

Convenient Synthesis of Difurylmethanes and Dithienylmethanes and Their Application to the Syntheses of Core-Modified Porphyrins

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One flask synthesis of dithienylmethane and difurylmethane is reported. The reaction of aldehydes with excess furan or thiophene affords the *meso*-phenyldithienylmethane (DTM) and *meso*-phenyldifurylmethane (DFM), respectively. The reaction is catalyzed with trifluoroacetic acid or with $\text{BF}_3 \cdot \text{O}(\text{Et})_2$. An acyl group is selectively introduced in 1 and 9 position of difurylmethane and dithienylmethane by use of an acid chloride and tin (IV) chloride. The reduction of resulting 1,9-bisacyldifurylmethane or 1,9-bisacyldithienylmethane affords the corresponding 1,9-bis-diol. An acid catalyzed condensation of diol with *meso*-phenyldipyrromethane followed by oxidation with DDQ gives the porphyrins. The reaction resulted *meso*-5,10,15,20-tetraphenyl-21,22-dithiaporphyrin (SSNN) or 15-mesityl-5,10,20-triphenyl-21,22-dioxaporphyrin (OONN), respectively. The formation of small amount of *meso*-tetraphenylporphyrin (TPPH_2) is also observed. The formation of TPP indicates that *meso*-phenyldipyrromethane is reversibly cleaved and form pyrrole and pyrrolylbenzylcarbocation during the condensation. The proton nmr and electronic spectrum of the SSNN and OONN porphyrins are somewhat different from the previously synthesized *meso*-5,10,15,20-tetraphenyl-21,23-dithiaporphyrin (SNSN) or *meso*-5,10,15,20-tetraphenyl-21,23-dioxaporphyrin (ONON).

Introduction

The structural variation of porphyrins has many interesting perspective. Controlled modification of the basic framework of porphyrins while keeping aromaticity intact will result a systematic variation of the spectroscopic properties. This is advantageous in building molecular devices because the systematic construction of molecular devices require precise control of energy migration scheme. The achievement of vectorial energy flow in such devices could be accomplished by replacing nitrogen ligands in the core with other heteroatoms. This will change the symmetry of molecule and accordingly change transition energy between A_{1u} or A_{2u} and π .¹ The construction of porphyrin-based model systems are closely tied to the development of synthetic methods of porphyrins. Our current interests are development of a synthetic method for asymmetric porphyrins with different core-ligands. As a part of these efforts, we have recently reported a synthesis of several core-modified porphyrins.²⁻⁴ Since works of Ulman involving the synthesis and spectroscopic character of core-modified porphyrins,⁵⁻⁸ there have been several reports related with the synthesis and metal complexes of thiaporphyrins and oxaporphyrins.^{9,10} The reported compounds have two sulfur or oxygen atoms in *trans* (across) or *cis* fashion in the core. But there have been no successful reports for the selective synthesis of porphyrins which have two oxygen atoms or sulfur atoms in *cis* (adjacent) fashion in the core (*vide infra*).

Latos-Grazinski *et al.* recently reported some spectroscopic properties of nickel complex of 5,10,15,20-tetraphenyl-21,23-dioxaporphyrin.^{11,12} The attempted synthesis of 21,22-dioxaporphyrin analogs was first described by Broadhurst *et al.* in 1969.⁹ But attempted condensation resulted complex mixture. If *meso*-phenyldifurylmethane or *meso*-phenyldithienylmethane is easily accessible with reasonable yields, it will be possible to obtain 21,22-dioxaporphyrin as single isomer by

condensing *meso*-phenyldifurylmethane or *meso*-phenyldithienylmethane with 1,9-bis[(α -hydroxy- α -phenyl)methyl]-5-phenyldipyrromethane or vice versa. Recently, we reported a synthesis and structural characterization of monooxaporphyrin and monothiaporphyrin bearing one inverted pyrrole.^{2,3} The synthesis utilizes the condensation of tripyrrane with disubstituted 5-membered aromatic heterocycles. The key step in the synthesis was direct synthesis of 1,14-unsubstituted tetrahydrotripyrins containing heteroatoms. The tetrahydrotripyrins containing heteroatoms were obtained by acid catalyzed condensation of 2,5-bis[(α -hydroxy)methyl]pyrrole, 2,5-bis[(α -hydroxy)methyl]furan or 2,5-bis[(α -hydroxy)methyl]thiophene with excess pyrrole. In this paper, we report the synthesis of 15-mesityl-5,10,15,20-triphenyl-21,22-dioxaporphyrin (OONN) and 5,10,15,20-tetraphenyl-21,22-dithiaporphyrin (SSNN) with full detail. The compounds will be useful in studying the influence of heteroatoms in the core in comparison with normal porphyrins.

Experimental

¹H NMR spectra (400 MHz, Bruker IFS48), IR spectra (JASCO IR 100), and absorption spectra (Kontron 941 and Hitachi U-3200) were collected routinely. Mass spectra was obtained by electron impact. Column chromatography was performed on silica (Merck, 230-400 mesh). Pyrrole was distilled at atmospheric pressure from CaH_2 . CH_2Cl_2 (Fisher, reagent grade) was distilled from K_2CO_3 . CHCl_3 (Fisher certified A.C.S.) containing 0.75% ethanol was distilled from K_2CO_3 . All other reagents were obtained from Aldrich unless noted otherwise. The synthesis of *meso*-phenyldipyrromethane obtained from the condensation of benzaldehyde and excess pyrrole was reported previously.¹ The spectroscopic data of the *meso*-phenyldipyrromethane synthesized in this study were identical with the authentic sample.

***meso*-Phenyldifurylmethane (1).** A mixture of ben-

zaldehyde (0.1 mL, 1 mmol) and furan (3.0 mL, 41 mmol) was degassed with nitrogen for 5 min. then titanium (IV) chloride (0.16 mL, 1.46 mmol) was added. The mixture was stirred for 30 min. at room temperature. The resulting dark purple mixture was diluted with CH_2Cl_2 (50 mL) and organic layer was washed with aqueous NaOH (0.1 N, 50 mL), water and dried over anhydrous MgSO_4 . The solvent was removed *in vacuo* and the resulting yellow oil was chromatographed on silica ($\text{CH}_2\text{Cl}_2/\text{Hexanes}=1/3$). Fast moving difurylmethane **1** was eluted first as yellow band and the trifurylmethane **3** was eluted next. Yield for **1**: 0.07 g (32.6%); for **3**: 0.02 g (11.2%). $^1\text{H NMR}$ for **1** (CDCl_3): δ 7.37-7.26 (m, 5H, Ar-H), 7.25 (d, 2H, $J=3$ Hz, furan-1,9-H), 6.32 (two doublets, 2H, $J=3$ Hz, furan-2,8-H), 6.03 (d, 2H, $J=3$ Hz, furan-3,7-H), 5.45 (s, 1H, *meso*-H); for **3** (CDCl_3): δ 7.37-7.21 (m, 12H, Ar-H and furan-1,7,8,14-H), 6.29 (two doublets, 2H, $J=3.0$ Hz, furan-2,13-H), 5.92 (d, 2H, $J=3.0$ Hz, furan-3,11H), 5.40 (s, 2H, *meso*-H).

meso-Phenylidithienylmethane (2). A solution of benzaldehyde (0.1 mL, 1 mmol) and thiophene (3.0 mL, 37 mmol) was degassed with nitrogen for 5 min. then $\text{BF}_3\cdot\text{O}(\text{Et})_2$ (0.2 mL, 1.6 mmol) was added. The solution was stirred at room temperature and the progress of reaction was carefully monitored by TLC. When no starting aldehyde was shown on TLC (~20 min.), the mixture was poured into CH_2Cl_2 (50 mL) and washed with aqueous NaOH (0.1 N). The organic layer was dried over anhydrous MgSO_4 and the solvent was evaporated to dryness. Column chromatographic separation of the resulting dark yellow solid gave two products which were identified as compound **2** (0.16 g, 62%) and **4** (oil, 0.05 g, 25.1%). mp for **2**: 70.2 °C. $^1\text{H NMR}$ for **2** (CDCl_3): δ 7.34-7.24 (m, 5H, Ar-H), 7.21 (two doublets, 2H, thiophene-H), 6.94 (two doublets, 2H, thiophene-H), 6.82 (d, 2H, thiophene-H), 5.86 (s, 1H, *meso*-H); For **4** (CDCl_3): δ 7.33-7.23 (m, 10H, Ar-H), 7.19 (d, 2H), 6.92 (t, 2H), 6.81 (two doublets, 2H), 6.61 (s, 2H), 5.76 (s, 1H, *meso*-H).

1,4-Bis(2,2'-difurylmethyl)benzene (5). A mixture of terephthalaldehyde (0.12 g, 0.9 mmol) and furan (3.0 mL, 41 mmol) was degassed by bubbling nitrogen for 5 min. then titanium (IV) chloride (0.14 mL, 1.3 mmol) was added. The mixture was stirred for 35 min. at room temperature, at which point no starting aldehyde was shown on TLC. The dark purple mixture was diluted with CH_2Cl_2 (50 mL) and washed with aqueous NaOH (0.1 N), water and dried (MgSO_4). The solvent was removed *in vacuo* and resulting light yellow solid was chromatographed on silica ($\text{CH}_2\text{Cl}_2/\text{Hexanes}=2/1$). The fast moving light yellow band was **5** (0.03 g, 9.5%) and second moving light brown band was **8** as an oily liquid (0.07 g, 30.5%). mp for **5**: 89.0-89.1 °C. $^1\text{H NMR}$ (CDCl_3): δ 7.36-7.35 (m, 4H, furan-H), 7.20 (s, 4H, Ar-H), 6.32 and 6.31 (two doublets, 4H, $J=3.0$ Hz, furan-H), 6.03 (d, 4H, $J=3.0$ Hz, furan-H), 5.43 (s, 2H, *meso*-H); $^1\text{H NMR}$ (CDCl_3) for **8**: δ 9.98 (s, 1H, aldehyde), 7.83 (d, 2H, Ar-H), 7.41 (d, 2H, Ar-H), 7.38 (s, 2H, furan-H), 6.34 and 6.33 (two doublets, 2H, $J=3.0$ Hz, furan-H), 6.07 (d, 2H, $J=3.0$ Hz, furan-H), 5.53 (s, 1H, *meso*-H).

1,4-Bis(2,2'-dithienylmethyl)benzene (6). A mixture of terephthalaldehyde (0.14 g, 1 mmol) and thiophene (3.2 mL, 40 mmol) was degassed by bubbling nitrogen for 5 min. then $\text{BF}_3\cdot\text{O}(\text{Et})_2$ (0.26 mL, 2.1 mmol) was added. The

solution was stirred at room temperature and the progress of reaction was carefully monitored by TLC. When no starting aldehyde was shown on TLC (~30 min.), the mixture was poured into CH_2Cl_2 (50 mL) and washed with aqueous NaOH (0.1 N). The organic layer was washed with water and dried (MgSO_4). The solvent was removed *in vacuo* and resulting solid was chromatographed on silica (methylene chloride/hexanes=1/1.6). The fast moving colorless band was compound **6** as a major product (0.2 g, 44%) and second moving yellow band was compound **7** (oil, 0.08 g, 20.1%). mp for **6**: 118-120 °C. $^1\text{H NMR}$ (CDCl_3) for **6**: δ 7.25 (s, 4H, Ar-H), 7.20 and 7.19 (two doublets, 4H, $J=5.0$ Hz, thiophene-H), 6.93 and 6.92 (two doublets, 4H, $J=5.0$ Hz, thiophene-H), 6.81-6.80 (m, 4H, thiophene-H), 5.85 (s, 2H, *meso*-H). $^1\text{H NMR}$ (CDCl_3) for **7**: δ 7.22 (s, 8H, Ar-H), 7.19-7.16 (m, 6H, thiophene-H), 6.93-6.89 (m, 6H, thiophene-H), 6.80-6.79 (m, 6H, thiophene-H), 6.57 (s, 2H, thiophene-H), 5.83 (s, 2H, *meso*-H), 5.73 (s, 2H, *meso*-H). MS (EI) Calcd. for $\text{C}_{42}\text{H}_{32}\text{S}_7$ 785.19, Found 784.0 (M^+).

1,3-Bis(2,2'-dithienylmethyl)benzene (10). A solution of isophthalaldehyde (0.13 g, 1 mmol) and thiophene (3.2 mL, 40 mmol) was degassed by bubbling nitrogen for 5 min. then $\text{BF}_3\cdot\text{O}(\text{Et})_2$ (0.26 mL, 2.1 mmol) was added. The solution was stirred at room temperature and the progress of reaction was carefully monitored by TLC. When no starting aldehyde was shown on TLC (~30 min.), the mixture was poured into CH_2Cl_2 (50 mL) and washed with aqueous NaOH (0.1 N). The organic layer was washed with water and dried (MgSO_4). The solvent was removed *in vacuo* and the resulting viscous oil was chromatographed on silica (methylene chloride/hexanes=1/1.5). The fast moving colorless band was **10** (0.2 g, 45.4%) and second moving yellow band was **11** (oil, 0.06 g, 14.5%). mp for **10**: 93.1-93.2 °C. $^1\text{H NMR}$ (CDCl_3): δ 7.46-7.36 (m, 4H, Ar-H), 7.29 (d, 4H), 7.03 (t, 4 H), 6.93 (d, 4H), 5.96 (s, 2H, *meso*-H). MS (EI) Calcd. for $\text{C}_{24}\text{H}_{18}\text{S}_4$ 434.67, Found 434.0. $^1\text{H NMR}$ (CDCl_3) for **11**: δ 7.25-7.13 (m, 14H, Ar-H and thiophene-H), 6.92-6.87 (m, 6H, thiophene-H), 6.77-6.76 (m, 6H, thiophene-H), 6.55-6.54 (m, 2H, thiophene-H), 5.80 (s, 2H, *meso*-H), 5.71 (s, 2H, *meso*-H); MS (EI) Calcd. for $\text{C}_{44}\text{H}_{32}\text{S}_7$ 784.70; Found. 784.0 (M^+).

1,9-Bis(benzoyl)-5-phenyldifurylmethane (12). A mixture of phenyldifurylmethane (0.23 g, 1.0 mmol) and benzoyl chloride (0.4 mL, 3.6 mmol) was dissolved in benzene (20 mL). This mixture was degassed by bubbling nitrogen for 5 min. then tin (IV) chloride (6.4 mL, 5.5 mmol) was added at 0 °C. After the mixture was stirred for 3.5 h at room temperature, it was combined with aqueous HCl (10%) and stirred for an additional 5 min. Then the dark purple mixture was diluted with CH_2Cl_2 (50 mL) and washed with water and dried (MgSO_4). The solvent was removed *in vacuo* and resulting deep brown solid was purified by column chromatography on silica ($\text{CH}_2\text{Cl}_2/\text{Hexanes}=2/1$). Fast moving dark-brown band was desired product obtained as dark yellow oil. Yield 0.21 g (46.5%). $^1\text{H NMR}$ (CDCl_3): δ 7.92-7.89 (m, 4H, Ar-H), 7.58-7.54 (m, 2H, Ar-H), 7.47-7.43 (m, 4H, Ar-H), 7.39-7.32 (m, 5H, Ar-H), 7.19 (d, 2H, $J=3.5$ Hz, furan-2,8-H), 6.34 and 6.33 (two doublet, 2H, $J=3.5$ Hz, furan-3,7-H), 5.71 (s, 1H, *meso*-H).

1,9-Bis(benzoyl)-5-phenyldithienylmethane (13). A mixture of phenyldithienylmethane (0.10 g, 0.4 mmol)

and benzoyl chloride (0.2 mL, 1.5 mmol) was dissolved in benzene (10 mL). The mixture was degassed by bubbling nitrogen for 5 min. at 0 °C, then tin (IV) chloride (0.18 mL, 1.5 mmol) was added. The mixture was stirred for 14 h at 85 °C then aqueous HCl (10%) was added. The resulting dark green mixture was diluted with CH₂Cl₂ (50 mL), washed with water and dried over anhydrous MgSO₄. The solvent was removed in vacuo and resulting deep brown solid was purified by column chromatography on silica (CH₂Cl₂/hexanes=2/1). Fast moving deep brown band was **14** (oil, 0.02 g, 10.5%) and second moving deep brown band was **13** as major product (oil, 0.11 g, 58.4%). ¹H NMR (CDCl₃) for **14**: δ 7.83-7.81 (m, 2H, Ar-H), 7.57-7.53 (m, 1H, Ar-H), 7.47 (d, 1H, *J*=4.0 Hz, thiophene-2-H), 7.45-7.41 (m, 1H, Ar-H), 7.36-7.26 (m, 5H, Ar-H), 7.22 and 7.23 (two doublets, 1H, *J*=5.0 Hz, thiophene-9-H), 6.95 and 6.94 (two doublet, 1H, *J*=5.0 Hz, thiophene-8-H), 6.89-6.88 (m, 1H, thiophene-3-H), 6.87-6.86 (m, 1H, thiophene-7-H), 5.88 (s, 1H, *meso*-H). ¹H NMR (CDCl₃) for **13**: δ 7.84-7.82 (m, 4H, Ar-H), 7.59-7.55 (m, 2H, Ar-H), 7.51-7.50 (m, 2H, thiophene-2,8-H), 7.49-7.46 (m, 4H, Ar-H), 7.38-7.32 (m, 5H, Ar-H), 6.96-6.95 (m, 2H, thiophene-3,7-H), 5.92 (s, 1H, *meso*-H).

1,9-Bis[(α-hydroxy-α-phenyl)methyl]-5-phenyl-difurylmethane (15). A solution of 1,9-bis(benzoyl)-5-phenyldifurylmethane (0.15 g, 0.34 mmol) and tetrahydrofuran (15 mL) was degassed by bubbling with nitrogen for 5 min. To this solution LiAlH₄ (0.34 g, 8.8 mmol) dissolved in tetrahydrofuran (15 mL) was added dropwise. The solution was stirred for 30 min. at room temperature under nitrogen. The brown mixture was diluted with CH₂Cl₂/H₂O (30 mL/10 mL) then washed with water and dried (MgSO₄). The solvent was removed *in vacuo* and resulting dark brown solid was directly used to the condensation without further purification. Yield 0.15 g (96.7%). IR (CH₂Cl₂): 3350 cm⁻¹ (s, OH). ¹H NMR (CDCl₃): δ 7.42-7.21 (m, 15H, Ar-H), 5.98-5.96 (m, 2H, furan-H), 5.88 (q, 2H, *J*=3.0 Hz, furan-H), 5.76 (s, 2H, methine-H), 5.40 (s, 1H, *meso*-H), 2.39 (s, 2H, OH).

1,9-Bis[(α-hydroxy-α-phenyl)methyl]-5-phenyl-dithienylmethane (16). A solution of 1,9-bis(benzoyl)-5-phenyldithienylmethane (0.12 g, 0.3 mmol) and tetrahydrofuran (15 mL) was degassed by bubbling with nitrogen for 5 min. To this solution LiAlH₄ (0.23 g, 5.9 mmol) dissolved in tetrahydrofuran (15 mL) was added dropwise. The solution was stirred for 30 min. The brown mixture was diluted with CH₂Cl₂/H₂O (30 mL/10 mL) then washed with water and dried (MgSO₄). Evaporation of the solvent afforded product. This crude product was directly used to the condensation without further purification. Yield 0.12 g (97.5%); The reduction of carbonyl function was identified by IR; The strong absorption appeared at 1670 cm⁻¹ was completely disappeared and new absorption was observed at 3350 cm⁻¹ by O-H stretching vibration.

meso-15-Mesityl-5,10,20-triphenyl-21,22-dioxaporphyrin (17). A mixture of 9-bis[(α-hydroxy-α-phenyl)methyl]-5-phenyldifurylmethane (0.1 g, 0.2 mmol) and *meso*-mesityldipyromethane (0.1 g, 0.2 mmol) dissolved in chloroform (14 mL) was purged with nitrogen for 5 min. then BF₃·O(Et)₂ (100 mL, 0.4 mmol) was added. The mixture was stirred for 40 min. at room temperature and then triethylamine (0.5 mL) and DDQ (0.2 g, 0.8 mmol)

were added. The mixture was stirred for an additional 4 h at room temperature. The mixture was washed with water and dried over anhydrous MgSO₄. The solvent was removed in vacuo and resulting black solid was chromatographed on silica (tetrahydrofuran/hexanes=2/1) afforded the porphyrin **17**. Yield 0.04 g (28.2%). ¹H NMR (CDCl₃): δ 9.77 and 9.68 (two doublets, 4H, *J*=5.0 Hz, Furan-H), 9.01 and 8.94 (two doublet, 4H, *J*=5.0 Hz, pyrrole-H), 8.32-8.28 (m, 6H, Ar-H), 8.01-7.88 (m, 9H, Ar-H), 7.35 (s, 2H, Ar-H), 2.65 (s, 3H, *p*-methyl), 1.87 (s, 6H, *m*-methyl). UV-Vis (CH₂Cl₂), λ_{max} (ε × 10³) 410 (30), 435 (18), 537 (3), 588 (3), 640 (1), FAB MS Calcd. for C₄₇H₃₄N₂O₂ 658.26, Found 659.11.

meso-5,10,15,20-Tetraphenyl-21,22-dithiaporphyrin (18). A mixture of 1,9-bis[(α-hydroxy-α-phenyl)methyl]-5-phenyldithienylmethane (0.12 g, 0.3 mmol) and *meso*-phenyldipyromethane (0.06 g, 0.3 mmol) dissolved in chloroform (14 mL, distilled from K₂CO₃) was purged with nitrogen for 5 min. then BF₃·O(Et)₂ (65 mL, 0.5 mmol) was added. The mixture was stirred for 30 min. at room temperature and then triethylamine (0.5 mL) and DDQ (0.2 g, 0.8 mmol) were added. The mixture was stirred for an additional 4 h at room temperature. The mixture was washed with water and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* and column chromatography on silica afforded the porphyrin. Yield 0.02 g (11.6%). ¹H NMR (CDCl₃): δ 9.42 and 9.38 (two doublets, 4H, *J*=5.0 Hz, thiophene-H), 8.62 and 8.51 (two doublet, 4H, *J*=5.0 Hz, pyrrole-H), 8.27-8.21 (m, 8H, Ar-H), 7.87-7.74 (m, 10H, Ar-H), 7.69 (t, 2H, Ar-H). UV-Vis (CH₂Cl₂), λ_{max} (ε × 10³) 441 (28), 465 (20), 546 (5), 643 (2), 698 (1). FAB MS Calcd. for C₄₄H₂₈N₂S₂ 648.84, Found 649.17.

Results and Discussion

Aldehydes and pyrrole readily undergo acid-catalyzed condensation.¹³ The normal condensation has been known to result in the mixture of oligomeric or polymeric products instead of dimeric or trimeric due to the high reactivity of pyrrole toward electrophile.¹⁴ 1,9-Unsubstituted, *meso*-substituted dipyrromethanes can be obtained selectively by performing the pyrrole-aldehyde condensation without any organic solvents in the presence of acid catalyst.¹² The success of this reaction prompted us to pursue the possibility of synthesizing difurylmethanes and dithienylmethanes. Easy availability of those building blocks will enable the regioselective synthesis of various core-modified porphyrins. *Meso*-substituted dipyrromethanes (DPM) can be obtained from either the reaction of 2-(α-hydroxymethyl)pyrrole with excess pyrrole or direct condensation of aldehydes and pyrrole.¹² This analogy has been successfully applied to the synthesis of furylpyrrylmethanes or thienylpyrrylmethanes.¹⁵ The same method can be applied to the synthesis of difurylmethanes (**1**, DFM) and dithienylmethanes (**2**, DTM). Condensation of 2-α-hydroxymethylfuran or 2-α-hydroxymethylthiophene with excess furan or thiophene in the presence of suitable catalyst would give the corresponding difurylmethanes (DFM) and dithienylmethanes (DTM). One other possible route would be the direct condensation of aldehydes with excess furan or thiophene. Stirring a solution of benzaldehyde with excess furan or thiophene in the pres-

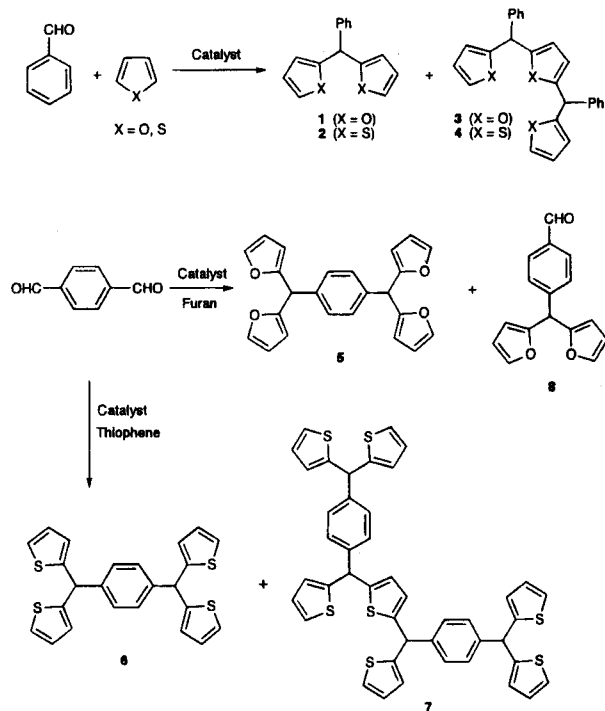
Table 1. Acid-catalyzed, one-flask condensation of 5-membered aromatic heterocycles with aromatic aldehydes

X	Ar	*Catalyst ^a	Product	Yield (%)	Product	Yield (%)
		BF ₃ ·OEt ₂	2	61.9	4	25.1
S	Ph	TiCl ₄	2	48.4	4	d
		CF ₃ COOH ^b	2	60.3	4	34.6
O	Ph	BF ₃ ·OEt ₂ ^c	1	23.7	3	d
		TiCl ₄	1	32.6	3	11.2
		CF ₃ COOH	1	27.6	3	18.2

*Amount of catalyst used in this reaction is one equivalent except b (10 equiv.) and all the reactions are run at room temperature except c (0 °C). ^dNot observed.

ence of acid catalysts afforded desired compounds as major products. But unlike the pyrrole-aldehydes condensation, the fraction of trifurylmethane (3) or trithienylmethane (4) was not negligible anymore in these cases. Washing the reaction mixture with base (0.1 M aqueous NaOH) immediately after the reaction (10-30 min.) seemed to be critical in obtaining high yields of DFM or DTM. Otherwise extensive polymerization during workup seemed to be inevitable. In general, the crude products were obtained by removing excess furan or thiophene under vacuum. Column chromatography on silica usually afforded the pure product. The results for the attempted condensation with different catalysts and temperature were shown in Table 1 and Scheme 1. The amounts of products slightly varied depending on the catalysts.

As shown in the Table 1, the highest yield of DTM was obtained when BF₃·O(Et)₂ was employed as catalyst. The formation of DFM seems not to be influenced by catalysts and the yields were not improved. The previous literature

**Scheme 1.**

procedure employing organic solvent in the condensation resulted many oligomeric mixture.¹ But only difurylmethane or trifurylmethane were isolated as major products under this solventless condensation. The solventless condensation with short reaction time would inhibit the extensive equilibration to higher oligomers. Current results are comparable with the one previously reported.^{1,2}

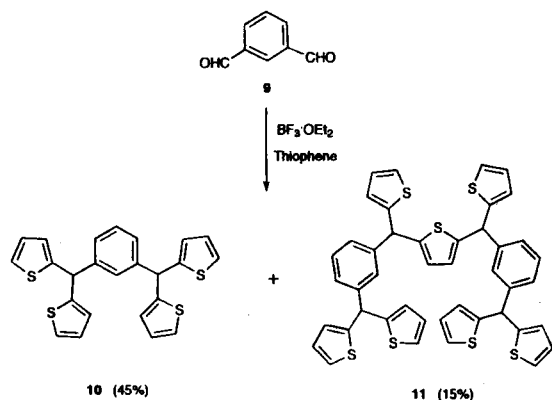
When the solventless condition was applied to dialdehyde condensation, corresponding bis-difurylmethane (5) and bis-dithienylmethane (6) were obtained as major products as shown in Scheme 2. But unexpected formation of secondary products such as (7) and (8) were also observed. The formation of (7) is assumed by the condensation of (6) with *meso*-(*p*-formyl)phenyl dithienylmethane and consecutive reaction with thiophene. The results for the condensation of aromatic dialdehyde with thiophene or furan were shown in Table 2. Almost same amount of (6) and (7) were obtained regardless the catalysts used. In the case of the reaction of furan with dialdehyde, extensive polymerization was observed in all attempted conditions. But the best condition found with this limited study was lowering the temperature during the condensation. The advantages of above synthesis obviously lie in the easy access to DFM and DTM that could be applied to the synthesis of core-modified porphyrins.

The easy availability of DFM and DTM played a key role in the synthesis of regioisomerically pure dioxaporphyrins, dithiaporphyrins and related macro cyclic systems. In order to functionalize 1 and 9 position of DFM or DTM, we adopted the acid catalyzed acylation. The electrophilic acylation works smoothly in the presence of tin (IV) chloride as catalyst. The fraction of bis-acyl compounds was increased when DFM was mixed with benzoyl chloride first followed by addition of SnCl₄. At least 2.2 equivalents of acid chloride should be applied in order to obtain 1,9-bisacyl-DFM (12) and 1,9-bisacyl-DTM (13) as the major products in the synthesis. The convenient availability of 1,9-bisacyl-DFM and 1,9-bisacyl-DTM makes a MacDonald's [2+2] type condensation¹⁶ possible in the synthesis of dioxaporphyrin and dithiaporphyrin, which hetero-ligands such as furan or thiophene are adjacent each other. The 1,9-bisbenzoyl-DFM or 1,9-bisbenzoyl-DTM were reduced with LiAlH₄ to afford corresponding bis-diol which were subsequently condensed with *meso*-phenyldiopyromethane.

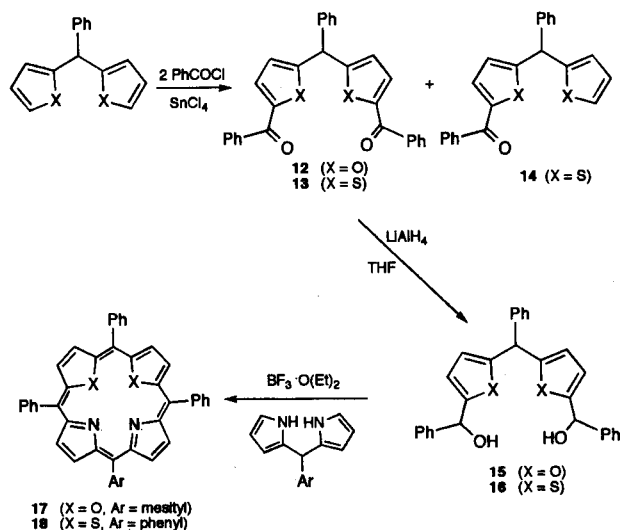
Table 2. Acid-catalyzed, one-flask condensation of 5-membered aromatic heterocycles with aromatic 1,4-dialdehydes

X	*Catalyst ^a	Reaction time (min)	Product	Yield (%)	Product	Yield (%)
	BF ₃ ·OEt ₂	30	6	44.3	7	20.1
S	TiCl ₄	15	6	32.3	7	22.5
	CF ₃ COOH ^b	22	6	25.6	7	18.1
O	BF ₃ ·OEt ₂ ^c	10	5	3.3	d	d
	TiCl ₄	35	5	9.5	8	30.5
	CF ₃ COOH	30	5	9.1	d	d

*Amount of catalyst used in this reaction is one equivalent except b (10 equiv.) and all the reactions are run at room temperature except c (0 °C). ^dNot observed.



Scheme 2.



Scheme 3.

The synthetic work for the porphyrin is shown in Scheme 3. The formation of *meso*-5,10,15,20-tetraphenyl-21,22-dithiaporphyrin (SSNN) and 15-mesityl-5,10,20-triphenyl-21,22-dioxaporphyrin (OONN) was easily monitored by TLC and UV-Vis spectroscopy during the reaction. The desired porphyrin was isolated from the crude reaction mixture by repeated column chromatography. The electronic spectrum of OONN and SSNN are shown in Figure 1. The spectrum shows typical Soret band at 410 nm for OONN porphyrin and 441 nm for SSNN porphyrin. The spectrum is quite different with previously reported 5,10,15,20-tetraphenyl-21,23-dioxaporphyrin.¹¹ The introduction of oxygen atoms in 21 and 23 position usually causes a strong bathochromic shift of the Q_I and Q_{II} bands and hypsochromic shift of the Q_{III} and Q_{IV} bands compared with TPPH₂.¹¹ In OONN porphyrin the introduction of two oxygen atoms adjacent each other causes strong hypsochromic shift of all Q bands compared with TPPH₂. A strong hypsochromic shift (418→410 nm) of Soret was also observed. Introduction of two sulfur atoms in the core adjacent each other causes strong bathochromic shift of the Q_I and Q_{II} bands and hypsochromic shift of the Q_{III} and Q_{IV} bands compared with TPPH₂. Introduction of two sulfur atoms adjacent each other in the core show somewhat different spectroscopic behavior. In case of 21,23-dithiaporphyrin which has two sulfur atoms

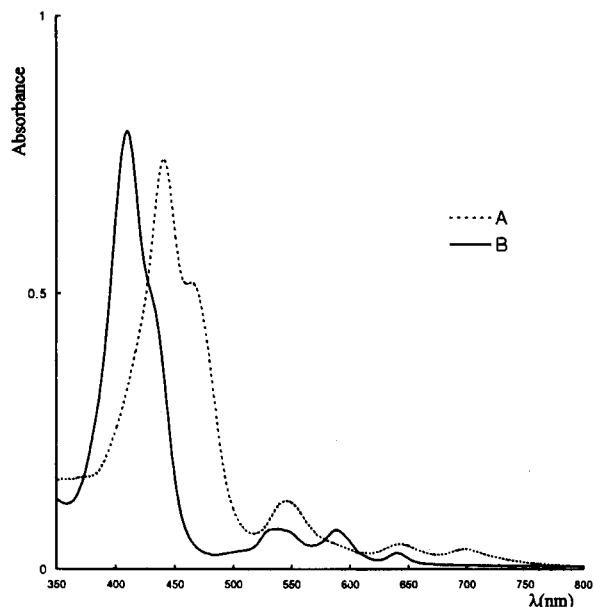


Figure 1. UV-vis spectrum of SSNN (A) and OONN (B) porphyrin in CH₂Cl₂.

across in the core shows strong bathochromic shift of the Q_I and Q_{II} bands and almost no change of Q_{III} and Q_{IV} bands.¹² The spectroscopic properties of OONN and SSNN porphyrin obviously suggest that both porphyrins have aromatic character. The SSNN-porphyrin is more distorted than OONN-porphyrin due to the bigger size of sulfur. This result indicates that steric effects in the core is a predominant factor of the flexibility of porphyrin plane.

Small amount of *meso*-tetraphenylporphyrin (TPPH₂) was unexpectedly isolated during the synthesis of porphyrin 17 and 18. The formation of TPPH₂ indicates the acid-catalyzed reversible cleavage of dipyrromethane and resulting pyrrolyphenylmethyl cation tetramerizes to form TPPH₂. Although the yields of dioxaporphyrin or dithiaporphyrin are not practically high, the mild reaction condition would allow us to prepare a building unit of porphyrins with various *meso*-substituents. The easy functionalization of 1,9-position in compounds (1) and (2) make the customized core-modification possible. In order to establish synthetic generality for the preparation of porphyrin building blocks, extensive adjustment is under investigation.

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Photodissociation Dynamics of *t*-butyl Hydroperoxide at 280-285 nm

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The photodissociation dynamics of *t*-butyl hydroperoxide at 280-285 nm has been investigated by measuring laser induced fluorescence spectra of the fragment OH. Measured fractions of the available energy distributed among the fragments are $f_t=0.56$, $f_r(\text{OH})=0.044$, $f_{int}(t\text{-BuO})=0.40$, and negligible populations of OH are found in vibrationally excited states. By analyzing the Doppler profiles of the spectra of OH, the positive v -J vector correlation has been obtained. From the measured v -J correlation and A'' propensity in the two Λ -doublets of OH, it is concluded that the dissociation takes place directly from the repulsive surface induced by the $\sigma^* \leftarrow n$ transition with the fragment OH rotating in the plane perpendicular to the dissociating O-O bond axis.

Introduction

Photochemical reactions are of fundamental importance to study chemical reaction dynamics in detail.^{1,2} Since the molecules of interest collide with photons with well-defined momenta, theories are much simpler than those of reactive scattering events and applicable to even moderately large molecules. The processes are governed by an initially prepared state and shape of potential energy surfaces along the reaction coordinate. By examining the dynamics of the process, one can study the shape of the potential energy surfaces in detail and thus electronic structures of the molecules as well.

Studies of photodissociation dynamics in detail require precise measurements of certain physical properties related to the potential energy surfaces. Population and energy distributions among quantum states of the reactants and products are scalar properties from which mechanism of the photodissociation can be deduced. However, in most cases, measuring the energy distribution is not enough to study the detailed dynamics of the process. The transition dipole moment of the parent molecule, recoil velocities and rotational angular momenta of the products are vector properties of the molecule and correlations between these vector properties reveal the detailed dynamics of the photodissociation. In order to measure the angular distribution and speed of the products, a rotatable time-of-flight mass spectrometer

has been used.³ In favorable cases such that the molecules of interest absorb or emit photons of easily accessible spectral region, Doppler resolved absorption or emission spectra provide the translational and internal energy distributions of the fragments. In addition, when linearly polarized lights are used for photolysis and probe, the vector correlations can be measured from the spectra by analyzing the Doppler profiles.⁴⁻⁶

The Doppler profiles in polarized absorption and emission spectra of molecules have been thoroughly analyzed by Herschbach and Zare.⁷⁻⁸ The molecules absorb a photon and are excited when the transition dipole moment μ is preferentially aligned in the laboratory frame parallel to the electric vector, ϵ_d of the linearly polarized dissociating light. The resulting angular distribution of the photofragments is described by the so-called anisotropy parameter which shows the correlation between μ and the recoil direction of the fragments. When the photofragments are polyatomic molecules, the fragments have rotational angular momenta which have definite relationship with the recoil velocities. Since this v -J correlation is developed when the fragmentation occurs, the v -J correlation may appear even when the angular distribution is isotropic. Correlations of rotation with translational motion have been thoroughly analyzed by Dixon⁹ and the anisotropy is defined by a number of bipolar moments of the translational and rotational angular distributions. The Doppler broadened lineshape in the spectra