phosphorus oxychloride (**2b**) with benzene as described above. Yield 85-87%, mp 80-81 ℃.

Preparation of phosphorodimorpholidic azide (5). A mixture of phosphorodimorpholidic bromide (**3a**) (2.89 g, 0.01 mol) and sodium azide (0.65 g, 0.01 mol) in acetone (20 mL) was stirred at room temperature for 20 h. The mixture was filtered and evaporated to give the **5**. Yield 70-75%, mp 36-38 ℃; IR(KBr) 2854, 2760, 2148, 1257 cm^{-1}.

A typical procedure for β-lactams from β-amino acids is as follow. To a suspended solution of 3-benzylamino-3-methylbutanoic acid (207 mg, 1.0 mmol) and phosphodimorpholidic bromide (360 mg, 1.2 mmol) in acetonitride (100 mL) was added triethylamine (120 mg, 1.2 mmol) at room temperature. After being stirred at 80 ℃ for 15 h, the reaction mixture was concentrated under reduced pressure and the residue was pass through flash chromatography column using ether-chloroform (2 : 1) as an eluent to yield 1-benzyl-4,4-dimethyl-2-azetidinone (172 mg, 91%) as an oil.

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Isolation and Characterization of Oxochromium (IV) Tetraphenylporphyrin Pyridine Complex and Its Derivatives

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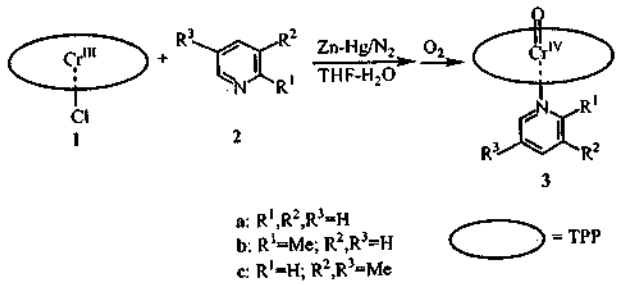
Cytochrome P-450 enzymes selectively oxidize hydrocarbons through the activation of molecular oxygen in the biosphere.[1] It has been proposed that the activation of oxygen by cytochrome P-450 enzymes involves oxoiron porphyrin intermediate.[2] Free oxoiron porphyrins, which are unstable above −30 ℃, are only studied in solution. While several oxometal porphyrins such as those of titanium(IV),[3] vanadium (IV),[4] molybdenum(IV and V),[5,6] and chromium(IV)[7,8] have been isolated and characterized, these compounds have not been shown to be effective oxidizing agents. The oxometal porphyrins such as those of chromium(V)[9] and manganese (IV)[10,11] have been shown to be effective oxidizing agents, but they were not synthesized through the activation of molecular oxygen. We report here the synthesis, isolation and spectral characterization of oxochromium(IV) tetraphenylporphyrin pyridine complex and its derivatives through the activation of molecular oxygen. The complexes are capable of oxidizing cyclohexene and styrene at room temperature to give 2-cyclohexen-1-ol and styrene oxide, respectively. They could be regarded as a model of the active oxygen species generated at the cytochrome P-450 catalytic center.

Results and Discussion

Reduction of ClCr(III)TPP in the mixture of tetrahydrofuran, pyridine derivatives, and water by activated zinc under nitrogen followed by stirring under air led to the isolation of a crystalline blackish green oxochromium(IV) complexes **3a-c** in 60, 63, and 61% yields, respectively (Scheme 1).[12] Elemental analyses of the oxochromium(IV) complexes **3a-c** were consistent with compounds for the formula oxochromium(IV) tetraphenylporphyrin pyridine complex and its derivatives. The visible spectra of **3a-c** display an intense Soret band at 430 nm and a broad shoulder band at 540 nm. The



Scheme 1.

Table 1. Oxidations of Cyclohexene and Styrene by 3

Oxochromium(IV) complexs 3	GLC yield (%)[a]	
	2-Cyclohexene-1-ol	Styrene oxide
3a	38	2
3b	78	6

[a]Based on half oxidizing equivalent for **3a** and **3b**.

X-band ESR spectra of **3a-c** show a seven-line hyperfine splitting near g=2.005. Both the visible and ESR spectra show that central chromium ions of **3a-c** are in tetravalent state. The infrared spectra of **3a-c** show a strong absorption band at 1026 cm^{-1} which is assigned to a Cr=O stretch.[8] Chemical shift assignments on ^1H NMR spectra were made on the basis of comparisions with the known O=Cr(IV)TPP.[8] The ^1H NMR spectra show that pyridine is involved in **3a** and methylpyridine derivatives are involved in **3b** and **3c**.

Cyclohexene and styrene were selectively oxidized by oxochromium(IV) complex **3a** and **3b** under nitrogen at room temperature. The result is listed in Table 1. It has been reported that the oxidation of cyclohexene by iron(IV),[13] manganese(IV)[11] and chromium(V)[9] porphyrin complexes generally produced a mixture of 2-cyclohexen-1-ol, 2-cyclohexen-1-one and cyclohexene oxide. However, the oxidation of cyclohexene by **3a** and **3b** produced only 2-cyclohexen-1-ol in 38% and 78% yields, respectively. Cyclohexene oxidizing activity of **3b** is far higher than that of **3a**. The oxidation of styrene by **3a** and **3b** produced styrene oxide in 2% and 6% yields, respectively. Therefore, while no alkene oxidizing activity was found with the known complex, O=Cr(IV)TPP, the activity was found with the complexes (**3a** and **3b**) because neutral pyridine or 2-methylpyridine was made as the axial ligand of **3a** or **3b**. It is well-known that the presence of pyridine as axial ligand in the NaOCl/Mn(TPP)OAc oxidizing system largely modifies the characteristic of the catalytic reaction.[14] We have first isolated oxometal porphyrin complexes which have hydrocarbon oxidizing activity through the activation of molecular oxygen. The oxochromium(IV) tetraphenylporphyrin pyridine or 2-methylpyridine complexes (**3a** and **3b**) could be regarded as another model of the active oxygen species generated at the cytochrome P-450 catalytic center.

Experimental Section

General

Commercially available organic and inorganic compounds were used without further purification except for the solvent, which was distilled by known methods before use. Chloro (tetraphenylporphinato)chromium(III) complex (**1**) was synthesized and purified by the method of Basolo.[15] Visible spectra were determined on a UV-3000 spectrophotometer. Infrared spectra were obtained by a FTS-20 infrared spectrophotometer. X-Band ESR spectra were determined on a JES-FE3AS ESR spectrometer. NMR spectra were obtained by a JNM-X100 NMR spectrometer.

Typical Procedure for the Synthesis of Complexes 3

To a solution of ClCr(III)TPP (**1**) (0.2 g, 0.28 mmol) in tetrahydrofuran (20 mL) was added pyridine (2 mL) and water (3 mL). After the mixture was degassed by N_2, 0.5 g of activated zinc was added and stirred for 2 h under N_2. The resulting solution was stirred overnight under air, filtered, rinsed with hot water and dried *in vacuo*. Recrystallization from tetrahydrofuran/hexane and vacuum drying afforded pure **3a** in 60% yield. The complexes prepared by the above procedure were characterized spectroscopically as shown below.

Oxochromium(IV) tetraphenylporphyrin pyridine (3a). 60% yield; Vis (CH_2Cl_2) λ_{max} 430, 540 nm; IR (KBr) 1026 (Cr=O) cm^{-1}; ESR (solid) g=2.005; ^1H NMR ($CDCl_3$) δ 8.75 (pyrrole H) 8.19 (phenyl *o*-H), 7.73 (phenyl *m*-H and *p*-H), 7.40 (pyridine H). Anal. Calcd for $C_{49}H_{33}N_5OCr$: C, 77.47; H, 4.35; N, 9.22; Cr, 6.85. Found: C, 76.78; H, 4.28; N, 9.31; Cr, 7.31.

Oxochromium(IV) tetraphenylporphyrin 2-methylpyridine (3b). 63% yield; Vis (CH_2Cl_2) λ_{max} 430, 540 nm; IR (KBr) 1026 (Cr=O) cm^{-1}; ESR (solid) g=2.005; ^1H NMR ($CDCl_3$) δ 8.86 (pyrrole H), 8.18 (phenyl *o*-H), 7.72 (phenyl *m*-H and *p*-H), 7.47 (pyridine H), 2.51 (methyl H). Anal. Calcd for $C_{50}H_{35}N_5OCr$; C, 77.62; H, 4.53; N, 9.06; Cr, 6.73. Found: C, 76.24; H, 4.65; N, 8.22; Cr, 6.84.

Oxochromium(IV) tetraphenylporphyrin 3,5-dimethylpyridine (3c). 61% yield; Vis (CH_2Cl_2) λ_{max} 430, 540 nm; IR (KBr) 1026 (Cr=O) cm^{-1}; ESR (solid) g=2.005; ^1H NMR ($CDCl_3$) δ 8.90 (pyrrole H), 8.16 (phenyl *o*-H), 7.73 (phenyl *m*-H and *p*-H), 7.46 (pyridine H), 2.31 (methyl H); Anal. Calcd for $C_{51}H_{37}N_5OCr$: C, 77.76; H, 4.70; N, 8.89; Cr, 6.61. Found: C, 76.98; H, 4.77; N, 7.75; Cr, 7.10.

Oxidation of Cyclohexene or Styrene by 3. The mixture of 6 mL of dichloromethane and 0.5 mL of cyclohexene or styrene was degassed by N_2, then oxochromium(IV) complex **3** was added and stirred for 2 h under N_2 at room temperature. After the reaction mixture was passed through short silica gel column to remove a reduced complex, the mixture was analyzed by GLC.

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Effect of Hydrophobic Environments and Reducing Agents on the Oxidation of Protoporphyrinogen IX

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The oxidation of protoporphyrinogen IX (Protogen) to protoporphyrin IX (Proto IX) is the last common step in the biosynthesis of heme and chlorophyll.[1] This six-electron oxidation is catalyzed by protoporphyrinogen oxidase (Protox) (EC 1.3.3.4) *in vivo* and can readily occur also nonenzymatically.[2] A variety of diphenyl ether compounds such as oxyfluorfen and acifluorfen are commonly used as effective herbicides and it is generally accepted that Protox is the primary target of photodynamic diphenyl ether herbicides.[3,4] The biochemical basis for the herbicidal effect has been shown to be the competitive inhibition of Protox by diphenyl ether compounds.[5,11] Paradoxically, the inhibition of Protox leads to massive accumulation of Proto IX, the product of enzymatic reaction instead of the substrate.[6] It has been demonstrated by numerous people that phytotoxic herbicidal effect of diphenyl ether herbicides is directly related to the abnormal accumulation of Proto IX which is a well known strong photosensitizer in the presence of light and molecular oxygen.[4,7]

However, the mechanism by which Protogen is converted to Proto IX and the reason for the accumulation of Proto IX *in vivo* are not clear. Since the putative Protox is known to be localized in the plastid envelope,[8] inhibition of the enzyme by diphenyl ether compounds would lead to the accumulation of substrate initially, which could be exported from the plastid through the cytosol to the plasma membrane and the oxidation would occur enzymatically by diphenyl ether resistant Protox-like peroxidase and/or nonenzymatically by autooxidation in the membrane. Our previous results indicated that the rate of nonenzymatic autooxidation of Protogen *in vitro* was highly dependent on the hydrophobic nature of reaction medium.[10] In a continuous effort to address the role of nonenzymatic autooxidation for the accumulation of Proto IX in diphenyl ether treated plants, we investigated effects of reducing agents, ionic strength, and ethyl alcohol on the oxidation of Protogen in enzymatic and nonenzymatic reaction conditions.

Etioplasts from barley (*Hordeum. Vulgare* L.) and wheat (*Triticum Aestivum* L.) were obtained as reported previously.[10] The substrate of Protox was prepared by reduction of Proto IX as previously described.[12] The rate for the oxidation of Protogen was measured following the procedure of Sherman *et al.*.[13] The relative rates of Protogen oxidation at various concentrations of dithiothreitol (DTT) and glutathione (GSH) is shown in Figure 1. and Figure 2, which clearly indicates that the rate of Proto IX formation can be remarkably inhibited by increasing concentration of DTT and GSH in both

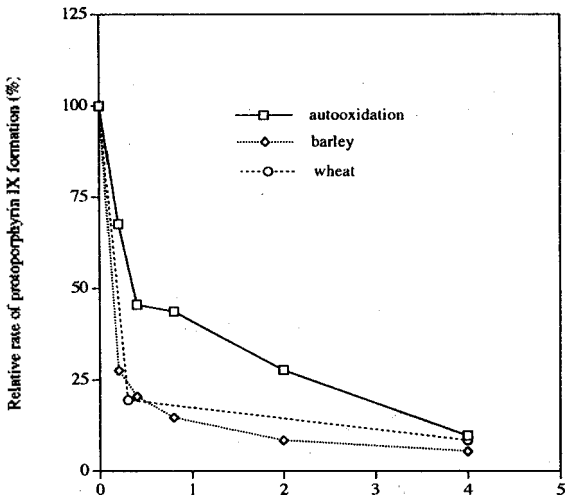

Figure 1. Effect of DTT on the rate of Protogen oxidation. The rates of Protogen oxidation were measured at various concentrations of DTT and calculated by leastsquare method using datapoints for the initial 5 minutes. Reaction mixture contained 100 mM HEPES (pH 7.5), 5 mM EDTA, 1% Tween-20, and 120 μL of etioplast extract (0.62 mg of protein) in 3 mL. The reaction was strated by adding 300 μL of 200 μM substrate. Fluorescence intensity was monitored using spectrofluorometer at 626 nm with excitation at 395 nm. Rates of autooxidation (□) and enzymatic oxidation (barley (◇), wheat (○)) were expressed relative to those at zero concentration of DTT.

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