and hydrogen charge ratios, respectively: CH_4/C_2H_6, (−0.255/−0.191) = 1.34 [1.39], (0.064/0.064) = 1.00 [1.04]; C_2H_6/C_2H_4, (−0.191/−0.138) = 1.38 [1.35], (0.064/0.069) = 0.93 [0.90]; C_2H_4/C_3H_6, (−0.138/−0.138) = 1.00 [0.98], (0.069/0.069) = 1.00 [0.98]; C_2H_4/C_2H_2, (−0.138/−0.074) = 1.87 [1.28], (0.069/0.074) = 0.93 [0.64]. Hydrogens are getting more positive, as required, and the matching to Mulliken ratios is improved for both carbon and hydrogen. This example shows how the simplicity of eq 1 can be employed to separate different effects influencing atomic charge and help identify their origin. Lewis–Langmuir/Mulliken charge ratios for F and Cl each in two different environments show notable commonality: FH, (−0.302/−0.517) = 0.58; F_3Cl, (−0.183/−0.308) = 0.59; ClH, (−0.125/−0.242) = 0.52; ClF_3, (0.546/1.34) = 0.41. Separation of charge between atoms in functional groups, e.g., CO and CN, is also an important test, and the ratio of charge shifts, Lewis–Langmuir/Mulliken, for H_2CO, (−0.333 − 0.205)/(−0.416 − 0.135) = 0.98, and HCN, (−0.307 − 0.243)/(−0.379 − 0.066) = 1.24, shows a similarity in these two charge definitions. Likewise, the corresponding ratio of the large charge shift on H when it changes its attachment from the most electropositive to the most electronegative element, LiH → FH, is (−0.388 − 0.302)/(−0.177 − 0.517) = 0.99. Overall, these examples demonstrate a parallelism between Lewis–Langmuir and Mulliken charges.

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Synthesis and Characterization of the "Chiral Wall" Porphyrin: A Chemically Robust Ligand for Metal-Catalyzed Asymmetric Epoxidations

Sean O'Malley and Thomas Kodadek*

Department of Chemistry
University of Texas at Austin
Austin, Texas 78712

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One of the most important problems in modern organic synthesis is the development of new methods for the enantioselective transformation of prochiral substrates into optically active products. In general, one of the most appealing solutions to this problem is chiral catalysis. Recent years have seen a tremendous growth in the number of practical asymmetric catalysts and some, in particular the Sharpless catalyst for the asymmetric epoxidation of allylic alcohols,[1] are commonly employed in the synthesis of optically active natural products. As part of a program aimed at developing a new family of rationally designed asymmetric catalysts, we have embarked on the construction of optically active tetraarylporphyrin macrocycles. In this report, we describe the synthesis of 5α,10β,15α,20β-tetrakis[(*R*)-1,1′-binaphth-2-yl]-porphyrin ($TBNPH_2$; **1**). Since metalloporphyrins catalyze a number of interesting reactions,[2] porphyrin **1** is a potential general chiral ligand for several enantioselective metal-mediated transformations.

Our approach to $TBNPH_2$ took advantage of the accessibility of optically pure (*R*)-binaphthaldehyde (**2**) by the elegant route of Meyers.[3] Condensation of this aldehyde with pyrrole was effected in methylene chloride at room temperature in the presence of a catalytic amount of BF_3–etherate (Lindsey conditions,[4] Figure 1). Following oxidation of the resultant tetrapyrrole with *p*-chloranil, the crude $TBNPH_2$ was purified by chromatography on a florisil flash column in 9% isolated yield.

The purified material was free of other atropisomers[5] as determined by 1-D and 2-D COSY NMR analyses (Figure 2).[6] The COSY spectrum (data not shown) allowed the unambiguous assignment of *all* resonances in the aromatic region to a single binaphthyl (δ 8.28–6.44, 13 protons). This indicated that the compound was either the α,β,α,β or the α,α,α,α atropisomer, since only those two possibilities have four identical binaphthyls. Proof that this was indeed the α,β,α,β form came from the observation of two singlet β-pyrrolic resonances (δ 8.58, 8.36; 4 protons each)—the spectrum of the α,α,α,α compound would have exhibited two doublets. The remaining atropisomers eluted as an inseparable mixture. Yields of recovered material suggest that the desired α,β,α,β isomer constitutes approximately 40% of the porphyrin product. The porphyrin was readily metallated[7] by standard procedures (Figure 1).

Each identical face of the porphyrin possesses C_2 symmetry. We predicted that a prochiral alkene substrate would prefer to orient one of its enantiofaces toward the active metal center due to nonbonded steric interactions between the olefin substituents and the chiral binaphthyl "walls".

The results of preliminary investigations into the properties of $Mn^{III}TBNPCl$ as an epoxidation catalyst are shown in Table I. Extremely high catalytic efficiency and moderate enantioselectivites for a variety of unfunctionalized olefin substrates were observed. The enantiomeric excesses (ee's) compare favorably with the state-of-the-art for asymmetric epoxidation of unfunctionalized alkenes. For example, Groves and Myers employed a chiral binaphthoic acid derivatized porphyrin as a catalyst for oxygen atom transfer from iodosylbenzene to alkenes. They obtained enantioselectivities ranging from 20 to 51%.[8] A

Table I. Catalytic Asymmetric Epoxidation of Olefins with MnTBNPCl[a]

substrate	enantiomeric excess, %	catalytic efficiency[d]
styrene[b]	20	240
p-chlorostyrene	20	160
2-vinylnaphthalene	20	220
trans-β-methylstyrene	15	190
cis-β-methylstyrene[c]	40	200

[a] Epoxidations were performed following Meunier conditions (hypochlorite as oxidant in a two-phase system, 0.03 mol % catalyst).[10] Chemical yields were calculated by GC analysis. The epoxides were purified by flash chromatography on silica (CH_2Cl_2) and the degree of asymmetric induction was determined by NMR with the chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III).[9] [b] Phenylacetaldehyde, a common side product of porphyrin-catalyzed styrene epoxidations, was not observed. [c] Analysis of the product by ^1H NMR showed a small amount of optically active *trans*-epoxide in addition to *cis*-epoxide (7:1 cis:trans). [d] Number of turnovers in 15 min.

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(2) See for example: Callot, H. J.; Metz, F.; Piechoki, C. *Tetrahedron* **1982**, 2365–2369 (cyclopropanation of alkenes). Battioni, P.; Renaud, J. P.; Bartoli, J. F.; Reina-Artiles, M.; Fort, M.; Mansuy, D. *J. Am. Chem. Soc.* **1988**, *110*, 8462–8470 (hydroxylation of alkanes). Aoyama, Y.; Tanaka, Y.; Yoshida, Y.; Toi, H.; Ogoshi, H. *J. Organomet. Chem.* **1987**, *329*, 251–266 (aldol condensation).

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(5) Four atropisomers are possible depending on which face of the porphyrin plane the second naphthalene of each binaphthyl is situated. Only the desired α,β,α,β has two identical faces—a crucial point since the reaction may occur on either face of the macrocycle. Our choice of Lindsey's mild thermodynamic cyclization conditions was based on the idea that the α,β,α,β suffers the least steric interaction between neighboring binaphthyls and would be formed in greater than statistical proportions.

(6) Independent confirmation that this compound is a single atropisomer was generously provided by Prof. W. H. Pirkle (University of Illinois) through analysis on chiral HPLC columns.

(7) Additional characterization data: FAB mass spectrum of $TBNPH_2$ (**1**) gave m/z = 1319.5 and MnTBNPCl (**3**) gave m/z = 1373 (loss of Cl). Visible spectra: λ_{max} = 433 nm for **1** and λ_{max} = 479 nm for **3**.

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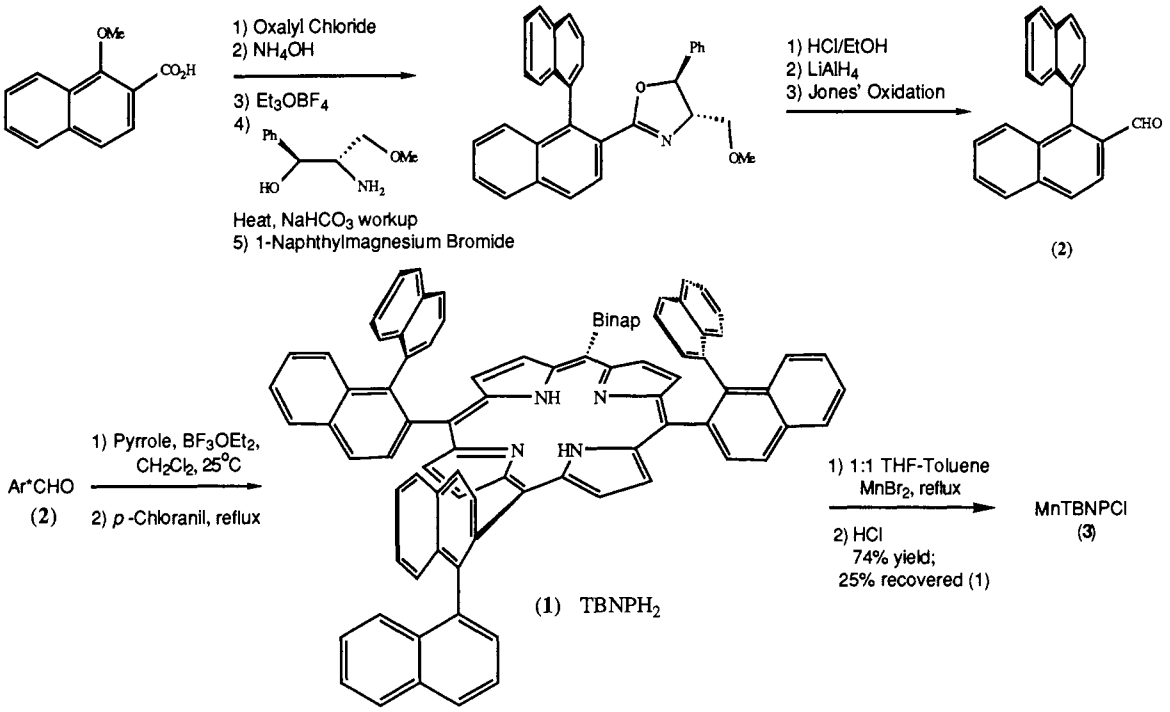

Figure 1. Synthesis of $TBNPH_2$ (**1**) and MnTBNPCl (**3**).

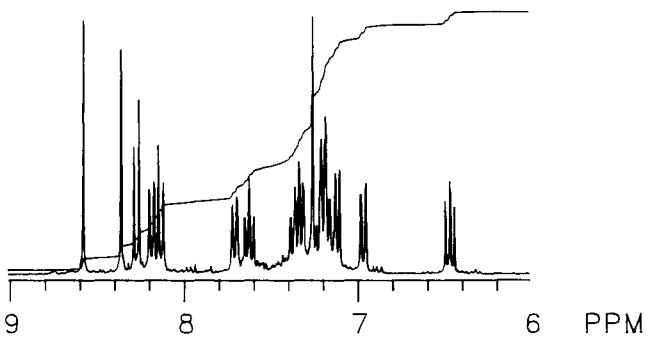

Figure 2. 500-MHz ^1H NMR of $TBNPH_2$ (**1**) in $CDCl_3$ at 22 °C.

"strapped" porphyrin incorporating L-phenylalanine synthesized by Mansuy's group yielded comparable enantioselectivites.[9] Unfortunately these previous porphyrins, though elegant and innovative, suffer from stability problems inherent in their synthetic design, which necessitates the presence of electron-donating substituents on the *meso*-phenyl groups (known to markedly sensitize the porphyrin toward oxidative degradation). Groves and Myers commented that after only 100 catalyst turnovers the enantioselectivity of epoxidation in their system deteriorated significantly. MnTBNPCl, in contrast, is quite robust under oxidation conditions; when catalyst that had been used for a standard styrene run (250 turnovers) was reused, identical rates and ee's were obtained. It is with regard to catalytic efficiency that the chiral wall porphyrin represents a significant advance in asymmetric oxygenation chemistry. By simply increasing the amounts of styrene and bleach we have been able to attain 2800 turnovers in 80 min with little catalyst degradation (examination of the Soret band at 479 nm at identical porphyrin concentrations before and after reaction showed 86% absorbance retained).

We are in the process of further evaluating $TBNPH_2$ as a chiral ligand for metal-mediated oxygenations as well as other types of catalytic reactions. Synthetic work directed toward creating substituted versions of **3** which are more selective epoxidation catalysts is also underway.

Acknowledgment. We thank Robert J. Nick for valuable discussion.

Supplementary Material Available: Synthesis details for **1** and **2** (1 page). Ordering information is given on any current masthead page.

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Introduction of Reporter Groups at Specific Sites in DNA Containing Phosphorothioate Diesters

Jacqueline A. Fidanza and Larry W. McLaughlin*

Department of Chemistry, Boston College
Chestnut Hill, Massachusetts 02167

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Facile and covalent attachment of reporter groups at specific sites within a DNA sequence would simplify detailed study of the structure and dynamics of unusual DNA forms as well as ligand-DNA or protein-DNA complexes. To date, the covalent introduction of such reporter groups has largely relied upon either (i) the prior de novo synthesis of a modified nucleoside containing the desired probe and then its incorporation into the nucleic acid[1]

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