While the short Ga-P bond distance and the yellow color of **2** are suggestive of a p_π-p_π interaction, this cannot be extensive since the P atoms remain pyramidal (sum of angles = 314.7°). Interestingly, the Ga atoms are also slightly nonplanar. Overall, the bonding description for **2** is closer to form B than to form A.

Acknowledgment. We thank the National Science Foundation, the Robert A. Welch Foundation, and the U.S. Army Research Office (Durham) for generous financial support.

Note Added in Proof. The trimer $[(2,4,6\text{-}Ph_3C_6H_2)GaP(C_6H_{11})]_3$ has been reported very recently by Power et al. (Hope, H.; Pestana, D. C.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 691). The Ga_3P_3 system is not planar and little delocalization is apparent.

Supplementary Material Available: Tables of bond distances, bond angles, atomic coordinates, and thermal parameters for **1** and **2** (8 pages); listings of observed and calculated structure factors for **1** and **2** (26 pages). Ordering information is given on any current masthead page.

Iron-Cyclam Complexes as Catalysts for the Epoxidation of Olefins by 30% Aqueous Hydrogen Peroxide in Acetonitrile and Methanol

Wonwoo Nam, Raymond Ho, and
Joan Selverstone Valentine*

*Department of Chemistry and Biochemistry
University of California, Los Angeles
Los Angeles, California 90024*

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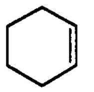
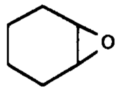
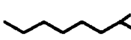
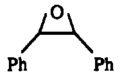
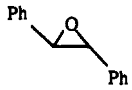
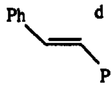
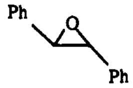
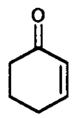
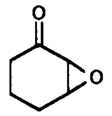
In recent years, several non-porphyrin iron-containing catalysts of alkane hydroxylation by dioxygen and/or peroxides have been reported that appear to react via nonradical pathways.[1-7] In this respect, their reactions resemble those of non-heme iron containing monooxygenase enzymes and iron bleomycin, but unlike the biological systems,[8-11] only a few of these non-porphyrin iron complexes are reported to catalyze olefin epoxidation.[4a,b,5a,12] Here we report that iron complexes of cyclam (1,4,8,11-tetraazacyclotetradecane) and related ligands are highly effective catalysts for olefin epoxidations by aqueous 30% hydrogen peroxide in acetonitrile or methanol and that, unlike previously reported systems, we observe (1) high turnovers based on the iron complex, (2) high percent yields based on H_2O_2, (3) tolerance for at least small amounts of water, (4) stereospecificity, and (5) only small amounts of allylic oxidation products.

Table I. Products Obtained from Reaction of H_2O_2 with Olefins in the Presence of $Fe(cyclam)(CF_3SO_3)_2$[a]

Substrate	Products	Yield (mmol)	Turnover[b]
		0.40[c]	20
		0.14	7
		0.26	13
		0.017	
	PhCHO	0.039	
 d		0.36	18
	PhCHO	0.02	
		trace	

[a] Reactions were quenched after 8 min for cyclohexene and 20 min for other substrates. See text for experimental conditions. [b] (Millimoles of epoxide)/(millimoles of iron catalyst). [c] See Table II for amounts of allylic oxidation products. [d] Reaction was run in the solvent mixture of acetonitrile (4 mL) and toluene (1 mL).

Hydrogen peroxide (1 mmol, 30% aqueous) was slowly added under an inert atmosphere over a period of 1 min to a solution of the Fe^{II} complexes of ligands **1-6** (0.02 mmol) and cyclohexene (1 mmol) in 5 mL of acetonitrile.[13] The reaction mixture was quenched after 8 min by addition of sodium sulfite, filtered through a 0.45-μm filter, and then analyzed by GC/MS or HPLC. The results were as follows: $Fe(\mathbf{1})^{2+}$ (ferrous cyclam) gave 0.40 mmol of cyclohexene oxide (40% yield based on H_2O_2, 20 turnovers based on Fe). $Fe(\mathbf{2})^{2+}$ gave 0.20 mmol, $Fe(\mathbf{3})^{2+}$ gave 0.10 mmol, and $Fe(\mathbf{4})^{2+}$ gave 0.04 mmol of cyclohexene oxide. The Fe^{II} complexes of **5** and **6** gave no epoxidation of cyclohexene. Only small amounts of allylic oxidation products were observed in any case, suggesting that typical radical reactions were not involved. $Fe(\mathbf{1})^{2+}$ in methanol under the same conditions but at 4 °C[17] gave the same

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(9) (a) May, S. W.; Abbott, B. J. *Biochem. Biophys. Res. Commun.* **1972**, *48*, 1230. (b) May, S. W.; Abbott, B. J. *J. Biol. Chem.* **1973**, *248*, 1725. (c) Katopodis, A. G.; Wimalasena, K.; Lee, J.; May, S. W. *J. Am. Chem. Soc.* **1984**, *106*, 7928.

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(11) Hecht, S. M. *Acc. Chem. Res.* **1986**, *19*, 383.

(12) Yamamoto, T.; Kimura, M. *J. Chem. Soc., Chem. Commun.* **1977**, 948.

(13) The complexes $Fe(\mathbf{2})(CF_3SO_3)_2$[14] and $Fe(\mathbf{4})(PF_6)_2$[15] and the ligand **5**[16] were prepared by literature methods. Ligands **1**, **3**, and **6** were purchased from Aldrich. The complexes $FeL(CF_3SO_3)_2$, L = **1**, **3**, **5**, **6**, were prepared by stirring equimolar quantities of $Fe(CF_3SO_3)_2$ and ligand in anhydrous acetonitrile followed by filtration, reduction of volume by evaporation, and addition of Et_2O to induce crystallization. The resulting solid was filtered, washed with Et_2O, and dried in vacuo. All manipulations were carried out under an inert atmosphere. Satisfactory elemental analyses were obtained for each complex.

(14) Tait, A. M.; Busch, D. H. *Inorg. Synth.* **1978**, *18*, 2.

(15) Reichgott, D. W.; Rose, N. J. *J. Am. Chem. Soc.* **1977**, *99*, 1813.

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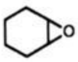
(17) Alcoholysis of cyclohexene oxide takes place in methanol under our reaction conditions at room temperature. Therefore the reaction was carried out at 4 °C, where the rate of alcoholysis was slow. Posner, G. H.; Rogers, D. Z. *J. Am. Chem. Soc.* **1977**, *99*, 8208.

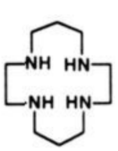
0002-7863/91/1513-7052$02.50/0

Table II. Cyclohexene Oxidation by Various Oxidants Catalyzed by Fe(cyclam)(CF$_3$SO$_3$)$_2$[a]

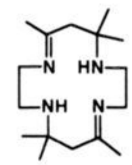
			products (yields, %)[b]			
oxidants	solvent	reactn time, min				mass balance,[c] %
H$_2$O$_2$	CH$_3$CN	8	40	1	0.4	96
	CH$_3$OH[d]	20	41	*e*	*e*	*e*
t-BuOOH	CH$_3$CN	120	1	6	9	95[f]
EtOOH	CH$_3$CN	120	0	7	1	95
PhIO	CH$_3$CN	15	38	0	0	88

[a] Reactions were run in a solution containing cyclohexene (1 mmol) and iron catalyst (0.02 mmol). Oxidant (1 mmol for H$_2$O$_2$, *t*-BuOOH, and EtOOH) was added to the reaction solution, and the reaction was quenched after the time indicated. In the case of PhIO, 0.4 mmol was added, and no sodium sulfite was added prior to filtration. See text for experimental conditions. [b] Percent yields based on oxidant added. [c] Percent of the sum of unreacted cyclohexene and products based on starting cyclohexene, ±3%. [d] Reaction was carried out at 4 °C. [e] Not determined. [f] 1-(*tert*-Butylperoxy)-2-cyclohexene (15%) was formed.

yield of cyclohexene oxide as in acetonitrile. Several other olefins were also epoxidized by H$_2$O$_2$ in acetonitrile in the presence of Fe(**1**)$^{2+}$ (see Table I). Particularly significant is the case of *cis*-stilbene, which gave a 26% yield of *cis*-stilbene oxide and less than 2% of *trans*-stilbene oxide. Formation of epoxides was not detected in the absence of the iron catalyst. Cyclam complexes of Mn(II), Co(II), Ni(II), and Cu(II) were ineffective as catalysts of either cyclohexene or *cis*-stilbene epoxidation by hydrogen peroxide.



1



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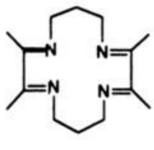
3



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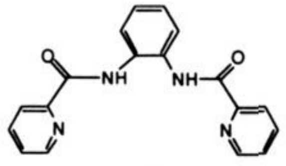

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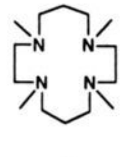

6

Replacement of hydrogen peroxide by other oxidants, i.e., *tert*-butyl hydroperoxide, ethyl hydroperoxide, and iodosylbenzene, was also studied (see Table II). In contrast to the hydrogen peroxide reactions, alkyl hydroperoxides gave only allylic oxidation products in acetonitrile or methanol. When *tert*-butyl hydroperoxide was used as an oxidant, a moderate amount of 1-(*tert*-butylperoxy)-2-cyclohexene was also formed, indicating that the *t*-BuOO• radical was generated.[18] By contrast, iodosylbenzene was found to give high yields of epoxide in the iron cyclam catalyzed reaction.

Oxidation of 2,4,6-tri-*tert*-butylphenol (TBPH)[19,20] was also studied under the same conditions in both acetonitrile and methanol. In the case of this substrate, as in the case of the olefins, little or no oxidation of substrate was observed in the absence of the iron catalyst. In the presence of ferrous cyclam, hydrogen peroxide, ethyl hydroperoxide, and *tert*-butyl hydroperoxide, all reacted rapidly with TBPH to give the highly colored 2,4,6-tri-*tert*-butylphenoxy radical.

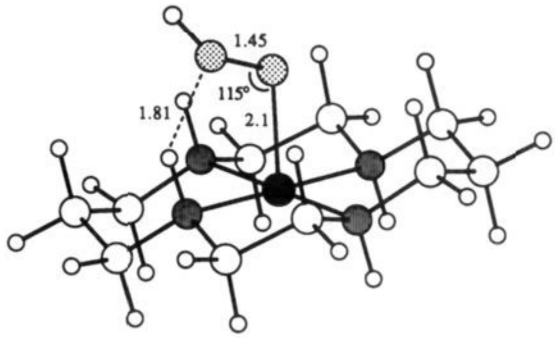

Figure 1. Computer drawing of an iron cyclam hydroperoxide complex illustrating favorable geometry for hydrogen bonding between the HOO$^-$ ligand and the N–H of the cyclam ligand. The trans conformation of the cyclam ligand was optimized by using the MM2 program.[24]

The iron cyclam catalyzed oxidation of methanol by hydrogen peroxide and *tert*-butyl hydroperoxide in methanol was also studied. Once again, little or no oxidation was observed in the absence of catalyst. When ferrous cyclam (0.002 mmol) was added to 4 mL of a solution of the peroxide (0.10 mmol) in methanol, *tert*-butyl hydroperoxide was observed to give 0.09 mmol of formaldehyde in 10 min while hydrogen peroxide reacted more slowly, giving 0.04 mmol in 10 min.[21] Thus the iron cyclam catalyst resembles the ferric EDTA complex in its ability to catalyze oxidation of methanol by peroxides.[20a]

The observation that both H$_2$O$_2$ and ROOH oxidized TBPH and methanol in the presence of iron–cyclam complexes but that only H$_2$O$_2$ and not ROOH gave epoxidation of cyclohexene under the same conditions leads us to conclude that the two types of reactions do not occur via a common intermediate. One possible explanation is that the species responsible for the TBPH and methanol oxidations are the product or products formed from cleavage of the O–O bond,[19,20] whereas the epoxidation reaction occurs by a direct reaction of the olefin with coordinated HOO$^-$. Since the O–O bond of HOOH is 5 kcal/mol stronger than that of ROOH,[22] an HOO$^-$ complex is expected to have a higher activation energy for O–O bond cleavage than a ROO$^-$ complex and therefore to have a longer lifetime.[23] The former might be less sterically hindered than the latter as well. The hypothesis that an HOO$^-$ complex of iron cyclam may be an intermediate is also supported by molecular modeling of such a species using computer graphics, which suggests strongly that the preferred conformation of the cyclam ligand **1** presents the HOO$^-$ ligand with an axial N–H bond that is well suited for hydrogen bonding (see Figure 1).

There are several possible explanations for the lower yields of cyclohexene oxide obtained when H$_2$O$_2$ was reacted with cyclohexene in the presence of Fe^{II} complexes of ligands **2**–**6**. Differences in redox potentials or ligand conformation may influence relative rates of formation and lifetimes of the intermediates

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J. Am. Chem. Soc. **1991**, *113*, 7054-7056

responsible for epoxidation, or alternatively, complexes may be poor catalysts for epoxidation because they are good catalysts for H_2O_2 disproportionation. Experiments to discriminate between these possibilities are planned.

The complex color changes that we observed when hydrogen peroxide was reacted with iron-cyclam complexes have led us to the conclusion that several intermediate species are involved. However, our attempts to characterize potential intermediates spectroscopically have so far been frustrated by a competing reaction of the ligand. During the course of these reactions, the initially purple complex was converted to a green complex which was no longer active as a catalyst for the epoxidation reaction in acetonitrile. This particular spectroscopic change resembles those that occur when ferrous complexes of related ligands undergo oxidative dehydrogenation upon reaction with dioxygen.[25]

Future studies will focus on attempts to stabilize intermediates in this reaction and to characterize their spectroscopic properties and their reactivities. If non-porphyrin iron complexes are indeed capable of epoxidizing olefins without prior O-O bond cleavage, such a mechanism should be considered in the cases of non-heme iron containing monooxygenase enzymes and iron bleomycin as well.

Acknowledgment. We thank Dr. Y. Wu and Professor K. N. Houk for providing us with Figure 1. Financial support from the National Science Foundation is gratefully acknowledged.

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[25] (a) Dabrowiak, J. C.; Busch, D. H. *Inorg. Chem.* **1975**, *14*, 1881. (b) Dabrowiak, J. C.; Lovecchio, F. V.; Goedkin, V. L.; Busch, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 5502.

The Temporary Silicon Connection Method in the Control of Regio- and Stereochemistry. Applications to Radical-Mediated Reactions. The Stereospecific Synthesis of *C*-Glycosides

Gilbert Stork,* Hong Suk Suh, and Guncheol Kim

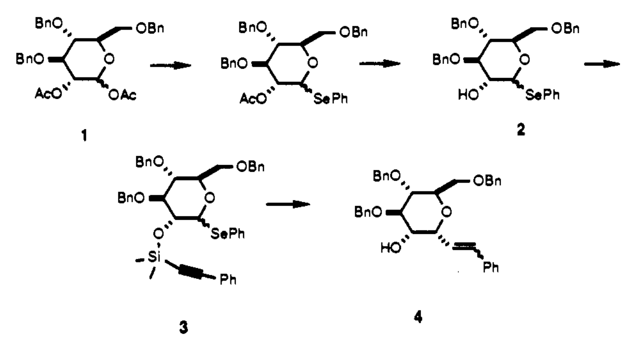
Chemistry Department, Columbia University
New York, New York 10027

Received June 7, 1991

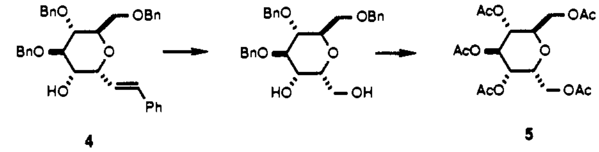
We report in this paper the application of the temporary silicon connection method for the control of regio- and stereochemistry[1] to the synthesis of *C*-glycosides.

C-Glycosides are an important class of carbohydrate derivatives,[2] and numerous methods have been devised for their stereoselective construction.[3] Most of those methods are empirical, and the result of their use in a previously unstudied case cannot be predicted with confidence.

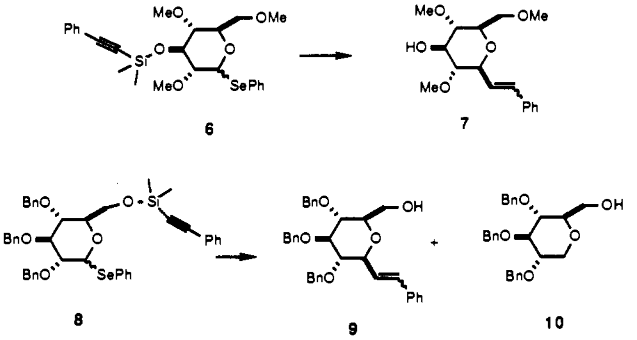
Scheme I



Scheme II



Scheme III



The method we describe here is entirely general. It achieves the stereospecific introduction of a styryl group at the anomeric center of a particular carbohydrate by the radical-induced[4] cyclization of a 3-phenylethynyl group tethered, via a temporary silicon connection,[5] to a suitable hydroxyl group of the carbohydrate.

In contrast to the poor stereocontrol available via *inter*molecular radical reactions at the anomeric center,[6] the geometric requirements for the *intra*molecular cyclization of an ethynyl group tethered to a β-hydroxyl onto the radical at the anomeric center can only lead, after detachment of the silicon connector, to a β *C*-glycoside (A), while tethering to an α-hydroxyl can only give an α *C*-glycoside (B). This is schematized in Figure 1.

The phenylethynyl group was chosen to be the tethered entity because (1) we have devised a simple method for attaching an acetylene to a hydroxyl via a silicon atom[7] and (2) the presence of a phenyl rather than an alkyl group leads to more general and efficient cyclizations. The styryl *C*-glycosides will sometimes be needed, as such. More generally, the styryl substituents, whatever their geometry, serve as convenient precursors for the stereospecific introduction of a versatile aldehyde or carbinol function at the anomeric center.

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[1] The Temporary Silicon Connection has been under investigation at Columbia for several years. Cf.: Keitz, P., ref 5. Stork, G. 32nd National Organic Symposium, Minneapolis, June 1991.

[2] Cf. inter alia: (a) Hanessian, S.; Pernet, A. G. *Adv. Carbohydr. Chem. Biochem.* **1976**, *33*, 111. (b) Nishimura, N.; et al. *J. Antibiot., Ser. A* **1966**, *17*, 148. (c) Boivin, T. L. B. *Tetrahedron* **1987**, *43*, 3309. (d) Connor, D. T.; Greenough, R. C.; v. Strandtmann, M. *J. Org. Chem.* **1977**, *42*, 3664.

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