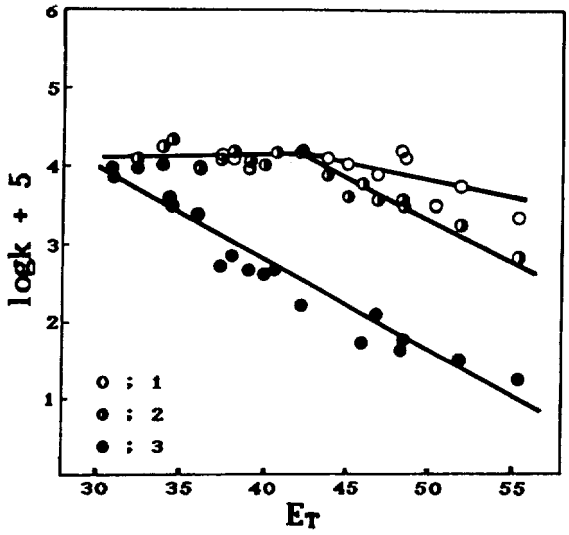

Figure 1. Plots of log k_{obs} versus E_T value for the ring closure reaction of the open form of 6′-substituted 5-Chloro-8′-nitro-1,3,3-trimethyl-indolinobenzospiropyrans [**1**; (6′-CH_3), **2**: (6′-H) and **3**; (6′-Br)] in various solvents.

ear plots were obtained. No branched linear plot is however obtained for the compound **3**.

In the highly polar-solvent region (E_T>40), good linear plots with negative slopes have been obtained as we observed[3,4]. The rate of the ring closure from the open-chain merocyanine form depends markedly on the substitutents in the present series **1-3**. The sensitivity of rate on medium polarity is highetest (slope=0.37) for the compound **3**, whereas it is lowest (slope=0.064) for the compound **1**. This finds an explanation that electron withdrawing groups (6′-Br and 8′-NO_2) will stabilize the dipolar structure **IIa** in the ground state. This provides further support for the dipolar structure of the merocyanines formed on ring opening of the spiropyrans in polar solvent media. Surprisingly, branched linear plots with zero slopes were obtained in the less polar-solvent region (E_T<40) for the compounds **1** and **2**, which have no electrowithdrawing substituent in the 6′-position. There are little sensitivities to both media and substituents.

This unusual observation of doubly branched solvatokinetics in the present system is hence indicative of a structural change of the ring opened merocyanine, between polyene-like structure **IIa** and the quinonoidal structures **IIb** in the ground state and hence alter the reaction mechanism for the spiro-ring formation. This is in coincedence with the recent report[7] of the solvatochromic merocyanine dye, 4-[2-(1-methyl-4-pyridino)ethyl]phenolate which exhibits both bathochromic (E_T<40) and hypsochromic shift (E_T>40) of long wavelength $\pi\rightarrow\pi^*$ absorption band as the solvent polarity increases.

Dual mechanistic processes are thus suggested to be operating in the spiro-ring formations. Namely the ionic process *via* TS_3 in polar solvent media and the concerted electrocyclic process *via* TS_1 in nonpolar solvent media are operated for **1** and **2** in the spiro-ring formation. Whereas the ionic process is operated for **3** in the whole region of solvent polarity examined. Further investigations for the doubly branched solvatokinetics and solvatochromism of the 5-substituted indolinobenzo-spiropyran derivatives and their open-chain merocyanines are currently underway.

Acknowledgement. This work was supported by the BasicResearch Institute Program of the Ministry of Education.

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Synthesis of Sterically Hindered Strapped Porphyrins

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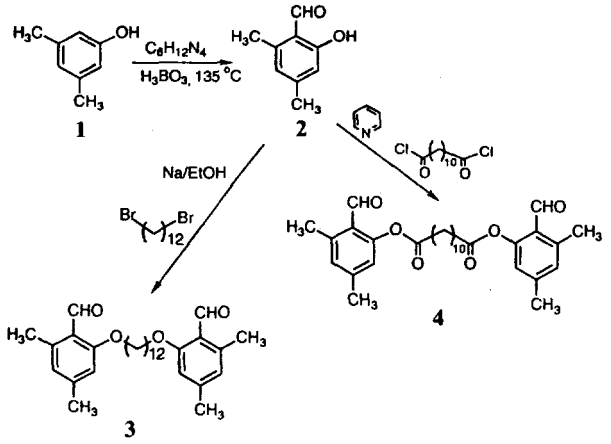
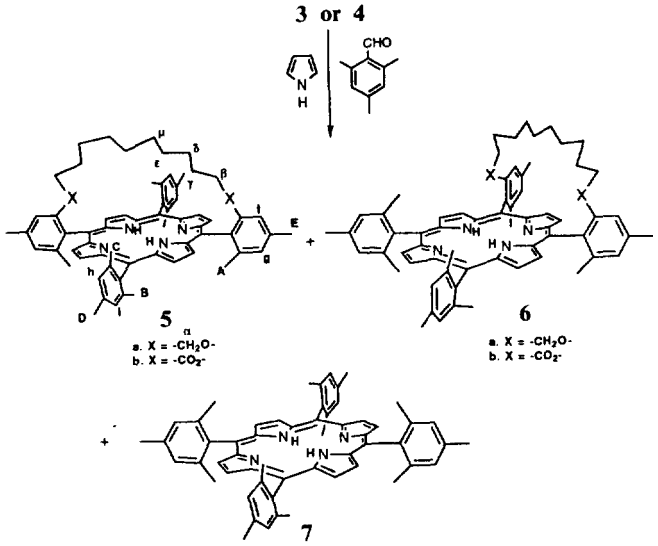
Heme proteins which contain iron porphyrins as prosthetic group are responsible for oxygen transport and storage, electron transport, oxygen reduction and hydrocarbon oxidation.[1,2] An ideal chemical model for these enzymes should satisfy a few structural characteristics such as similar active site geometry, protective structural feature and similar domain. The design and synthesis of model compounds for heme proteins become increasingly important in the investigation of various enzymatic processes. In these regards, many systems have been designed and synthesized since 1960.[2] Also there are various means by which a tetraphenylporphyrin ring can be constructed.[3-5] The common procedure is to react pyrrole with an appropriate benzaldehyde.



Scheme 1.



Scheme 2.

Among them, the method introduced by Baldwin and coworkers,[3] so called "C_2-capped porphyrins" seems reasonable because there is almost no other isomeric porphyrin formation by incorporating four benzaldehydes into a single molecule. Only capped porphyrin was obtained on reaction with pyrrole under dilute condition in this method.

One of the major task for designing model compounds is the prevention of destructive reaction of catalyst, *i.e.*, irreversible μ-oxo dimer formation and autoxidation of metal center. In this report we describe the synthesis of sterically hindered strapped porphyrins and their ^{1}H-NMR characterization. The compounds synthesized here might be useful models for dioxygen carrier or other dioxygen activation enzymes.

The identities of all intermediates were determined by ^{1}H-NMR and mass spectroscopy. As shown in Scheme 1, phenolic aldehyde **2** was prepared by *ortho*-formylation of 3,5-dimethylphenol **1** to give aldehyde **2** (12%).[5a] Treatment of **2** with sodium metal in absolute ethanol gave phenoxide salt quantitatively, which was directly coupled with 1,12-dibromododecane to afford ether-linked dialdehyde **3** (12%).[4b] Diester-linked dialdehyde **4**[4c] was obtained in 78% yield by the reaction of **2** with dodecanedioyl chloride in the presence of pyridine at room temperature. Condensation of dialdehyde **3** or **4** and mesitylaldehyde with 4 equivalent of freshly distilled pyrrole (dilute condition, 10^{-3} M of pyrrole in dry chloroform distilled from potassium carbonate) to provide porphyrins such as **5a**, **6a** and **7** for ether-linked and **5b**, **6b** and **7** for ester bridged porphyrins (Scheme 2). The reaction conditions attempted here were developed originally by Linsey *et al.*[4a]. High dilution is critical to obtain monomeric porphyrins in these reactions. After repeated chromatographic separation of each monomeric porphyrins, the yield was 0.2%, 0.15% and 0.4% for ether-bridged porphyrins (**5a**, **6a** and **7**); 0.1%, 0.2% and 0.5% for ester-bridged porphyrins (**5b**, **6b** and **7**) respectively. Only monomeric porphyrins were isolated. The low overall yield is expected by steric hindrance of the ortho-methyl substituent in the aldehydes.

The strapped porphyrins (**5** and **6**) were characterized by ^{1}H-NMR, mass and UV/vis spectroscopy. ^{1}H-NMR spectra of **5a**[5b] and **5b**[5c] suggest C_{2v} symmetry of the molecules. Compound **6a** and **6b** on the other hand, showed completely different ^{1}H-NMR spectra from **5a** and **5b**. For instance, the pyrrolic proton resonance shown at $\delta=8.60$ ppm ($J=4.5$ Hz) in **5a** and $\delta=8.65$ ppm ($J=4.7$ Hz) in **5b** was AB quartet system. On the other hand **6a** and **6b** showed the pyrrolic resonance at $\delta=8.55$-8.71 and 8.62-8.76 respectively as multiplet. Also the protons in each bridging methylene group showed different characteristics. The two protons in each methylene in **5a** and **5b** are enantiotopic and appeared as individual multiplets (quintet). But they are diastereotopic in **6a** and **6b** and appeared as two different sets of multiplets of each proton in each methylene group. The resonance of the methylene protons in both cases were shifted upfield due to their exposure to the porphyrin ring anisotropy. The individual chemical shifts of the bridging methylene protons are an indication of their relative distance from the porphyrin plane and the influence of the magnetic anisotropic effect. The μ-methylene protons in **5b** experience the strongest influence from the shielding effect with upfield shift to -2.14 ppm since these protons are held in close proximity to the center of the porphyrin plane. The ε, δ and γ-methylene protons experience similar shielding effects but the effect is diminished gradually. The observed shielding effect in **5a** is very different from **5b** inspite of similar number of atoms in the bridge. The μ-methylene protons in **5b** only shifted to -1.62 ppm. The α-methylene protons experience deshielding effect with down field shift to 3.89 ppm, which indicates that it is outside to the porphyrin periphery. These results indicate that ester strapped porphyrin **5b** is more tightly held to the porphyrin plane than ether strapped **5a**. The methyl groups at aromatics in **5a** (A, B, C, D and E) are assigned as δ 1.77, 1.84, 1.88, 2.62 and 2.64 ppm respectively. These assignments are based on the ^{1}H-NMR spectra of pendent capped porphyrin and tetramesytyl porphyrin **7** where the chemical shift of the comparable methyl groups are completely known by various NMR techniques such as 2-D COSY and ROESY.[6,7] The *meso*-phenyl protons (f, g, h, and i) can not be assigned by ^{1}H-NMR spectra alone. Only two different singlets (6.97 and 7.03 ppm) were observed in spite of their individual anisotropy.

Chemical properties, epoxidation studies and metal complexes formed from **5a** and **5b** will be reported in due course. The urgent is to synthesize iron complex and investigate

the monooxygen activation as a model of cytochrome P-450.

Acknowledgement. This investigation was supported by the Basic Science Research Institute Program, Ministry of Education, 1991.

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Palladium-Catalyzed Carbonylative Vinylation of Arylmercuric Chlorides with Carbon Monoxide and Olefins

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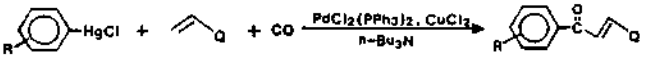
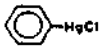
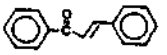
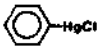
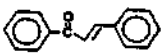
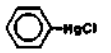
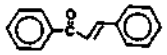
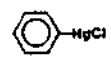
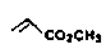
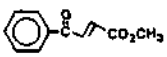
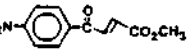
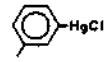
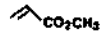
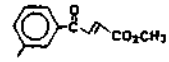
The palladium-catalyzed vinylation of vinyl halides with olefins provides a convenient method for the preparation of the corresponding conjugated dienes.[1] We reported methods for the palladium-catalyzed vinylation of vinylmercuric chlorides with olefins under mild conditions, which afforded the conjugated dienes in good yields,[2] and for the palladium-catalyzed cabonylative vinylation of aryl halides with olefins in the presence of carbon monoxide, which resulted in the formation of aryl vinyl ketones or aryl vinyl-α-diketones.[3]

We have now found that arylmercuric chlorides react under mild conditions with carbon monoxide and olefins in the presence of a palladium catalyst, a base, and $CuCl_2$ to afford the corresponding aryl vinyl ketones in moderate to good yields.



The results obtained are summarized in the Table 1. In a typical procedure (entry 1) a mixture of phenylmercuric chloride (1.57 g, 5 mmol), styrene (0.69 m*l*, 6 mmol), tri-*n*-

Table 1. Palladium-Catalyzed Carbonylative Vinylation of Arylmercuric Chlorides with Carbon Monoxide and Olefins[a]

Entry	Arylmercuric chloride	Olefin	Product (% Yield[b])	
1				(71)
2[c]				(30)
3[d]				(35)
4				(70)
5				(81)
6				(68)

[a] All reactions were carried out for 12 hours in the same manner as described in the text, unless otherwise noted. Disappearance of the starting material was monitored by TLC. [b] Yiels of isolated products. [c] $PdCl_2(CH_3CN)_2$ was used as a catalyst. [d] Reacted under atmospheric pressure of CO.