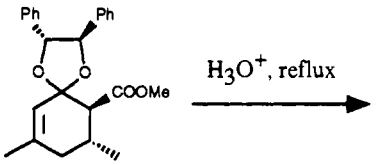
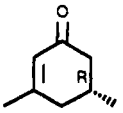
steric considerations prevail. Enantiomerically pure hydrobenzoin is also isolated in good yield.





lit $[\alpha]_D = -138^\circ$

$[\alpha]_D = -61^\circ$

Current work in these laboratories include studies on solvent effects,[20] Lewis acid catalysis,[21] and pressure[22] on the course of these reactions. The use of this methodology in the total synthesis of more complex organic molecules is also in progress, and results from these efforts will be reported as they become available.[23]

Supplementary Material Available: Experimental details for the synthesis of **6** and the Diels-Alder reaction between **6** and *N*-methylmaleimide (4 pages). Ordering information is given on any current masthead page.

(20) For recent discussions on the effect of solvents on the Diels-Alder reaction, see: (a) Breslow, R.; Guo, T. *J. Am. Chem. Soc.* **1988**, *110*, 5613-7. (b) Dunams, T.; Hoekstra, W.; Pentaleri, M.; Liotta, D. *Tetrahedron Lett.* **1988**, *29*, 3745-8.

(21) (a) Evans, D. A.; Chapman, K. T.; Bisha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238-56. (b) Narasaka, K.; Inoue, M.; Yamada, T.; Sugimori, J.; Iwasawa, N. *Chem. Lett.* **1987**, 2409-12. (c) Chapuis, C.; Jurczak, J. *Helv. Chim. Acta* **1987**, *70*, 436-40.

(22) For a general discussion of the use of high pressure in the Diels-Alder reaction, see: Matsumoto, K.; Sera, A. *Synthesis* **1985**, 999-1027.

(23) Research support by the UC Santa Cruz Committee on Research and the American Cancer Society is gratefully acknowledged.

Substrate Selectivity in Epoxidation by Metalloporphyrin and Metallosalen Catalysts Carrying Binding Groups[1]

Ronald Breslow,* Alan B. Brown,[2] Richard D. McCullough, and Peter W. White[3]

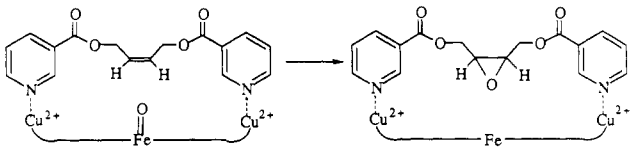
Department of Chemistry, Columbia University
New York, New York 10027

Received February 7, 1989

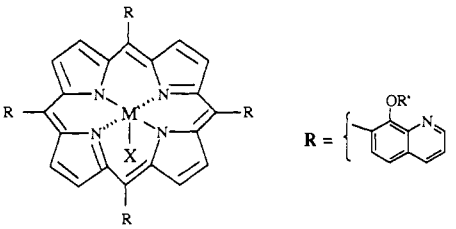
Despite extensive studies of hydroxylation and epoxidation reactions catalyzed by metalloporphyrins and other metal complexes, there are almost no examples of systems using auxiliary binding groups to select particular substrates. The most striking case is the recent example reported by Groves,[4] in which a steroid substrate is epoxidized or hydroxylated by a metalloporphyrin catalyst carrying substituents that create a shape-selective pocket in a micelle.

For some time we have been interested in constructing systems that can mimic the selectivities of enzymes in oxidations and other reactions[5] and have used metal binding as a force to hold substrates and catalysts together.[6] We have also described a system in which double binding (by ion pairing) of a substrate to a reagent was particularly effective in promoting selective functionalization of the substrate.[7] We now wish to report examples of the selective functionalization of substrates that can doubly bind to a metalloporphyrin at appended metal ligand groups (Scheme I) and also to a related non-porphyrin metal epoxidation catalyst.

Scheme I

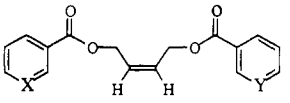


Reaction of 8-methoxyquinoline-7-carboxaldehyde with pyrrole in propionic acid afforded the free base porphyrin **1a**.[8,9] This was metalated to form **1b**,[10] which with BBr_3 yielded **1c**.[11]

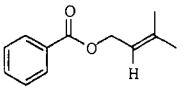


1a M = $2H^+$, X not present, R' = Me
1b M = Fe(III), X = Br, R' = Me
1c M = Fe(III), X = Br, R' = H

Addition of Cu^{2+} to **1c** produces a catalyst in which some of the atropisomers can bind appropriate substrates across the face of the metalloporphyrin, in a position to be epoxidized by the Fe=O intermediate.[12] As a double binding substrate we selected the bis-nicotinate **2a**.[13] We also examined the single binding substrate **2b** and with the salen catalyst the nonbinding analogue **2c**.



2a X = Y = N
2b X = N, Y = CH
2c X = Y = CH



3

All substrates were epoxidized with catalyst and PhI=O in direct competition with the nonbinding substrate prenyl benzoate (**3**), and 400 MHz proton NMR spectra were used (excess phenanthroline was added to complex the Cu^{2+}) to determine the extent of epoxidation of **2** and **3**; we define the ratio of **2**-epoxide/**3**-epoxide as the *selectivity*, *S*. Solutions containing 0.0125 mmol of both substrates in 14 mL of acetonitrile were allowed to react with 10% of porphyrin **1c** and 60% of PhI=O, with or without the addition of 4 equiv of $Cu(ClO_4)_2 \cdot 6EtOH$. Under these conditions the maximum conversion of **2a** to its epoxide was 18%, so the substrate ratios stayed fairly constant throughout the reaction. Control reactions with PhI=O and Cu^{2+} (in the presence or absence of bipyridyl) without **1c** led to <1% epoxidation of either substrate, so we are not dealing with copper-catalyzed oxidation chemistry.[14] Such copper catalysis would in any case

(1) Support of this work by the NSF and the NIH are gratefully acknowledged. Mass spectral determinations of salens were performed by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (CHE 8620177).

(2) Recipient of an NIH postdoctoral fellowship.

(3) Recipient of an NSF predoctoral fellowship.

(4) Groves, J. T.; Neumann, R. *J. Am. Chem. Soc.* **1987**, *109*, 5045.

(5) Breslow, R. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1986**, *58*, 1-60.

(6) Breslow, R.; Chipman, D. *J. Am. Chem. Soc.* **1965**, *87*, 4195.

(7) Breslow, R.; Rajagopalan, R.; Schwarz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2904.

(8) For the preparation of other isomers, with the wrong geometry for our reactions, cf.: Sugata, S.; Matsushima, Y. *Chem. Pharm. Bull.* **1987**, *35*, 2623-2626.

(9) MS, FAB 939 (M + 1). ^1H NMR consistent with the structure.

(10) ^1H NMR (200 MHz, CD_2Cl_2) of $Fe^{II}(pyridine)_2$ complex consistent with the structure, including several peaks in the δ 3.81-2.76 region with a total area of 12 protons for the CH_3 groups of the various atropisomers.

(11) Crystallized from chloroform/hexane. Anal. Found (Calcd for $C_{56}H_{32}N_8O_4FeBr \cdot 7H_2O$): C, 59.08 (58.86); H, 3.41 (4.06); N, 9.74 (9.81); Fe 4.24 (4.89). The ^1H NMR spectrum of the reduced $Fe^{II}(pyridine)_2$ complex showed the expected peaks.

(12) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884.

(13) All substrates and the corresponding epoxide products were characterized by ^1H NMR and mass spectroscopy.

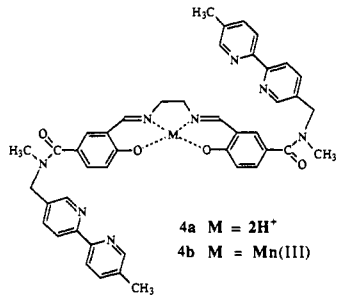
0002-7863/89/1511-4517$01.50/0

be inconsistent with the findings reported below, particularly the dependence of selectivity on the particular substrate and the particular catalyst used.

The bis-nicotinate **2a** had essentially half the reactivity of prenyl benzoate (**3**) with catalyst **1c** in the absence of added Cu^{2+} (S = 0.5), but with 4 equiv Cu^{2+} per catalyst there was a 20/1 preference for epoxidizing the doubly binding substrate **2a** (S = 20), a 40-fold increase in S. With the singly binding substrate **2b** the addition of Cu^{2+} enhanced S by only 2-fold, to S = 1. In our earlier studies with ion pairing we had also seen that binding both ends of a substrate, to stretch it across a reactive center, is much more effective than is simple binding of one end.[7]

Molecular models show that a substrate related to **2a** but with isonicotinate groups cannot productively bridge across catalyst **1c** as in Scheme I. As expected, we find that its reactivity in competition with **3** is *not* increased on the addition of Cu^{2+}. Also consistent with double binding of substrate **2a** to catalyst **1c** via Cu^{2+} bridging (Scheme I) is our finding that in the absence of Cu^{2+} up to 9% of the epoxide of **2a** is trans, but in the presence of Cu^{2+} the product is >99% cis. The stereospecific formation of *cis*-epoxide is expected if the two ends are immobilized.

The salen catalyst precursor **4a**[15] was prepared from the cor-



responding salicylaldehyde derivative and converted to the Mn^{III} derivative as the PF_6^- salt **4b**.[16] Since **4b** was not soluble in acetonitrile in the absence of Cu^{2+}, the bis-copper complex of **4b** was compared with the Mn^{III} complex of salen itself (**4b** without the bipyridyl appendages) under conditions similar to those above. The double binding substrate **2a** had S of 0.029 with salen-Mn^{III} (the intrinsically lower reactivity of **2a** relative to **3** is accentuated with this more discriminating catalyst), but with the **4b** bis-copper complex this relative reactivity increased by 43-fold to S = 1.24. The nonbinding substrate **2c** increased its selectivity (S = 0.036 with salen-Mn^{III}) by less than 2-fold to S = 0.06. Interestingly, in the salen series even the singly binding substrate **2b** showed a 30-fold increase in S (to 1.0) on changing salen-Mn^{III} to the bis-copper complex of **4b**.

The contrast with the porphyrin case, where double binding was much more effective than single coordination, may reflect the high flexibility of catalyst **4b** compared with the rigid **1c**. Consistent with this, even the bis-isonicotinate ester related to **2a** gave an increased selectivity of 30-fold with the Cu^{2+}/**4b** complex, so this flexible catalyst can adapt to the different geometry of the isonicotinate. The substrates must be chiefly singly bound to the salen catalyst, judging from the small presumably just statistical advantage of **2a** over **2b**. As expected from this we find that with catalyst **4b** all the substrates, under all conditions, show the nonstereospecific formation of epoxide containing ca. 7% of the trans isomer.

Molecular models indicate that double binding of substrate **2a** to catalyst **1c** should indeed hold the double bond over the oxygen of a Fe=O intermediate. Thus the observed selective epoxidation is expected (but the formation of a metallooxetane intermediate, as in some mechanistic proposals,[17] looks almost impossible). Furthermore, with only 1% of the tetra-Cu^{2+} complex of **1c** we see eight turnovers in the epoxidation of **2a**, so we are dealing with true turnover catalysis. It remains to be seen whether the use of metal ions in these two ways—one to perform epoxidation and the others to bind substrates—proves to be a useful general procedure, as is the Sharpless oxidation[18] in which substrates bind to the catalytic metal. In any case, with the addition of selective multipoint substrate binding the catalyst **1c** increasingly resembles the P-450 enzymes which inspire this entire field.

(14) Tai, A. F.; Margerum, L. D.; Valentine, J. S. *J. Am. Chem. Soc.* **1986**, *108*, 5006.

(15) Anal. Found (Calcd for $C_{44}H_{42}N_8O_4$): C, 70.83 (70.76); H, 5.85 (5.67); N, 14.77 (15.00). MS, FAB 747 (M + 1).

(16) Anal. Found (Calcd for $C_{44}H_{40}N_8O_4MnPF_6 \cdot 3H_2O$): C, 53.28 (52.91); H, 4.40 (4.04); N, 11.04 (11.22); F, 11.21 (11.41); Mn, 5.34 (5.50). MS, FAB 800 (M + 1).

(17) Collman, J. P.; Brauman, J. I.; Meunier, B.; Raybruck, S. A.; Kodadek, T. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 3245.

(18) Sharpless, K. B.; Woodard, S. S.; Finn, M. G. *Pure Appl. Chem.* **1983**, *55*, 1823.

A New Structure Type in Polyoxoanion Chemistry: Synthesis and Structure of the $V_5O_{14}^{3-}$ Anion

V. W. Day,*[1a] W. G. Klemperer,*[1b] and O. M. Yaghi[1b]

Department of Chemistry, University of Nebraska
Lincoln, Nebraska 68588
Crystalytics Company
Lincoln, Nebraska 68501
Department of Chemistry, University of Illinois
Urbana, Illinois 61801

Received February 22, 1989

The $Mo_2O_7^{2-}$[2] and α-$Mo_8O_{26}^{4-}$[3] anions are soluble in aprotic, polar solvents as tetra-*n*-butylammonium salts and have proved to be suitable starting materials for the synthesis of numerous covalent polyoxomolybdate derivatives.[4] Since analogous unprotonated polyvanadate salts might serve as the starting point for the synthesis of polyoxovanadate derivatives, we have begun to explore the chemistry of tetra-*n*-butylammonium isopolyvanadates. We report here the first structurally characterized[5] species of this type,[6] $V_5O_{14}[(n\text{-}C_4H_9)_4N]_3$.

When 4.5 mL of 0.41 M $[(n\text{-}C_4H_9)_4N]OH$ in CH_3CN (1.8 mmol)[7] is added with stirring to a solution of 0.97 g (0.58 mmol) of $H_3V_{10}O_{28}$ $[(n\text{-}C_4H_9)_4N]_3$[8] in 25 mL of CH_3CN at ambient temperature, the resulting solution contains at least four different polyvanadates according to ^{51}V NMR spectroscopy. This dark orange solution can be converted to a virtually colorless solution containing a single polyvanadate species (see eq 1) by filtering

$$H_3V_{10}O_{28}^{3-} + 3OH^- \xrightarrow{\Delta} 2V_5O_{14}^{3-} + 3H_2O \qquad (1)$$

off a small amount of insoluble material and then reducing the

(1) (a) University of Nebraska and Crystalytics Company. (b) University of Illinois.

(2) (a) Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 6146. (b) Hur, N. H.; Klemperer, W. G.; Wang, R.-C. *Inorg. Synth.*, in press.

(3) (a) Fuchs, J.; Hartl, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 375. (b) Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1976**, *98*, 8291. (c) Hur, N. H.; Klemperer, W. G.; Wang, R.-C. *Inorg. Synth.*, in press.

(4) For representative studies, see: (a) Day, V. W.; Klemperer, W. G. *Science (Washington, D. C.)* **1985**, *228*, 533. (b) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1831. (c) Chilou, V.; Gouzerh, P.; Jeannin, Y.; Robert, F. *J. Chem. Soc., Chem. Commun.* **1987**, 1469. (d) Kang, H.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1988**, 1192.

(5) $V_{10}O_{28}[(n\text{-}C_4H_9)_4N]_6$ has been reported but not structurally characterized: Fuchs, J.; Mahjour, S.; Palm, R. *Z. Naturforsch.* **1976**, *31B*, 544.

(6) Several polyvanadic acid salts have been prepared that are soluble in organic solvents. (a) $HV_4O_{12}^{3-}$: Fuchs, J.; Mahjour, S.; Pickardt, J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 374. (b) $H_3V_{10}O_{28}^{3-}$: Day, V. W.; Klemperer, W. G.; Maltbie, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 2991 and references cited therein. (c) $H_2V_{10}O_{28}^{4-}$ and $HV_{10}O_{28}^{5-}$: ref 5 and Corigliano, F.; DiPasquale, S. *Inorg. Chim. Acta* **1975**, *12*, 99.

(7) Prepared from 1.0 M methanolic $(n\text{-}C_4H_9)_4NOH$ (Aldrich) by solvent removal under vacuum at 35-40 °C in a rotary evaporator and addition of acetonitrile. This sequence of solvent removal and addition of acetonitrile was repeated three times.

(8) This material can be prepared in 86% yield by using the procedure described in ref 6b but recrystallizing from acetonitrile/ether: Klemperer, W. G.; Yaghi, O. M. *Inorg. Synth.*, in press.

0002-7863/89/1511-4518$01.50/0