Convenient Route to Core-modified Corroles by Acid-catalyzed Condensation of Furylpyrromethanes and Dipyrromethanes

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Corroles and oxacorroles were synthesized by acid-catalyzed 2+2 condensation. The condensation afforded different corroles bearing core-heteroatoms at the predesignated locations. Regioselective α-α' linkage between pyrrole and furan or between pyrrole and pyrrole was achieved by keeping the linking carbon at different position of starting dipyrromethanes. The condensation was only fruitful when furan-containing dipyrromethanes were condensed.

Introduction

Corroles are porphyrinoid macrocycles bearing one bipyrrole ring junction and considered as 18π macro-aromatic systems. The metal complexes of corroles and corrins are important biological cofactors and the study of their physico-chemical properties has been contributed to the development of the chemistry of oligopyrrolic macrocyclic compounds.[1] The corrin ring has been known to be more flexible than chlorins and thus allows easy change of the steric environment around the central metal ion.[2] This steric flexibility facilitates the catalysis of carbon-carbon bond formation in vitamin B_{12}.[3] Most of the corrole synthesis known so far has been focused on the cyclization of tetrapyrrolic units. These include biladiene cyclization,[4] *meso*-carbon or sulfur extrusion of *meso*-thiaporphyrin[5] or direct synthesis from substituted pyrroles.[6] More recently, corrole has been isolated from the solventless condensation of aldehydes with pyrrole.[7] The primary target for the corrole research has been focused on the synthetic access to the ring structure of corrin and corroles. The bipyrrole ring junction in the corrole usually exihibits the same dynamic range as found in porphyrins and chlorins indicating macro-aromatic character of the parent macrocycles. The synthesis of core modified corroles containing oxygen or sulfur has been reported by Broadhurst *et al.*[8] But McDonald type condensation of dipyrromethanes and 2,2'-bifuran or 2,2'-bithiophene at elevated temperature resulted in complex mixture of products due to scrambling of starting material.[9] The synthesis of *meso*-aryl corroles from monopyrrole precursors has been reported.[10] The peripheral substitution usually induces alteration of the electronic properties and is known to possess reversed energy level compared with porphyrin.[11] But little has been known for the synthetic methods of corrole by 2+2 condensation from two different dipyrromethanes. We herein report the synthesis and characterization of new free-base oxacorroles bearing oxygen atom at the designated position and having three *meso*-substituents. It is of interest to evaluate the relationship between the core-modification of corrole and electrochemical properties. These types of studies are now possible with the convenience of customized modification of core-ligand reported here. It is also possible to synthesize corroles bearing three different *meso*-substituents in a regiospecific manner. Consequently, the study of electronic effect induced by the *meso*-substituents or hetero-atoms in the core is even possible. The approach provided with this article may be adaptable as a generic procedure for the synthesis of corrole nucleus.

Experimental Section

^{1}H NMR spectra (400 MHz, Bruker IFS 48), IR spectra (JASCO IR 100), and absorption spectra (Kontron 941) were collected routinely. Mass spectra were obtained by FAB. Column chromatography was performed on silica (Merck, 230-400 mesh). Pyrrole was distilled at atmospheric pressure from CaH_2. CH_2Cl_2 (reagent grade) was distilled from K_2CO_3. All other reagents were obtained from Aldrich unless noted otherwise. *meso*-(*p*-Tolyl)dipyrromethane (**10**) was synthesized from the condensation of *p*-tolualdehyde with pyrrole as reported previously.[12] Compound (**1a**) was synthesized from the condensation of [2-α-hydroxy-2-α-(*p*-tolyl)methyl]furan with pyrrole.

***p*-Tolyl-[5-(*p*-toluoyl)furan-2-yl]-(pyrrol-2-yl)methane (3a).** To a solution of (*p*-tolyl)-(furan-2-yl)-(pyrrol-2-yl]methane (0.237 g, 1.0 mmol) and *p*-toluoyl chloride (0.199 mL, 1.505 mmol) in CH_2Cl_2 (20 mL) cooled in ice bath was added $AlCl_3$ (0.302 g, 2.265 mmol). The mixture was stirred for 4 h at room temperature and then saturated $NaHCO_3$ solution (10 mL) was added slowly. The mixture was extracted with ethyl acetate (30 mL × 3). The organic layer was washed with water and dried (Na_2SO_4). Solvent was removed in *vacuo* and the remaining black oil was purified by column chromatography on silica. The first moving band eluted with CH_2Cl_2 was identified as the monoacyl compound **3a** (0.11 g, 36.6%) and the second moving band eluted with CH_2Cl_2/EtOAc (30/1) was identified as the bisacylated compound **2a** (0.076 g, 16.0%). For **3a**: mp 44-45 °C; ^{1}H NMR ($CDCl_3$) δ 8.17 (bs, 1H, N-H), 7.81 and 7.25 (two doublets, J = 8.2 Hz, 4H, Ar-H), 7.16-7.12 (m, 5H, Ar-H and furan-H), 6.74-6.72 (m, 1H, pyrrole-H), 6.27 (d, J = 3.5 Hz, 1H, furan-H), 6.17-6.15 (m, 1H, pyrrole-H), 5.977-5.976 (m, 1H, pyrrole-H), 5.53 (s, 1H,

meso-H), 2.42 (s, 3H, Ar-CH_3), 2.34 (s, 3H, Ar-CH_3). IR (C=O) 1634 cm^{-1}. For **2a**: mp 66 °C; ^1H NMR ($CDCl_3$) δ 9.45 (bs, 1H, N-H), 7.82 (d, 2H, J = 8.1 Hz, Ar-H), 7.78 (d, 2H, J = 8.1 Hz, Ar-H), 7.28-7.24 (m, 5H, Ar-H and Furan-H), 7.17-7.16 (m, 4H, Ar-H), 6.82 and 6.81 (dd, 1H, J = 3.7 Hz, pyrrole-H), 6.28 (d, 1H, furan-H), 6.12-6.11 (m, 1H, pyrrole-H), 5.62 (s, 1H, *meso*-H), 2.421-2.417 (m, 6H, Ar-CH_3), 2.35 (s, 3H, Ar-CH_3). Anal. calcd for $C_{33}H_{27}NO_3$: C, 81.16; H, 5.75; N, 2.96 found: C, 80.98; H, 5.91; N, 2.90. IR (C=O) 1640 (s) and 1605 (s) cm^{-1}.

***p*-Tolyl-[5-(*p*-toluoyl)thien-2-yl]-(pyrrol-2-yl)methane (3b).** The mixture of (*p*-tolyl)-[(pyrrol-2-yl)-(thien-2-yl)]methane (1.01 g, 4.0 mmol), *p*-toluoyl chloride (1.33 mL, 10.02 mmol) and $AlCl_3$ (2.03 g, 15.21 mmol) were treated identically as for the synthesis of **3a**. Column chromatography of crude mixture on silica afforded two products. Elution with CH_2Cl_2 gave clean separation of **2b** (0.53 g, 27.1%) and successive elution with CH_2Cl_2/EtOAc (40/1) afforded **3b** (0.58 g, 39.0 %). For **2b**: mp 82-83 °C; ^1H NMR ($CDCl_3$) δ 9.49 (bs, 1H, N-H), 7.78 and 7.28 (two doublets, 4H, J = 8.1 Hz, Ar-H), 7.75 and 7.27 (two doublets, 4H, J = 8.1 Hz, Ar-H), 7.48 (d, 1H, J = 3.8 Hz, thiophene-H), 7.20-7.15 (m, 4H, Ar-H), 6.90-6.89 (m, 1H, thiophene-H), 6.82 and 6.81 (dd, 1H, J = 3.7 Hz, pyrrole-H), 6.13-6.12 (m, 1H, pyrrole-H), 5.72 (s, 1H, *meso*-H), 2.43 (s, 6H, Ar-CH_3), 2.35 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$) δ 187.67, 184.41, 155.36, 142.85, 142.72, 142.40, 140.75, 137.72, 137.39, 135.55, 135.28, 134.55, 130.87, 129.57, 129.25, 129.12, 128.99, 128.93, 128.18, 126.99, 120.04, 110.57, 46.01, 21.55, 21.04; Anal. calcd for $C_{32}H_{27}NO_2S$ C, 78.49; H, 5.56; N, 2.86 found: C, 78.24; H, 5.53; N, 2.77. IR (C=O) 1605 (s) cm^{-1}. For **3b**: mp 36-37 °C ^1H NMR ($CDCl_3$) δ 7.93 (bs, 1H, N-H), 7.76 and 7.28 (two doublets, 4H, J = 8.1 Hz, Ar-H), 7.48 (d, 1H, J = 3.7 Hz, thiophene-H), 7.18-7.13 (m, 4H, Ar-H), 6.88 (d, 1H, thiophene-H), 6.73-6.71 (m, 1H, pyrrole-H), 6.18-6.16 (m, 1H, pyrrole-H), 5.998-5.995 (m, 1H, pyrrole-H), 5.66 (s, 1H, *meso*-H), 2.43 (s, 3H, Ar-CH_3), 2.34 (s, 3H, Ar-CH_3). IR (C=O) 1623 (s) and 1605 (s) cm^{-1}.

***p*-Tolyl-(furan-2-yl)[5-(*p*-toluoyl)pyrrol-2-yl]methane (4a).** EtMgBr (1.0 M solution in THF, 3.5 mL, 3.5 mmol) was added to a solution of (*p*-tolyl)-(furan-2-yl)-(pyrrol-2-yl)-methane (0.167 g, 0.703 mmol) and THF (20 mL) in ice bath under nitrogen. The mixture was stirred for 30 min and then *p*-toluoyl chloride (0.186 mL, 1.406 mmol) was added. The whole mixture was stirred for 12 h at room temperature. The mixture was combined with sat. NH_4Cl (10 mL) then extracted with CH_2Cl_2 (20 mL × 3). The organic layer was washed with water (30 mL) and dried ($MgSO_4$). The solvent was removed in *vacuo* and resulting brown oil was purified by column chromatogaphy on silica (methylene chloride/hexanes, 2/1). Yield 0.158 g (63.0%); mp 84-85 °C; ^1H NMR ($CDCl_3$) δ 9.30 (bs, 1H, N-H), 7.78 and 7.26 (two doublets, J = 8.1 Hz, 4H, Ar-H), 7.409-7.406 (m, 1H, furan-H), 7.17-7.12 (m, 4H, Ar-H), 6.81-6.79 (m, 1H, pyrrole-H), 6.34-6.33 (m, 1H, furan-H), 6.094-6.086 (m, 1H, furan-H), 6.07-6.05 (m, 1H, pyrrole-H), 5.47 (s, 1H, *meso*-H), 2.42 (s, 3H, Ar-CH_3), 2.34 (s, 3H, Ar-CH_3). IR (C=O) 1600 cm^{-1}.

***p*-Tolyl-[5-(*p*-toluoyl)pyrrol-2-yl]-(thien-2-yl)methane (4b).** EtMgBr (1.0 M solution in THF, 9.5 mL, 9.5 mmol), (*p*-tolyl)-(pyrrol-2-yl)-(thien-2-yl)methane (0.48 g, 1.90 mmol) and *p*-toluoyl chloride (0.38 mL, 2.84 mmol) in THF (50 mL) were treated identically as for **4a**. Column chromatography on silica (CH_2Cl_2/Hexanes, 2/1) afforded pure product. Yield 0.47 g (66.7%); mp 57-58 °C; ^1H NMR ($CDCl_3$) δ 9.24 (bs, 1H, N-H), 7.78 and 7.26 (two doublets, 4H, J = 8.1 Hz, Ar-H), 7.231 and 7.228 (dd, 1H, thiophene-H), 7.18-7.14 (m, 4H, Ar-H), 6.96 and 6.95 (dd, 1H, thiophene-H), 6.85-6.84 (m, 1H, thiophene-H), 6.81-6.80 (dd 1H, pyrrole-H), 6.08-6.07 (m, 1H, pyrrole-H), 5.68 (s, 1H, *meso*-H), 2.42 (s, 3H, Ar-CH_3), 2.35 (s, 3H, Ar-CH_3). IR (C=O) 1599 cm^{-1}.

Reduction of carbonyl group. $NaBH_4$ (5.602 g, 0.148 mol) was carefully added portion wise to a stirred solution of *p*-tolyl-(furan-2-yl)-[5-(*p*-toluoyl)pyrrol-2-yl]methane (**4a**) (0.526 g, 1.48 mmol) in MeOH/EtOH (2/1, 300 mL). The mixture was stirred for 20 min at room temperature. The reaction mixture was quenched with water (20 mL) followed by extraction with ethyl acetate. The organic phase was dried (K_2CO_3) and the solvent was removed to afford pale yellow amorphous solid **5a**. The strong O-H stretching band observed at 3407 cm^{-1} indicates the reduction accompanied with the disappearance of carbonyl stretching at 1634 cm^{-1}. Due to limited stability of the reduced alcohol, it was immediately used in the next step without further purification. Reduction of compounds **4b**, **3a** and **3b** was carried out similarly. 100 molar equivalents of $NaBH_4$ were used to ensure complete reduction in all the reactions.

5,10,15-Tri(*p*-tolyl)-21-oxacorrole (9). To an ice-cold mixture of alcohol (**5a**) (0.503 g, 1.406 mmol), *meso*-(*p*-tolyl)-dipyrromethane (0.333 g, 1.407 mmol), NH_4Cl (0.753 g, 14.068 mmol) in acetonitrile (140.6 mL) was added BF_3OEt_2 (17.8 μL, 0.141 mmol). The mixture was stirred for 1 h at 0 °C and then DDQ (0.958 g, 4.219 mmol) and triethylamine (2 mL) were added. The whole mixture was stirred for 1 h followed by the addition of water (30 mL). The mixture was extracted with ethyl acetate (60 mL × 3) and the organic phase was dried (Na_2SO_4). The solvent was removed in *vacuo* and the resulting solid was purified by column chromatography on silica (CH_2Cl_2/hexanes, 1/2). The purple soild was recrystallized from methanol. Yield 72.4 mg (9.0%); ^1H NMR ($CDCl_3$) δ 9.52 (d, 1H, J = 4.2 Hz), 9.22 (d, 1H, J = 4.4 Hz), 9.04 (d, 1H, J = 4.2 Hz), 8.89-8.84 (m, 3H), 8.74-8.73 (m, 1H), 8.63 (d, 1H, J = 4.5 Hz), 8.21-8.17 (m, 4H), 8.06 (d, 2H, J = 7.8 Hz), 7.63-7.60 (m, 4H), 7.54 (d, 2H, J = 7.8 Hz), 2.69 (s, 3H, Ar-CH_3), 2.68 (s, 6H, Ar-CH_3), -2.996 (bs, 1H, N-H). ^{13}C NMR ($CDCl_3$): δ 152.32, 150.15, 147.27, 139.44, 139.34, 137.65, 137.52, 137.01, 136.70, 135.99, 134.78, 134.49, 134.24, 134.08, 133.63, 131.66, 130.32, 128.91, 128.45, 127.63, 126.20, 125.27, 123.28, 123.26, 120.19, 117.11, 115.02, 113.35, 112.32, 106.97, 21.48, 21.43. UV-vis (CH_2Cl_2/EtOH, 3/1) λ_{max} ($\varepsilon \times 10^3$) 402 (93), 418 (49), 488 (3.2), 524 (7.2), 551 (19), 604 (7.4). FAB MS calcd for $C_{40}H_{31}N_3O$ 569.25, found 570.07 ($M^+ + H$).

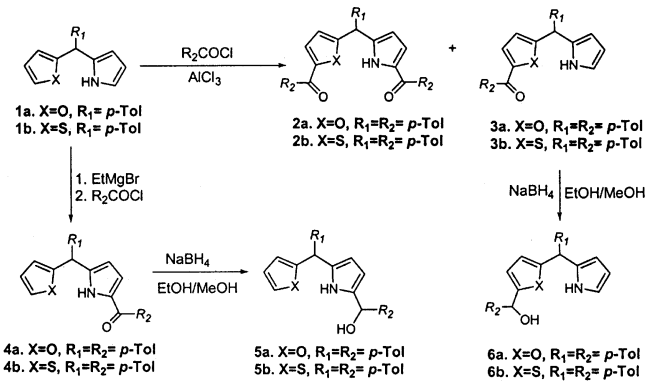
5,10,15-Tri(*p*-tolyl)-22-oxacorrole (11). To an ice-cold mixture of alcohol (**6a**) (0.145 g, 0.408 mmol), *meso*-(*p*-tolyl)dipyrromethane (0.104 g, 0.410 mmol), NH_4Cl (0.219 g, 4.085

mmol) in acetonitrile (41.0 mL) was added $BF_3{\cdot}OEt_2$ (5.2 μL, 0.041 mmol). The mixture was stirred for 1 h at 0 °C and then DDQ (0.278 g, 1.225 mmol) and triethylamine (50 μL) were then added. The whole mixture was stirred for 1 h and then combined with water (20 mL). The mixture was extracted with ethyl acetate (40 mL × 3) and the organic phase was dried (Na_2SO_4). The solvent was removed in *vacuo* and the resulting solid was purified by column chromatography on silica (CH_2Cl_2/hexanes, 1/2). The purple soild was recrystallized from methanol. Yield 35.09 mg (15.1%); ^{1}H NMR ($CDCl_3$) δ 9.07 (d, 1H, J – 5.1 Hz), 9.02-9.01 (m, 1H), 9.00 (d, 1H, J – 4.0 Hz), 8.81 (d, 1H, J – 4.3 Hz), 8.78 (d, 1H, J – 4.8 Hz), 8.76 (d, 1H, J – 5.1 Hz), 8.55-8.54 (m, 1H), 8.34 (d, 1H, J – 4.5 Hz), 8.19-8.15 (m, 4H), 7.99 (d, 2H, J – 7.8 Hz), 7.61-7.59 (m, 4H), 7.54 (d, 2H, J – 7.7 Hz), 2.68 (s, 3H, Ar-CH_3), 2.67 (s, 6H, Ar-CH_3), -1.85 (br s, 1H, N-H). ^{13}C NMR ($CDCl_3$): δ 150.44, 149.84, 145.44, 142.75, 138.50, 137.78, 137.63, 137.29, 137.05, 135.78, 134.70, 134.00, 133.88, 133.74, 132.23, 129.20, 129.00, 128.56, 128.27, 124.75, 123.71, 123.19, 123.17, 122.76, 121.21, 120.09, 120.02, 114.75, 108.79, 108.73, 105.29, 21.54, 21.48, 21.44. UV-vis (CH_2Cl_2/EtOH, 3/1) λ_{max} ($\varepsilon \times 10^3$) 412 (211), 498 (13), 529 (13), 583 (6.2), 634 (20). FAB MS calcd for $C_{40}H_{31}N_3O$ 569.25, found 570.48 ($M^+ \cdot H$).

Results and Discussion

The first synthesis of corroles was reported in 1965 by photochemical cyclization of a,c-biladiene.[13] This classical approach has been extensively applied for various model systems and yields have been improved.[14] The synthesis of *meso*-substituted corroles from tetrapyrrolic precursor has been reported in 1993 by Paolesse *et al.*[15] But the reaction proceeds only in the presence of cobalt (II) ion and required tedious separation. The accidental discovery that acid catalyzed 2+2 condensation of diol (**7**) with *meso*-(*p*-tolyl)dipyrromethane (**10**) afforded trace amount of corrole (**9**) prompted us to investigate the scope of the reaction further.[16] As shown in Scheme 2, a selective bond cleavage between C2 and 2α-methyl must precede the cyclization during the formation of corrole **9**. Thus, mono-hydroxy compounds such as (**5a**), (**5b**), (**6a**), and (**6b**) could be condensed with *meso*-(*p*-tolyl)dipyrromethanes to afford corroles bearing heteroatoms at the designated locations. In order to verify this assumption, we synthesized several precursors.

The synthesis of *p*-tolyl-(furan-2-yl)-(pyrrol-2-yl)methane (**1a**) and *p*-tolyl-(thien-2-yl)-(pyrrol-2-yl)methane (**1b**) was achieved by acid catalyzed condensation of 2[α-hydroxy-α-(*p*-tolyl)]furan or 2[α-hydroxy-α-(*p*-tolyl)]thiophene and pyrrole. As shown in Scheme 1, Lewis acid ($SnCl_4$) catalyzed acylation of (**1a**) or (**1b**) resulted in the products (**2a**), (**2b**), (**3a**) and (**3b**) respectively. Selective acylation on the furanyl side (**3a** and **3b**) was achieved by employing $SnCl_4$ as the catalyst. The acylation led to mono-acylation on pyrrole moiety and 1,9-bisacylated products (**2a, 2b**) were also isolated in good yields. But mono-acylation product on furan or pyrrole-moiety was not observed in this reaction. The reactions were successful with sterically hindered mesitoyl chloride. 1,9-Bisacylated products were always dominant regardless of the nature of acid chloride. When $AlCl_3$ was used as catalyst (Table 1), similar results were obtained. Almost equal amounts of mono- and bis-acylated products were usually isolated in all cases but no pyrrolic acylation occurred.



Scheme 1

The site of acylation was easily determined by analyzing the chemical shifts of the each protons in furan, thiophene and pyrrole. Since the two 5-membered aromatic systems in (**1a**) or (**1b**) were magnetically and chemically non-equivalent, acylation on furan did not change the chemical shifts of the pyrrole protons and vice versa.

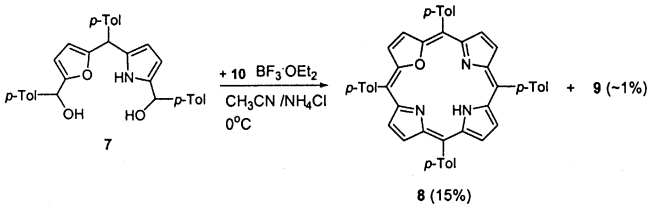
For example, the chemical shifts of the furan protons in (**1a**) were observed at 7.37, 6.32 and 6.06 ppm respectively and those of pyrrole protons were observed at 6.70, 6.15 and 5.93 ppm respectively. When it is acylated on furan side, the chemical shifts of the pyrrolic-protons remained unchanged while one of the furanyl-protons has disappeared. The same pattern was observed when acylation occurred on pyrrole side.

On the other hand, acylation carried out *via* pyrrole-Grignard's afforded compounds (**4a** and **4b**) exclusively. Treatment of (**1a**) or (**1b**) with EtMgBr (5.0 equiv) in THF followed by adding acyl chloride (2 equiv) gave high yield of (**4a**) or (**4b**) as the only product.

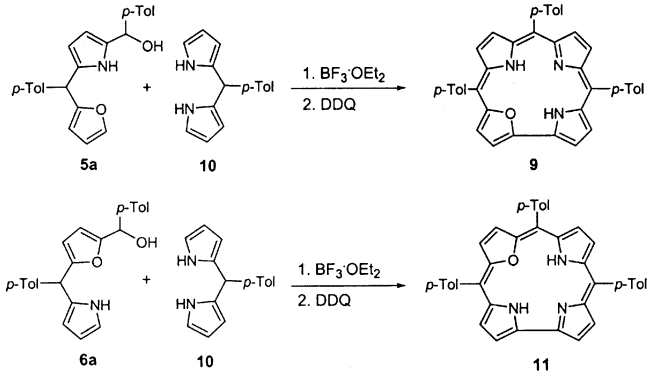
Since site-selective acylation of (**1a**) and (**1b**) has been achieved, we attempted to reduce the carbonyl group to the corresponding alcohol. 1,9-Bisacylated dipyrromethanes were successfully reduced to the corresponding diols employing large excess of reducing agents.[16] Treatment of **3a**, **3b**, **4a** or **4b** with excess $NaBH_4$ (100 molar equiv) in MeOH/EtOH (2/1) gave clean reduction and afforded the corresponding alcohols **6a**, **6b**, **5a** and **5b** respectively. The use of large excess amount of reducing agent was crucial to make the

Table 1. Yields of Lewis acid catalyzed acylation of dipyrromethanes in the presence of catalysts

Catalyst	X	R_1	R_2	Yield (%)					
				4a	**4b**	**3a**	**3b**	**2a**	**2b**
$SnCl_4$	O	Ph(*p*-I)	mesityl	5				81	
	S	Ph(*p*-I)	mesityl		13				82
$AlCl_3$	O	*p*-Tol	*p*-Tol			37		16	
	S	*p*-Tol	*p*-Tol				39		27



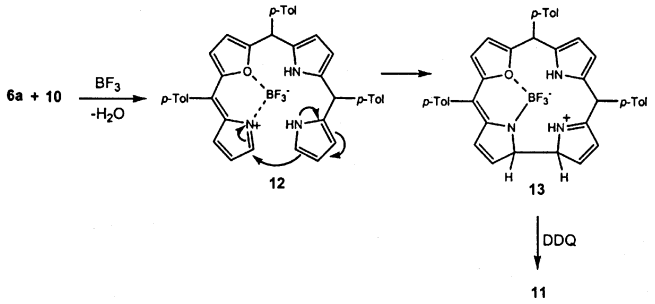
Scheme 2



Scheme 3

reduction complete. The progress of the reaction was easily followed by TLC and IR spectrometer: the disappearance of carbonyl stretching associated with the appearance of -OH stretching. The reduced compounds were rather unstable in air. Thus they were not purified further and used immediately in the next step. The '2 + 2' type approaches in the porphyrin synthesis have been well documented,[17] but the same approach applied in the synthesis of corrinoids has not been studied much. We applied the previously identified low-scrambling, acid-catalyzed conditions[18] in the condensation of the two different dipyrromethanes such as (**6a**), (**6b**) and (**10**). When the diol (**7**) was reacted with (**10**) under the low-scrambling '2+2' condensation conditions and subsequent oxidation with DDQ, the desired porphyrin (**8**) were isolated in 15% yield (Scheme 2). The green pigment characterized as (**9**) was isolated in less than 1%. The formation of corrole (**9**) from the condensation of (**10**) with (**7**) might have occurred *via* cleavage of the furan-C2 and 2α-C bond during the reaction. The identity of compound (**9**) was verified by independent synthesis of authentic (**9**) *via* different route. At the same time, the site of cleavage between the two hydroxyl groups in (7) was also identified (*vide infra*).

Acid-catalyzed condensation of (**5a**) with *meso*-(*p*-tolyl)-dipyrromethane (**10**) exclusively afforded corrole (**9**) in 9% yield. The spectroscopic data of the minor product obtained from the reaction shown in Scheme 2 were completely identical with the compound isolated from the condensation of (**10**) and (**5a**). Scheme 3 shows two different types of '2+2' condensation. Different α-α linkage was achieved by applying the regio-isomers such as (**5a**) and (**6a**) in the condensation. Although the exact mechanism leading to the corrole is not conclusive, all the experimental evidence indicated that the presence of BF_3 and oxygen in the core is important in the formation of α-α linkage.



Scheme 4

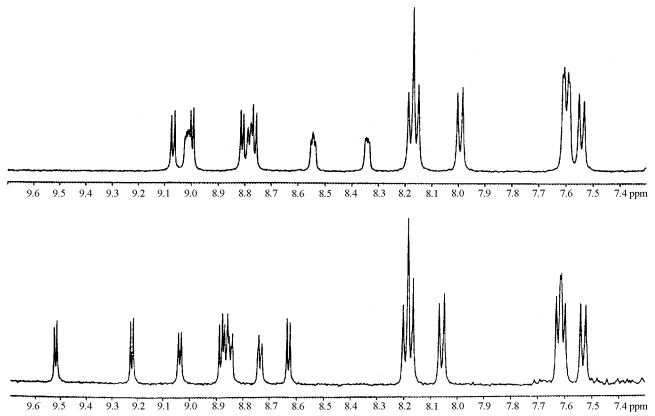


Figure 1. Partial 400 MHz proton NMR spectra of corrole (**9**) (bottom) and (**11**) (top) in $CDCl_3$. The *meso*-tolyl groups have almost identical chemical shifts while the β-pyrrolic and β-furanyl signals show large differences.

The absorption spectra of (**9**) and (**11**) have distinctive features. The Soret band was observed at 402 nm for (**9**) and at 412 nm for (**11**) as shown in Figure 2. A typical series of Q-bands were also observed between 470 and 750 nm. These values are somewhat red-shifted compared with those which do not have *meso*-substituents.[4] The blue-shifted Soret band in (**9**) indicates that it is less flexible and more resonance-stabilized than (**11**). The proton NMR spectra also support this assumption. As shown in Figure 1, the β-pyrrolic resonances of (**9**) are shifted further down field and the inner N-

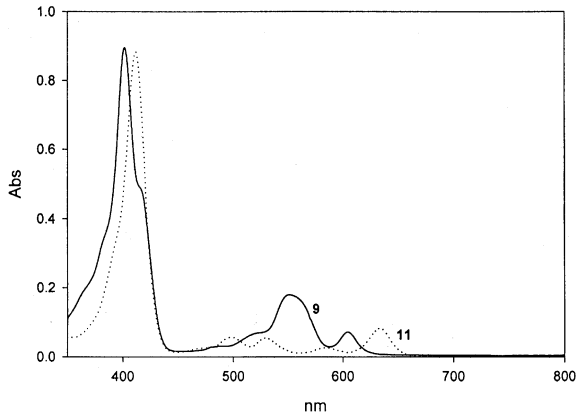


Figure 2. UV-vis spectra of the two core-modified corroles **9** (8.99×10^{-6} M) and **11** (5.90×10^{-6} M). Each spectrum was obtained in CH_2Cl_2/EtOH (3/1).

H protons were observed at -1.85 ppm in (**11**) while that of (**9**) was observed at -3.00 ppm.

A proposed mechanism for the cyclization is shown in Scheme 4. The first step would be the acid-catalyzed condensation of the two dipyrromethanes to afford oxa-tetrapyrrolic compound (**12**) complexed with BF_3. The development of yellow color at the early stage of the reaction indicates that a biladiene-type intermediate (**12**) may be involved.

The boron-dipyrromethene complex (**12**) has been known to be stable and studied as a fluorescence probe previously.[19] The subsequent nucleophilic attack by the other end-pyrrole might lead to (**13**) which will give rise to corrole (**11**) on subsequent oxidation. The proposed mechanism is somewhat different from the oxidative cyclization using Ni(II) as template reported.[20] This is the first example of the synthesis of core-modified corroles by the '2+2' condensation. BF_3 must be acting as a catalyst and as a template in the reaction.

Attempted condensation of 5-(*p*-tolyl)-2-[α-hydroxy-α-(*p*-tolyl)methyl]dipyrromethane (**14**) with *meso*-(*p*-tolyl)dipyrromethane (**10**) didn't result in any corrole components but self-condensed porphyrin (**15**) was isolated in 9% yield instead (Scheme 5). The similar condensation of dipyrromethane (**16**) with (**10**) also gave trace amount of porphyrin (**17**) as a single product. The condensation of (**18**) with (**10**) did not give any corrinoid components and starting material was recovered. The furan moiety is strongly basic than that of pyrrole or thiophene. Thus, exceptionally strong complexation of furan with BF_3 makes the intramolecular cyclization possible. Attempted condensation carried out in the presence of $Co(OAc)_2$ and HBr[14] in methanol didn't give any observable corrinoid components. Attempted condensation in the presence of protic acid (trifluoroacetic acid and *p*-toluene sulfonic acid) in acetonitrile at 0 °C resulted in much lower yields of corroles. These results indicate that a strong templating effect of BF_3 might have led to the formation of corroles.

The optimization of the 2+2 condensation discussed in this article would provide new approaches to core-modified corroles that have diffenrent *meso*-substituents and core-ligands. This will also open a new horison of building blocks for the construction of porphyrin-corrole array and potential application to molecular devices.

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