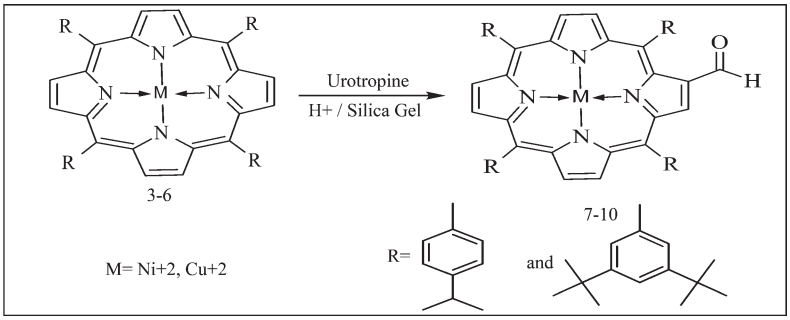
Microwave-Assisted Synthesis, Metallation, and Duff Formylation of Porphyrins

Muhammad Yaseen,[a]* Mukhtar Ali,[b] Muhammad NajeebUllah,[a]
Munawar Ali Munawar,[a] and Irshad Khokhar[a]

[a]Institute of Chemistry University of the Punjab, Lahore, Pakistan
[b]Government College of Science, Lahore, Paksitan
*E-mail: yaseen747pk@hotmail.com
Received July 27, 2008
DOI 10.1002/jhet.78
Published online 00 Month 2009 in Wiley InterScience (www.interscience.wiley.com).



Microwave assisted synthesis, metallation, and β-formylation of porphyrins is described. All synthetic reactions were carried out on inorganic polymer solid support using microwave energy. It is the first documented application of the Duff reaction in the field of porphyrins and metalloporphyrins. The overall process is simple, easy, and environment friendly. FTIR, UV–visible, elemental analysis, ^{1}H NMR, and mass spectrometry were used to characterize the compounds.

J. Heterocyclic Chem., **46**, 251 (2009).

INTRODUCTION

The solid-state synthetic methods have attracted much attention and are widely used for the synthesis of a variety of compounds [1–3]. Microwave assisted organic synthesis has became an increasingly popular technique in academic and industrial laboratories because of certain advantages particularly shorter reaction times, minimum solvent requirement, and ease of purification [4–6]. Application of microwave power in synthesis, metallation, and substitution reactions of porphyrins is not a new concept [7–9]. In the past few years, porphyrin chemistry under microwave heating has been under intense study with significant benefits. Microwave assisted reactions are believed to facilitate the polarization of the substrate thereby increasing the rate of the reactions [10–12]. Herein, we wish to report the use of inorganic polymer solid support for synthesis, metallation, and formylation of porphyrins.

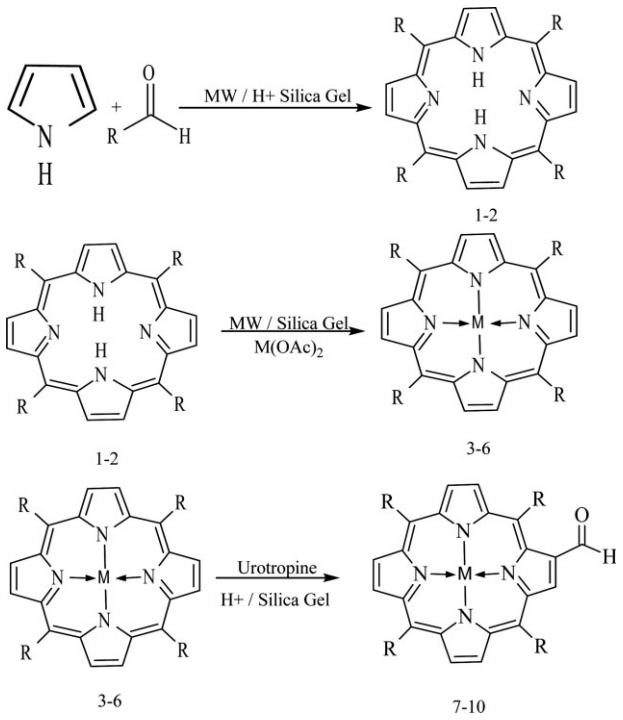
Porphyrins are tetrapyrrolic molecules, the electronic properties of which can be tailored by the variation of peripheral substitution or by central atom [13]. A single porphyrin molecule offers twelve peripheral substitution positions; four meso and eight β-positions. As a result peripheral substitution reactions of porphyrin with different functional groups are highly important reactions. Known functionalization reactions of porphyrins include sulfonation, nitration, halogenation, and Vilsmeier formylation [14,15]. One functional group that allows asymmetric modification and is widely used in porphyrin chemistry is the formyl group [16,17]. Formyl porphyrins are not only prepared synthetically but also occur naturally [18]. Formyl porphyrins are important precursors for the synthesis of multiporphyrin systems [19]. Many methods are available in the literature to formylate the porphyrins at meso and β-positions [20–22]. Both synthetic and natural porphyrins have been formylated by different methods but the most popular is the Vilsmeier reaction [23]. According to the best of our knowledge, there has not been a single example to formylate the porphyrins by Duff reaction over inorganic solid support under microwave radiations.

RESULTS AND DISCUSSION

The classical porphyrin synthesis popularized by Alder, Longo, and Lindsey makes use of toxic and corrosive solvents [24–26]. However, with the advent of microwave radiation as source of energy for chemical reactions, it has been possible to synthesize the porphyrins and metalloporphyrins under solventless conditions

© 2009 HeteroCorporation

Scheme 1



[27]. The first report of solid-state synthesis of porphyrins under microwave radiations used silica gel, alumina, clay, and montmonillonite. According to that report, the yields were poor and not more than 10% [28].

The experimental technique applied for the organic synthesis described below is based on microwave power. The aim of this work was to investigate the solid phase synthesis, metallation, and formylation of porphyrins. The overall process for the synthesis of formyl porphyrins is rapid, efficient, and eco-friendly (Scheme 1).

Two reaction techniques were used namely (i) Solventless heating with controlled temperature, and (ii) Dry media procedure with controlled temperature. Initially, we used microwave radiation under solventless conditions for the synthesis of Porphyrin **1** and **2** without using any solid support (Table 1). In another experiment, the mixtures of aldehyde and pyrrole were supported on dry neutral silica gel and irradiated with microwave radiation to get Porphyrin **1** and **2** but the yields were not greater than 10%. Alternatively, silica gel was first acidified with propanoic acid, dried in an oven at 50°C for 12 h. This silica gel was used to support the mixtures of reacting aldehyde and pyrrole. Upon microwave irradiation, Porphyrin **1** and **2** were obtained in good yields (Table 2).

Table 1

Solventless synthesis of porphyrins.

Mixture	Porphyrin	% Age yield
Pyrrole and Cuminaldehyde	Porphyrin [1]	22
Pyrrole and 3,5-di-*tert*-butyl benzaldehyde	Porphyrin [2]	20

W = 200 Watts; Time = 6 min; Temperature = 100°C.

Table 2

Solid phase supported porphyrin synthesis.

Mixture over H^+/silica gel	Porphyrin	% Age yield
Pyrrole and Cuminaldehyde	Porphyrin [1]	37
Pyrrole and 3,5-di-*tert*-butyl benzaldehyde	Porphyrin [2]	32

W = 200 Watts; Time = 10 min; Temperature = 100°C.

Metallation of Porphyrin **1** and **2** was achieved when mixture of Porphyrin **1** and **2** and metal acetate adsorbed on neutral silica gel were irradiated under microwave radiation (Table 3). In another experiment, propanoic acid/silica gel containing synthesized crude Porphyrin **1** and **2** were washed thoroughly with the saturated solution of metal acetate in methanol. After drying, silica gel was irradiated with microwave radiation to get Metallo-porphyrin **3**, **4**, **5**, and **6** (Table 3). Hence, after the synthesis of Porphyrin **1** and **2** on acidic silica gel one may use the same silica gel for the synthesis of Metalloporphyrin **3**, **4**, **5**, and **6** without any purification step. One pot synthesis of Metalloporphyrin **3**, **4**, **5**, and **6** was also investigated when mixture of reacting aldehyde, pyrrole, and metal acetate were simultaneously heated under microwave radiations over neutral silica gel. The results were not more than 6% probably because of poor synthesis of Porphyrin **1** and **2** over neutral silica gel. On the other hand, when acidic silica gel was used for one pot synthesis of Metalloporphyrin **3**, **4**, **5**, and **6**, under microwave radiations, metallation failed because of the acidic environment.

Table 3

Metalloporphyrins.

Mixture over silica gel	Metalloporphyrin	% Age yield
$Ni(OAc)_2$ and Porphyrin [1]	Metalloporphyrin [3]	90
$Ni(OAc)_2$ and Porphyrin [2]	Metalloporphyrin [4]	92
$Cu(OAc)_2$ and Porphyrin [1]	Metalloporphyrin [5]	94
$Cu(OAc)_2$ and Porphyrin [2]	Metalloporphyrin [6]	93

W = 250 Watts; Time = 15 min; Temperature = 111°C.

Table 4
Formylporphyrins.

Mixture on H^+/ silica gel	Product	% Age yield
Urotropine and porphyrin [3]	Formyl porphyrin [7]	54
Urotropine and porphyrin [4]	Formyl porphyrin [8]	50
Urotropine and porphyrin [5]	Formyl porphyrin [9]	54
Urotropine and porphyrin [6]	Formyl porphyrin [10]	51

W = 200 Watts; Time = 18 min; Temperature = 111°C.

After successful synthesis (Table 2) and metallation of Porphyrin **1** and **2** (Table 3), we applied the standard Vilsmeier method for the introduction of formyl group onto Metalloporphyrin **3**, **4**, **5**, or **6**. Dry neutral silica gel containing Metalloporphyrin **3**, **4**, **5**, or **6** was mixed with the Vilsmeier salt adsorbed on silica gel. On microwave irradiation, demetallattion was exclusively observed. When all attempts to formylate the Metalloporphyrin **3**, **4**, **5**, and **6** over silica gel solid support under microwave radiations were failed, we applied Duff reaction. Duff reaction require strongly acidic conditions whereas under such conditions metalloporphyrins demetallate [29]. To overcome this problem, we used acidified silica gel instead of acid itself under solventless conditions to get formyl porphyrin **7**, **8**, **9**, and **10** (Table 4).

UV–visible spectra of Porphyrin **1** and **2** showed characteristic Soret and Q bands. On metallation, two visible bands appeared along with a Soret band. ^{1}H NMR spectra of free-base Porphyrin **1** and **2** showed a singlet in the high field region for imino-protons that disappeared on metallation. Formyl porphyrin **7**, **8**, **9**, and **10** showed two clear singlets at downfield region; one for formyl proton and second for β-pyrrolic proton immediately next to formyl group. FTIR of formyl porphyrin **7**, **8**, **9**, and **10** showed clear sharp peak around 1660 cm^{-1} for C=O group.

EXPERIMENTAL

Melting points were determined on a Kofler micromelting point apparatus without correction. IR spectra were recorded on a Nicolet Impact-410 FTIR spectrophotometer in KBr. ^{1}H NMR spectra were measured in $CDCl_3$ using TMS as internal standard with a Bruker 500 MHz spectrometer. MS spectra were taken on a KRATOS-AEI-MS50 spectrometer. Elemental analyses were performed on a PE-2400 CHN elemental analyzer. UV/Vis measurements were performed with a Shimadzu Multispec-1501. All the reactions were performed in the commercial microwave oven having maximum output power 500 Watts. Reagents from Merck and Aldrich Chemical were used. Anhydrous Silica gel 60–100 (0.063–0.2 mm) was used as solid support after dehydration under microwave irradiation for 4 min.

General procedures

(i) Solventless heating with controlled temperature. The reagents were mixed together in a low boiling point solvent at room temperature. Solvent was removed under vacuum. The reaction mixture was heated under microwave radiation in a quartz flask having an outer solvent circulating jacket for the control of temperature. The sample was cooled in an ice bath. TLC was used to monitor the reaction progress. The reaction product was extracted with solvent; the extract was filtered, dried over anhydrous sodium sulfate, and then the solvent was removed. The product was purified by column chromatography.

(ii) Dry media procedure with controlled temperature. The reagents were dissolved in a low boiling point solvent at room temperature; anhydrous microwave transparent inorganic solid support (silica gel) was added and the solvent was removed under vacuum. The adsorbed reaction mixture was introduced in an open quartz flask having an outer solvent circulating jacket for the control of temperature. It was subjected to microwave irradiation. The reaction mixture was cooled in an ice bath. TLC was used to monitor the reaction progress. The reaction product was purified by column chromatography. For column chromatography, the reaction mixture was applied as such onto silica column and eluted with mixture of solvents. Solvents were removed under vacuum to get product.

Preparation of propanoic acid/silica. Silica gel (15 g, Merck, 60–100 mesh size) was mixed well with 5 g of propanoic acid in a mortar. The resultant mixture was dried in an oven at 60°C for 12 h. Acidic silica gel was obtained as white powder.

Preparation of H_2SO_4/silica gel. H_2SO_4 (5 g, 95%) and silica gel (15 g, Merck, 60–100 mesh size) were mixed in a mortar. The resultant mixture was dried in an oven at 90°C for 12 h. Acidic silica gel was obtained as white powder.

Porphyrin [1] (1A). A mixture of pyrrole (0.04 mole, 2.68 g) and cuminaldehyde (0.04 mole, 5.93 g) was subjected to microwave irradiation according to solventless heating with controlled temperature method (i) (Table 1). After cooling, the reaction mixture was applied onto silica column and eluted with chloroform: *n*-hexane (1:2). The fast moving band was collected and the solvent was evaporated to get Porphyrin [1] (22%). mp > 350°C; Anal. Calcd. for $C_{56}H_{54}N_4$: C, 85.89; H, 6.96; N, 7.16. Found: C, 85.79; H, 6.93; N, 7.18. IR(KBr): ν_{max} 3315 (N—H), 2956, 1470, 1348, 1186, 1053, 966, 802, 735 cm^{-1}; UV($CHCl_3$) λ_{max} 420, 450, 515, 555, 670 nm; ^{1}H NMR ($CDCl_3$): δ −2.74 (bs, 2NH), 1.53 (d, J = 6.9 Hz, 8CH_3), 3.25 (sep, J = 6.9 Hz, 4CH), 7.58 (d, J = 7.8 Hz, 4m-Ph2H), 8.12 (d, J = 7.8, 4o-Ph2H), 8.84 (s, β-pyrrolic H 2, 3, 7, 8, 12, 13, 17, 18). MS (*m*/*z*, %): 782.3 (M^+, 100%), 780.4 (2.14%), 391.3 (7.74%).

Porphyrin [1] (1B). A mixture of pyrrole (0.04 mole, 2.68 g) and cuminaldehyde (0.04 mole, 5.93 g) was supported on propanoic acid/silica gel (5 g) and subjected to microwave irradiation according to dry media procedure (ii) (Table 2). After cooling, the reaction mixture was applied as such onto silica column and eluted with chloroform: *n*-hexane (1:2). The fast moving band was collected and the solvent was evaporated to get Porphyrin [1] (37%).

Porphyrin [2] (2A). A mixture of pyrrole (0.04 mole, 2.68 g) and 3,5-di-*tert*-butylbenzaldehyde (0.04 mole, 8.73 g) was

subjected to microwave irradiation according to solventless heating with controlled temperature method (i) (Table 1). After cooling, the reaction mixture was applied onto silica column and eluted with chloroform: *n*-hexane (1:2). The fast moving band was collected and the solvent was evaporated to get Porphyrin [2] (20%). mp > 350°C; Anal. Calcd. for $C_{76}H_{94}N_4$: C, 85.82; H, 8.90; N, 5.20. Found: C, 85.66; H, 8.87; N, 5.23. IR(KBr):ν_{max} 3320 (N—H), 3060, 2960, 2900, 2860, 1600, 1470, 1420 cm^{-1}; UV($CHCl_3$) λ_{max} 420, 520, 555, 590, 645 nm; ^1H NMR ($CDCl_3$): δ −2.67 (bs, 2NH), 1.51 (s, 8t-Bu), 7.74 (t, J = 1.7 Hz, 4p-PhH), 8.07 (d, J = 1.7 Hz, 8o-PhH), 8.87 (s, β-pyrrolic H 2, 3, 7, 8, 12, 13, 17, 18). MS (*m*/*z*, %): 1063 (M^+, 100%), 189 (5%).

Porphyrin [2] (2B). A mixture of pyrrole (0.04 mole, 2.68 g) and 3,5-di-*tert*-butylbenzaldehyde (0.04 mole, 8.73 g) was supported on propanoic acid/silica gel (5 g) and subjected to microwave irradiation according to dry media procedure (ii) (Table 2). After cooling, the reaction mixture was applied as such onto silica column and eluted with chloroform: *n*-hexane (1:2). The fast moving band was collected and the solvent was evaporated to get Porphyrin [2] (32%).

Metalloporphyrin [3] (3A). A mixture of Porphyrin [1] (0.04 mmole, 31.32 mg) and nickel acetate (1 mmole, 176.78 mg) was supported on propanoic acid/silica gel (5 g) and subjected to microwave irradiation according to dry media procedure (ii) (Table 3). After cooling, the reaction mixture was applied as such onto silica column and eluted with chloroform: petroleum ether; b.p 60–90°C (1:3). The fast moving band was collected, and the solvent was evaporated to get Metalloporphyrin [3] (90%). mp > 350°C; Anal. Calcd. for $C_{56}H_{52}N_4Ni$: C, 80.10; H, 6.25; N, 6.67. Found: C, 80.05; H, 6.28; N, 6.68. IR(KBr):ν_{max} 2956, 1654, 1660, 1351, 1261, 1055, 1004, 812 cm^{-1}; UV($CHCl_3$) λ_{max} 420, 445, 530 nm. ^1H NMR ($CDCl_3$): δ 1.48 (d, J = 6.9 Hz, 8CH_3), 3.18 (sep, J = 6.9 Hz, 4CH), 7.50 (d, J = 7.9 Hz, 4m-Ph2H), 7.90 (d, J = 7.9 Hz, 4o-Ph2H), 8.74 (s, β-pyrrolic H 2, 3, 7, 8, 12, 13, 17, 18). MS (*m*/*z*, %): 839 (M^+, 75%) 837.7 (100%), 55.1 (16.79%).

Metalloporphyrin [3] (3B). Silica gel obtained directly from Experiment-1B having adsorbed crude Porphyrin [1] was thoroughly washed with 50 mL of a saturated solution of nickel acetate in methanol. Silica gel was dried and heated under microwave according dry media procedure (ii) (Table 3). After cooling, the reaction mixture was applied as such onto silica column and eluted with chloroform: petroleum ether; b.p 60–90°C (1:3). The fast moving band was collected, and the solvent was evaporated to get Metalloporphyrin [3] (90%).

Metalloporphyrin [4] (3C). A mixture of Porphyrin [2] (0.04 mmole, 42.54 mg) and nickel acetate (1 mmole, 176.78 mg) was supported on propanoic acid/silica gel (5 g) and subjected to microwave irradiation according to dry media procedure (ii) (Table 3). After cooling, the reaction mixture was applied as such onto silica column and eluted with chloroform: petroleum ether; b.p 60–90°C (1:3). The fast moving band was collected, and the solvent was evaporated to get Metalloporphyrin [4] (92%). mp >350°C; Anal. Calcd. for $C_{76}H_{92}N_4Ni$: C, 81.48; H, 8.28; N, 5.00. Found: C, 81.52; H, 8.30; N, 5.01. IR(KBr):ν_{max} 3060, 2960, 2900, 2860, 1600, 1480, 1440, 1400 cm^{-1}; UV($CHCl_3$) λ_{max} 415, 530 nm. ^1H NMR ($CDCl_3$): δ 1.46 (s, 8t-Bu), 7.70 (t, J = 2.0 Hz, 4p-PhH), 7.86 (d, J = 2.0 Hz, 8o-PhH), 8.79 (s, β-pyrrolic H 2, 3, 7, 8, 12, 13, 17, 18). MS (*m*/*z*, %) 1118 (M^+, 100%), 57 (84%).

Metalloporphyrin [4] (3D). Silica gel obtained directly from Experiment-2B having adsorbed crude Porphyrin [2] was thoroughly washed with 50 mL of saturated solution of nickel acetate in methanol. Silica gel was dried and heated under microwave according dry media procedure (ii) (Table 3). After cooling, the reaction mixture was applied as such onto silica column and eluted with chloroform: petroleum ether; b.p 60–90°C (1:3). The fast moving band was collected, and the solvent was evaporated to get Metalloporphyrin [4] (92%).

Metalloporphyrin [5] (3E). Experiment-3A procedure was repeated with copper acetate (1 mmole, 181.63 mg) to get Metalloporphyrin [5] (Table 3) (94%). mp > 350°C; Anal. Calcd. for $C_{56}H_{52}CuN_4$: C, 79.62; H, 6.21; N, 6.63. Found: C, 79.50; H, 6.23; N, 6.65. IR(KBr):ν_{max} 2922, 1670, 1460, 1342, 1000, 802, 722 cm^{-1}; UV($CHCl_3$) λ_{max} 415, 540 nm. MS (*m*/*z*, %): 844.6 (M^+, 15.85%), 842.6 (72%), 837.6 (100%).

Metalloporphyrin [5] (3F). Silica gel obtained directly from experiment 1-B having crude synthesized Porphyrin 1 was washed thoroughly with 50 mL of a saturated solution of copper acetate in methanol. After drying, silica gel was irradiated with microwave (Table 3). Pure Metalloporphyrin [5] was obtained by column chromatography using chloroform: petroleum ether; b.p 60–90°C (1:3) as mobile phase. The fast moving band was collected and the solvent was evaporated to get pure Metalloporphyrin [5] (94%).

Metalloporphyrin [6] (3G). Experiment-3C procedure was repeated with copper acetate (1 mmole, 181.63 mg) to get Metalloporphyrin [6] (Table 3) (93%). mp > 350°C; Anal. Calcd. for $C_{76}H_{92}CuN_4$: C, 81.13; H, 8.24; N, 4.98. Found: C, 81.20; H, 8.22; N, 5.0. IR.(KBr)ν_{max} 3060, 2980, 2940, 2860, 1600, 1520, 1480, 1440, 1400 cm^{-1}; UV($CHCl_3$) λ_{max} 420, 540 nm. MS (*m*/*z*, %) 1123 (M^+, 23%), 57 (34%).

Metalloporphyrin [6] (3H). Silica gel obtained directly from the experiment 2-B having crude synthesized Porphyrin 2 was washed thoroughly with 50 mL of a saturated solution of copper acetate in methanol. After drying, silica gel was irradiated with microwave (Table 3). Purification was done by column chromatography using chloroform: petroleum ether; b.p 60–90°C (1:3) as mobile phase. The fast moving band was collected, and the solvent was evaporated to get pure Metalloporphyrin [6] (93%).

Formyl porphyrin [7] (4A). Urotropine (1 mmole, 140.19 mg) and Metalloporphyrin [3] (0.04 mmole, 33.59 mg) were powder together in an agate mortar. These were doped on H_2SO_4/silica gel (15 g) and heated under microwave according to dry media procedure (ii) (Table 4). After cooling, 50 mL of water was added and reaction mixture was stirred at room temperature for 30 min. Water was removed by filtration and residue was dried in vacuum desiccator. It was applied onto silica column and eluted with chloroform: petroleum ether; b.p 60–90°C (2:1). The fast moving band was collected and the solvent was evaporated to get 2-formyl-5,10,15,20-tetrakis(4′-isopropylphenyl)porphyrinatonickel(II) [7] (54%). mp > 350°C; Anal.Calcd. for $C_{57}H_{52}N_4NiO$: C, 78.90; H, 6.04; N, 6.46. Found: C, 78.80; H, 6.03; N, 6.50. IR(KBr)ν_{max} 2956, 2923, 1669 (C=O), 1545, 1507, 1459, 1351, 1056, 1001, 937, 813, 797, 719 cm^{-1}; UV($CHCl_3$)λ_{max} 435, 545, 585 nm. ^1H NMR($CDCl_3$): δ 1.48 (d, J = 6.7 Hz, 8CH_3), 3.18 (sep, J = 6.7 Hz, 4CH), 7.52 (d, J = 6.9 Hz, 4m-Ph2H), 7.89 (d, J = 6.9 Hz, 4o-Ph2H), 8.72 (m, β-pyrrolic H 7, 8, 12, 13, 17, 18), 9.20 (s, CH 3), 9.34 (s, CHO). MS (*m*/*z*, %), 867 (M^+, 1%), 413 (100%), 277 (24%).

Formyl porphyrin [8] (4B). Urotropine (1 mmole, 140.19 mg) and Metalloporphyrin [4] (0.04 mmole, 44.81 mg) were treated according to the procedure describe in experiment (4A) to get 2-formyl-5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)porphyrinatonickel(II) [8] (50%). mp > 350°C; Anal.Calcd. for $C_{77}H_{92}N_4NiO$: C, 80.54; H, 8.08; N, 4.88. Found: C, 80.45; H, 8.09; N, 4.89. IR(KBr)ν_{max} 3080, 2970, 2920, 2880, 1680 (C=O), 1600, 1480, 1440, 1400, 1370, 1360 cm^{-1}; UV ($CHCl_3$)λ_{max} 435, 545, 585 nm. ^1H NMR($CDCl_3$): δ 1.45 (m, 8t-Bu), 7.71 (m, C_5 p-PhH, C_{10} p-PhH, C_{15} p-PhH); 7.74 (t, J = 1.8 Hz, C_{20} p-PhH), 7.79 (d, J = 1.8 Hz, C_5 o-Ph2H, 6H), 7.82 (d, J = 1.8 Hz, C_{10} o-Ph2H), 7.82 (d, J = 1.8 Hz, C_{15} o-Ph2H), 7.88 (d, J = 1.8 Hz, C_{20} o-Ph2H), 8.77 (m, β-pyrrolic H 7, 8, 12, 13, 17, 18), 9.03 (s, CH 3), 9.34 (s, CHO). MS (*m*/*z*, %) 1147 (M^+, 1%), 235 (23%), 193 (18%), 189 (25%), 57 (100%).

Formyl porphyrin [9] (4C). Experiment (4A) procedure was repeated by using Metalloporphyrin [5] (0.04 mmole) to get 2-formyl-5, 10, 15, 20-tetrakis(4′-isopropylphenyl)porphyrinatocopper(II) [9] (54%) (Table 4). mp > 350°C; Anal.-Calcd. for $C_{57}H_{52}CuN_4O$: C, 78.46; H, 6.01; N, 6.42. Found: C, 78.51; H, 6.03; N, 6.44. IR (KBr) ν_{max} 2957, 2923, 1670 (C=O), 1559, 1540, 1507, 1458, 1342, 1055, 1000, 798, 721 cm^{-1};UV($CHCl_3$)λ_{max} 430, 550, 595 nm. MS (*m*/*z*, %) 872 (M^+, 3%), 349 (100%), 236 (71%).

Formyl porphyrin [10] (4D). Experiment (4B) procedure was repeated by using Metalloporphyrin [6] to get 2-formyl-5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)porphyrinatocopper (II) [10] (51%) (Table 4). mp > 350°C; Anal.Calcd. for $C_{77}H_{92}CuN_4O$: C, 80.20; H, 8.04; N, 4.86. Found: C, 80.18; H, 8.04; N, 4.85. IR(KBr)ν_{max} 2961, 1671 (C=O), 1591, 1560, 1540, 1362, 1345, 1288 cm^{-1}. UV($CHCl_3$) λ_{max} 430, 550, 595 nm. MS (*m*/*z*, %) 1154 (M^+, 3%), 349 (100%), 236 (71%), 189 (24%).

Acknowledgments. The author would like to thank Higher Education Commission of Pakistan for the financial support to this work.

REFERENCES AND NOTES

[1] Desai, B.; Danks, T. N.; Wagner, G. Tetrahedron Lett 2005, 46, 955.

[2] Nascimento, B. F. O.; Pineiro, M.; Gonsalves, A. M. A. R.; Silva, M. R.; Beja, A. M.; Paixao, J. A. J Porphyrin Phthalocyanines 2007, 11, 77.

[3] Kishan, M. R.; Rani, V. R.; Murty, M. R. V. S.; Devi, P. S.; Kulkarni, S. J.; Raghavan, K. V. J Mol Catal A Chem 2004, 223, 263.

[4] Toda, F. Top Curr Chem 1988, 149, 211.

[5] Rasmussen, M. O.; Axelsson, O.; Tanner, D. Synth Commun 1997, 27, 4027.

[6] Mohammadpoor-Baltork, I.; Sadeghi, M. M.; Esmayilpour. K. Synth Commun 2003, 33, 953.

[7] Zhao.; Fang, S.; Chen.; Cheng, N, Y.; Abzhu, X.; Li, Q. F.; Ying, Z. Chin J Chem 2005, 25, 805.

[8] Samaroo, D.; Soll, C. E.; Todaro, L. J.; Drain, C. M. Org Lett 2006, 8, 4985.

[9] Dean, M. L.; Schmink, J. R.; Leadbeater, N. E.; Bückner, C. Dalton Trans 2008, 1341.

[10] Liu, M. O.; Hu, A. T. J Organomet Chem 2004, 689, 2450.

[11] Liu, M. O.; Tai, C. H.; Wang, W. Y.; Chen, J. R.; Hu, A. T.; Wei, T. H. J Organomet Chem 2004, 689, 1078.

[12] Boufatah, N.; Gellis, A.; Maldonado, J.; Vanelle, P. Tetrahedron 2004, 60, 9131.

[13] Susumu, K.; Maruyama, H.; Kobayashi, H.; Tanaka, K. J Mater Chem 2001, 11, 2262.

[14] Fuhrhop, J. In Porphyrins and Metalloporphyrins; Smith. K. M., Ed.; Elsevier Scientific: Amsterdam, 1975; p 625.

[15] Vicente, M. G. H. In The Porphyrin Handbook; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 1, p 161.

[16] Couch, P. W.; Games, D. E.; Jackson, A. H. J Chem Soc Perkin Trans 1 1976, 2492.

[17] Fischer, H.; Orth, H. In Die Chemie des Pyrrols, Bd. II, Tl. 1; Akademischer: Leipzig, 1943; pp 287–293.

[18] Falk, J. E. In Porphyrins and Metalloporphyrins; Elsevier: Amsterdam, 1964; p 94.

[19] Arnold, D. P.; Johnson, A. W.; Mahendran, M. J Chem Soc Perkin Trans I 1978, 366.

[20] Montforts, F. P.; Scheurich, G.; Meier, A.; Haake, G.; Hoper, F. Tetrahedron Lett 1991, 32, 3477.

[21] Smith, K. M.; Langry, K. C. J Chem Soc Perkin Trans I 1983, 439.

[22] Nichol, A. W. J Chem Soc C 1970, 903.

[23] Vilsmeier, A.; Haack, A. Berichte 1927, 60, 119.

[24] Adler, A. D.; Longo, F. R.; Shergalis, W. J Am Chem Soc 1964, 86, 3145.

[25] Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. J Org Chem 1967, 32, 476.

[26] Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. J Org Chem 1987, 52, 827.

[27] Warner, M. G.; Succaw, G. L.; Hutchison, J. E. Green Chem 2001, 3, 267.

[28] Petit, A.; Loupy, A.; Maiuardb, P.; Momenteaub, M. Synth Commun 1992, 22, 1137.

[29] Johnson, A. W.; Kay, I. T. J Chem Soc C 1961, 2418.