Experimental

Materials. Materials were purchased from Wako or Merck. Acetone was refluxed over $KMnO_4$ for 1 day until the violet colour persists, distilled, dried with anhydrous Na_2CO_3 for 3 days, and fractionated by using Widmer column.[4a),6] Thiobenzamides were used after recrystallization with ethanol.

M.p.s for Y-$C_6H_4C(S)NH_2$ were Y=p-CH_3, 167-168 °C (Lit.,[7] 168 °C); H, 115-116 °C (Lit.,[7] 115-116 °C); p-Cl, 129.5-130 °C (Lit.,[7] 130 °C).

Kinetic Measurements. Rates were measured conductimetrically as described before.[5] Pseudo-first-order rate constants, k_{obs}, were determined by the least-squares computer program. The precision of the fit to pseudo-first-order kinetics was generally satisfactory, with correlation coefficient $\geq$ 0.9999 over 3 half-lives of the reaction. Second-order rate constants, k_2, were determined by dividing k_{obs} by the initial thiobenzamide concentration.

Product analysis. Products of the reaction of substituted benzyl benzenesulfonates and substituted thiobenzamides were identified by IR, ^{1}H NMR, mass spectra.

Benzylthiobenzamidiniumsulfonate was prepared by a mixture of 0.015 mol benzyl- benzenesulfonate and 0.015 mol of thiobenzamide dissolved 100 mL acetone at 45 °C for 2 days. The product was collected by suction, and recrystallized from ethyl acetate. Yellowish-white solid were obtained with mp 149-150 °C. IR (KBr): 3170, 3160, 1640 (N-H), 1440, 1030, 160, and 130 (-S-), 1230, 1180, and 560 cm^{-1} (SO_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ=11.4-12.6 (s, 2H, =NH_2), 7.6-7.9 (m, 5H, -S-C(=)-Φ), 7.2-7.5 (m, 10H, Φ-CH_2, O_3S-Φ), 4.8 (s, 2H, -CH_2-).

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A Novel Synthesis of Oligopyridines

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An efficient synthetic method applicable for the preparation of symmetrical as well as unsymmetrical terdentates, and 2-aryl-2,2'-bipyridines was developed, in which a Michael addition of enamine onto enaminone was employed as a key step.

Introduction

The terdentate, 2,2';6',2"-terpyridine has been attractive because of its potentials to form ML_2 metal complexes with various d_6 transition metals [especially Ru(II)] showing various intriguing properties.[1] Although a plenty of 2,2';6',2"-terpyridine derivatives as well as their Ru(II) complexs were prepared and studied, only a limited number of unsymmetric terpyridines were reported presumably due to the lack of synthetic method with general applicability.[2] Because of low reactivity of pyridine nucleus, direct introduction of the substituent(s) on the pyridine nucleus is not an effective method to prepare the unsymmetric terpyridines. Among the limited number of synthetic methods for unsymmetric terpyridines, a coupling reaction[3] between 6-halo-2,2'-bipyridines and/or 2-halopyridines and the Krö

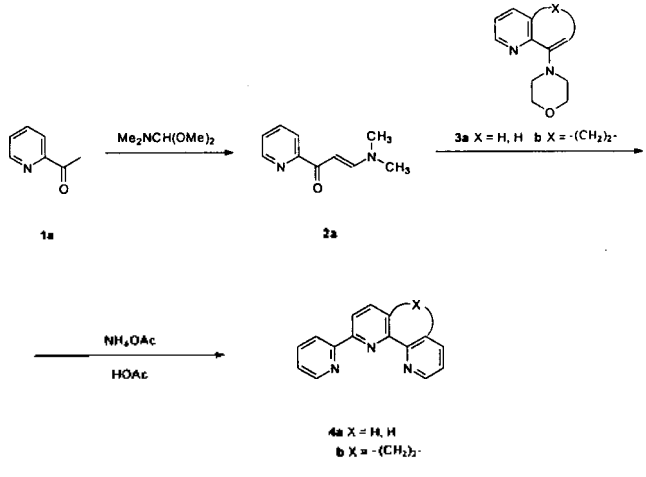
hnke synthesis[2] are the most frequently employed reactions for the preparation of oligopyridines. These methods are, however, usually suffered from low yields and/or difficulties to afford suitable starting materials. Recently, central pyridine ring formation from 1,5-diketones was introduced for the preparation of symmetrical terdentates.[4] Although such a method has been employed over a decade, low yields and/or multi-step procedures restrict the usages for the preparation of either prerequisite 1,5-diketones or final products.

The bidentate 2,2'-bipyridine can create a chiral center when it forms octahedral metal complex with d_6 transition metal, thus showing discriminative ability to recognize nucleic acid with respect to each enantiomer[5] while 2,2';6',2"-terpyridine is not able to create a chiral center. The symmetry of ML_2 complex of 2,2';6',2"-terpyridine resulted in lack of biological interests upon reacting with nucleic acid. An importance of unsymmetric terdentates stems from the ability to form chiral complexes with d_6 transition metal ions by creating a chiral center when they form octahedral complexes. We herein report a novel synthetic procedure applicable to both symmetric and unsymmetric terdentates as well as 6-aryl-2,2'-bipyridines.

Results and Discussion

The method described herein included a Michael addition of enamine **3** onto enaminone **2** as a key step.[6] The starting 2-acetylpyridine and other acetyl(hetero)aromatics were converted to corresponding 2-[3-(*N*,*N*-dimethyl-amino)propenoyl](hetero)aromatics **2** in 68-90% yields by reacting with *N*,*N*-dimethylformamide dimethyl acetal (DMFDMA).[7] Enaminone **2a** was then reacted with enamines **3** in dry THF at room temperature. Resulting Michael addition adducts were neither isolated nor characterized, but instead allowed to react with NH_4OAc in acetic acid to afford the desired terdentate products **4** in over 65% yields. The fact that one does not need to isolate the intermediates lends simplicity to the method. The prerequisite enamines **3** were prepared from corresponding pyridyl ketones by known procedure.[4a,8]

The scope of the reaction could be extended to the preparation of 6-aryl-2,2'-bipyridines **5**. The reactions of enamine **3a** with enaminone **2b-e** gave bipyridine derivatives **5** in 64-82% yields (Table 1). The alternative combinations of



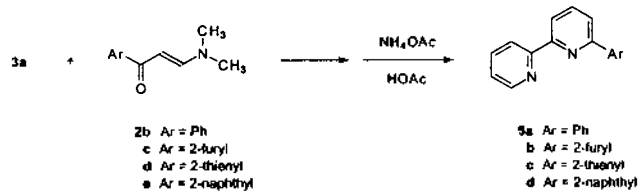


Table 1. Properties of 6-Aryl-2,2'-bipyridines

Compounds	Ar	Yields (%)	mp (°C)	Reference mp (°C)
4a	2-pyridyl	82	89-90	89-91[3]
5a	Ph	75	85-86	85-86[10]
5b	2-furyl	64	65-67	this work
5c	2-thienyl	79	77-78	78[2a]
5d	2-naphthyl	77	96-97	this work

enaminone **2a** with enamines from corresponding acetylaromatics [*i.e.* acetophenone, 2-acetylfuran, 2-acetylthiophene, and 2-acetylnaphthalene] resulted lower yields (45-56%).[9] Studies on the preparation of metal complexes and their properties will be due in the future publication.

In conclusion, a novel procedure applicable for the preparation of the 2,2'-bipyridine derivatives and 2,2';6',2"-terpyridine derivatives was described, which has advantages over previously described method in the synthesis of symmetric as well as unsymmetric oligopyridines under mild reaction condition.

Experimental

Melting points were measured on Fisher-Jones melting point apparatus and are uncorrected. IR spectra were obtained on a Perkin Elmer 1310 spectrophotometer in KBr, except noted. ^{1}H nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AM-300 spectrometer at 300 MHz, and chemical shifts are reported in parts per million down field from Me_4Si referenced to the solvent peak. All the starting materials were commercially available from Aldrich Chemical Co., Milwaukee, WI. Enamines[8] and 2-[3-(*N*,*N*-dimethylamino)propenoyl]pyridine **2a**[11] were prepared by either a previously published method or a modification of such a method. Chemicals and solvents were commercial reagents grade and used without further purification. Elemental analyses were taken on a Hewlett-Packard Model 185B elemental analyzer.

[3-(*N*,*N*-Dimethylamino)propenoyl]benzene (2b). A mixture of 1.20 g (0.01 mol) of acetophenone and 1.20 g (0.01 mol) of *N*,*N*-dimethylformamide dimethyl acetal in 100 mL of toluene was refluxed at 110 °C for 12 h under Ar. The resulting mixture was stripped of methanol and unreacted starting material under reduced pressure to afford 1.25 g (70%) of title compound as a yellow solid which was recrystallized from toluene to give yellow needles: mp 83-84 °C. IR (thin film) 3050, 3020, 1650, 1580, 1420, 1260, 1150, 1080, 980, 770 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.90 (dd, 1H, *J*=7.9, 1.8 Hz), 7.82 (d, 1H, *J*=12.4 Hz), 7.45-7.38 (m, 3H), 5.73 (d, 1H, *J*=12.4 Hz), 3.15 (s, 3H), 2.94 (s, 3H).

2-[3-(*N*,*N*-Dimethylamino)propenoyl]furan (2c). The same procedure described above for **2b** was em-

ployed with 2.20 g (0.02 mol) of 2-acetylfuran and 2.38 g (0.02 mol) of DMF dimethyl acetal to give 2.64 g (80%) of yellow needles: mp 77-79 °C. IR (thin film) 3050, 3020, 1650, 1600, 1440, 1260, 1100, 1080, 970, 850, 770 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.81 (d, 1H, *J*=18 Hz), 7.50 (dd, 1H, *J*=1.5, 0.6 Hz, H5), 7.07 (dd, 1H, *J*=3.4, 0.7 Hz, H3), 6.49 (dd, 1H, *J*=3.4, 1.5 Hz, H4), 5.69 (d, 1H, *J*=18.0 Hz), 3.15 (s, 3H), 2.93 (s, 3H).

2-[3-(*N*,*N*-Dimethylamino)propenoyl]thiophene (2d). The same procedure described above for **2b** was employed with 1.26 g (0.01 mol) of 2-acetylthiophene and 1.19 g (0.01 mol) of DMF dimethyl acetal to give 1.22 g (68%) of yellow needles: mp 107-109 °C. IR (thin film) 3050, 3020, 1650, 1580, 1450, 1260, 1100, 1050, 990, 850, 770 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.79 (d, 1H, *J*=12.3 Hz), 7.63 (dd, 1H, *J*=3.7, 1.1 Hz, H5), 7.48 (dd, 1H, *J*=5.0, 1.1 Hz, H3), 7.08 (dd, 1H, *J*=5.0, 3.7 Hz, H4), 5.63 (d, 1H, *J*=12.3 Hz), 3.15 (s, 3H), 2.94 (s, 3H).

2-[3-(*N*,*N*-Dimethylamino)propenoyl]naphthalene (2e). The same procedure described above for **2b** was employed with 1.70 g (0.01 mol) of 2-acetylnaphthalene and 1.19 g (0.01 mol) of DMF dimethyl acetal to give 2.02 g (90%) of yellow needles: mp 82-84 °C. IR (thin film) 3050, 2914, 2806, 1642, 1555, 1420, 1350, 1270, 1100, 780 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.40 (s, 1H, H1), 8.02 (dd, 1H, *J*=8.5, 1.7 Hz, H3), 7.96-7.93 (m, 1H), 7.89-7.86 (m, 3H), 7.57-7.48 (m, 3H), 5.88 (d, 1H, *J*=12.3 Hz), 3.17 (s, 3H), 2.98 (s, 3H).

Oligopyridines(general procedure). The mixture of enaminone (0.01 mol) and enamine (0.01 mole) in dry THF (50 mL) was allowed to stirr for 12-14 h. The resulting mixture was hydrolyzed by 5% aq. HCl and the aq. layer collected was made basic with 50% KOH. The mixture was extracted with CH_2Cl_2 (50 mL×3). The organic layers were combined and washed with water, followed by saline. The organic phase was dried over anhydrous $MgSO_4$. Evaporation of solvent afforded usually brown oily material which was then treated with NH_4OAc in acetic acid at 145-150 °C for 1-2 h. The mixture was cooled to room temperature and extracted with CH_2Cl_2 (100 mL×3). The organic layers were combined and washed with water, followed by saline. The organic phase was dried over anhydrous $MgSO_4$. Evaporation of solvent afforded brown oily gum, which was chromatographed on basic alumina, eluting with CH_2Cl_2 and CH_2Cl_2 : hexane (1 : 1, followed by 3 : 7). The fractions of 3 : 7 mixture provided the desired polypyridines. The physical and spectral data of **4a** and **5a** were identical to those[3,10] of previously reported compounds

3,3'-Dimethylene-2,2';6',2"-terpyridine (4b). Foam (65%); IR (KBr) 3020, 2910, 1530, 1410, 1350, 1250, 1060, 970, 890 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.76 (dd, 1H, *J*=4.8, 1.8 Hz, H6'), 8.72 (ddd, 1H, *J*=8.0, 4.8, 1.2 Hz, H6"), 8.68 (ddd, 1H, *J*=4.8, 1.8, 0.9 Hz, H3"), 8.39 (d, 1H, *J*=8.0 Hz, H5), 7.83 (td, 1H, *J*=8.0, 1.8 Hz, H4"), 7.71 (d, 1H, *J*=8.0 Hz, H5), 7.59 (dd, 1H, *J*=7.6, 1.6 Hz, H 4'), 7.30 (ddd, 1H, *J*=8.0, 4.8, 1.2 Hz, H5"), 7.26 (dd, 1H, *J* =8.0, 4.8 Hz, H5'), 3.04 (s, 4H). Anal. Calcd for $C_{17}H_{13}N_3$: C, 78.74; H, 5.05; N, 16.21. Found: C, 78.86; H, 5.12; N, 16.02.

6-(2"-Furyl)-2,2'-bipyridine (5b). Pale yellow needles (64%). IR (KBr) 3040, 2940, 2900, 2840, 1550, 1430, 1260, 1070, 1040, 960, 880, 810, 770 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.67 (d, 1H, *J*=4.8 Hz, H6'), 8.53 (d, 1H, *J*=8.0 Hz, H3'), 8.27 (d, 1H, *J*=7.8 Hz, H3), 7.84 (t, 1H, *J*=6.5 Hz, H4), 7.80 (t, 1H, *J*=6.7 Hz, H4'), 7.69 (d, 1H, *J*=7.8 Hz, H5), 7.29 (dd, 1H, *J*=8.0, 4.8 Hz, H5'), 7.54 (d, 1H, *J*=1.2 Hz, H5"), 7.18 (d, 1H, *J*=3.3 Hz, H3"), 6.55 (dd, 1H, *J*=3.3, 1.7 Hz, H4"). Anal. Calcd for $C_{14}H_{10}N_2O \cdot H_2O$: C, 69.99; H, 5.03; N, 11.66. Found C, 69.73; H, 5.16; N, 12.02.

6-(2"-Thienyl)-2,2'-bipyridine (5c). Pale brown needles (79%).Unreported spectral data are as follows: IR (KBr) 3040, 2940, 1560, 1450, 1270, 1100, 1040, 960, 870, 810, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.67 (dd, 1H, *J*=4.8, 1.5 Hz, H6'), 8.57 (dd, 1H, *J*=8.0, 2.1 Hz, H3'), 8.29 (d, 1H, *J*=7.8 Hz, H3), 7.85 (t, 1H, *J*=8.5 Hz, H4'), 7.81 (t, 1H, *J*=6.7 Hz, H4), 7.75 (d, 1H, *J*=7.8 Hz, H5), 7.65 (dd, 1H, *J*=3.7, 1.2 Hz, H3"), 7.41 (dd, 1H, *J*=5,5, 1.2 Hz, H5"), 7.31 (ddd, 1H, *J*=8.6, 4.8, 1.8 Hz, H5"), 7.13 (dd, 1H, *J*=5.5, 3.7 Hz, H4").

6-(2"-Naphthyl)-2,2'-bipyridine (5d). White needles (77%). IR (KBr) 3040, 2900, 2840, 1550, 1430, 1260, 1100, 1050, 970, 880, 805, 770 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.71-8.68 (m, 2H, H6', H3"), 8.64 (s, H1"), 8.40 (dt, *J*=8.8, 4.2 Hz, H4'), 8.32 (dd, *J*=8.6, 1.8 Hz, H3'), 7.80-7.95 (m, 2H), 7.92-7.84 (m, 4H), 7.55-7.48 (m, 4H), 7.32 (ddd, *J*=8.6, 4.8, 1.2 Hz, H5"). Anal. Calcd for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 84.88; H, 5.09; N, 10.03.

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Thermodynamic and Kinetic Study on the Protonation of Free Base Tetraphenylporpyrin Derivatives in Solution

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The protonation of tetraphenylporphyrin (TPP) in acidic organic solutions was analyzed by acid titrimetric and temperature-dependent absorption measurements. Competition between the protonation of free base TPP ($TPPH_2$) and the solvation of proton by near solvent molecules determines the equilibrium of the diprotonated TPP ($TPPH_4^{2+}$) formation. The diprotonated TPP exists as an ion pair complex with the acid counterions, which are found to affect the degree of red shift of the Soret band. The rotation of the phenyl rings also plays an important role in the diprotonation, as suggested by the decrease in the degree of diprotonation for the fluorophenyl TPP derivatives whose phenyl ring rotation is significantly hindered relative to normal TPP. The difference of fluorescence lifetime between $TPPH_2$ (τ_{FL}=19.6 ns) and $TPPH_4^{2+}$ (τ_{FL}=2.1 ns) was used advantageously to measure the rate of protonation in the excited state. The protonation of $TPPH_2$ are found to occur much slower than the diffusion of protons from bulk solution to the porphyrin ring. The monoprotonated TPP is suggested to be the transient species for the diprotonation process.

Introduction

The protonation of free base porphyrins greatly affects their physicochemical properties such as the spectroscopic modifications,[1-5] the behavior of self-association or aggregation,[6-9] and the photoinduced electon transfer to adjacent molecules.[10,11] Upon protonation, the Soret band of porphyrins in UV-vis spectrum is largely shifted to a longer wavelength, which changes the color of porphyrin solutions from the red to the deep green. Also the characteristic Q_x and Q_y bands of the D_{2h} symmetric free base porphyrins are converted to a series of Q bands as a result of the formation of D_{4h} symmetric dicationic forms.[1,2] The protonation also changes the fluorescence properties; fluorescence spectrum of the diprotonated TPP ($TPPH_4^{2+}$) has a broad emission band with the maximum located between the two emssion bands originally observed in the free base TPP ($TPPH_2$).[6] This spectral change has been attributed to the protonation-induced structural change of the porphinato macrocycle.[12-15] Also the rotation of the phenyl rings has been accounted for the variation of the spectroscopic properties in terms of resonance interaction of the phenyl ring with the porphyrin's corresponding orbitals, based on the X-ray crystallographic result which showed that the phenyl substituents reorient from out-of-plane to in-plane position with respect to the porphyrin ring upon protonation.[16,17]

The protonation of free base porphyrins is completely reversible, and the degree of diprotonation at equilibrium is strongly dependent on the type of solvent as well as the acid concentration.[2,18] The effect of acid counterion on the conformational and spectroscopic changes is also menifest in the protonation of various porphyrin derivatives.[4,17] However, the equilibrium thermodynamic properties for the formation of diprotonated porphyrins have been yet rarely studied with respect to any of the environmental factors such as solvent, acid concentration, and the acid counterion effect, not to mention the kinetic property for the protonation process. Therefore, we investigated the equilibrium thermodynamic and kinetic properties for the protonation of tetraphenyl porphyrin and its fluorophenyl derivatives in organic solvents using acid titrimetric absorption and fluorescence lifetime measuring techniques. Our report will demonstrate that the formation of the diprotonated TPP goes through an activation state in the form of the monoprotonated TPP, and the equilibrium properties for the diprotonation are characterized by the proton exchange between

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