J. Am. Chem. Soc. 1991, 113, 7195–7205

Lewis Acidic Catalysts for Olefin Epoxidation by Iodosylbenzene

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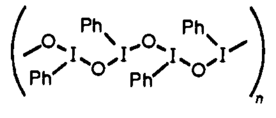
Received November 19, 1990. Revised Manuscript Received May 14, 1991

Abstract: A ferric complex, (Et$_3$HN)Fe^{III}(bpb)Cl$_2$, has been synthesized, and its structure has been determined by X-ray crystallography. This complex and its triflate derivative, (Et$_3$HN)Fe^{III}(bpb)(OTf)$_2$, are found to catalyze the epoxidation of a variety of olefins by iodosylbenzene, OIPh. These reactions give little allylic oxidation of cyclohexene and stereochemical retention with *cis*-stilbene. Al(OTf)$_3$, a nonredox metal salt, has also been found to catalyze the epoxidation of cyclohexene by iodosylbenzene, and the reactivity is quite similar to that of Fe(OTf)$_3$, which we studied previously. In addition to epoxides, other products were observed. For the reactions containing Fe(OTf)$_3$, Al(OTf)$_3$, or (Et$_3$HN)Fe^{III}(bpb)(OTf)$_2$, *cis*-1,2-cyclohexanediol ditriflate and 3-acetamidocyclohexene were found. The amide oxygen in 3-acetamidocyclohexene was derived from iodosylbenzene as verified by isotopic labeling using ^{18}OIPh. For the reactions containing (Et$_3$HN)Fe^{III}(bpb)Cl$_2$, FeCl$_3$, or AlCl$_3$, *trans*-1,2-dichlorocyclohexane and 3-chlorocyclohexene were observed. 1,4-Diiodobenzene was found in all of the reactions. The presence of these products suggests strongly that the mechanisms of these reactions are related to those occurring between soluble iodine(III)-containing compounds and olefins in the absence of any metal catalysts. A new mechanism that accounts for all of the products is proposed which involves electrophilic attack on the olefin by the iodine(III) center in a metal–iodosylbenzene complex. The reactions of PhI(OAc)$_2$ with norbornenecarboxylic acid or norbornene in different solvents were also investigated. The products isolated were shown to be 5-(acetyloxy)-3,3a,4,5,6,6a-hexahydro-[3β,3aα,5α,6β,6aα]-3,6-methano-2*H*-cyclopenta[*b*]furan-2-one (**1**), 5-acetamido-3,3a,4,5,6,6a-hexahydro-[3β,3aα,5α,6β,6aα]-3,6-methano-2*H*-cyclopenta[*b*]furan-2-one (**2**), and *exo*-2-acetoxy-*syn*-7-acetamidonorbornane (**3**). The structures of **1** and **3** were determined by X-ray crystallography. The formation of these products provides additional evidence for the electrophilic character of iodine(III) compounds.

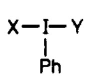
Introduction

Iodosylbenzene, OIPh, has been widely used as an oxygen atom donor in mechanistic studies of cytochrome P-450, a heme-containing monooxygenase enzyme, and its metalloporphyrin models.[1] It has been concluded from such studies that a high-valent iron(IV) oxo cation radical species is involved as an intermediate.[1] Less is known about intermediates formed in reactions of the non-heme iron containing monooxygenase enzymes, for example, the hydrocarbon monooxygenase system from *Pseudomonas oleovorans* (POM),[2] methane monooxygenase (MMO),[3] and phenylalanine hydroxylase (PAH),[4] which catalyze reactions analogous to those observed for their heme-containing counterparts. Our laboratory[5] and others[6] have studied the reactions of iodosylbenzene with olefins catalyzed by non-porphyrin metal complexes in the hope of gaining some understanding of the nature of possible intermediates in the non-heme enzymatic reactions and of the process of oxygen atom transfer to organic substrates.

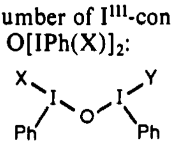
Iodosylbenzene is a polymeric substance with the proposed structure shown below.



It is obviously related to a large number of I^{III}-containing compounds of the forms PhI(X)Y and O[IPh(X)]$_2$:



X = OH, Y = OTs;
X = Y = OAc, etc.



X = OTf, NO$_3$, OOCCF$_3$, etc.

The chemistry of such iodine(III) compounds with organic substrates has been investigated since they show promise as reagents for use in organic synthesis.[7,8] For example, reactions of alkenes with hydroxy(tosyloxy)iodobenzene [PhI(OH)(OTs)] or other iodine(III) compounds yield *cis*-1,2-substituted alkanes,[7] and PhI(OH)(OTs) reacts with various alkynes to afford stable phenyl[(β-tosyloxy)vinyl]iodonium tosylates,[7b] suggesting that

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[†] This work constitutes part of the Ph.D. thesis of Y. Yang, University of California, Los Angeles, 1990. A portion of this work was communicated previously: Yang, Y.; Diederich, F.; Valentine, J. S. *J. Am. Chem. Soc.* **1990**, *112*, 7826–7828.

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0002-7863/91/1513-7195$02.50/0

iodine(III) in these compounds acts as an electrophilic center. Koser and co-workers have proposed a mechanism involving electrophilic addition of iodine(III) to the double bond of alkenes in the first step.[7a] Interestingly, in addition to these products, stable iodine-substituted compounds have been formed in some cases.[7c] For example, in the reaction of $C_3F_7I(OH)(OTs)$ with cyclohexene, *trans*-1-iodo-2-(tosyloxy)cyclohexane has been observed.[7c] The formation of this iodine compound provides direct evidence of addition of iodine to the double bond of alkenes and strongly supports the assignment of electrophilic character to iodine(III). Moriarty et al. have proposed that the mechanism in the metal-catalyzed oxygenation reactions with iodosylbenzene may be related to that in these organic reactions.[9] Our recent discovery[5c] that nonredox metals can catalyze olefin epoxidation by iodosylbenzene have led us to investigate this possibility further.

We have synthesized a new iron complex, $(Et_3HN)Fe(bpb)X_2$ (H_2bpb = 1,2-bis(2-pyridinecarboxamido)benzene; X = Cl, OTf), and have found that it can catalyze the epoxidation of olefins by iodosylbenzene. In addition to epoxides, we noted the formation of other products whose presence suggests strongly that the mechanisms of these reactions are related to those occurring between olefins and soluble I^{III}-containing compounds in the absence of any metal catalyst. We therefore examined a nonredox metal salt, $Al(OTf)_3$, as a catalyst for olefin epoxidation reactions and reinvestigated the reaction of $Fe(OTf)_3$. We find that $Al(OTf)_3$ can catalyze olefin epoxidation with iodosylbenzene, giving yields and product distributions similar to those obtained with $Fe(OTf)_3$. The new products found in the $(Et_3HN)Fe(bpb)(OTf)_2$ reactions were also observed in the case of $Fe(OTf)_3$ and $Al(OTf)_3$. On the basis of these results, we propose a mechanism involving metal complex catalyzed electrophilic attack of I^{III} on alkenes.

Experimental Section

Materials. Unless otherwise stated, all chemicals were purchased from Aldrich and used without further purification. *cis*-Stilbene, *trans*-β-methylstyrene, and styrene were distilled under reduced pressure. *trans*-Stilbene was sublimed. *cis*-1,2-Dichlorocyclohexane (Frinton Laboratory) and 3-chlorocyclohexene (K & K Rare & Fine Chemicals) were purified by distillation before use. Bicyclo[2.2.1]-5-heptene-2-carboxylic acid (or norbornenecarboxylic acid, 98%, predominantly endo isomer, Lancaster) was used as received. HPLC grade solvents were purchased from Fisher. Acetonitrile was distilled from calcium hydride and then passed through Woelm Super I active grade alumina. Ethanol was distilled from magnesium ethoxide before use. Iodosylbenzene was prepared by literature methods[10] and stored at −30 °C in the dark. μ-Oxobis[(triflato)(phenyl)iodine] $[O(IPh(OTf))_2]$ was prepared by literature methods.[7f]

Instrumentation. Infrared spectra were recorded on a Beckman 4260 spectrophotometer. Visible spectra were obtained by using a Beckman 5270 spectrophotometer. ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ against TMS as an internal standard on a Bruker AF 200 spectrometer. EPR spectra were determined by using a Bruker 200D spectrometer equipped with a liquid nitrogen dewar. Low-resolution electron impact mass spectra were performed on a MS 902 spectrometer.

Organic products from the reactions of olefins with iodosylbenzene catalyzed by iron complex were analyzed by GC/MS or HPLC. The GC/MS analysis was performed on a Hewlett-Packard 5890 gas chromatograph with a 0.2-mm 5% phenyl methyl silicone capillary column (25 m in length), interfaced to a Hewlett-Packard 5970 mass selective detector. The HPLC analysis was performed on a Beckman 344 high-performance liquid chromatograph system with an UV detector. Alltech Econosphere C18 columns were used to separate reaction mixtures.

$(Et_3HN)Fe^{III}(bpb)Cl_2$. The ligand 1,2-bis(2-pyridinecarboxamido)benzene (H_2bpb) was prepared by the method of Barnes et al.[11] Anhydrous $FeCl_3$ (162 mg, 1 mmol) was added to a solution of H_2bpb (318 mg, 1 mmol) and 300 μL of Et_3N in 30 mL of dry acetonitrile in a Vacuum Atmospheres glovebox under a helium atmosphere. The solution turned dark green immediately. The solution was stirred for approximately 2 h and cooled at −30 °C overnight. A small amount of brown precipitate was removed by filtration. After reducing the volume of the solution, it was cooled at −30 °C for 2 days. A mixture of dark green crystals of $(Et_3HN)Fe^{III}(bpb)Cl_2$ and white crystals of $Et_3N{\cdot}HCl$ was formed and isolated by filtration. The mixture was separated by taking advantage of solubility differences in ethanol. Stirring the solid mixture in dry ethanol followed by quick filtration removed $Et_3N{\cdot}HCl$ and gave $(Et_3HN)Fe^{III}(bpb)Cl_2$ as a crystalline solid in 50% yield: IR (KBr) ν (amide) 1620 cm^{-1} and no N–H stretch. Anal. Calcd for $(Et_3HN)Fe^{III}(bpb)Cl_2{\cdot}CH_3CN$ ($FeC_{26}N_6O_2Cl_2H_{31}$): Fe, 9.52; C, 53.25; H, 5.34; N, 14.33; Cl, 12.09. Found Fe, 9.80; C, 53.01; H, 5.13; N, 14.05; Cl, 12.91. The EPR spectra were taken for both solution and solid samples at 90 K. The visible spectrum of a 1×10^{-3} M solution of $(Et_3HN)Fe^{III}(bpb)Cl_2$ in acetonitrile was recorded in a 1-cm cell.

$(Et_3HN)Fe^{III}(bpb)(OTf)_2$ Solutions. Ag(OTf) (2 equiv) was added to solutions of $(Et_3HN)Fe^{III}(bpb)Cl_2$ in acetonitrile, and AgCl was removed by filtration. The dark brown solutions were used for reactions.

$Al(OTf)_3$ Solutions. Ag(OTf) (3 equiv) was added to a solution of $AlCl_3$ in acetonitrile, and AgCl was removed by filtration. The colorless solutions were used for reactions. By removal of the solvent under vacuum, a white solid was obtained and sent for analysis. Anal. Calcd for $Al(OTf)_3{\cdot}3CH_3CN$ ($AlC_9H_9N_3O_9F_9S_3$): Al, 4.52; C, 18.09; H, 1.52; N, 7.04; S, 16.10; Cl, 0.00. Found: Al, 4.32; C, 17.15; H, 1.50; N, 6.12; S, 16.01; Cl, 0.023.

General Procedure for Reactions of Olefins with Iodosylbenzene in the Presence of Metal Catalysts. All reactions were carried out in a Vacuum Atmospheres glovebox under a helium atmosphere. In a typical epoxidation reaction, $(Et_3HN)Fe^{III}(bpb)Cl_2$ (0.005 mmol) was dissolved in 5 mL of acetonitrile, and olefin (0.5 mmol) was added. Iodosylbenzene (0.1–0.2 mmol) was then added all at once to the solution with constant stirring. The reaction mixture was filtered through a Gelman Acrodisc 0.45-μ filter to eliminate unreacted iodosylbenzene. Aliquots were taken at timed intervals and analyzed by GC/MS or HPLC. An internal standard (*n*-decane, *n*-nonane, or chlorobenzene) was used in analysis by GC/MS.

For observation of other products, different concentrations of substances were used. In the cases of $(Et_3HN)Fe^{III}(bpb)(OTf)_2$, $Fe(OTf)_3$, or $Al(OTf)_3$, iodosylbenzene (0.8 mmol) was added to solutions consisting of 4 mL of acetonitrile, 1 mL of cyclohexene, and metal complexes (0.025 mmol) (plus 0.4 mmol of Li(OTf) when indicated). In the cases of $(Et_3HN)Fe^{III}(bpb)Cl_2$, $FeCl_3$, or $AlCl_3$, iodosylbenzene (0.4 mmol) was added to 5-mL acetonitrile solutions containing cyclohexene (0.5 mmol) and metal complexes (0.025 mmol). The reaction mixtures were filtered and analyzed by GC/MS.

Effect of Cyclohexene Concentration. In order to assay the effect of substrate concentration on epoxide formation, the reaction with different concentrations of cyclohexene (50 mM to 2 M) was carried out.

Relative Reactivity of Olefins in the Epoxidation Catalyzed by $Fe(OTf)_2$. The relative reactivities of substituted styrenes to styrene, measured by intermolecular competition, were calculated by eq 1, where

$$k_x/k_y = \log (X_f/X_i)/\log (Y_f/Y_i) \qquad (1)$$

X_i and Y_i are the initial concentrations of the olefins X (substituted styrenes) and Y (styrene), and X_f and Y_f are the final concentrations of these olefins. The olefins used in this study included styrene, 4-methoxystyrene, 4-methylstyrene, 4-chlorostyrene, and 3-chlorostyrene. In a typical competition reaction, styrene and substituted styrene (0.45 mmol each) were mixed in an acetonitrile (15 mL) solution containing $Fe(OTf)_2$ (0.03 mmol) and the internal standard chlorobenzene (0.45 mmol). The solution was divided into three parts of 5 mL each. Iodosylbenzene (0.08 mmol) was added to each solution, and the mixtures were stirred for 30 min. Aliquots were taken before addition of the iodosylbenzene and 30 min after it was added. The amounts of olefins were determined by GC/MS. The relative reactivities were calculated by the above equation.

***cis*-1,2-Cyclohexanediol Ditriflate.** The product was isolated from the reaction of cyclohexene with iodosylbenzene and $Al(OTf)_3$ in acetonitrile and purified on a silica gel column as an oil. It was identified by comparison with published ^1H NMR data.[7f] This product from reactions containing other metal complexes was identified by GC/MS. Quantitative analysis was performed by GC/MS using the above purified compound as a standard.

3-Acetamidocyclohexene. This product was isolated from the reaction of cyclohexene with iodosylbenzene and $Zn(OTf)_2$ and purified on a silica gel column as a white solid: mp 78.5–80.5 °C (lit.[12] mp 78 °C); IR (KBr) ν (NH) 3260, (CONH) 1633, 1539 cm^{-1}; ^1H NMR δ 5.75–5.85 (m, 1 H, CH=), 5.59 (br, 1 H, NH), 5.45–5.55 (m, 1 H, CH=), 4.35–4.4 (m, 1 H, CHN), 1.91 (s, 3 H, CH_3), 1.35–2.05 (m, 6 H, CH_2); ^{13}C NMR δ 169.3 (C=O), 130.9, 12.7 (CH=CH), 44.7 (CHN), 23.5

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Table I. Crystal and Refinement Data for $(Et_3HN)Fe(bpb)Cl_2{\cdot}CH_3CN$, **1**, and **3**

	$(Et_3HN)Fe(bpb)Cl_2{\cdot}CH_3CN$	**1**	**3**
formula	$FeC_{26}N_6O_2Cl_2H_{31}$	$C_{10}O_4H_{12}$	$C_{22}H_{34}O_6N_2$
formula weight	586.32	196.20	422.52
crystal syst	monoclinic	monoclinic	triclinic
space group	*C*2/*c*	*P*21/*c*	$P\bar{1}$
crystal color	dark green	colorless	colorless
crystal habit	diamond	rectangular	rectangular
a, Å	32.06 (1)	5.614 (1)	9.734 (0)
b, Å	12.802 (3)	8.252 (1)	11.608 (1)
c, Å	15.613 (4)	20.228 (1)	10.671 (1)
α, deg	90.00 (0)	90.00	98.72 (0)
β, deg	115.89 (1)	97.03 (1)	90.53 (0)
γ, deg	90.00 (0)	90.00	99.56 (0)
Z	8	4	2
V, $Å^3$	5764.14	930.05	1174.50
ρ(calcd), g cm^{-3}	1.35	1.40	1.19
radiation, λ	Mo Kα 0.7107	Mo Kα 0.7107	Mo Kα 0.7107
F(000), e	2440	416	456
temperature, K	298	298	298
diffractometer	Picker	Picker	Picker
scan mode, speed (deg/min)	θ–2θ, 3.0	θ–2θ, 3.0	θ–2θ, 3.0
2θ range, deg	1–45	1–50	1–45
data collected	*h*, *k*, ±*l*	*h*, *k*, ±*l*	*h*, ±*k*, ±*l*
total data collected	7576	1928	3551
unique data used ($I > 3\sigma(I)$)	4937	1198	1020
no. of params refined	289	127	271
final shift/error, max and av	0.022, 0.002	0.044, 0.009	0.012, 0.002
max resid density, e/$Å^3$	0.52	0.56	0.43
R	0.082	0.048	0.075
R_w	0.081	0.066	0.082

(CH_3), 29.4, 24.8, 19.7 (CH_2); MS *m*/*z* (relative intensity) 139 (100, M^+), 97 (13, $M^+ - O{=}C{=}CH_2$). This same product was identified by GC/MS in the case of reactions containing other metal complexes. Quantitative analysis was performed by GC/MS using the purified compound as a standard. It was important for the column to be very clean in order to detect this compound.

Reaction of Cyclohexene with μ-Oxobis[(triflato)(phenyl)iodine]. μ-Oxobis[(triflato)(phenyl)iodine] $[O(IPh(OTf))_2]$ dimer is soluble in acetonitrile and forms a yellow solution. When cyclohexene (1 mL, 10 mmol) was added to an acetonitrile (4 mL) solution of $O[IPh(OTf)]_2$ (18.1 mg, 0.025 mmol), the yellow color disappeared immediately. The reaction was also carried out in an acetonitrile solution (5 mL) of cyclohexene (200 mM, 100 mL) and $O[IPh(OTf)]_2$ (5 mM). The amounts of *cis*-1,2-cyclohexanediol ditriflate formed in these reactions were determined by GC/MS.

^{18}OIPh Labeling Studies. ^{18}OIPh was made from 97.5 atom % $H_2{}^{18}O$ by the method of Schardt and Hill[13] and checked by IR. ^{18}O incorporation into products was determined by analysis of mass spectra from GC/MS. ^{18}O incorporation into cyclohexene oxide was determined on the basis of the 85:83 fragment ratio. ^{18}O incorporation into 3-acetamidocyclohexene was determined on the basis of the 141:139 parent peak ratio.

3,6-Methano-2*H*-cyclopenta[*b*]furan-2-one, 5-(Acetyloxy)-3,3a,4,5,6,6a-hexahydro-[3β,3aα,5α,6β,6aα]- (1). Iodobenzene diacetate (6.3 g, 19.6 mmol) and bicyclo[2.2.1]-5-heptene-2-carboxylic acid (2.7 g, 19.6 mmol) were placed in a 300-mL round-bottom flask, and glacial acetic acid (approximately 100 mL) was added. The reaction was stirred for 3 days at room temperature and filtered to remove unreacted iodobenzene diacetate. Water was added to the reaction mixture, which was then extracted with ethyl ether. The ether layer was washed twice with distilled water, once with 10% NaOH, and twice more with distilled water. Subsequent drying (magnesium sulfate, $MgSO_4$), filtration, and evaporation of the solvent gave a liquid. Addition of petroleum ether caused a white solid to precipitate. Compound **1** was then purified by silica gel column chromatography (60–200 mesh) using hexanes and then chloroform as eluents. The product was finally obtained in a low yield (50 mg, 1.3%): mp 109–110 °C (lit.[14b] mp 116–116.5 °C); IR (KBr) ν (C=O, lactone) 1795, (C=O, acetate) 1730 cm^{-1}; ^{1}H NMR (for numbering, see eq 5; assignments are based on ^{1}H–^{13}C heteronuclear 2D COSY spectrum) δ 5.00 (s, br, 1 H, 7-H), 4.85–4.9 (m, 1 H, 2-H), 2.75–2.8 (m, 1 H, 4-H), 2.65–2.7 (m, 1 H, 5-H), 2.6–2.65 (m, 1 H, 1-H), 2.05 (s, 3 H, CH_3), 2.0–2.1 (m, 1 H, 3-H_{endo}), 1.75–1.8 (m, 1 H, 6-H_{exo}), 1.65–1.7 (m, 1 H, 3-H_{exo}), 1.4–1.55 (m, 1 H, 6-H_{endo}); ^{13}C NMR (assignments are based on ^{1}H–^{13}C heteronuclear 2D COSY spectrum) δ 178.0 (C=O), 169.9 (C=O), 83.9 (C-7), 75.6 (C-2), 45.7 (C-4), 43.2 (C-5), 42.2 (C-1), 29.3 (C-3), 24.9 (C-6), 21.0 (CH_3); MS *m*/*z* (relative intensity) 196 (0.6, M^+), 136 (97, $M^+ - CH_3COOH$), 108 (100, $M^+ - CH_3COOH - CO$). The control reaction of norbornenecarboxylic acid in acetic acid in the absence of iodobenzene diacetate was carried out, and the product **1** was not observed.

3,6-Methano-2*H*-cyclopenta[*b*]furan-2-one, 5-Acetamido-3,3a,4,5,6,6a-hexahydro-[3β,3aα,5α,6β,6aα]- (2). Iodobenzene diacetate (0.86 g, 6.2 mmol) and bicyclo[2.2.1]-5-heptene-2-carboxylic acid (2.0 g, 6.2 mmol) were placed in a 300-mL round-bottom flask. Acetonitrile was added until all of the iodobenzene diacetate dissolved completely (approximately 100 mL). The reaction was stirred for 3 days at room temperature. A thick liquid was obtained after the solvent was removed under vacuum. An off-white solid precipitated after addition of ethyl ether to the liquid. Compound **2** was obtained in 0.22 g (18%) after filtration: mp 168–169 °C; IR (KBr) ν (N—H) 3275, (C=O, lactone) 1810, (CONH) 1635, 1555 cm^{-1}; ^{1}H NMR (for numbering, see eq 6) δ 5.99 (s, br, 1 H, NH), 4.91 (s, 1 H, 7-H), 4.05 (m, 1 H, 2-H), 2.6–2.9 (m, 3 H, 1,4,5-H), 1.6–2.3 (m, 4 H, 3,6-H), 1.97 (s, 3 H, CH_3); ^{13}C NMR δ 178.5 (C=O), 169.9 (C=O), 84.1 (C-7), 53.3 (C-2), 46.3 (C-4), 43.8 (C-5), 42.7 (C-1), 29.3 (C-3), 26.8 (C-6), 23.1 (CH_3); MS *m*/*z* (relative intensity) 195 (100, M^+), 153 (68, $M^+ - O{=}C{=}CH_2$). The control experiment demonstrates that reaction of norbornenecarboxylic acid in acetonitrile in the absence of iodobenzene diacetate does not occur.

Isotopic Labeling Studies. The above reaction was carried out in deuterated acetonitrile (CD_3CN) solvent. The solid CD_3CONH derivative was obtained by the same method used in isolating compound **2**.

***exo*-2-Acetoxy-*syn*-7-acetamidonorbornane (3).** Iodobenzene diacetate (15.4 g, 47 mmol) was added to a solution of norbornene (4.5 g, 47 mmol) in acetonitrile (50 mL) and glacial acetic acid (20 mL). The mixture was heated at 55 °C for 3 days. The acetonitrile was removed under vacuum. An aqueous solution of sodium hydrogen carbonate $(NaHCO_3)$ was added to the residue, and the mixture was extracted with chloroform to remove acetic acid. The organic layer was washed with distilled water and dried with magnesium sulfate. The products were separated by silica gel column chromatography (60–200 mesh). Iodobenzene was washed out with hexanes. A white product mixture consisting of **3** and other isomers was obtained in approximately 2.4 g (24%) by elution with chloroform. Crystals of **3** for X-ray analysis were obtained from the first fraction eluted with chloroform: IR (KBr) ν (N—H) 3320, (C=O, acetate) 1740, 1645, (CONH) 1545 cm^{-1}; MS *m*/*z* (relative intensity) 211 (6, M^+), 151 (100, $M^+ - CH_3COOH$).

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(13) Schardt, B. C.; Hill, C. L. *Inorg. Chem.* **1983**, *22*, 1563–1565.

(14) (a) Moriarty, R. M.; Walsh, H. G.; Gopal, H. *Tetrahedron Lett.* **1966**, 4363–4367. (b) Moriarty, R. M.; Gopal, H.; Walsh, H. G. *Tetrahedron Lett.* **1966**, 4369–4374. (c) Moriarty, R. M.; Gopal, H. *Tetrahedron Lett.* **1972**, 347–350. (d) Moriarty, R. M.; Gopal, H.; Flippen, J. L.; Karle, J. *Tetrahedron Lett.* **1972**, 351–354.

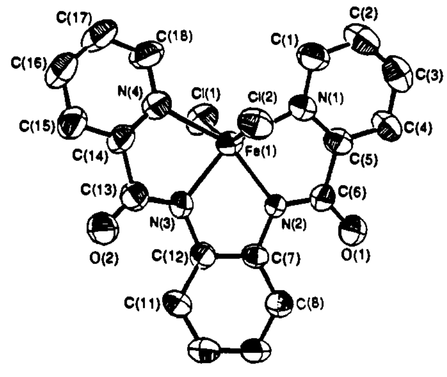


Figure 1. ORTEP diagram for Fe(bpb)Cl$_2^-$.

X-ray Crystallographic Determination of Structures of (Et$_3$HN)-Fe^{III}(bpb)Cl$_2$·CH$_3$CN, 1, and 3. A summary of crystallographic parameters for (Et$_3$HN)Fe^{III}(bpb)Cl$_2$·CH$_3$CN, 1, and 3 is given in Table I. Single crystals of (Et$_3$HN)Fe^{III}(bpb)Cl$_2$·CH$_3$CN with dark green color were grown from acetonitrile at −30 °C in the glovebox freezer. Single crystals of 1 were grown from chloroform in a NMR tube at room temperature. Single crystals of 3 were grown when a saturated warm chloroform solution was cooled to room temperature. Both crystals of 1 and 3 were colorless. All data were collected on a Picker diffractometer at room temperature. The structure of the iron complex was solved in the monoclinic space group $C2/c$ by conventional heavy-atom methods. The position of the Fe atom was determined from a Patterson map, while the remaining non-hydrogen atoms were located from subsequent difference-Fourier maps. This was followed by several cycles of full-matrix least-squares refinement. At least one hydrogen on methyl and methylene groups was found in a difference electron density map. The other positions of hydrogen atoms were calculated on the basis of idealized bond lengths and angles for sp^3 and sp^2 hybridized carbons. Neither the positions nor the temperature factors were refined for the hydrogen atoms. A final least-squares refinement led to $R = 0.082$ and $R_w = 0.081$. Both structures of 1 and 3 were solved by direct methods (MULTAN80), 1 in the monoclinic space group $P2_1$ and 3 in the triclinic space group $P\bar{1}$. The positions of non-hydrogen atoms were located from difference electron density maps. This was followed by several cycles of full-matrix least-squares refinement. For 3, the positions of the amide nitrogen atom and the acetate oxygen atom were determined by refining the occupation of the two atoms. Since nitrogen atoms should have hydrogen atoms attached while oxygen atoms should not, location of the hydrogen atom in a difference map around nitrogen was also helpful in distinguishing acetamide and acetate groups. The positions of hydrogen atoms were located by the same method as described for the iron complex. Final least-squares refinements led to $R = 0.048$ and $R_w = 0.066$ for 1 and $R = 0.075$ and $R_w = 0.086$ for 3. Tables of the fractional coordinates, bond distances, bond angles, and isotropic and anisotropic temperature factors for all three compounds are listed in the supplementary material.

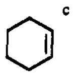
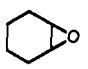
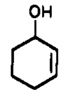
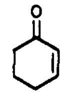
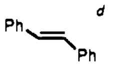
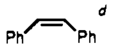
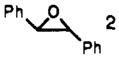
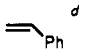
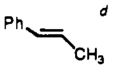
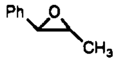
Isomerization of *cis*-Stilbene. PhI(OH)(OTs) (0.025 mmol) was added to an acetonitrile (5 mL) solution of *cis*-stilbene (100 mM). Aliquots were taken before and after addition of PhI(OH)(OTs), and the reaction was stirred for 30 min. These samples were diluted and analyzed by HPLC.

Table II. Selected Bond Distances (Å) and Angles (deg) for (Et$_3$HN)Fe(bpb)Cl$_2$·CH$_3$CN[a]

bond distance		bond angle	
Fe-N1	2.178 (5)	N1-Fe-N2	76.8 (2)
Fe-N2	2.037 (4)	N2-Fe-N3	77.6 (2)
Fe-N3	2.047 (4)	N3-Fe-N4	77.1 (2)
Fe-N4	2.173 (5)	N4-Fe-N1	128.5 (2)
Fe-Cl1	2.350 (2)	Cl1-Fe-Cl2	152.3 (1)
Fe-Cl2	2.340 (2)	N1-Fe-Cl1	84.2 (1)
		N1-Fe-Cl2	84.9 (1)
		N2-Fe-Cl1	100.1 (1)
		N2-Fe-Cl2	102.1 (1)

[a] Estimated standard deviations in parentheses.

Table III. Olefin Epoxidation with OIPh Catalyzed by (Et$_3$HN)Fe(bpb)Cl$_2$[a]

substrate	product yield (%) based on PhI formed						turnover[b] number
 [c]		15		trace		trace	2.5
 [d]		12	PhCHO	4			2.5
 [d]		10		2	PhCHO	2	2.2
 [d]		7	PhCHO	1			1
 [d]		9	PhCHO	3			1.6
 [d]		10					2
1-octene[c]	1,2-epoxyoctane	7					1.2

[a] OIPh (0.1–0.2 mmol) was added to a 5-mL acetonitrile solution of 0.005 mmol (1 mM) of (Et$_3$HN)Fe(bpb)Cl$_2$ and 0.5 mmol (100 mM) of substrate. The mixture was stirred at room temperature under an inert atmosphere. The reaction mixture was filtered and analyzed by GC/MS or HPLC. [b] Turnover number is amount (mmol) of epoxide formed per millimoles of catalyst. [c] 0.5-h reactions. [d] 4-h reactions.

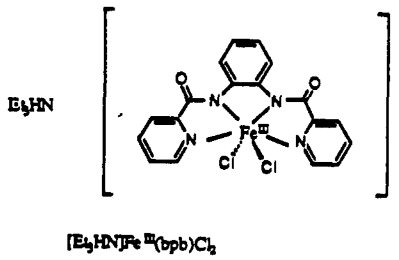
Table IV. Effect of Concentration of Cyclohexene on the Formation of Epoxide for (Et$_3$HN)Fe^{III}(bpb)Cl$_2$-Catalyzed Reaction by OIPh[a]

c-C$_6$H$_{12}$ (mM)	epoxide (mM)	IPh (mM)	% yield based on IPh formed	turnover number
50	1.4	10	13	1.4
100	1.9	13	15	1.9
2000[b]	2.0	11	18	2.0

[a] Reaction conditions: 0.005 mmol (1 mM) of iron catalyst, 0.1 mmol of OIPh with cyclohexene in 5 mL of acetonitrile for 30 min. [b] 0.2 mmol of OIPh was used.

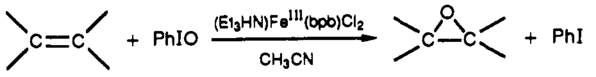
Results

I. Synthesis and Structure of (Et$_3$HN)Fe^{III}(bpb)Cl$_2$. The ferric complex used in this study was synthesized from the reaction of anhydrous FeCl$_3$ with H$_2$bpb in the presence of triethylamine in acetonitrile. The (Et$_3$HN)Fe^{III}(bpb)Cl$_2$ complex has dark green color. It is sensitive to moisture and slowly decomposes after exposure to air for several days. The ORTEP diagram from the X-ray crystallography for the complex is shown in Figure 1. The metal ion is located in the bpb ligand plane. Selective bond distances and angles are listed in Table II. The dark green solution of the (Et$_3$HN)Fe^{III}(bpb)Cl$_2$ complex in acetonitrile shows an absorption band at 680 nm with molar extinction coefficient (ϵ) 1.0×10^3 M^{-1} cm^{-1}, which is probably due to a charge transfer transition. EPR study of the solution and solid indicates the complex is high spin and rhombic with $g = 4.3$.



[Et$_3$HN]Fe^{III}(bpb)Cl$_2$

II. Catalytic Epoxidation of Olefins. Reactions of iodosylbenzene with a variety of olefins in the presence of the (Et$_3$HN)Fe^{III}(bpb)Cl$_2$ complex in acetonitrile at room temperature resulted predominantly in epoxides (eq 2). The color of the reaction solution changed from dark green to yellow during the reaction. The olefins used in this study included cyclohexene, *cis*-



(2)

Table V. Relative Reactivity of Substituted Styrenes in Epoxidation Catalyzed by Fe(OTf)$_2$[a]

styrene	log ($k_{\mathrm{subs\text{-}styr}}/k_{\mathrm{styr}}$)	σ^+
4-MeO–styrene	0.787	−0.78
4-Me–styrene	0.269	−0.31
4-Cl–styrene	−0.168	0.11
3-Cl–styrene	−0.479	0.40

[a] Reaction conditions: 0.01 mmol (2 mM) of Fe(OTf)$_2$, 0.15 mmol (30 mM) of olefins, and 0.08 mmol of OIPh in 5 mL of acetonitrile for 30 min.

and *trans*-stilbene, styrene, *trans*-β-methylstyrene, norbornene, and 1-octene. The results of the epoxidation of olefins catalyzed by (Et$_3$HN)Fe$^{\mathrm{III}}$(bpb)Cl$_2$ are listed in Table III. The results with variation of cyclohexene concentration are listed in Table IV. The yield of cyclohexene oxide obtained after 30 min did not increase significantly when the concentration of cyclohexene was varied from 50 mM to 2 M. The control experiments in all the cases demonstrated that the iron complex is required for the epoxidation reactions. Addition of more iodosylbenzene at the end of the reaction did not give additional epoxide, indicating that the catalyst had either decomposed or been modified during the course of the reaction. Use of ^{18}OIPh with cyclohexene as a substrate gave more than 90% ^{18}O incorporation to cyclohexene oxide. Attempts to observe intermediates spectroscopically at either room temperature or low temperature were not successful. At room temperature, the reaction occurred too fast; at lower temperature, no reaction occurred between (Et$_3$HN)Fe$^{\mathrm{III}}$(bpb)Cl$_2$ and OIPh. When a solution of (Et$_3$HN)Fe$^{\mathrm{III}}$(bpb)Cl$_2$ in acetonitrile was treated with iodosylbenzene in the absence of substrates, the solution also turned to yellow, and iodobenzene was formed in high yield.

The relative reactivities of substituted styrenes in epoxidation catalyzed by Fe(OTf)$_2$ and their σ^+ values, are listed in Table V. A Hammett plot of log ($k_{\mathrm{substituted\ styrene}}/k_{\mathrm{styrene}}$) vs σ^+ (Figure 2) gives the ρ value −1.1 according to the Hammett equation. The negative ρ value suggests the involvement of a positive charged species in the transition state.

$$\log (k/k_0) = \rho\sigma \qquad (3)$$

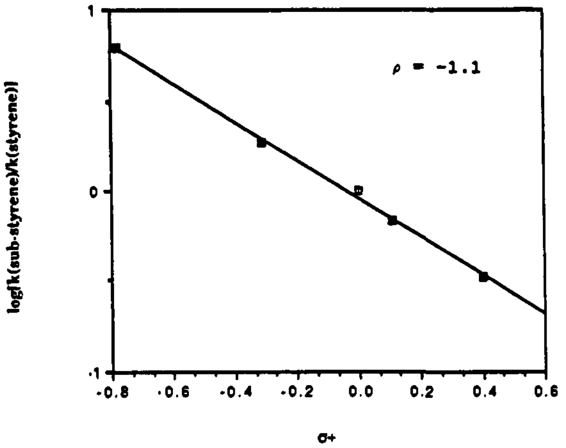


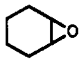
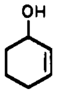
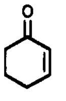
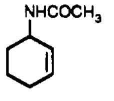
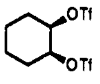
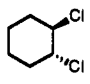
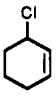
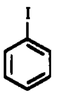
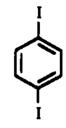
Figure 2. Hammett plot for the reaction of iodosylbenzene with substituted styrenes catalyzed by Fe(OTf)$_2$.

The results of epoxidation of cyclohexene catalyzed by some metal complexes and the identities and yields of other products are given in Table VI. The reaction conditions were chosen to optimize yields of products other than epoxide. Decreasing the concentration of catalysts led to higher turnover numbers for epoxide formation since the catalysts caused epoxide decomposition, especially at high concentration. We also know, from earlier work,[5b] that slow addition of small amounts of iodosylbenzene tends to give higher yields in these reactions and that too rapid addition results in formation of an iodine-containing iron complex that is ineffective as a catalyst.[5b] Epoxidation of other olefins with iodosylbenzene catalyzed by Fe(OTf)$_3$ and other triflates has also been previously reported by our laboratory.[5a,b]

III. Difunctionalization of Cyclohexene. In the case of cyclohexene as a substrate, the observation of cyclohexanediol ditriflate or dichloride as products in addition to cyclohexene oxide was striking. Table VI lists the results of the reactions of cyclohexene with iodosylbenzene in the presence of Fe(OTf)$_3$, Al(OTf)$_3$ or (Et$_3$HN)Fe(bpb)(OTf)$_2$. The reaction with metal triflates gave *cis*-1,2-cyclohexanediol ditriflate as a major product, and only a trace amount of the trans isomer was found. The yield was enhanced when an extra source of triflate, i.e., Li(OTf), was added. Li(OTf) itself reacting with cyclohexene and iodosylbenzene did not produce ditriflate. No 1,2-cyclohexanediol ditriflate was detected in control reactions of metal complexes with cyclohexene in the absence of iodosylbenzene, suggesting an I$^{\mathrm{III}}$ compound was required for the formation of the ditriflate.

Table VI also lists the results of the reaction of cyclohexene with iodosylbenzene in the presence of (Et$_3$HN)Fe(bpb)Cl$_2$, FeCl$_3$, or AlCl$_3$ under a variety of conditions. Dichlorination of cyclohexene gave *trans*-1,2-dichlorocyclohexane as a major product, and only a trace amount of the cis isomer was found. The control reactions in the absence of iodosylbenzene showed no or trace amounts of 1,2-disubstituted cyclohexane. Substantial amounts

Table VI. Products Observed in Reactions of Cyclohexene with OIPh Catalyzed by Metal Complexes in CH$_3$CN

metal complex	product (mM)								
									
Fe(OTf)$_3$[a]	28	1	3	11	0.4			116	0.6
Fe(OTf)$_3$ + Li(OTf)[a]	34	3	5	9	1.3			122	0.6
Al(OTf)$_3$[a]	28	3	3	13	0.2			120	0.6
Al(OTf)$_3$ + Li(OTf)[a]	14	3	3	3	0.3			77	0.3
(Et$_3$HN)Fe(bpb)(OTf)$_2$[a]	15	3	2	4	trace			60	0.4
(Et$_3$HN)Fe(bpb)(OTf)$_2$ + Li(OTf)[a]	20	5	5	10	0.1			88	0.6
(Et$_3$HN)Fe(bpb)Cl$_2$[b]	10	2.6	0.9			1.0	1.7	67	0.3
(Et$_3$HN)Fe(bpb)Cl$_2$ + O$_2$[c]	8.5	1.7	1.5			0.15	0.4	58	0.3
FeCl$_3$[b]	trace	trace	trace			1.4	0.4	18	0.09
AlCl$_3$[b]	trace	trace	trace			3.0	0.5	13	0.09
O[IPh(OTf)]$_2$[d]	nd[e]	nd	nd	nd	0.2–0.3			10	0.02

[a] OIPh (0.8 mmol) was added to a 5-mL acetonitrile solution of 0.025 mmol (5 mM) of metal complex (and 0.4 mmol (80 mM) of Li(OTf) when indicated) and 10 mmol (2 M) of cyclohexene. The mixture was stirred for 2 h at room temperature under an inert atmosphere. The reaction mixture was filtered and analyzed by GC/MS. [b] OIPh (0.4 mmol) was added to a 5-mL acetonitrile solution of 0.025 mmol (5 mM) of metal complex and 0.5 mmol (100 mM) of cyclohexene. The mixture was stirred for 4 h. [c] The reaction was carried out by continuously bubbling oxygen through the solution. [d] Reaction was carried out by using 0.025 mmol (5 mM) of O[IPh(OTf)]$_2$, 0.5 mmol (100 mM) or 10 mmol (2 M) of cyclohexene in 5 mL of acetonitrile. Even in the presence of 0.4 mmol (80 mM) of O[IPh(OTf)]$_2$, no 3-acetamidocyclohexene was detected. [e] nd refers to not detected.

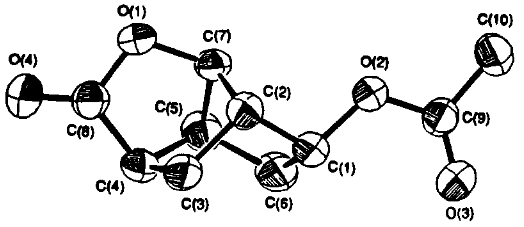
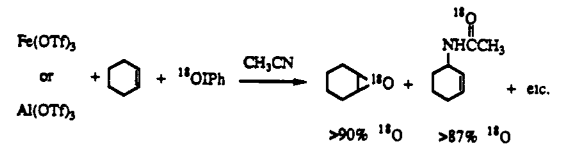


Figure 3. ORTEP diagram for **1**.

of *trans*-1,2-dichlorocyclohexane were also found in the presence of $FeCl_3$ or $AlCl_3$, although there were no significant amounts of epoxide produced. 3-Chlorocyclohexene was formed in these reactions especially when $(Et_3HN)Fe(bpb)Cl_2$ was used. Dioxygen has been used as a radical trap in such reactions to assay if dichlorination proceeds via a radical mechanism.[15] We therefore carried out a reaction of $(Et_3HN)Fe(bpb)Cl_2$ with cyclohexene and iodosylbenzene while dioxygen was bubbled through the solution. The results (see Table VI) demonstrate that dioxygen inhibits the formation of dichloride and 3-chlorocyclohexene but does not significantly affect epoxide formation.

IV. Formation of 3-Acetamidocyclohexene. Substantial amounts of 3-acetamidocyclohexene were produced in the reactions of cyclohexene with iodosylbenzene in the presence of $Fe(OTf)_3$, $Al(OTf)_3$, or $(Et_3HN)Fe(bpb)(OTf)_2$ as shown in Table VI. The reactions were catalytic. Control reactions in the absence of metal complexes or iodosylbenzene gave no 3-acetamidocyclohexene.

The formation of this amide is analogous to the product formed in the Ritter reaction.[16] In the Ritter reaction, the amide oxygen is derived from H_2O.[16] Our reactions were carried out in dry acetonitrile, however, and we doubted that sufficient water was present to account for the product. We therefore carried out an isotopic labeling study using $^{18}OIPh$ to ascertain the source of oxygen. The results indicate that oxygen was derived from iodosylbenzene: ^{18}O incorporation into the amide group in more than 87%, and ^{18}O incorporation into the epoxide in more than 90% (eq 4).



(4)

V. Formation of 1,4-Diiodobenzene. One additional product, 1,4-diiodobenzene was observed in all of the reactions as shown in Table VI. This product was found whether or not cyclohexene was present. Trace amounts of 1,2-diiodobenzene were also detected. Control reactions of iodosylbenzene with iodobenzene in acetonitrile gave only trace amounts of 1,4-diiodobenzene.

VI. Reactions of Iodobenzene Diacetate ($PhI(OAc)_2$) with Bicyclo[2.2.1]-5-heptene-2-carboxylic Acid or Norbornene. Iodine(III) compounds are known to react with olefins in the absence of metal catalysts although epoxides have previously never been reported as products.[7] Our growing suspicion that the mechanism of metal-catalyzed reactions of iodosylbenzene in the case of non-porphyrin systems might be related to the I^{III} chemistry led us to investigate the chemistry of a typical I^{III} reagent, $PhI(OAc)_2$, with norbornenecarboxylic acid and norbornene, seeking clues to the mechanism of the reaction. Norbornenecarboxylic acid and norbornene have been used by Moriarty et al. in lead(IV) and thallium(III) acetate oxidation of olefins.[14] Electrophilic addition of these metal ions to the double bond of olefins has been proposed as the mechanism on the basis that acetoxylactones and 7-acetoxynorbornene were formed as products. The reactions with PhI(OH)(OTs) yielded a (tosyloxy)lactone in the case of norbornenecarboxylic acid,[8a] and 2,7- and 2,3-bis(tosyloxy)norbornane in the case of norbornene.[7a]

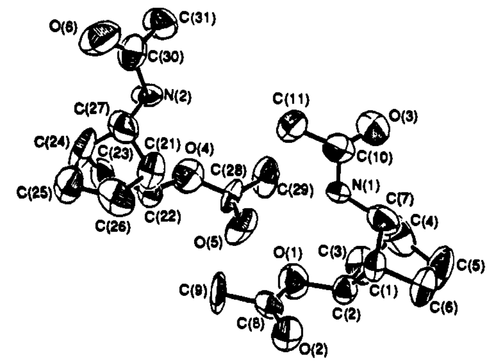
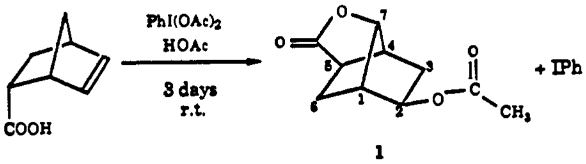


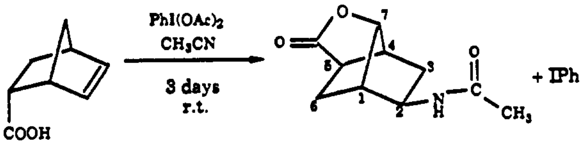
Figure 4. ORTEP diagram for **3**.

The reactions of iodobenzene diacetate with norbornenecarboxylic acid in acetic acid or acetonitrile yielded compounds **1** or **2** respectively (eqs 5 and 6).



1

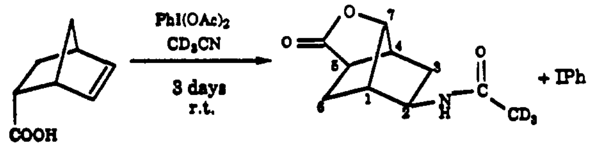
(5)



2

(6)

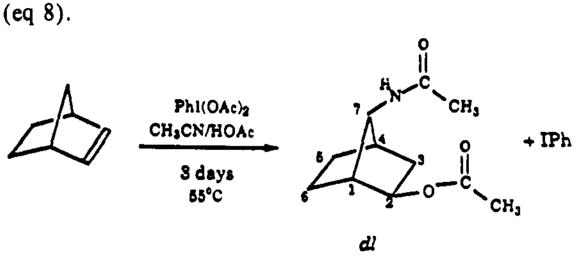
The products were identified by IR, ^1H and ^{13}C NMR, and mass spectra. The structure of **1** was determined by X-ray crystallography, and its ORTEP diagram is presented in Figure 3. The structure of **2** was assigned by comparison of its ^1H and ^{13}C NMR data with those of **1**. It has been demonstrated that the amide group in **2** is derived from acetonitrile by carrying out the reaction in isotopically labeled acetonitrile, CD_3CN (eq 7), and analyzing the ^1H NMR spectrum of the product.



2-*d*$_3$

(7)

The reaction of iodobenzene diacetate with norbornene in the solvent mixtures of acetic acid and acetonitrile, where no internal carboxylic acid existed, resulted in compound **3** and other products (eq 8).



dl

3

+ others

(8)

The structure of **3** was determined by X-ray crystallography, and Figure 4 shows its ORTEP diagram.

VII. Isomerization of *cis*-Stilbene by Hydroxy(tosyloxy)iodobenzene (PhI(OH)(OTs)). When PhI(OH)(OTs) (5 mM) reacted with *cis*-stilbene (100 mM) in acetonitrile, 90% of *cis*-stilbene isomerized to *trans*-stilbene in 30 min. No stilbene oxide was detected under the same condition or at higher concentration of PhI(OH)(OTs) (80 mM) and longer reaction time (2 h). The reactions of *cis*-stilbene with iodosylbenzene in the presence of

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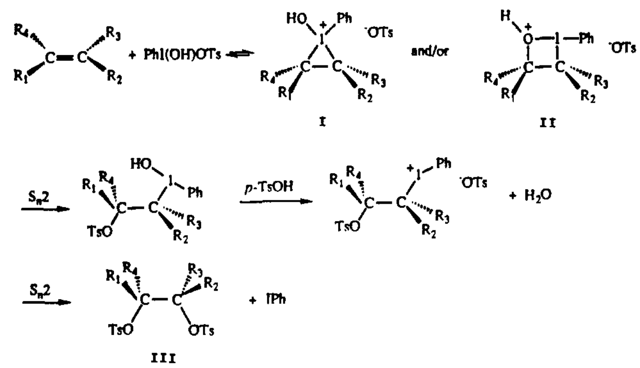
[15] Tanner, D. D.; Gidley, G. C. *J. Org. Chem.* **1968**, *33*, 38–43.

[16] Cota, D. J. In *Organic Reactions*; Wiley Inc.: New York, 1969; Vol. 17, pp 213–325.

Scheme I



cobalt, manganese, or copper triflate also resulted in isomerization of *cis*- to *trans*-stilbene,[5a] although this isomerization did not occur with iron triflate[5a] or $(Et_3HN)Fe^{III}(bpb)Cl_2$ present.

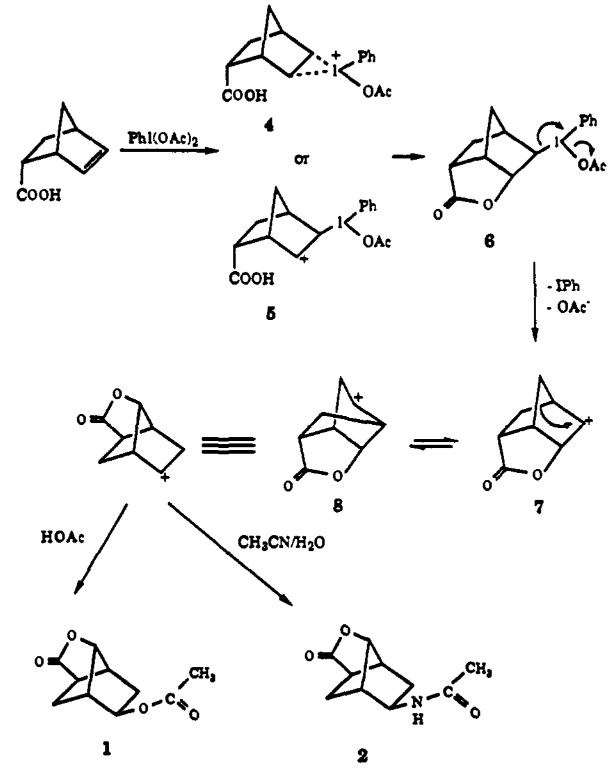
Discussion

Reactions of Organoiodine(III) Compounds with Olefins. The reactions of PhI(OH)(OTs) with olefins were reported initially by Koser and co-workers.[7b] Since that time, several studies of a variety of I^{III}-containing compounds have been reported by his group and others.[7] On the basis of their studies, Koser and co-workers proposed a mechanism of electrophilic attack of I^{III} on olefins occurring via two possible intermediates (I and/or II) (see Scheme I).[7a] Two steps of nucleophilic addition of tosylate to intermediate I yield *cis*-1,2-bis(tosyloxy)alkanes III. O–I bond cleavage in II followed by nucleophilic addition of tosylate and loss of iodobenzene leads to *trans*-1-hydroxy-2-(tosyloxy)alkane IV. Both of these products have been observed in the reaction of PhI(OH)(OTs) with cyclohexene.[7a]

In order to demonstrate further the electrophilic character of I^{III} and relate it to metal-catalyzed oxygenation reactions, we have studied the reactions of iodobenzene diacetate with norbornenecarboxylic acid or norbornene in different solvents. The formation of the amides **2** and **3** when acetonitrile was used as a solvent (eqs 6 and 8) is particularly significant and gives insight into the probable mechanism of the reaction. The formation of amides is reminiscent of the products formed in the Ritter reaction.[16] The mechanism of the Ritter reaction is believed to proceed via a carbocation intermediate.[16] The formation of amides in the iodobenzene diacetate reactions suggests strongly that the reactions involve carbocations as intermediates. We also found that norbornane rings in all of three products have been rearranged during the reactions. This skeletal rearrangement is also indicative of the involvement of carbocations. In these reactions, the only reagent present capable of generating such intermediates is the iodine(III) reagent. Indeed, the control experiment shows that no reaction occurs in the absence of iodobenzene diacetate. The carbocations thus must be generated by iodine(III) in iodobenzene diacetate. The formation of carbocations by iodine(III) and skeletal rearrangement of the norbornane ring strongly demonstrate the electrophilic character of iodine(III)-containing compounds.

On the basis of the above discussions, we propose the mechanism shown in Scheme II. Electrophilic attack of iodine(III) on the double bond of norbornenecarboxylic acid generates an intermediate (**4** and/or **5**). An internal nucleophilic addition of carboxylate forms a lactone (**6**) with an iodine(III) species attached to carbon. Dissociation of iodobenzene and acetate gives a carbocation (**7**) that can rearrange to another carbocation (**8**). A similar reaction mechanism that involves electrophilic attack of metal ions in $Pb(OAc)_4$ or $Tl(OAc)_3$ on the double bond followed by dissociation of metal acetates in the reaction of these metal acetates with norbornenecarboxylic acid has been previously postulated.[14] In the case of the reaction (eq 5) in acetic acid, addition of acetate gives **1**, while in acetonitrile (eq 6), addition of acetonitrile yields compound **2**. A possible mechanism for formation of **3** is quite similar to that of **1** and **2** and involves intermediates similar to **4** and/or **5** formed by electrophilic attack of iodine(III) on the double bond of norbornene.

Scheme II



Metal-Catalyzed Reactions of OIPh with Olefins. Che et al. have reported that manganese(III) amide complexes ($Mn^{III}(bpb)Cl$, $Mn^{III}(bpb)N_3$, and $Mn^{III}(bpcb)Cl$, where H_2bpcb = 1,2-bis(pyridine-2-carboxamido)-4,5-dichlorobenzene) are efficient catalysts for alkene epoxidation by iodosylbenzene (OIPh) in acetonitrile solvent.[17] A similar osmium complex, $Os^{III}(bpb)(PPh_3)Cl$, has also been reported to catalyze the epoxidation of cyclohexene by iodosylbenzene, although the yield is not as high.[18] Although no mechanistic studies were reported, the results of these studies for manganese and osmium–bpb complexes were promising. We were interested in examining iron complexes with the bpb ligand as potential catalysts for oxidations of organic substrates in the hope that we could obtain some mechanistic insight concerning iron-catalyzed oxidation reactions. The dianionic ligand bpb seemed to be a good candidate ligand for oxidation studies. The bpb ligand is oxidation resistant, and therefore ligand destruction by oxidant during the reaction could be minimized. Since this ligand is tetradentate, there are still two coordination positions left on iron for reaction with potential oxidants. In addition, nitrogen atom coordination is very common for metalloenzymes, and the pyridine ligands resemble imidazole, which is one of the most common amino acid residues bound to metal in this type of enzyme. We therefore chose iron–bpb complexes as catalysts for oxidation studies of organic compounds.

We find that $(Et_3HN)Fe^{III}(bpb)Cl_2$ catalyzes a variety of olefin epoxidations by iodosylbenzene in acetonitrile (see Table III). Epoxides are the predominant products in all of the reactions, and the epoxide oxygen is derived from iodosylbenzene as verified by $^{18}OIPh$ labeling studies using cyclohexene as a model substrate. The fact that the reaction with cyclohexene forms mainly cyclohexene oxide and only trace amounts of 2-cyclohexen-1-one and 2-cyclohexen-1-ol indicates that typical free radical pathways are not involved. The reactivity does not vary much among these different olefins even for two extreme examples, norbornene and 1-octene. For many epoxidation reactions, the former is very reactive, and the latter, a terminal olefin, is relatively unreactive.

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(17) Che, C.-M.; Cheng, W.-K. *J. Chem. Soc., Chem. Commun.* **1986**, 1443–1444.

(18) Che, C.-M.; Cheng, W.-K.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1986**, 200–202.

We conclude that the rate-determining step in the reaction catalyzed by $(Et_3HN)Fe^{III}(bpb)Cl_2$ is not a reaction with substrate. This conclusion was substantiated by our observation that the yield of epoxide formation was relatively insensitive to the olefin concentration (see Table IV). It is likely that the rate-limiting step is reaction of the complex with the insoluble OIPh polymer and that subsequent reactions are faster. *cis*-Stilbene is used as a probe in this study to assay the stereochemistry of the reaction since oxygen atom transfer from various oxygen donors to *cis*-stilbene often leads to a significant amount of *trans*-stilbene oxide. Our results show that *cis*-stilbene oxide is the major product when *cis*-stilbene is used as a substrate in the $(Et_3HN)Fe^{III}(bpb)Cl_2$-catalyzed reactions, indicating that the catalytic epoxidation occurs with stereochemical retention. $(Et_3HN)Fe^{III}(bpb)Cl_2$ reacts with iodosylbenzene in the absence of substrates, giving iodobenzene. The fate of the oxygen in iodosylbenzene is unknown. This reaction competes with the epoxidation reaction with the result that yields of epoxide based on iodobenzene formed are not high.

Replacement of the chloride ligand by triflate gave $(Et_3HN)Fe^{III}(bpb)(OTf)_2$, which proved to be a better catalyst than $(Et_3HN)Fe^{III}(bpb)Cl_2$ (see Table VI). Addition of excess triflate to $(Et_3HN)Fe^{III}(bpb)(OTf)_2$ further increased the yield of epoxide, suggesting strongly that triflate plays a role in the mechanism of this reaction. This conclusion is discussed further below.

Having established that the non-porphyrinic ferric complexes $(Et_3HN)Fe^{III}(bpb)X_2$ could catalyze olefin epoxidation by OIPh, we turned our attention to the question of the possible involvement of a high-valent metal oxo intermediate in the reaction. It had been recently found in our laboratory that nonredox metal complexes could catalyze the epoxidation of olefins by iodosylbenzene.[5c] We therefore extended our studies to examination of the reactivity of $Al(OTf)_3$, which we found to be very similar to that of $Fe(OTf)_3$. In addition, we found evidence for the presence of other organic products, which turned out to be present in reactions of all three catalysts, i.e., $(Et_3HN)Fe^{III}(bpb)(OTf)_2$, $Al(OTf)_3$, and $Fe(OTf)_3$ (see Table VI). The strong resemblance of the product distributions in the presence of these three catalysts strongly suggests that these reaction mechanisms are related. The similarity of $Al(OTf)_3$ as a catalyst implied that the Lewis acidity rather than the redox character was important for these reactions, and therefore that a high-valent metal oxo intermediate was not involved.

We find that cyclohexene oxide is the major product in our iron-catalyzed reactions of iodosylbenzene with cyclohexene. In addition, however, we find substantial amounts of 3-acetamidocyclohexene, *cis*-1,2-cyclohexanediol ditriflate, dichlorocyclohexane, and small amounts of diiodobenzene produced in these reactions. Each of these products is discussed below.

Difunctionalization by Triflates. *cis*-1,2-Cyclohexanediol ditriflate was formed in the reactions of cyclohexene with iodosylbenzene and metal complexes containing triflate (see Table VI). The reactions gave the cis isomer nearly stereospecifically, i.e., only trace amounts of the trans isomer were observed. The fact that the reaction in the absence of iodosylbenzene did not give ditriflate indicates that an I^{III}-containing species is required to form this product. The same product has also been found in the reaction of cyclohexene with μ-oxobis[(triflato)(phenyl)iodine] in ethylene chloride.[7d] Stereospecific formation of *cis*-1,2-cyclohexanediol ditriflate in our reaction is analogous to cis-1,2-difunctionalization of olefins by a variety of I^{III} compounds,[7] suggesting that this product is the result of electrophilic attack of I^{III} on olefins followed by nucleophilic addition of triflate.

The formation of the same product in the reaction of cyclohexene with $O[IPh(OTf)]_2$ raises the question whether the product actually resulted from the reaction of cyclohexene with $O[IPh(OTf)]_2$, which might have been formed by the reaction of iodosylbenzene with $Fe(OTf)_3$. We therefore carried out a reaction of $O[IPh(OTf)]_2$ with cyclohexene. Our results indicate that the formation of *cis*-1,2-cyclohexanediol ditriflate from $O[IPh(OTf)]_2$ in acetonitrile is independent of the concentration of cyclohexene. We attribute this finding to rate-determining dissociation of the μ-oxo dimer prior to reaction with olefin. By contrast, the reaction of cyclohexene with iodosylbenzene catalyzed by $Fe(OTf)_3$ shows a dependence of the rate of formation of both epoxide and *cis*-1,2-cyclohexanediol ditriflate on cyclohexene concentration. These results suggest that *cis*-1,2-cyclohexanediol ditriflate is not produced from $O[IPh(OTf)]_2$ in our reaction.

The observation that the same ditriflate product was formed in the system of iodosylbenzene plus metal complex and in a soluble I^{III}-containing compound leads us to believe that the reaction mechanisms are similar. We therefore conclude that a metal complex with an I^{III}-containing ligand is responsible for the product formation and the mechanism involves electrophilic attack of iodine(III) on the double bond of olefin.

Dichlorination. *trans*-1,2-Dichlorocyclohexane and 3-chlorocyclohexene are observed in the reactions of cyclohexene with iodosylbenzene and metal complexes containing chloride (see Table VI). Although it has been reported that halogenations of olefins with copper(II) halides give trans-1,2-dihalogenated alkanes,[19] our control experiments in the absence of iodosylbenzene indicate no or trace amounts of dichlorocyclohexane and 3-chlorocyclohexene are formed. The results suggest that iodine(III) is required for the product formation. Similar dichlorination of olefins by iodobenzene dichloride ($PhICl_2$) has also been reported in early papers.[15] Mechanistic studies have suggested that the reaction can proceed by a radical or an ionic mechanism.[15] The distribution of the products from these two pathways should be different. In a radical reaction, one would expect most of the product to be the trans isomer because of its greater thermodynamic stability. In an ionic reaction, if the reaction proceeds via electrophilic attack of iodine(III) on olefins, similar to the mechanism proposed by Koser et al., the cis isomer would be the major product. The fact that the trans isomer is the major product in our reactions and that *trans*-1,2-dichlorocyclohexane and 3-chlorocyclohexene are significantly inhibited in the presence of dioxygen suggests that dichlorination may go through a radical mechanism. By contrast, the epoxide yield is not significantly affected by the presence of dioxygen, suggesting that the mechanism for epoxidation is different from that of dichlorination.

Formation of 3-Acetamidocyclohexene. Substantial amounts of 3-acetamidocyclohexene are produced in the reactions of cyclohexene with iodosylbenzene in the presence of $Fe(OTf)_3$, $Al(OTf)_3$, or $(Et_3HN)Fe(bpb)^{III}(OTf)_2$ in acetonitrile solvent. Control experiments demonstrate that both iodosylbenzene and metal complexes are needed in order to produce this product. The formation of these amides is reminiscent of products formed in the Ritter reaction[16] and strongly implies that carbocation intermediates are involved. Unlike the Ritter reaction where the amide oxygen is derived from water, the amide oxygen in our reactions carried out in dry acetonitrile is derived from iodosylbenzene as evidenced by isotopic labeling studies using $^{18}OIPh$. The reaction of cyclohexene with $O[IPh(OTf)]_2$ in acetonitrile does not produce 3-acetamidocyclohexene, indicating clearly that the species responsible for the product is not $O[IPh(OTf)]_2$.

Similar amides have been found in metal-catalyzed reactions with alkanes in acetonitrile. Hill and co-workers have observed the formation of *N*-alkylacetamides from adamantane in polyoxometalate complex catalyzed reactions with *tert*-butyl hydroperoxide.[20] Their studies suggest that the products are likely formed from carbocations generated by oxidation of intermediate alkyl radicals under the reaction conditions. Kochi and co-workers have reported that a substantial amount of *N*-cyclohexylacetamide is formed from the reaction of cyclohexane with iodosylbenzene and manganese complexes.[6c] They have suggested that the cyclohexyl cation is formed by oxidation of cyclohexyl radical by high-valent manganese oxo species ($Mn^{V}{=}O$).[6c] However, this mechanism is not reasonable for our reaction because $Al(OTf)_3$,

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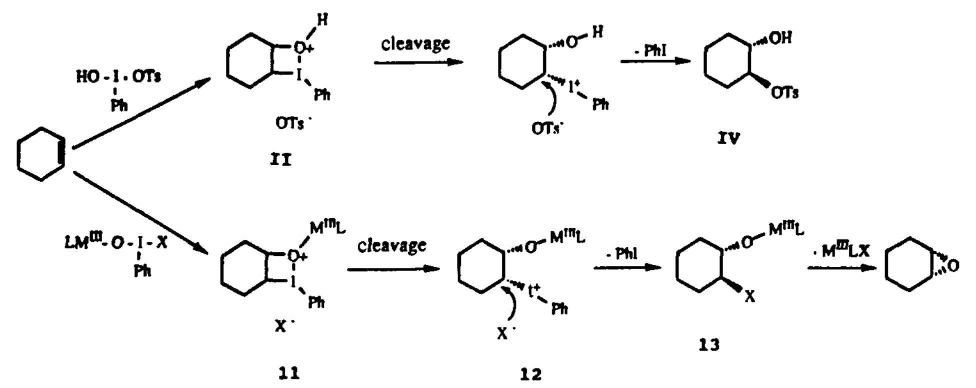
(19) (a) Baird, Jr., W. C.; Surridge, J. H.; Buza, M. *J. Org. Chem.* **1971**, *36*, 3324–3330. (b) Gamlen, P. H.; Henty, M. S.; Roberts, H. L. *J. Chem. Soc., Dalton Trans.* **1983**, 1373–1376.

(20) Faraj, M.; Lin, C.-H.; Hill, C. L. *New J. Chem.* **1988**, *12*, 745–749.

Scheme III

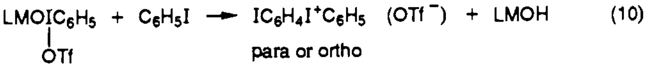


which is incapable of generating high-valent metal oxo species, catalyzes 3-acetamidocyclohexene formation. We have also found similar amides (**2** and **3**) from the reactions of iodobenzene diacetate with norbornene or norbornenecarboxylic acid and demonstrated the reactions involve carbocations that are generated by iodine(III). Furthermore, 1-acetamido-2-iodocyclohexane has been reported to be formed from the reaction of cyclohexene with $I(Py)_2BF_4$ in acetonitrile,[21] which strongly supports a mechanism in which a carbocation is generated by iodine species. Therefore we believe that, in our reactions, the carbocations are generated by iodine(III) species in a metal–iodosylbenzene complex.

Formation of 1,4-Diiodobenzene. Small amounts of 1,4-diiodobenzene are found in all of the reactions of cyclohexene with iodosylbenzene and metal complexes. The same amounts of the products are formed in the absence of cyclohexene. Products similar to 1,4-diiodobenzene have been found in reactions of iodonium ions.[22] Iodonium ions such as ArI^+Ar decompose to form mono- or disubstituted benzene in the presence of some nucleophiles, e.g.

$$IC_6H_4I^+C_6H_5 + Cl^- \rightarrow C_6H_5I + IC_6H_4I + C_6H_5Cl + IC_6H_4Cl \quad (9)$$

Iodonium ion $IC_6H_4I^+C_6H_5$ in our reactions could be generated from an electrophilic substitution reaction of the iron–iodosylbenzene complex with iodobenzene, which is a product of the reaction (eq 10). The low yields of 1,4- or 1,2-diiodobenzene

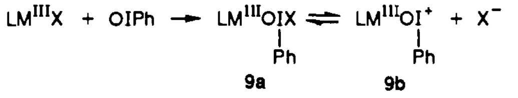


$$\underset{\displaystyle \mathrm{OTf}}{\mathrm{LMOIC_6H_5}} + C_6H_5I \longrightarrow \underset{\text{para or ortho}}{IC_6H_4I^+C_6H_5\ (OTf^-)} + LMOH \quad (10)$$

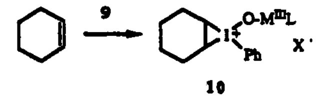
are expected because I deactivates the benzene ring; therefore, the formation of $IC_6H_4I^+C_6H_5$ is expected to be slow. The formation of diiodobenzene should be independent of the presence of cyclohexene, which is in agreement with our results.

Proposed Mechanism. The mechanism of cytochrome P450 and porphyrin models is believed to go through a high-valent iron(IV)–oxo porphyrin cation radical species.[1] In the cases of non-heme monooxygenases, similar high-valent iron(IV)–oxo or iron(V)–oxo species have not been demonstrated. If a similar high-valent iron–oxo species does exist in mononuclear non-heme iron-containing enzyme, it would be Fe(V)=O or Fe(IV)=O with oxidation of some group on the protein. We had hoped that the complexes $(Et_3HN)Fe(bpb)X_2$ would be good candidates for stabilization of high-valent metal–oxo species. We found, however, that they were inferior to the simple ferric triflate salt $Fe(OTf)_3$, which we found to have a reactivity virtually identical with that of $Al(OTf)_3$. We therefore abandoned the high-valent iron–oxo hypothesis for these reactions. On the other hand, electrophilic properties of iodine(III)-containing compounds had previously been demonstrated in reactions of olefins. Our observation of products other than epoxides and their similarity to products resulting from I^{III} chemistry leads us to propose the mechanism discussed below that can account for all of the observed products.

We believe that **9a** is the first species formed in these reactions where the metal complex reacts with the insoluble OIPh polymer. Related complexes have been isolated and spectroscopically characterized by Hill and his co-workers from reaction of manganese porphyrins with iodosylbenzene.[23] On the basis of the work of Koser[7a] and Zefirov,[7c] we expect that I^{III} in **9a** will be electrophilic. We therefore propose that **9a** or **9b** reacts with the double bond of cyclohexene, forming **10**, which resembles the intermediate proposed by Koser and co-workers in their reactions.[7a] This intermediate can then react by several pathways, each leading to a different product.



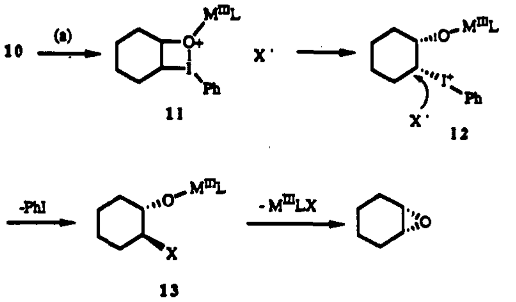
$$LM^{III}X + OIPh \longrightarrow \underset{\textbf{9a}}{\underset{\displaystyle Ph}{LM^{III}OIX}} \rightleftharpoons \underset{\textbf{9b}}{\underset{\displaystyle Ph}{LM^{III}OI^+}} + X^- \quad (11)$$



(12)

10

In pathway a, **10** rearranges to give **11**, which then forms **12** by O–I bond cleavage. Nucleophilic addition of the anion X^- and loss of PhI followed by oxygen–carbon bond formation yield epoxide. Participation of the anion in the reactions may explain why the amount of epoxide increases when an excess of triflate is added. Compared to chloride, triflate is a poorer ligand and weaker nucleophile; therefore, the complex with triflate as a ligand is expected to form **9** more easily in the first step of the reaction and to leave more quickly in the last step of the reaction to give epoxide. It is interesting to compare this pathway with that proposed by Koser et al.[7a] for the reaction of cyclohexene with PhI(OH)(OTs) (see Scheme III). Comparing intermediate **11** with II, we notice that the only difference is that, in **11**, a metal binds to oxygen while in II a proton binds to oxygen. After formation of **13**, epoxide forms because one would expect **13** to be unstable. However, if a proton binds to oxygen in **13**, a stable *trans*-1-hydroxy-2-(tosyloxy)cyclohexane, IV, forms. Therefore,



(13)

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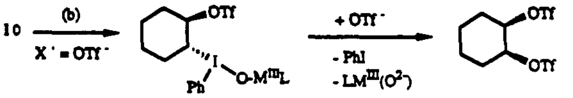
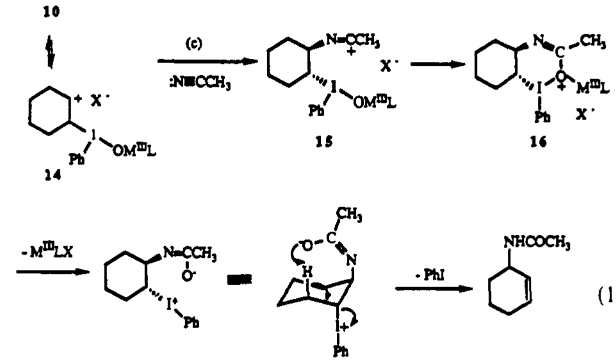
no epoxide is produced in the reaction of PhI(OH)(OTs) with cyclohexene.

In pathway b, **10** is attacked by a nucleophile, triflate, and *cis*-1,2-cyclohexanediol ditriflate is formed by two steps of nucleophilic substitution of triflates. This mechanism is further supported by the fact that the amount of *cis*-1,2-cyclohexanediol ditriflate increases when extra source of triflate such as Li(OTf) is added.



(14)

In pathway c, in order to achieve the postulated loss of IPh to give 3-acetamidocyclohexene as shown in eq 15, **15** is formed either by attack of acetonitrile on cyclic **10** or by trans attack on the carbocation **14** of which one face is sterically protected by the bulk I^{III}-substituted species. This step of the reaction is analogous to the Ritter reaction. Under the conditions of our reaction in dry acetonitrile solvent, the oxygen originating from iodosylbenzene attacks the immonium center in **15** to form the six-membered-ring intermediate **16**. As shown in eq 15, when the intermediate then formed is in the diaxial conformation, this same oxygen atom can act as an internal base, and intramolecular proton abstraction will give the final product 3-acetamidocyclohexene.



(15)

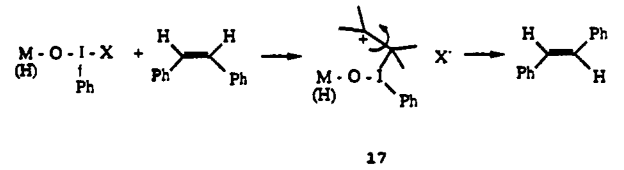
To account for the formation of diiodobenzene, the reactive I^{III} species **9b** could react with iodobenzene, a product formed in these reactions, to form an iodonium ion, $IC_6H_4I^+C_6H_5$ as shown in eq 10. This iodonium ion then decomposes to diiodobenzene etc. This reaction does not involve olefin, and therefore should proceed whether or not cyclohexene is present, which is consistent with our results.

Previous studies with metal triflates demonstrated that $Fe(OTf)_2$ and $Fe(OTf)_3$ show similar reactivity for olefin epoxidation.[5a] Also, *cis*-1,2-cyclohexanediol ditriflate and 3-acetamidocyclohexene are found in the reaction with $Fe(OTf)_2$. The negative ρ value from the Hammett equation for the competition reaction of substituted styrenes catalyzed by $Fe(OTf)_2$ suggests development of positive charge in the transition state. This observation is in agreement with our proposed mechanism.

The observation that epoxidation of norbornene by iodosylbenzene catalyzed by $(Et_3HN)Fe(bpb)Cl_2$ gave exo epoxide only (see Table III) also is in agreement with our proposal that the mechanism involves electrophilic attack on norbornene.[24]

Isomerization by *cis*-Stilbene. The metal triflate catalyzed epoxidation of *cis*-stilbene by iodosylbenzene has been reported.[5a] It was found that *trans*-stilbene oxide is the major product and that large amounts of *cis*-stilbene isomerize to *trans*-stilbene when Co, Mn, and Cu triflates are used.[5a] In contrast, *cis*-stilbene is produced as the major product and no isomerization of *cis*-stilbene to *trans*-stilbene is found in the reactions of Fe(III) triflate[5a] and $(Et_3HN)Fe(bpb)Cl_2$. Small amounts of isomerization of *cis*-stilbene to *trans*-stilbene have also been found in Fe(BLM),[25] Ni(cyclam),[6e] and Fe–porphyrin[26] catalyzed reactions with iodosylbenzene. Castellino and Bruice have used *cis*-stilbene as a mechanistic probe in iron porphyrin catalyzed epoxidation studies and suggested the isomerization is caused by a carbocation radical intermediate.[26] We have found a large amount of isomerization of *cis*-stilbene to *trans*-stilbene catalyzed by PhI(OH)(OTs) in acetonitrile. This observation suggests that electrophilic addition of Ph(OH)(OTs) to *cis*-stilbene could form the carbocation **17** (Scheme IV), similar to **14** in eq 15, which is also capable of leading to *trans*-stilbene, the thermodynamically favored isomer. Therefore, the isomerization of *cis*-stilbene in metal-catalyzed reactions with iodosylbenzene can also be explained by the intermediate **17** in the proposed mechanism. If the oxygen–carbon bond forms quickly, e.g., in the conversion of the iron derivative **10** to **11** (eq 13), isomerization of *cis*-stilbene does not occur. If the oxygen–carbon bond-forming reactions are slow, however, the carbon–carbon bond in **17** has enough time to rotate, and isomerization occurs.

Scheme IV



The "Lost Oxygen" Reaction. A reaction that we term the "lost oxygen" reaction occurs in many of the oxidation studies using iodosylbenzene as an oxygen donor. This term refers to the unknown reaction that consumes iodosylbenzene and gives iodobenzene but does not give oxygenated substrate. For example, in the reaction of cyclohexene with iodosylbenzene catalyzed by $Fe(OTf)_3$ (see Table VI), the yield of epoxide is 24% based on iodobenzene formed, and 76% of oxygen goes by unknown pathways. (Some of the oxygen may be lost by iodosylbenzene disporportionation to give iodobenzene and iodoxybenzene, $PhIO_2$, but the high yield of PhI (see Table VI) indicates that such a reaction could only account for a minor portion of the lost oxygen.) This discrepancy has also been observed by other investigators studying iodosylbenzene reactions who have tentatively attributed it to solvent oxidation.[6d] Kochi and co-workers have suggested that acetonitrile is oxidized to hydrogen cyanide and formaldehyde in the nickel catalysis of olefin epoxidation by iodosylbenzene.[6d]

$$CH_3CN + PhIO \xrightarrow{[Ni]} PhI + HOCH_2CN \xrightarrow{fast} HCN + CH_2O \quad (16)$$

Our observation of formation of 3-acetamidocyclohexene where the amide oxygen is derived from iodosylbenzene accounts for only a small part of lost oxygen. However, its occurrence suggests an alternative explanation for the lost oxygen reaction. Coordination of the acetonitrile nitrogen atom to metal ion would be expected to weaken the N≡C triple bond. As a result, acetamide might be formed by inter- or intramolecular transfer of oxygen originated from the iodosylbenzene in the iron–iodosylbenzene complex. However, acetamide is likely to be unstable under the reaction conditions due to its further reaction with iodosylbenzene or other I^{III} species in the solution. Primary amides are known to react with several iodine(III) compounds such as $PhI(OOCCF_3)_2$,[27] PhI(OH)(OTs),[28] and PhIO with formic acid[29] and finally convert to amines or ammonium salts through the Hofmann rearrange-

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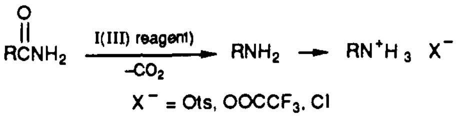
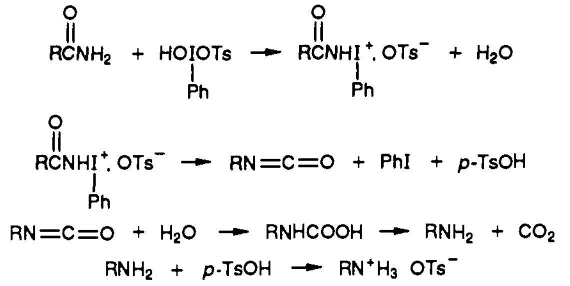
ment. A mechanism for the reaction with PhI(OH)(OTs),



$$\mathrm{R\overset{\displaystyle O}{\overset{\|}{C}}NH_2} \xrightarrow[-\mathrm{CO_2}]{\mathrm{I(III)\ reagent)}} \mathrm{RNH_2} \longrightarrow \mathrm{RN^+H_3\ X^-} \qquad (17)$$

$$\mathrm{X^- = Ots, OOCCF_3, Cl}$$

analogous to the Hofmann rearrangement, was proposed by Koser and co-workers.[28a]



$$\mathrm{R\overset{\displaystyle O}{\overset{\|}{C}}NH_2 + HO\underset{\displaystyle Ph}{\underset{|}{I}}OTs \longrightarrow R\overset{\displaystyle O}{\overset{\|}{C}}NH\underset{\displaystyle Ph}{\underset{|}{I}}{}^{+}, OTs^- + H_2O}$$

$$\mathrm{R\overset{\displaystyle O}{\overset{\|}{C}}NH\underset{\displaystyle Ph}{\underset{|}{I}}{}^{+}, OTs^- \longrightarrow RN{=}C{=}O + PhI + \mathit{p}\text{-}TsOH}$$

$$\mathrm{RN{=}C{=}O + H_2O \longrightarrow RNHCOOH \longrightarrow RNH_2 + CO_2}$$

$$\mathrm{RNH_2 + \mathit{p}\text{-}TsOH \longrightarrow RN^+H_3\ OTs^-} \qquad (18)$$

We have found that iodosylbenzene reacts with neat formamide immediately, releasing gas as the iodosylbenzene becomes solubilized. The reaction of iodosylbenzene with acetamide in acetonitrile resulted in slow release of gas and uptake of iodosylbenzene into the solution.

Conclusions

We have found new iron complexes, $(Et_3HN)Fe^{III}(bpb)X_2$ (X = Cl, OTf), capable of catalyzing the olefin epoxidation by iodosylbenzene. Although the yields of epoxide are not high due to iodosylbenzene-consuming competition reaction that also occurs in the absence of substrate, epoxides are found to be the predominant products. The epoxidation reaction occurs with stereochemical retention. We have also found that a nonredox metal salt, $Al(OTf)_3$, can catalyze the same reaction, suggesting strongly that high-valent metal oxo intermediates are not involved. In addition to epoxide, other products have also been observed in all of the reactions. The presence of these products suggests that the mechanisms of these reactions are related to those occurring between olefins and soluble iodine(III) compounds, and this leads us to propose a new mechanism. Iodine(III) species are found to be capable of isomerizing *cis*-stilbene in the absence of metal catalyst, which can explain *cis*-stilbene isomerization and loss of stereochemistry in some metal-catalyzed reactions by iodosylbenzene. All of our observations are consistent with a mechanism that does not require changes in oxidation state of the metal ion and that involves electrophilic attack of I^{III} at the olefin.

Acknowledgment. We thank Dr. Saeed I. Khan for assistance in solving the crystal structures. Financial support from the National Science Foundation (J.S.V.) and the Office of Naval Research (F.D.) is gratefully acknowledged.

Registry No. 1, 135270-98-3; **2**, 135225-28-4; **3**, 135225-27-3; $(Et_3HN)Fe^{III}(bpb)Cl_2$, 135225-30-8; $(Et_3HN)Fe^{III}(bpb)Cl_2$, 135271-00-0; $Al(OTf)_3$, 74974-61-1; $Fe(OTf)_2$, 59163-91-6; $Fe(OTf)_3$, 63295-48-7; $(Et_3HN)Fe^{III}(bpb)Cl_2{\cdot}CH_3CN$, 135225-31-9; $O[IPh(OTf)]_2$, 88016-29-9; Li(OTf), 33454-82-9; iodosylbenzene, 536-80-1; cyclohexene, 110-83-8; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8; styrene, 100-42-5; *trans*-β-methylstyrene, 873-66-5; norbornene, 498-66-8; 1-octene, 111-66-0; cyclohexene oxide, 286-20-4; *trans*-2,3-diphenyloxirane, 1439-07-2; *cis*-2,3-diphenyloxirane, 1689-71-0; phenyloxirane, 96-09-3; *trans*-2-methyl-3-phenyloxirane, 23355-97-7; *exo*-1,2-epoxynorbornane, 3146-39-2; 1,2-epoxyoctane, 2984-50-1; 4-methoxystyrene, 637-69-4; 4-methylstyrene, 622-97-9; 4-chlorostyrene, 1073-67-2; 3-chlorostyrene, 2039-85-2; 3-acetamidocyclohexene, 39819-72-2; bicyclo[2.2.1]-5-heptene-2-carboxylic acid, 67999-50-2; iodobenzene diacetate, 3240-34-4; norbornene, 498-66-8; 1,4-diiodobenzene, 624-38-4; iodobenzene, 591-50-4; *cis*-1,2-cyclohexanediol ditriflate, 91146-10-0.

Supplementary Material Available: Tables of the fractional coordinates, bond distances, bond angles, and isotropic and anisotropic temperature factors for $(Et_3HN)Fe^{III}(bpb)Cl_2{\cdot}CH_3CN$, **1** and **3** (19 pages); listing of calculated and observed structure factors for $(Et_3HN)Fe^{III}(bpb)Cl_2{\cdot}CH_3CN$, **1** and **3** (33 pages). Ordering information is given on any current masthead page.

$Ca_{14}GaAs_{11}$: A New Compound Containing Discrete $GaAs_4$ Tetrahedra and a Hypervalent As_3 Polyatomic Unit

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Contribution from the Department of Chemistry, University of California,
Davis, California 95616. *Received December 5, 1990*

Abstract: In the course of investigating the synthesis and properties of several ternary Ga–As Zintl compounds, a new Zintl compound has been prepared: $Ca_{14}GaAs_{11}$. This compound has been prepared in high yield from the stoichiometric combination of the elements in a sealed Nb tube, sealed in an evacuated quartz ampule, at 1100 °C for 4 days. It crystallizes in the tetragonal space group $I4_1/acd$ with lattice parameters a = 15.642 (2) Å and c = 21.175 (4) Å (room temperature). Single-crystal X-ray diffraction data were collected at 130 K ($I4_1/acd$, Z = 8, a = 15.620 (3) Å, and c = 21.138 (4) Å). Its structure is composed of isolated $GaAs_4$ tetrahedra that are separated by As_3 linear units, As and Ca. The As_3 units are situated between the tetrahedra and alternate by 90° down the c axis. Although the As–As distance in the As_3 unit is rather long (2.956 (2) Å), it is consistent with the long I–I distance observed in the isoelectronic, hypervalent I_3^- anion and therefore is considered to be formally an As_3^{7-} anion. Optical data are consistent with a semiconducting compound, indicating an optical band gap of about 1.49 eV, slightly higher in energy than that observed for GaAs. The synthesis, structure, and bonding in this compound will be discussed.

Introduction

Basic research on crystalline semiconductors has played a key role in the development of solid-state devices.[1] GaAs and III/V semiconductors[2] are important for electronic and optoelectronic applications such as quantum devices,[1b] high-speed computers,[1c] and photovoltaics.[1d] A large group of materials that may have unique semiconductor properties are the so called ternary Zintl phases.[3] This class of materials contains ternary I–III–V and

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* To whom correspondence should be addressed.

(1) See for example: (a) *Crystalline Semiconducting Materials and Devices*; Butcher, P. N., March, N. H., Tosi, M. P., Eds.; Plenum Press: New York 1986. (b) Bate, R. T. *Sci. Am.* **1988**, *258*, 96. (c) Seitz, C. L.; Matisoo, J. *Phys. Today* **1984**, 38. (d) Hamakawa, Y. *Sci. Am.* **1987**, *256*, 87.

(2) According to the recent IUPAC convention, groups III and V are groups 13 and 15, respectively; groups I and II are groups 1 and 2, respectively.

0002-7863/91/1513-7205$02.50/0