Pergamon

Tetrahedron Vol. 51, No. 11, pp. 3129-3136, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00069-0

Synthesis of *Beta*-Aryl Substituted Porphyrins by Palladium Catalyzed Suzuki Cross-coupling Reactions

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Abstracts: β–Bromoporphyrins undergo Suzuki cross coupling reactions with aryl boronic acids to give β-arylporpyrins in high yields.

Introduction

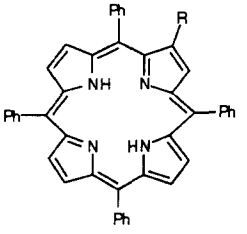
Porphyrin synthesis arouses continuing interests in biological, material and inorganic chemistry. Substitutents at the β-positions of porphyrins exert much larger steric and electronic effects on the porphyrin ring than substiutents at the *meso*-aryl positions.[1,2,3] The β-substitutents also induce the porphyrin ring into a non-planar conformation which may control the biological properties in tetrapyrrole systems like the photosynthetic centers,[1] vitamin B_{12},[4] coenzyme F_{430}[5] and the P-450.[6] In fact, the recent crytallographic studies of iron[IV] oxo cation radical has demonstrated the stabilizing effect of β halogen substitutents.[6] The synthesis of these β–subtituted porphyrins often requires the relatively inaccessible 3-substutited or 3,4-disubstituted[7] pyrroles for either protic[8] or Lewis acid-catalyzed[9] co-tetramerization with aldehydes. Furthermore, regioisomeric mixtures which require difficult and tediuos chromatographic purification often result in the preparation of unsymmetrical porphyrins. Since β-brominated porphyrins are obtained easily from the controlled bromination of porphyrins[10] or metalloporphyrins,[11] the transformation of the bromine subtituents into other functional groups would provide a facile entry into β-substituted porphyrins. We now report our full results on the synthesis of β-aryl substituted tetraphenylporphyrins[12] by Suzuki cross coupling[13] with β-bromoporphyrins.

Results and discussion

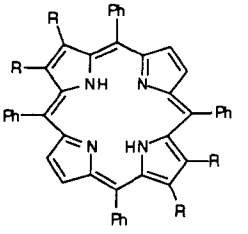
β -Monobromo [H_2TPP(Br)] **1** (TTP = 5, 10, 15, 20-tetraphenylporphyrin),[10] β-tetrabromo [H_2TPP(Br)$_4$] **2**,[10] and β-octabromophenyl [H_2TPP(Br)$_8$] **3**[11] porphyrins all underwent smooth Suzuki cross coupling reactions with *p*-substituted arylboronic acids **4** to give high yields of β -aryltetraphenyl porphyrins [Scheme1, eq 1, Table 1]. Both electron-donating and electron-withdrawing groups were introduced with little difference in the rate and the yields (**1a-1e**). The reactions were carried out in anhydrous toluene with solid K_2CO_3 as the base at 90-100 °C under nitrogen for 1 to 7 days. The use of other bases (KO^tBu, aq NaOH) and other solvents (THF, DMF, DME) were found to be less satisfactory.[14]

The mono- and tetra-arylation took 1 day while the octa-arylation required 7 days for complete reaction. Anhydrous conditions were essential as little reaction was observed in a mixed solvent of toluene and aqueous K_2CO_3.[14] The use of 4 instead of 2 equivalents of phenylboronic acid reduced the reaction time of **2** with **4a** to give **2a** from 36 h to 24 h but had little effect on the yield.[15] No protection of the acidic N-H of porphyrin ring was necessary which is advantageous to the cross coupling of bromo-substituted zinc porphyrins with organozinc reagents recently reported by Therien.[16] Furthermore, difference in cross-coupling with organozinc reagents exists in the literature. Rieke noted that 1,2-dibromobenzene did not cross couple with organozinc reagent to yield di-cross coupled product[17] while both aryl zinc reagents[18] and arylboronic acids[19] did cross couple with 1,2-dihalobenzene successfully. Thus the tetra- and octa-arylation *via* Suzuki coupling are unique.

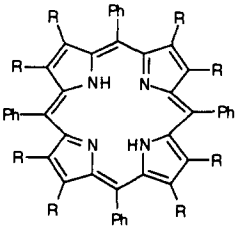
Scheme I



R = Br, H_2TPP(Br) **1**
Ar, H_2TPP(Ar) **1a-e**



R = Br, H_2TPP(Br)$_4$ **2**
Ar, H_2TPP(Ar)$_4$ **2a-b**



R = Br, H_2TPP(Br)$_8$ **3**
Ar, H_2TPP(Ar)$_8$ **3a-c**

p-X-PhB(OH)$_2$

X = H	**4a**
= Me	**4b**
= MeO	**4c**
= ^{t}Bu	**4d**
= Cl	**4e**

$$H_2TPP(Br)_n \xrightarrow[Pd(Ph_3P)_4,\ K_2CO_3]{p\text{-X-PhB(OH)}_2} H_2TPP(Ar)_n \qquad (1)$$

toluene, 110 °C, 1-7 d

Table 1 Suzuki Cross Coupling of $H_2TPP(Br)_n$ with *p*-X-Ph-$B(OH)_2$ (eq 1)

X =		% yield of $H_2TPP(Ar)$		% yield of $H_2TPP(Ar)_4$		% yield of $H_2TPP(Ar)_8$	
Reaction time		28 h		28 h		7 d	
H	**4a**	84	**1a**	88	**2a**	65	**3a**
Me	**4b**	84	**1b**	67	**2b**	50	**3b**
OMe	**4c**	70	**1c**			53	**3c**
^{t}Bu	**4d**	83	**1d**				
Cl	**4e**	79	**1e**				

The centrosymmteric structure of the β-tetraphenylated porphyrin, **2a**, was determined by single crystal X-ray analysis.[12] The regiochemistry of the bromination of TPP is thus confirmed as the one proposed by Crossley [20] using NMR method as shown who rightly corrected an earlier misassignment of the structure of $H_2TPP(Br)_4$.[10] Furthermore, it is interesting to note that the porphyrin ring in $H_2TPP(Ph)_4$ is planar with the β-phenyl ring near orthogonal to the porphyrin core.[12] This planar structure is in direct contrast with the non-planar features of β-octaphenyl[1] and octabromo[11b] substituted porphyrins. The recently reported structures of β-tetra chloro- and bromo-tetrakismesityl porphyrins exihibit slight deviation from planarity with larger distortion for the tetrabromo porphyrin. It seems the interplay of the size, the orientation, and possibly the electronic interaction of the β-substituents may influence the extent of distortion of the porphyrin core from planarity. Further crystallographic studies are required to define the number of β-substitutents as well as any steric and electronic influences in inducing the ruffling and saddling of porphyrins.[1]

Crossley has found that for mono-β-substituted TPP, the N-H protons preferentially lie on the pyrrole ring with more electron donating substitutents and the equilibrium does not follows a known substituents scale.[22] The N-H protons of **2a** however reside on the more electron deficient phenylated pyrroles (the Hammett constant of phenyl group = 0.05).[23] The β-and meso phenyl groups are all nearly orthogonal to the porphyrin ring in the solid state suggestive of difficult resonace interaction. We are currently studying the structural and electronic influences on this N-H tautormerism.

In comparison with the synthesis of porphyrins *via* the co-tetramerization of pyrroles with aryl aldehydes, our method is complimentary. While dodecaphenylporphyrin[24] is prepared in high yield from the acid catalyzed condensation of 3,4-diphenyl pyrrole[25] with benzaldehyde, this Suauki croos coupling method possesses the ease of structural modification at the β- positions by virtue of readily available arylboronic acids. Limitation exists, however, on the preparation of *meso*-unsubstituted porphyrins[25] since the corresponding β-bromo porphyrins may not be conveniently obtained through controlled bromination. The distinct advantage of synthesizing β- tetrasubstituted porphyrins from β-tetrabromo tetraphenyl porphyrin proves superior over the condensation method in avoiding tedious chromatographic separation of regioisomeric mixtures.

Conclusion

In summary, we have synthesized mono-, tetra-, and octa- β-aryl substituted tetraphenylporphryins through Suzuki cross coupling reactions with corresponding β-bromo porphyrins. Further applications of this synthetic method in porphyrin synthesis are being conducted in our laboratory.

Acknowledgments

We thank the Hong Kong Research Grants Council and the Direct Grant (CUHK) for financial support and the Dean of Student Office of CUHK and the Dow Chemical Company for summer research grants to MKA and CKT.

Experimental Section

Melting points were uncorrected. IR spectra were recorded on a FT-IR spectrophotometer as neat films on KBr plates. ^{1}H NMR spectra were measured at 250 MHz. In all ^{1}H NMR measurements, chemical shifts were reference with tetramethylsilane δ = 0.00 ppm. Mass spectra were obtained either in EI mode at 70 eV or in FAB mode using NBA as the matrix. Elemental analyses were performed by the Medac Ltd, Department of Chemistry, Brunel University, U. K. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl and toluene was distilled from sodium immediately prior to use. All cross-coupling reactions were run with the reaction mixture deoxygenated by the freeze-pump-thaw method (-195 to 25 °C, three cycles). Flash chromatography was performed with silica gel (70-230 or 230-400 mesh).

General procedure for arylboronic acid synthesis.[26] Magnesium turnings (30 mmol) were placed in a round-bottomed flask and then flame-dried under N_2. Aryl bromide (30 mmol) dissolved in THF (20 mL) was added with an addition funnel to the flask slowly. The reaction mixture was gently refluxed for 3 to 4 h. After cooling, the Grignard reagent was transferred to a solution of $(CH_3O)_3B$ in THF (10 mL) at -78 °C and stirred over night with warming up to rt slowly. After acidified with 10% HCl (10 mL), the product was extracted into ether (3 x 100 mL) and dried (sodium sulfate). The solvent was then removed under reduced pressure, and the products was precipitated by hexane with further recrystallization from water.

***p*-Tolylboronic acid (4b).** white needles were obtained in 81% yield; mp 243-244 °C (lit[26] 242-243 °C) ^{1}HNMR ($CDCl_3$) δ 8.12 (d, 2 H, J = 7.8 Hz), 7.26 (d, 2 H, J = 7.8 Hz), 4.55 (s, 2 H), 2.39 (s, 3 H) MS: m/z 354 (M^+).

***p*-Methoxyphenylboric acid (4c).** White needles were obtained in 72 % yield; mp 197-198 °C (lit[27]: 202 - 205 °C). ^{1}HNMR ($CDCl_3$) δ 8.15 (d, 2 H, J = 8.3 Hz), 7.01 (s, 2 H , J = 8.2 Hz), 4.52 (s, 2 H), 3.85 (s, 3 H) MS: m/z 402 (M^+).

***p*-^{t}Butylphenylboric acid (4d).** The white needle crystal was collected in 48% yield; mp : 168-170 °C. ^{1}HNMR ($CDCl_3$) δ 8.15 (d, J = 7.8 Hz, 2 H), 7.86 (d, 2 H, J = 7.8 Hz), 4.68 (s, 2 H),

1.34 (d, 9 H, J = 12.1 Hz); MS: m/z 480 (M^+). Anal. Calcd. for $C_{30}H_{39}B_3O_3$ (as the trimer): C, 74.91; H, 8.18. Found: C, 74.34; H, 8.40.

***p*-chlorophenylboric acid (4e).** White plate was collected in 76% yield; mp 264-268 °C (lit[27]: 268-272 °C). ^{1}HNMR ($CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 2 H), 7.48 (d, J = 7.9 Hz, 2 H), 4.61 (s, 2 H); MS: m/z 157 (M^+).

General Suzuki Coupling Procedure for H_2TPP(Br). A 50 mL telfon-stoppered flask was charged with H_2TPP(Br) (1 equiv), $Pd(Ph_3P)_4$ (10-20 mol %), toluene (25 to 30 mL), and anhydrous potassium carbonate (8 equiv), arylboronic acid (4 equiv). The purple suspension was degassed by the freeze-pump-thaw method (3 cycles) and was then heated between 90-100 °C under N_2 for 1-2 d. The reaction mixture was worked up by adding equal volume CH_2Cl_2 and washed with satd NaCl (40 mL). The organic layer was dried with anhydrous $MgSO_4$ and rotary evaporated to dryness. The crude product was purified by column chromatography on silica gel using a solvent mixture of toluene:hexane (1 : 1) as the eluent. The purple band was collected to give a purple solid which was recrystallized from CH_2Cl_2-methanol to give the pure purple crystal of H_2TPP(Ar).

2-Phenyl-5,10,15,20-tetraphenylporphyrin (1a) (84%): R_f = 0.22 (toluene : hexane = 1 : 1). ^{1}HNMR ($CDCl_3$) δ 8.77 (m, 7 H), 8.21 (m, 6 H) 7.89 (s, 2 H), 7.73 (m, 9 H), 7.17 (m, 8 H), -2.63 (s, 2 H); UV/Vis(λ_{max}, nm, CH_2Cl_2, logε) 419 (5.63), 517 (4.36), 5.92 (3.85), 592 (3.85), 647 (3.65); FABMS: m/z 691 $(M+1)^+$. Anal. Calcd for $C_{50}H_{34}N_4 \cdot H_2O$: C, 84.55; H, 4.96; N, 7.65. Found: C, 84.64; H, 5.07; N, 7.89.

2-(4-Methylphenyl)-5,10,15,20-tetraphenylporphyrin (1b) (84%): R_f = 0.22 (toluene : hexane = 1 : 1). ^{1}HNMR ($CDCl_3$) δ 8.74 (m,7 H), 8.19 (s, 6 H), 7.86 (d, 2 H, J = 6.6 Hz), 7.72 (m, 9 H), 7.21 (m, 5 H), 6.92 (d, 2 H, J = 7.8 Hz), 2.33 (s, 3 H), -2.65 (s, 2 H); UV/Vis (λ_{max}, nm, CH_2Cl_2, logε) 420 (5.76), 517 (4.46), 552 (4.00), 592 (3.87), 648 (3.58); FABMS: m/z 705 $(M+1)^+$. Anal. Calcd for $C_{51}H_{36}N_4$: C, 86.90; H, 5.15; N, 7.95. Found: C, 86.83; H, 5.37; N, 7.59.

2-(4-Methoxyphenyl)-5,10,15,20-tetraphenylporphyrin (1c) (70%): R_f = 0.20 (toluene : hexane = 1 : 1). ^{1}HNMR ($CDCl_3$, 250MHz) δ 8.76 (m,7 H), 8.22 (m, 6 H) 7.88 (d, 2 H, J = 6.63 Hz), 7.74 (m, 9 H), 7.25 (m, 5 H), 6.67 (d, 2 H, J = 8.6 Hz), -2.63 (s, 2 H); UV/Vis(λ_{max}, nm, CH_2Cl_2, logε) 420 (5.56), 517 (4.01), 552 (3.58), 592 (3.47), 647 (3.22); FABMS: m/z 721 $(M+1)^+$. Anal. Calcd for $C_{51}H_{36}N_4O$: C, 84.89; H, 5.03; N, 7.77. Found: C, 84.47; H, 5.08; N, 7.64.

2-(4-^{t}Butylphenyl)-5,10,15,20-tetraphenylporphyrin (1d) (83%): R_f = 0.25 (toluene : hexane = 1 : 1). ^{1}HNMR ($CDCl_3$) δ 8.77 (m, 5 H), 8.21 (m, 6 H), 7.84 (d, 2 H, J = 6.6 Hz), 7.73 (m, 9 H), 7.21 (m, 5 H), 1.37 (s, 9 H), -2.64 (s, 2 H) UV/Vis (λ_{max}, nm, CH_2Cl_2, logε) 420 (5.49), 517 (4.24), 552 (3.79), 592 (3.71), 647 (3.49). FABMS: m/z 747 $(M+1)^+$. Anal. Calcd. for $C_{54}H_{42}N_4.H_2O$: C, 84.80; H, 5.79; N, 7.32. Found: C, 85.36; H, 5.67; N, 7.20.

2-(4-Chlorophenyl)-5,10,15,20-tetraphenylporphyrin (1e) (79%): R_f = 0.28 (toluene : hexane = 1 : 1). ^{1}HNMR ($CDCl_3$) δ 8.76 (m, 7 H), 8.20 (m, 6 H), 7.84 (s, 2 H), 7.73 (m, 9 H), 7.24 (m, 5 H), 7.07 (d, 2 H, J = 8.3 Hz), -2.66 (s, 2 H) UV/Vis (λ_{max}, nm, CH_2Cl_2, logε) 420 (5.85), 517 (4.78), 551 (4.36), 592 (4.25), 647 (4.05). FABMS: m/z 725 $(M+1)^+$. Anal. Calcd. for $C_{50}H_{33}N_4Cl \cdot H_2O$: C, 81.09; H, 4.71; N,7.44. Found: C, 80.80; H, 4.71; N, 7.53.

General coupling procedure for $H_2TPP(Ar)_4$. A 50 mL telfon-stoppered flask was charged with H_2TPPBr_4 (1 equiv), $(Ph_3P)_4Pd$ (10-20 mol%), toluene (25-30 mL), and anhydrous potassium carbonate (24 equiv), arylboronic acid (12 equiv). The brown-yellow suspension was degassed by the freez-pump-thaw method (3 cycles), and then was heated between 90-100^{0}C under N_2 for 4-5 d. The reaction mixture was worked up by extracting with equal volume of CH_2Cl_2 and washed with satd $NaHCO_3$ (40 mL), water (2x40 mL), brine (40 mL). The organic layer was dried with anhydrous $MgSO_4$ and rotary evaporated to dryness. The crude product was purified by column chromatography on silica gel using CH_2Cl_2. The purple band was collected and the purple solid was further recrystallized from CH_2Cl_2-MeOH.

2,3,12,13-Tetraphenyl-5,10,15,20-tetraphenylporphyrin (2a) (88%): R_f = 0.25 (CH_2Cl_2). ^{1}HNMR($CDCl_3$) δ 8.37 (s, 4 H), 7.83 (d, 8 H, J = 6.4 Hz), 7,.22 (m, 2 H), 6.89 (m, 12 H), -2.06 (s, 2 H) UV/Vis (λ_{max}, nm, CH_2Cl_2, logε): 433 (5.47), 528 (4.28), 602 (3.84), 675 (3.55); FABMS: m/z 918 $(M)^+$. Anal. Calcd. for $C_{68}H_{46}N_4$: C, 88.83; H, 5.04; N, 6.09. Found: C, 88.67; H, 5.07; N, 5.91.

2,3,12,13-Tetrakis(4-Methylphenyl)-5,10,15,20-tetraphenylporphyrin (2b) (67%): R_f = 0.11 (CH_2Cl_2). ^{1}HNMR ($CDCl_3$) δ 8.22 (brs, 8 H), 7.96 (s, 4 H), 7.53 (d, J = 2.8 Hz, 12 H), 6.76 (d, J = 7.1 Hz, 8 H), 6.64 (d, J = 8.0 Hz, 8 H), -2.05 (s, 2 H). UV/Vis (λ_{max}, nm, CH_2Cl_2, logε): 434 (5.62), 529 (4.43), 570 (4.03), 598 (4.02), 673 (3.61). FABMS: m/z 975 $(M+1)^+$. Anal. Calcd. for $C_{72}H_{54}N_4$: C, 88.72; H, 5.58; N, 5.74. Found: C, 88.83; H, 5.21; N, 5.88.

General Coupling Procedure for $H_2TPP(Ar)_8$. A 50 mL telfon-stoppered flask was charged with $H_2TPP(Br)_8$ (1 equiv), $(Ph_3P)_4Pd$ (15 mol%), toluene (25-30 mL), and anhydrous potassium carbonate (40 equiv), arylboronic acid (20 equiv). The green suspension was degassed by the free-pump-thaw method (3 cycles), and then was heated between 90-100^{0}C under N_2 for 7 d. The reaction mixture was worked up by adding equal volume CH_2Cl_2 and washed with $NaHCO_3$ (40 mL), water (2 x 40 mL), and brine. The organic layer was dried ($MgSO_4$) and evaporated off the solvent to afford the crude product which was purified by column chromatography on silica gel using $CHCl_3$ as the eluent. The last slow-moving green band was collected and evaporated to dryness to give a green solid which was recrystallized from CH_2Cl_2-EtOH to yield the pure green crystal of $H_2TPP(Ar)_8$.

2,3,5,7,8,10,12,13,15,17,18,20-Dodecaphenylporphyrin (3a)[24] (65%): R_f = 0.10 ($CHCl_3$). ^{1}HNMR ($CDCl_3$): δ 7.59 (d, 8 H, J = 6.8Hz), 6.74 (m, 52 H); UV/Vis (λ_{max}, nm, CH_2Cl_2, logε): 468(5.38), 564 (4.13), 616 (4.15), 722 (4.00).

2,3,7,8,12,13,17,18-Octakis(4-methylphenyl)-5,10,15,20-tetraphenylporphyrin (3b) (50%): R_f = 0.12 ($CHCl_3$). ^{1}HNMR ($CDCl_3$): δ 7.85 (m, 8 H), 7.03 (s, 12 H), 6.46 (m, 32 H), 1.96 (s, 24 H). UV/Vis (λ_{max}, nm, CH_2Cl_2, logε): 469 (5.73), 5.66 (4.52), 616 (4.52), 723 (4.44), FABMS: m/z 1335 $(M+1)^+$. Anal. Calcd. for $C_{100}H_{78}N_4.3H_2O$: C, 86.60; H, 6.08; N, 3.88. Found: C, 86.80; H, 6.22; N, 3.86.

2,3,7,8,12,13,17,18-Octakis(4-methoxyphenyl)-5,10,15,20-tetraphenylporphyrin (3c) (53%): R_f = 0.12 ($CHCl_3$). ^{1}HNMR ($CDCl_3$): δ 7.55 (d, 8 H, J=6.5 Hz), 6.80 (d, 12 H, J = 7.6 Hz), 6.60 (d, 16 H, J = 7.4 Hz), 6.22 (d, 16 H, J = 8.8 Hz), 3.59 (s, 24 H). UV/Vis (λ_{max},

nm, CH_2Cl_2, log ε): 470 (5.66), 567 (4.53), 616 (4.49), 723 (4.28). FABMS: m/z 1464 $(M)^+$.
Anal. Calcd. for $C_{100}H_{94}N_4.H_2O$: C, 81.06; H, 5.50; N, 3.80. Found: C, 80.85; H, 5.90; N, 4.20.

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(*Received in Japan* 13 *December* 1994; *accepted* 20 *January* 1995)