 carbon atoms (for a diffusion on the radical character of Mn=O with PhIO/Mn, see ref 20d and with NaOCl/Mn see ref 46).

Table VII. *cis-trans*-Epoxide Ratio in the Epoxidation of *cis*-Stilbene in the Presence of Various Pyridines

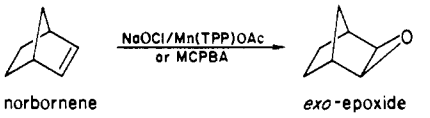
	cis-epoxide, %	*trans*-epoxide, %
without amine	35	65
pyridine (0.03 equiv/olefin)	70	30
pyridine (0.15 equiv)	78	28
pyridine (6 equiv)	91	9
pyridine (60 equiv)	94	6
4-cyanopyridine (0.15 equiv)	60	40
4-methylpyridine (0.15 equiv)	83	17
2,6-dimethylpyridine (0.15 equiv)	56	44
2,6-diterbutylpyridine (0.15 equiv)	45	55
3,5-dimethylpyridine (0.15 equiv)	75	25

(5) Stereochemical Evidence against a Chlorohydrin Route in the NaOCl/Mn System. Prior to further discussing possible manganese–oxo complexes in the NaOCl/Mn(TPP)OAc system, we have checked that epoxidation formation did not occur via chlorhydrin intermediates. The pH value (ca. 13) of the aqueous phase in our system is not compatible with the formation of large quantities of HOCl, which is the active species in the chlorohydrin epoxidation route.



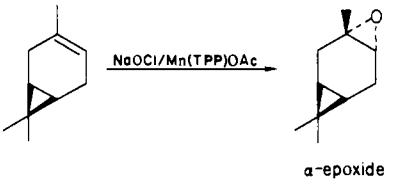
It is known that after the trans addition of HOCl to the olefin, the ring oxirane closure occurs in basic medium via a chloride trans displacement. Consequently, this epoxidation route gives epoxides with the stereochemistry opposite to that obtained by the peracid method.[40c]

In order to distinguish between the transfer of an electrophilic oxygen atom or a chlorohydrin activation in the NaOCl/Mn system, we have studied the epoxide stereochemistry with norbornene and 3-carene. The epoxidation of norbornene with NaOCl/Mn only leads to the *exo*-epoxide, identical with a sample prepared by peracid.[42]



MCPBA = *m*-chloroperbenzoic acid

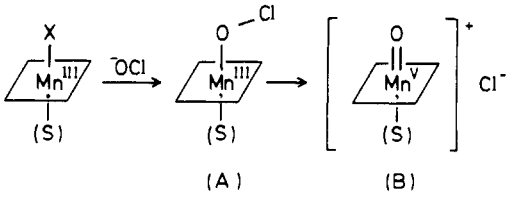
In the same way, the only epoxide observed in the case of 3-carene is the α-epoxide, whereas the β-epoxide is obtained via



the chlorohydrin route.[40c] No traces of the latter isomer are formed in the manganese-catalyzed reaction. So, with these two

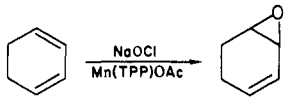
(42) (a) Kwart, H.; Wosburg, W. G. *J. Am. Chem. Soc.* **1954**, *76*, 5400–5403. (b) Budnick, R. A.; Kochi, J. K. *Ibid.* **1976**, *41*, 1384–1389.

Scheme I. Proposed Mechanism for Manganese-Oxo Bond Formation from a Coordinated Hypochlorite Anion



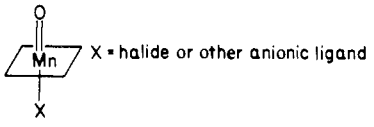
olefins, the observed epoxidation stereochemistry is the same as that obtained with peracid where the transfer of an electrophilic oxygen atom in a syn addition is well established. *These results definitely favor the syn addition of an electrophilic manganese–oxo species in the NaOCl/Mn system instead of an epoxide formation via chlorohydrin intermediates.*

Furthermore, monoepoxides are the only products in the catalytic epoxidation of 1,3-cyclohexadiene and 1,3-cyclooctadiene.



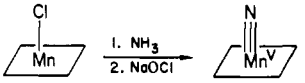
The absence of endoperoxide formation with these two olefins indicates that singlet oxygen $^1O_2$ is not present in the medium. If any hydrogen peroxide has been produced during the catalytic reaction, it is known that a mixture of NaOCl and H_2O_2 is a good chemical source of singlet oxygen, leading by this way to endoperoxide formation.[43]

(C) Oxidized Manganese Porphyrin Species in Active Intermediates in this Catalytic Epoxidation. Recent works have been devoted to the PhIO/Mn(TPP)Cl system in attempt to characterize the different oxidized species obtained by PhIO oxidation of manganese(III) porphyrin complexes.[20c,d] In these cases, various monomeric and dimeric manganese complexes were isolated which all behave as phosphine oxidants.[20l,m,n] Hill reported these complexes as secondary products of an initial electrophilic manganese(V)–oxo complex:



In the case of NaOCl/Mn(TPP)OAc, the typical features of the reaction also favor such an electrophilic oxygen species coordinated to manganese porphyrin.

Since the preliminary studies of Calvin,[44a] Tabushi[44b] and Harriman[44] on the oxidation of manganese porphyrins by NaOCl with regard to photosynthesis studies and to the role of high-valent manganese species in the oxidative decomposition of water, little has been done so far to describe the exact nature of these oxidized manganese porphyrins. We wish now to present some hypotheses on the possible formation of manganese–oxo complexes by oxidation of Mn(TPP)X with NaOCl. First, one may consider that the phase-transfer agent largely increases the hypochlorite anion concentration in the organic phase so the substitution of the axial anionic ligand X by OCl^- is allowed and leads to the formation of A (Scheme I). Then two possibilities can be examinated: (i) the coordination of the hypochlorite anion to manganese is sufficient to increase the electrophilic properties of the oxygen atom and makes possible its transfer to the olefin, (ii) or the heterolytic dissociation of the oxygen–chlorine bond is necessary to give a more electrophilic manganese–oxo complex B. Up to now, no examples of complex A have been described, and furthermore this complex is a manganese(III) compound when it is known that NaOCl is a strong oxidant able to generate Mn(IV) and Mn(V) complexes.[44c] As an example, the first well-characterized manganese(V) porphyrin compound[45] has been prepared by NaOCl oxidation.[45a]



The NaOCl route for the preparation of the nitrido complex supports the formation of high-valent manganese–oxo complexes like B in the catalytic epoxidation reaction.[47] One may easily admit that the electronic structure and reactivity of this manganese–oxo bond could be modulated according to the nature of the ligand S coordinated in trans position (Scheme I,S = water or pyridine). If we are reminded that the proximal ligand plays an important role in the iron–oxo bond reactivity in metalloporphyrin enzymes such as cytochrome P-450, peroxidases, and catalase, the pyridine influence on the selectivity observed in these epoxidation reactions may underline the biomimetic character of the NaOCl/Mn(TPP)OAc system.

Concerning the spectroscopic evidence for the generation of a complex like B in the catalytic system, it should be noted first that the visible spectra of the brownish catalytic solutions present an intense absorption band at 425 nm as previously described for oxidized manganese porphyrins.[20c,d,44c] In the case of PhIO oxidations, this band has been attributed to a manganese–oxo bond. Recently, we have been able to precipitate at −80 °C the oxidation product of Mn(TPP)OAc by NaOCl. However, this brown solid is very unstable above −20 °C, which does not facilitate its complete characterization by usual physical methods. The temperature-dependent decomposition of this complex in dichloromethane solution leads to a complex which gives a Soret band at 478 nm characteristic of Mn^{III}(TPP)X complexes.

By changing the "normal" *meso*-tetraphenylporphyrin ligand for a more sterically hindered porphyrin, namely, the *meso*-tetramesitylporphyrin, it has been possible to obtain a more stable brown oxidation product[47] whose physical and chemical properties are still under investigation (electrochemical behavior, EXAFS data, ...).

Conclusion

Among all the oxidants that are potentially donors of one oxygen atom, we have shown that NaOCl is a good reagent for the efficient catalytic oxygenation reactions.

In the presence of catalytic amounts of manganese porphyrin complexes, sodium hypochlorite is a good source of oxygen for olefin epoxidation. This new catalytic method of epoxidation occurs in mild conditions, and the use of a versatile and cheap oxidant should probably make it useful among the new catalytic methods for selective oxidation.[48]

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 225 or 257 spectrophotometer. ^1H NMR spectra were obtained with a Perkin-Elmer R12B (60 MHz) and for FT mode on a Bruker WH90 (90 MHz) or a Bruker WM250 (250 Hz) spectrometers. GLC analyses were performed with an Intersmat IG 120 on four different columns: a 6 ft × 0.125 in.

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column packed with 10% SE-30 on Chromosorb PAW (80–100 mesh), a 9 ft × 0.125 in. column with 8% OV17 on Chromosorb PAW (80–100 mesh), or silica capillary columns WCOT 25 m × 0.23 mm CPSil5 or CPWax51 (from Chrompack).

UV–visible spectra were recorded on a Varian Cary 14 spectrophotometer (sample concentration, 10^{-4}–10^{-5} M).

Schiff base complexes **5–8** were prepared according to ref 49.

Metalloporphyrins were usually synthetized as described by Adler et al.[50] or by more recently modified methods (for Mn(TPP)Cl, see ref 51). Mn(TPP)OAc was purchased from Strem Chem. or prepared by DMF metalation procedure[50] from $Mn(OAc)_2$ followed by alumina column chromatography. The dichloromethane fraction is evaporated to dryness and refluxed in a $CH_3COOH/(CH_3CO)_2O$ (5/1) mixture to eliminate the hydroxide complex produced on alumina.[52] After evaporation, the crude material is crystallized from toluene (yield, 91%).

Olefins were obtained from Fluka or Aldrich, and peroxides were carefully removed by passing the olefins through a short neutral alumina column (5 cm) before use.

Benzyldimethyltetradecylammonium chloride, *meso*-tetraphenylporphyrin, cyclohexene oxide, and styrene oxide were obtained from Fluka, Merck, or Aldrich and used without purification. The different pyridines were obtained from Prolabo, Merck, Fluka, or Aldrich and distilled before use.

Sodium hypochlorite was obtained from Prolabo (Rectapur quality, 0.35 M) and titrated by iodometric method. All other commercial sources of sodium hypochlorite could be used after dilution but a small decrease in reaction rate and selectivity was observed with domestic bleach. Iodosylbenzene was prepared according to Saltzmann et al.[53] Hydrogen peroxide (30%, Merck) and *tert*-butyl hydroperoxide (85%, Fluka) were used without purification. Noncommercial epoxides used in this work were prepared from corresponding olefins with *m*-chloroperbenzoic acid (85%, Merck) following conventional procedures[54] and were identified by NMR and mass spectra. For spectroscopic data of the following, see the indicated references: styrene oxide,[55] *p*-methoxystyrene oxide,[56] cyclooctene oxide, 1-methylcyclohexene oxide,[20j] *cis*- and *trans*-stilbene oxide,[56] tetramethylethylene oxide,[20j] norbornene oxide,[56] α-3-carene oxide.[58]

(A) Epoxidation Reactions. General Procedures. All reactions were carried out at room temperature under nitrogen (except for results described in Table I) in a 30-mL Schlenk tube equipped with a stirring bar. One millimole of standard for GLC analysis, 4 mmol of olefin, and 10 mL of N_2-purged dichloromethane are successively added by syringe to 0.025 mmol of Mn(TPP)OAc and 0.05 mmol of benzyldimethyltetradecylammonium chloride; 20 mL of 0.35 M NaOCl is then added by syringe to the organic phase. Magnetic stirring is stopped before each aliquot (20 μL) is withdrawn from the organic phase and diluted with diethyl ether (20 μL) before GLC analysis. The large difference in reactivity between olefins and saturated hydrocarbons in these Mn(TPP)OAc-catalyzed reactions allowed the use of saturated hydrocarbons as internal standard. A maximum of 1–2% of the standard is converted at the end of olefin conversion. However, this procedure for internal standard cannot be applied to catalysts that are more efficient in catalytic hydroxylations.

(B) Oxidation of Styrene with NaOCl in the Presence of Various Transition-Metal Complexes. The results summarized in Table I were carried out under the following conditions: styrene (1 mmol), complex (0.025 mmol), benzyldimethyltetradecylammonium chloride, BDTAC (0.05 mmol), CH_2Cl_2 (10 mL), NaOCl 0.35 M (20 mL, 7 mmol).

(C) Influence of Styrene Concentration on Epoxidation Selectivity. The results are given in Table II and Figure 1.

For $[styrene]_0$ = 0.025 M: styrene (0.25 mmol), Mn(TPP)OAc (1.5×10^{-3} mmol), BDTAC (3×10^{-3} mmol), CH_2Cl_2 (10 mL), NaOCl 0.35 M (25 mL).

For $[styrene]_0$ = 0.1 M: styrene (1 mmol), Mn(TPP)OAc (6.2×10^{-3} mmol), BDTAC (12.5×10^{-3} mmol), CH_2Cl_2 (10 mL), NaOCl 0.35 M (25 mL).

For $[styrene]_0$ = 0.8 M: styrene (4 mmol), Mn(TPP)OAc (25×10^{-3} mmol), BDTAC (0.05 mmol), CH_2Cl_2 (10 mL), NaOCl 0.35 M (25 mL).

For $[styrene]_0$ = 0.4 M: styrene (8 mmol), Mn(TPP)OAc (50×10^{-3} mmol), BDTAC (0.1 mmol), CH_2Cl_2 (10 mL), NaOCl 0.35 M (25 mL).

(D) Influence of Catalyst Concentration on Styrene Epoxidation. Figure 2, styrene (4 mmol), Mn(TPP)OAc ((a) 0.01, (b) 0.025, (c) 0.1 mmol), BDTAC (0.05 mmol), CH_2Cl_2 (10 mL), NaOCl 0.35 M (20 mL).

(E) Influence of Phase-Transfer Agent (PTA) on Styrene Oxide Formation. Figure 3, styrene (4 mmol), Mn(TPP)OAc (0.025 mmol), BDTAC ((b) 5×10^{-3} (c) 20×10^{-3} mmol), CH_2Cl_2 (10 mL), NaOCl 0.35 M (20 mL).

(F) Epoxidation of Styrene in the Presence of Pyridine. Table III, 0.1 equiv/styrene, styrene (1 or 4 mmol), Mn(TPP)OAc (0.025 mmol), BDTAC (0.05 mmol), pyridine (0.62 mmol), CH_2Cl_2 (10 mL), NaOCl 0.35 M (20 mL).

(G) Epoxidation of Styrene in the Presence of Various Substituted Pyridines. Table IV, styrene (4 mmol), Mn(TPP)OAc (0.025 mmol), BDTAC (0.05 mmol), amine (0.62 mmol), CH_2Cl_2 (10 mL), NaOCl 0.35 M (20 mL).

(H) Epoxidation of Cyclohexene with Different 4-Substituted Pyridines. Reaction time of 4 h Table V, results were obtained in the same conditions as for Table IV (see above).

(I) Epoxidation of Various Olefins by NaOCl in the Presence of Pyridine. Table VI, same conditions as for Table IV.

(J) Pyridine Influence on Cyclooctene Epoxidation. Figure 4, cyclooctene (4 mmol) Mn(TPP)OAc (0.025 mmol), BDTAC (0.05 mmol), pyridine ((a) 1.25 (b) 0.62 mmol), CH_2Cl_2 (10 mL), NaOCl 0.35 M (20 mL).

(K) *cis*-/*trans*-Epoxide Ratio in Epoxidation of *cis*-Stilbene in the Presence of Various Pyridines. Table VII, the same conditions as described in the general procedure were followed (see above) with the corresponding amount of pyridine (see Table VII for the ratio pyridine/olefin). At the end of the reaction, the reaction mixtures were worked up by passage of the solution through a column of silica gel 70–230 Mesh (eluant, hexane/diethyl ether, 3/1). After solvent evaporation, the compositions of the crude products were determined by ^1H NMR ($CDCl_3$, Me_4Si as reference). *cis*-Stilbene was characterized by a singlet at δ 4.35–4.45 for the epoxidic proton and the trans isomer by a singlet at δ 3.80–3.90. In one of the experiments, both isomers were separated by semipreparative HPLC (Waters μBondapak C_{18} column; eluant, H_2O/MeOH, 60/40; refractometer as detector) and separately identified by NMR and mass spectrum.

(L) Epoxidation of *p*-Methoxystyrene with $LiOCl/H_2{}^{18}O$. *p*-Methoxystyrene (0.5 mmol), Mn(TPP)OAc (0.005 mmol), BDTAC (0.062 mmol), pyridine (20 μL), CH_2Cl_2 (1 mL), LiOCl (Fluka) (0.195 g dissolved in 1 mL of $H_2{}^{18}O$, 98%, provided for by CEA, Saclay). The reaction is complete within 15 min. The dichloromethane solution is chromatographed on Florisil (CH_2Cl_2/hexane, 80/20, as eluant). The pure epoxide (yield, 80%) is identified by NMR[56] and mass spectrum (electron ionization). A molecular peak was observed in the MS at 150 which was identical with that for the epoxide prepared by NaOCl/Mn or peracid (from the relative intensity of peaks 150 and 152, the incorporation of ^{18}O is less than 5%).

(M) Epoxidation of Norbornene. Norbornene (4 mmol), Mn(TPP)OAc (0.04 mmol), BPTAC (0.046 mmol), pyridine (50 μL), CH_2Cl_2 (10 mL), and NaOCl 0.35 M (20 mL). After 4 h at room temperature, the organic phase was chromatographed on a silica gel (70–230 mesh) column (eluant, CH_2Cl_2). After purification of the crude epoxide by sublimation, the norbornene oxide was identified by NMR and mass spectroscopy (yield, 40–50%).

(N) Epoxidation of 3-Carene. Same experimental conditions as for norbornene. After 4 h at room temperature, the dichloromethane solution is chromatographed on silica gel. The only epoxide observed by NMR is the crude material is the α-isomer. The compound is purified by recrystallization in hexane at −20 °C (yield, 60%), $[\alpha]_D^{20}$ +19° in chloroform (*c* 0.46).

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Registry No. 1a, 58356-65-3; **1b**, 32195-55-4; LiOCl, 13840-33-0; styrene, 100-42-5; 4-cyanopyridine, 100-48-1; 4-methylpyridine, 108-89-4; 2,6-dimethylpyridine, 108-48-5; 2,6-di-*tert*-butylpyridine, 585-48-8; 3,5-dimethylpyridine, 591-22-0; *cis*-stilbene, 645-49-8; α-methylstyrene, 98-83-9; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; cyclooctene, 931-88-4; 2-methyl-2-heptene, 627-97-4; 2-methyl-1-heptene, 15870-10-7; 1-octene, 111-66-0; pyridine, 110-86-1; benzyldimethyltetradecylammonium chloride, 139-08-2; *p*-methoxystyrene, 637-69-4; sodium hypochlorite, 7681-52-9; norbornene, 498-66-8; 3-carene, 13466-78-9.

Substituent Effects on the Carbon–Silicon Double Bond. Monosubstituted Silenes

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Abstract: A series of isomeric silenes $H_2C{=}SiHR$ (**1**) and $H_2Si{=}CHR$ (**2**) where R = CH_3, SiH_3, F, OH, $OSiH_3$, CN, and NO_2 were studied at the RHF/3-21G and 6-31G* levels. The two basis sets give in general similar results. The calculated r(C=Si) are (3-21G, values (in Å) for **1** followed by **2**) 1.717 (R = H), 1.716, 1.725 (CH_3), 1.724, 1.721 (SiH_3), 1.698, 1.730 (F), 1.705, 1.746 (OH), 1.705, 1.749 ($OSiH_3$), 1.711, 1.727 (CN), 1.707, and 1.726 (NO_2). The experimental r(C=Si) of 1.764 Å in $(Me_3Si)_2Si{=}C$(adamantyl)$(OSiMe_3)$ is electronically elongated and consistent with our calculations and with a r(C=Si) of 1.70 Å in unperturbed silenes but contrasts with the electron diffraction measurement of 1.83 Å. The **2** - **1** energy differences (ΔE) are determined by the bond energies of Si–R vs. C–R and of Si–H vs. C–H: ΔE (6-31G*, kcal mol^{-1}) 8.9 (R = CH_3), -3.6 (SiH_3), 53.9 (F), 41.2 (OH), 51.1 ($OSiH_3$), 3.0 (CN), 2.7 (NO_2). Substituent effects (SE) on the thermodynamic stability of the C=Si bond are generally small. The calculated energies of the equations **1** + $SiH_4 \rightarrow$ **1**, R = H and H_3SiR, **2** + $CH_4 \rightarrow$ **2**, R = H and H_3CR, that also model the SE on the dimerization energies of **1** and **2** are, respectively, (6-31G*, kcal mol^{-1}), R = CH_3, 0.1, 0.3, H_3Si, 2.9, 6.0, F, -2.0, -7.8, OH, 0.3, 0.4, $OSiH_3$, -0.2, -2.8, CN, -1.4, 3.8, and NO_2, -3.4, 2.4. SE on the charge distributions and on the energies and coefficients of the frontier orbitals of **1** and **2** are evaluated and used for analyzing the factors that control their kinetic stability. A "reversed polarity" of the π-bond, i.e., $C^{\delta+}{=}Si^{\delta-}$, is the most important single electronic factor that reduces the reactivity of silenes; the energies of the π- and π*-orbitals are less significant.

Silicon–carbon double bonds (silenes) have become recently the subject of considerable experimental and theoretical interest.[1] The theoretical as well as most of the experimental studies have centered on the parent $H_2C{=}SiH_2$[2] and on the methyl-substituted silenes.[1c,3] Recently Brook et al. have succeeded for the first time to isolate stable silenes of the general formula $(Me_3Si)_2Si{=}CR(OSiMe_3)$.[4] This important achievement focused attention to the possible role of the substituents in stabilizing the C=Si bond. While steric effect definetively play an important role in stabilizing these silenes[4] the contribution of electronic effects which may be even more significant is unknown. Knowledge of substituent effects is of great importance in selecting new silenes as possible candidates for synthesis or for understanding silene reactions. Disappointingly, very little is known in this respect either experimentally or theoretically. Experimentally, Brook reported that attempts to stabilize silenes with aryl or trifluoromethyl groups were unsuccessful.[4c] Theoretically only methyl[3] and fluorine[5a] substituions were studied. When this paper was being written, Gordon and George pulbished calculations on hydroxy substitution,[5b] but as the prime interest of these authors was entirely different from ours there is no overlap between the discussions of the two papers. In an attempt to supply this vital basic information we have undertaken an extensive theoretical study of a series of substituted silenes. Both mono- and disubstituted silenes were studied. The substituents that were chosen, i.e., OH, $OSiH_3$, SiH_3, CN, and NO_2, span wide range of electronic properties.[6] Hydroxy and silyloxy are strong π-donors, due to the presence of lone-pair electrons on the oxygen, but weak σ-acceptors. The nitro and the nitrile groups on the other hand are strong π-acceptors and also powerful σ-acceptors. Silyl exerts a much milder electronic effect, it is a weak π-acceptor and a weak σ-donor. For completion we have included methyl and fluorine which were studied previously.[3,5] Methyl is a weak π- and σ-donor, while fluorine is a strong σ-acceptor and a weak π-donor.[6]

In this paper we report the results of molecular orbital calculations at the ab initio level for the monosubstituted silenes. Substitution at both the silicon (**1**) and the carbon (**2**) ends of

$$\underset{\mathbf{1}}{H_2C{=}SiHR} \qquad \underset{\mathbf{2}}{RCH{=}SiH_2}$$

R = H, CH_3, SiH_3, OH, $OSiH_3$, F, CN, NO_2

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