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Progress Toward Artificial Metalloenzymes: New Ligands for Transition Metal Ions and Neutral Molecules

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Abstract. New nickel catalysts have been developed for the oxidation of alkenes to epoxides, alcohols, aldehydes and ketones. Mechanistic studies indicate that the oxidation reactions are very sensitive to the nature of the catalyst; only certain ligands including salen and the macrocycles cyclam and dioxocyclam render Ni(II) effective as a catalyst. A Ni(III) or Ni(IV)-oxo species has been postulated as the catalytically active oxidant which leads to oxygen atom transfer to alkenes in a stepwise process. Both iodosylbenzene and hypochlorite have been used as terminal oxidants; both systems give high yields of epoxidation of alkenes and varying amounts of C=C bond cleavage products. In order to reach an ultimate goal of hydrocarbon oxidation within a molecular recognition system, new molecular receptors for organic substrates have been investigated. The receptors are constructed from two subunits of cholic acid and display amphophilic character – a hydrophobic exterior and a hydrophilic interior. Conformational properties in the presence of polar guests in $CDCl_3$ are described.

Key words. Metalloenzymes, catalysis, oxidation, nickel, alkene.

1. Introduction

Nature has engineered proteins with complex structural features in order to carry out sophisticated organic transformations. One example is cytochrome P-450, an enzyme capable of selectively hydroxylating a variety of hydrocarbon substrates [1]. This process is an enviable one; reagents for organic synthesis which achieve even non-selective hydroxylation of hydrocarbons are few. Due to the extraordinary interest in both metal-catalyzed oxidation of organic substrates [2] and in the molecular recognition of organic compounds [3], it is a compelling challenge to construct a mimic of an oxidative enzyme. The approach involves the assembly of an artificial enzyme possessing a reactive site oriented with respect to a binding site for the substrate. Such an approach has been undertaken by others in efforts to generate artificial hydrolases and oxidases [4]. An alternative approach is to control the steric environment around a catalytic site without incorporation of a discrete substrate binding site. Notable examples of this approach are in the area of transition metal-catalyzed olefin epoxidation [5]. It was our intention to begin by studying the two aspects of the former approach individually in order to develop both new reagents for oxidation as well as new molecular receptors.

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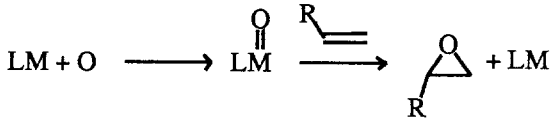
2. Olefin Oxidation using Nickel Complexes

Numerous model systems for cytochrome P-450 have focussed upon the use of porphyrin complexes of chromium, manganese and iron in the presence of O_2, peracids, hydroperoxides, *N*-oxides or iodosylarenes as terminal oxidant [5, 6]. It is generally agreed that these systems generate a high valent metal-oxo species which participates in a rebound mechanism to shuttle an oxygen atom to a hydrocarbon [7].



L = ligand, O = oxidant

We sought macrocyclic ligands for transition metals that might offer a wider range of synthetic architectures for the construction of a substrate binding site adjacent to the metal oxidation site. There are only a few examples of non-porphyrinic metal complexes which catalyze hydrocarbon hydroxylation or olefin epoxidation [8]. Although most first row transition metals have been shown to mediate olefin epoxidation under some conditions, nickel was conspicuously absent from this list when we began this work. This was surprising in light of the vast amount of research directed toward nickel polyamine complexes [9] and the discovery of a tetraaza-macrocyclic nickel complex, Factor F_{430}, present in a redox enzyme [10]. Since the cyclam[1] ligand is well known to stabilize the Ni(III) oxidation state [11] and certain polyamine complexes have allowed generation of the Ni(IV) state [12] we undertook a program of study using tetraaza-macrocyclic nickel complexes as oxidation catalysts.

2.1. USE OF NICKEL(II) CYCLAM COMPLEXES WITH IODOSYLBENZENE

Concurrent work in our laboratory [13] and in Kochi's [14] has shown that Ni(II) cyclam complexes act as catalysts for olefin epoxidation and, to a lesser extent, alkane hydroxylation when iodosylbenzene (PhIO) is used as terminal oxidant.

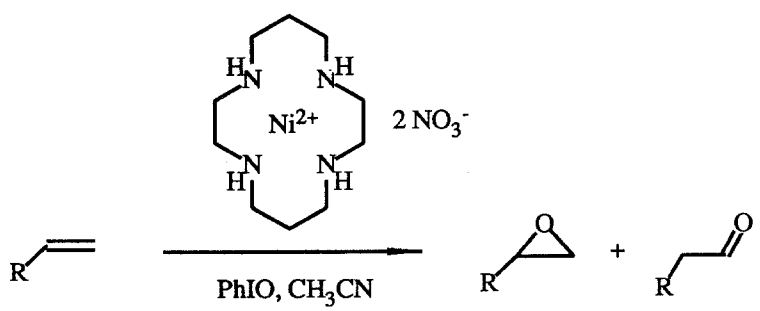
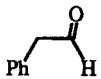
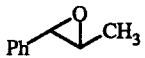
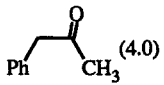
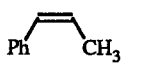
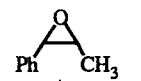
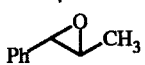
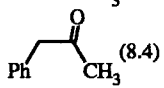
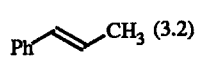
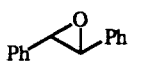
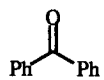
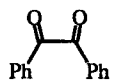
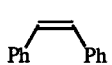
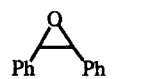
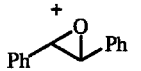
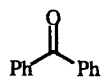
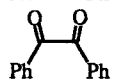
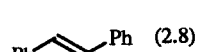
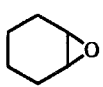
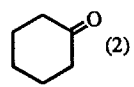


Table I. Products of Ni(cyclam)$(NO_3)_2$-catalyzed oxidation of phenyl-substituted alkenes using PhIO as terminal oxidant[a,b]

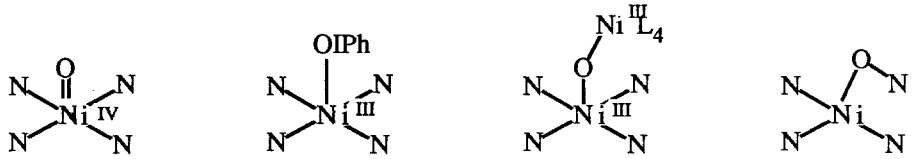
entry	substrate	products (% yield)[c]					
1		 (26)	 (2.7)	 (4.2)			
2		 (60)	 (3.0)	 (4.0)			
3		 (18) +  (15)	 (8.0)	 (8.4)		 (3.2)	
4		 (31)[d]	 (8.8)	 (5.2)	 (2.3)		
5		 (4.1) +  (3.8)	 (9.0)	 (3.6)	 (1)	 (2.8)	
6		 (30)	 (2)	 (5)	 (3)		

[a] Reaction time = 5 hr. [b] See text for standard reaction conditions. [c] Based on olefin. [d] About 1% Z-isomer formed.

The reaction conditions are mild but an excess of oxidant is required for high yields of oxidized products. In a typical experiment, 0.1 mmol $Ni(NO_3)_2$, 0.5 mmol olefin, and 2.0 mmol PhIO in 5.0 mL dry degassed CH_3CN were allowed to react at room temperature for 2–5 hours. Most of the PhIO is consumed within the first hour of the reaction. The yields of oxidized products based on starting olefin are listed in Table I [15]. Low turnover is likely due to the competitive oxidation of CH_3CN as solvent. Nearly quantitative yields of products could be obtained if additional aliquots of PhIO were added to the reaction at intervals.

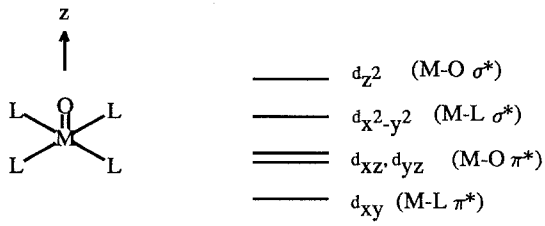
Consideration of the oxidation products of the reactions lends insight into the mechanism of the reaction. Any mechanistic proposal must account for the following facts: (i) The reaction proceeds faster with *E*-olefins than with *Z*. This is contrary to most reports of metal-catalyzed epoxidations. In addition, partial isomerization of *Z* to *E*-alkenes is observed. (ii) Only partial retention of configuration is observed. This is evident from the study of *Z*-stilbene and *Z*-β-methylstyrene. (iii) Over-oxidation to give products of C=C bond cleavage (e.g. benzaldehyde) is observed, and the yield of such products increases if O_2 is added to the reaction medium. (iv) Rearranged products such as phenylacetaldehyde are produced in small amounts. (v) Both oxygen atom transfer to alkenes (epoxidation) and C—H hydrogen atom abstraction reactions are observed (cf. cyclohexene).

If the reaction mechanism is in any way similar to that proposed for Cr(III), Mn(III) and Fe(III) porphyrin complexes, the first step of the reaction involves formation of a nickel-oxo intermediate. There are several possible formulations of such an intermediate, shown as **I–IV** below.

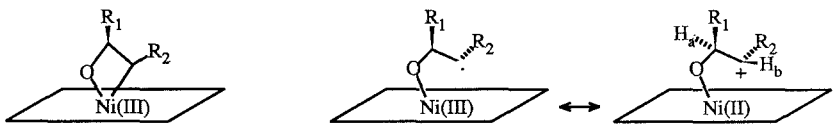


I II III IV

Species **I**, a macrocyclic $L_4Ni{=}O$ structure, is drawn by analogy to iron-oxo-porphyrin complexes. The bonding scheme for the nickel complex suggests that formulation of a Ni=O double bond may not be justified. Theoretical studies of d^4 metals support the molecular orbital picture shown below [16]. A d^6 Ni(IV) species would not have empty d_{xz}, d_{yz} orbitals available for π bonding to oxygen.



The nickel-oxo species **I** might be better formulated as the oxyanion Ni(IV)—O^- or a Ni(III)—$O^\cdot$ oxy radical. No nucleophilic behavior typical of an oxyanion has been observed in this reaction. In fact, a Hammett study of *p*-substituted styrenes gave a linear correlation ($r^2 = 0.998$) with σ^+ [15]. The observed ρ^+ value of -0.82 is consistent with electrophilic character of the oxygen atom attack at an olefin and is in the same general range observed for metal-oxo-catalyzed olefin oxidations [17]. The results in Table I are also consistent with the formation of a nickel-oxo species with considerable radical character. Addition of a radical species to an oelfin would be expected to proceed more rapidly with, for example, *E*-stilbene. The intermediate carbon radical generated would be resonance stabilized. Resonance stabilization could only be achieved with the non-planar substrate *Z*-stilbene after C—C bond rotation, consequently, its transition state for formation would be higher in energy. Concerted formation of an oxametallacyclobutane **V** is ruled out by the observation of only partial retention of configuration in epoxide products [18]. Rather, an intermediate **VI** is implied – one with dual radical/carbocation character.[2]

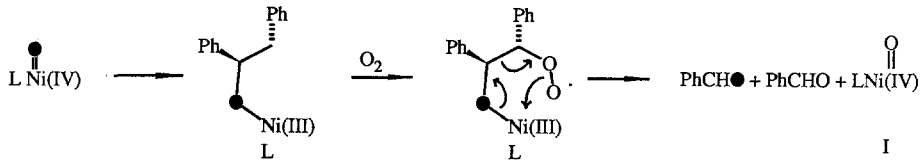


V VIa VIb

The fate of radical **VIa** may be reductive elimination to produce an epoxide or trapping by O_2 to lead to over-oxidation products. Structure **VIb** is essentially a resonance structure of **VIa** and suggests a pathway for the migration of H or Ph to yield the products phenylacetaldehyde, phenylacetone or benzophenone.

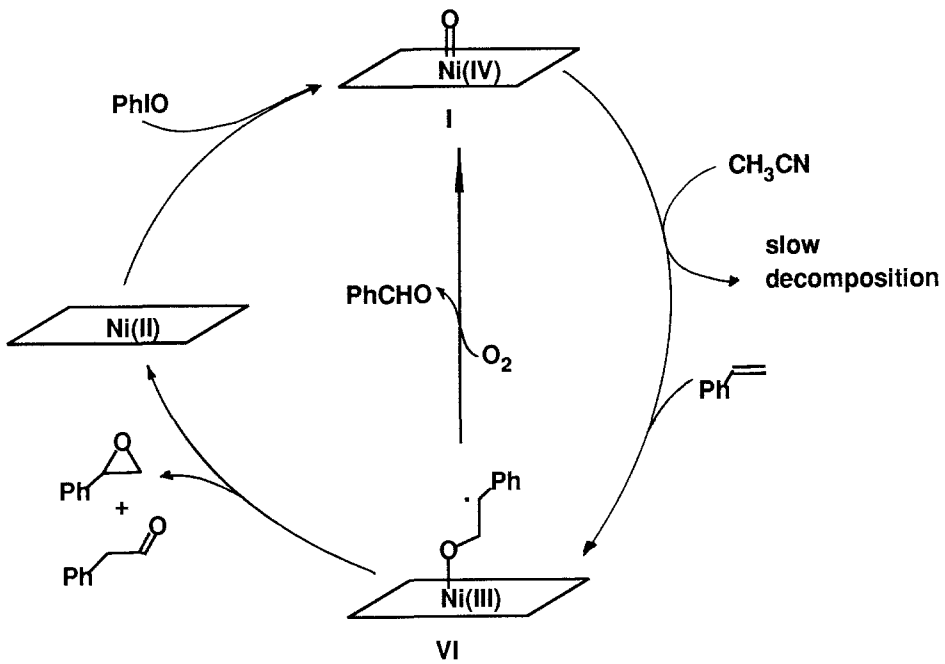
The mechanism of C=C bond cleavage in the presence of O_2 was also studied by analyzing the ^{18}O content of products when $PhI^{18}O$ was used as terminal oxidant. In the absence of O_2, essentially 100% of the oxygen content of the epoxide products originated from $PhI^{18}O$. Examination of the ^{18}O content of benzaldehyde was more informative. When derived from *E*-stilbene, benzaldehyde showed a 45% incorporation of ^{18}O; the corresponding value for styrene as starting material was 2%. These results agree with intermediate **VIa** in which R_2 is always Ph and R_1 is either Ph or H. An ^{18}O atom from PhIO would always produce a label at the R_1 carbon. In these studies, dioxygen was present at very low concentration and was unlabeled. If the concentration of O_2 was increased by continuous bubbling through the reaction mixture, *the* ^{18}O *content of all products was diminished.* We have proposed a pericyclic mechanism of the Ni-oxo-olefin-O_2 adduct which is consistent with these observations [15]. This mechanism regenerates the nickel-oxo intermediate **I** in unlabeled form and provides further support for the existence of **I** as the first intermediate in the reaction sequence.

This scheme suggests an overall pathway for nickel cyclam-catalyzed oxidation of olefins which uses PhIO stoichiometrically to produce a high valent nickel-oxo intermediate capable of three different types of reactions. One pathway is H atom



^{18}O label shown as ●.

abstraction from hydrocarbons; this reaction may occur slowly with solvent molecules as well. A second pathway is the anticipated olefin epoxidation route. A third reaction uses O_2 stoichiometrically to cleave C=C bonds and regenerates the catalytically active oxidant. Studies are under way to exploit this third process since it is catalytic in PhIO.

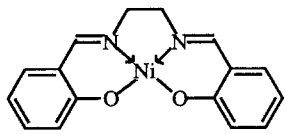


Scheme I.

2.2. USE OF NICKEL(II) SALEN COMPLEXES WITH HYPOCHLORITE

A number of problems arose in the use of iodosylbenzene as terminal oxidant for olefin oxidation. The compound is a relatively expensive oxidant and was used in large excess in order to give good reaction yields. In addition, PhIO is only sparingly soluble in most solvents so that the heterogeneous nature of the reaction makes quantitative kinetic or spectroscopic analysis difficult. In a survey of other

oxygen atom donor reagents, we found that tert-butyl hydroperoxide, *N,N*-dimethyl-*p*-cyanoaniline-*N*-oxide, $NaIO_4$ and H_2O_2 were unreactive as terminal oxidants. On the other hand, use of sodium hypochlorite under phase transfer conditions similar to those discovered by Meunier [19] lead to efficient olefin oxidation [20]. This reaction solves some of the problems of PhIO: NaOCl is inexpensive, only a two to four-fold excess of the oxidant is used, and the reaction is more nearly homogeneous, at least in the organic phase. The best catalyst under these conditions was Ni(II) salen.



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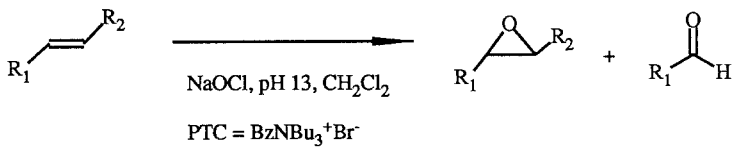


Typical reaction conditions involved 4.0 mmol olefin, 1 mmol nickel complex and 0.15 mmol benzyltributylammonium bromide in 10 mL CH_2Cl_2 to which 20 mL 0.77 M NaOCl (pH 13) were added. A fine black precipitate is formed immediately upon mixing which may be nickel peroxide. This material was shown to be inert toward olefin oxidation and disappeared later in the reaction when all the oxidant was consumed. Table II lists the yields of styrene oxide formed from oxidation of styrene as a function of the nickel complex. The best results were obtained using Ni(II) salen as catalyst.

A summary of the reactions of various hydrocarbon substrates is given in Table III. For aryl-substituted alkenes, epoxidation is the major pathway, but substantial amounts of C=C bond cleavage to carbonyl compounds was also observed. As in the nickel cyclam-catalyzed reactions with PhIO, the reaction showed a slight preference for *E*-stilbene over the *Z*-isomer; however, the epoxide product in both cases was exclusively the *E*-isomer. This may reflect a longer-lived nickel-oxo-olefin

Table II. Yields of styrene oxide as a function of catalyst[a]

Catalyst	% Yield
Ni(II) salen	44.3
Ni(II) cyclam $(OTf)_2$	4.7
Ni(II) TPP	0
$Ni(OAc)_2$	trace
no catalyst[b]	0.7

[a] 6 hr reaction time; see text for standard reaction conditions.
[b] 18 hr reaction time.

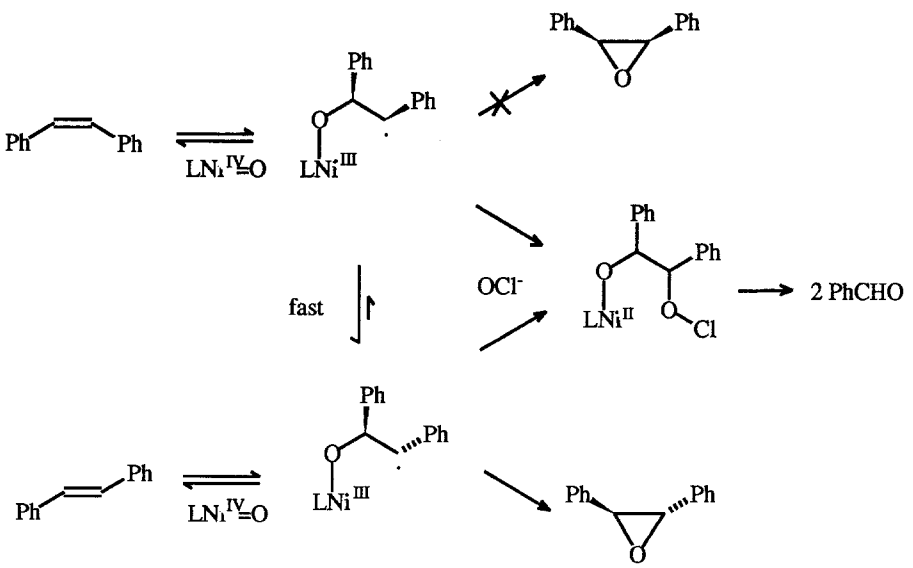
Table III. Percent conversion and yields of products from Ni^{II} (salen)-catalyzed oxidation of alkenes by OCl^- after 5 hours

substrate	% conversion[a]	epoxide[b]	PhCHO[c]	selectivity[d]
styrene	98	44	6	45
Z-β-methylstyrene	100	84[e]	10	84
E-β-methylstyrene	100	89[e]	0	89
Z-stilbene	45	12[e]	12	27
E-stilbene	80	46[e]	0	58
cyclohexene	87	23		26
norbornene	94	30[f]		32

[a] Disappearance of starting material. [b] Based on starting alkene. [c] Remainder of product is $PhCO_2H$. [d] Epoxide yield/% conversion. [e] *E*-epoxide only. [f]*exo*-epoxide only.

intermediate capable of rapid C—C bond rotation prior to reductive elimination. The epoxidation of alkyl olefins was complicated by the production of substantial amounts of chlorinated products.

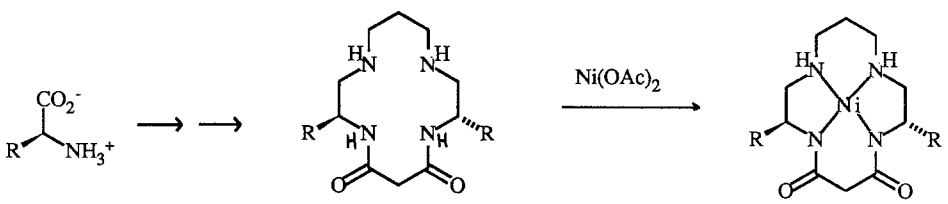
Overall, the reaction of Ni(II) salen/NaOCl with olefins bears considerable similarity to that of the Ni(II) cyclam/PhIO system. Production of C=C bond cleavage products is only modestly affected by the presence or absence of O_2. A mechanistic scheme is suggested below that accounts for the formation of benzaldehyde from stilbene by reaction with two equivalents of hypochlorite. In future work, it will be important to control the relative amounts of the epoxidation vs. C=C cleavage pathways and to minimize chlorination reactions.



Scheme II.

2.3. USE OF NICKEL(II) DIOXOCYCLAM COMPLEXES WITH HYPOCHLORITE

From the studies described above, it is evident that certain 14-membered square planar chelating rings containing strong donor atoms render Ni(II) salts active as oxidation catalysts. To approach our ultimate goal of incorporating substrate binding sites adjacent to the catalytic site, it is necessary to use a macrocycle that possesses additional functional groups as points of attachment. Ideally, this macrocycle should also be optically active in order to avoid the complications of mixtures of diastereomeric ligands and to provide the possibility of chiral recognition. We chose to explore analogs of the dioxocyclam ligand since its ability to stabilize the Ni(III) oxidation state was well known [21]. Our unsubstituted ligands are derived from amino acids and contain two stereogenic units. We have developed a general synthetic route to the ligands **VIIa–d** from phenylalanine, tryptophan, valine and leucine.



VII

a R=CH_2Ph

b R= 3-indolemethyl

c R=$CH(CH_3)_2$

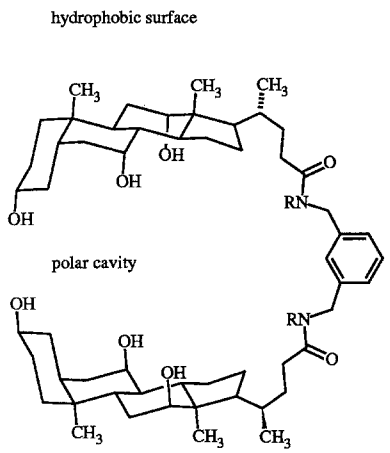
d R=$CH_2CH(CH_3)_2$

Macrocycle **VIIa** readily forms the doubly deprotonated nickel complex upon addition of $Ni(OAc)_2$. The methylene chloride soluble complex was unreactive under reaction conditions similar to those employed in the nickel cyclam/PhIO system. However, oxidation of *E*-β-methylstyrene occurred readily when the hypochlorite phase transfer conditions were used. Epoxidation represented about 50% of the reaction pathway with the remainder yielding a mixture of benzaldehyde and other over-oxidation products.

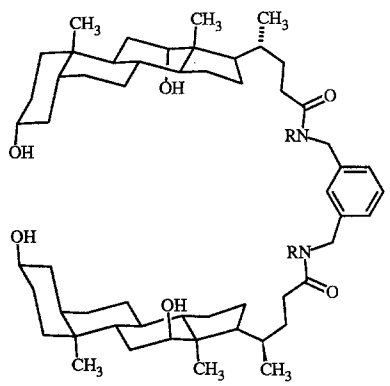
In summary, a variety of square planar macrocyclic nickel complexes are capable of catalysis of olefin oxidation using strong terminal oxidants. With knowledge of the reaction mechanism and suitable functionalization of the periphery of the macrocycle, new catalysts might be developed which show high substrate selectivity as well as interesting regio- and stereochemistry.

3. Design of New Molecular Receptors for Neutral Molecules

For the organic chemist, synthetic reactions are most conveniently carried out in organic solvents. Reactions involving nucleophiles or bases are often more rapid in non-polar solvents due to poor solvation of polar species. For these reasons, we have focussed our attention upon the design of new molecular receptors which are soluble in non-polar solvents, but which possess a hydrogen-bonding cavity for the inclusion of polar substrates. In the design of a new receptor, we sought a structure with convergent hydrogen-bonding groups surrounded by a superstructure of overall hydrophobic character. Cholic acid was therefore an ideal building block for this purpose since it is a highly functionalized, rigid steroid with the amphophilic properties of a detergent. Our first generation receptors are diamides derived from condensation of two cholic acid molecules with simple diamines [22].



VIII



IX

The properties of the cholic acid dimers **VIII** have been compared to the deoxycholate analogs **IX** in order to give information about the importance of the hydrogen-bonding hydroxyl groups. Examination of the ^{1}H-NMR spectra of compounds **VII** and **IX** (R = H) under various conditions displayed interesting behavior of the two receptors. The diastereotopic benzylic hydrogens of **VIII** were doublets of doublets under all conditions, but the chemical shifts of these two hydrogens in particular were temperature and solvent dependent. At low temperature in dry $CDCl_3$ the resonances were separated by about 1 ppm. Near 65°, the peaks converged to the point of having nearly the same chemical shift. The same phenomenon was observed for the deoxycholate analog **IX**, except that the low temperature separation was smaller and the temperature of convergence was lower. These data are plotted in Figure 1.

This phenomenon of peak convergence as a function of temperature could be reproduced at room temperature by incremental addition of a hydrogen-bonding

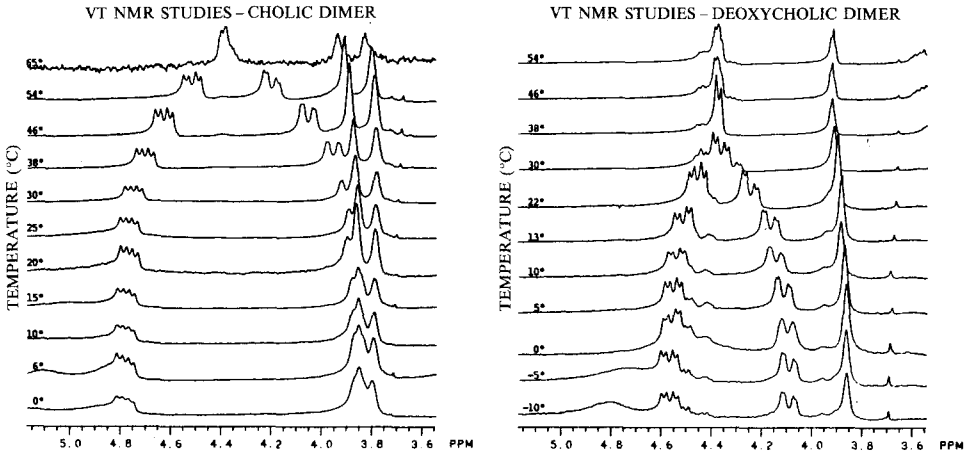


Fig. 1.

solvent such as methanol (see Figure 2). In contrast, the spectrum of *N*-benzylcholamide shows a collapsed multiplet at 4.4 ppm for the benzylic protons under all conditions.

An explanation consistent with these results is that the cholamide dimers may exist in two limiting conformations. In non-polar solvents and in the absence of hydrogen-bonding substrates, **VIII** may exist in a folded conformation with intramolecular hydrogen bonds (Figure 3). We are not currently able to detect whether or not one or two water molecules might also be present and acting as bridging groups between cholate hydroxyls as is seen in the crystal structure of cholic acid [23]. The addition of heat or methanol would be expected to break

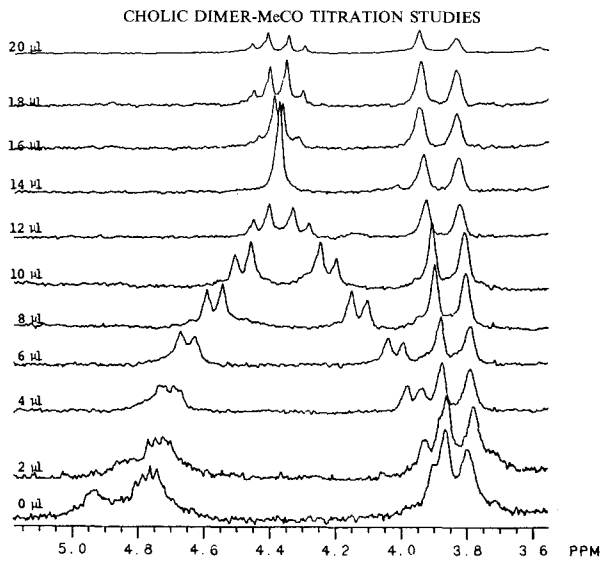


Fig. 2.

hydrogen bonds and generate an open, freely rotating species. The closed conformation would have a rigid structure with the two benzylic hydrogens in potentially quite different chemical environments. The open form would allow for near averaging of these environments through rotation.

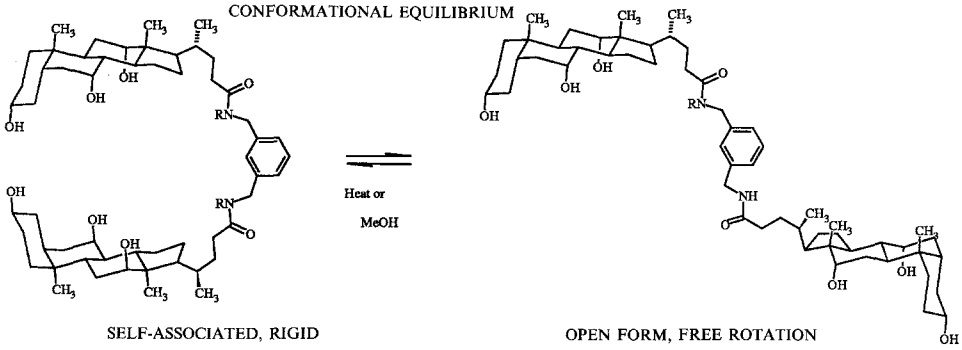


Fig. 3.

An interesting consequence of these experiments is that we can use this phenomenon of temperature convergence of signals as an indication of substrate binding. If a substrate hydrogen bonds in the central cavity between the two cholate moieties, one would anticipate a stabilization of the closed form resulting in well-separated NMR signals. This would lead to a higher temperature of convergence of the signals. A very interesting result that we have obtained in this area is such an observation using n-pentylglucopyranoside as substrate. A 1 : 1 molar ratio of **VIII** and the glucoside were studied at various temperatures in anhydrous $CDCl_3$. The results at 56° are shown in Figure 4. In the presence of substrate, convergence of signals had occurred *to a lesser extent, consistent with binding.*[3] Introduction of water or other solvent impurities would have led to the opposite result. This is an unusual example of binding of a carbohydrate derivative to a synthetic molecular receptor. By further synthetic elaboration of the receptor we hope to increase its binding strength and selectivity for polar substrates.

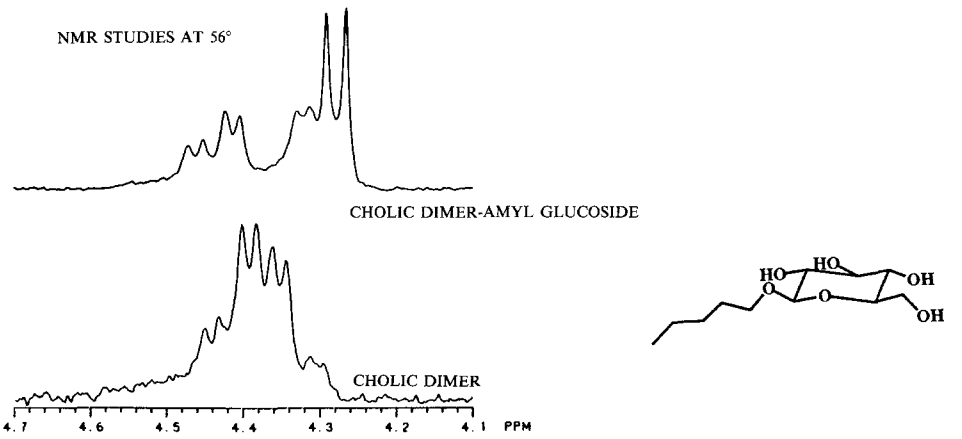


Fig. 4.

4. Prospects for the Future

Inclusion phenomena range from the encapsulation of single atoms to the binding of complex organic molecules. In the case of transition metal ions, the encapsulating ligand may have a profound effect on the reactivity of the metal ion particularly in the case of redox processes. For organic substrates, synthetic molecular receptors offer the possibility of dissolution in unusual media and orientation relative to approaching reagents. Progress in both the design of new catalytic species and of effective binding agents will accelerate the success of chemists in mimicry of biological catalysts.

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Notes

[1]Abbreviations used: cyclam = 1,4,8,11-tetraazacyclotetradecane; salen = *N,N'*-ethylenebis(salicylideneamine); TPP = 5,10,15,20-tetraphenylporphyrin.

[2]These structures are formally resonance forms only if no nuclear motion accompanies electronic reorganization.

[3]We have not eliminated the possibility of aggregation phenomena. Low solubility of **VIII** (R = H) has limited determination of solution molecular weights by vapor pressure osmometry.

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