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Efficient Synthesis of *meso*-Tetraarylporphyrins Using I_2 as Catalyst and IBX as Oxidant

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Abstract: *meso*-Tetraarylporphyrins are synthesized from pyrrole and substituted benzaldehydes by a catalytic amount of I_2 as catalyst and *o*-iodoxybenzoic acid (IBX) as oxidant in two steps and one flask. The advantages of this method include the use of inexpensive and easily available catalyst, avoidance of heavy consumption of CH_2Cl_2, innocuous oxidant, and good yields.

Keywords: Aldehydes, IBX, *meso*-tetraarylporphyrins, pyrrole, synthesis

The synthesis of porphyrins attracts widespread interest because of their potential applications as catalysts[1] and in energy conversion,[2] photodynamic cancer therapy,[3] molecular electronic devices,[4] and modeling of enzymes.[5] Tetraarylporphyrins were first synthesized by Rothemund[6] in 1939. Then Adler et al.[7] proposed a simplified synthetic method for *meso*-tetraarylporphyrin. Later, Lindsey et al.[8] published an improved method for sensitive *meso*-tetraarylporphyrins in a two-step, one-flask synthesis. Recently, synthetic methods for tetraarylporphyrins include the use of various acids,[9] clays,[10] silica chloride,[11] ionic liquids,[12] and cation exchange resins[13] as catalysts and 2,3-dichloro-5,6-dicyano-1,

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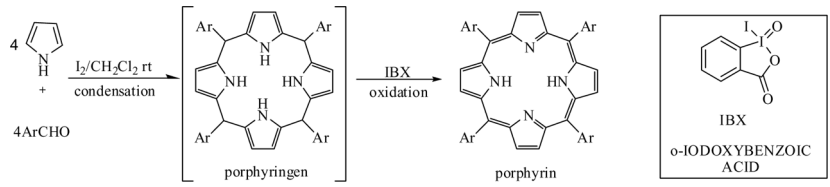
4-benzoquinone (DDQ)[14] and *p*-chloranil[10a] as oxidants. There are numerous advantages in this approach but still disadvantages, such as poor product yields, expensive catalysts, complex purification procedures, and heavy consumption of dichloromethane.

o-Iodoxybenzoic acid[15] [IBX, l-hydroxy-l, 2-benziodoxol-3(1 H)-one oxide], a compound first prepared in 1893, is a mild oxidant and can widely oxidize alcohols to aldehydes and ketones.[16] We now report that IBX can successfully oxidize porphyrinogen to porphyrin. In our previous article,[17] we demonstrated that I_2 was a great catalyst for tetraarylporphyrins. Herein we describe a method (Scheme 1) for preparing tetraarylporphyrins under milder conditions; pyrrole and benzaldehyde in the presence of I_2 react to form tetraarylporphyrinogen and IBX as oxidant in one pot, avoiding the use of deleterious and valuable DDQ[14] or tetrachlorobenzoquinone (TCQ).[18] Under these conditions, the yields are 25–63%.

Followed our previous research,[17] we mainly investigate the concentration of the reactant and the optimal reaction condition of step 1. We discovered that this method can achieve a good result under these reaction conditions.

The best CH_2Cl_2 quantity was studied first (Table 1). The results apparently show that 15 ml CH_2Cl_2 is the proper amount for the tetraarylporphyrin synthesis. It is also observed that with more than 15 ml CH_2Cl_2, the time of step 1 increased and the yields decreased. On the other hand, with less than 15 ml CH_2Cl_2, the reaction time was shorted but the yield was less.

We found that when IBX was simply suspended in the solution it can easily oxidize porphyrinogen to porphyrin at 39°C. When the oxidation step was done at room temperature, it required quite a long time and the yield was less (entry 6, Table 2). The optimal oxidant quantity of IBX was also investigated in CH_2Cl_2 (Table 2). The results distinctly show that 1 mmol IBX was the appropriate amount of oxidant. The yield was less when using a small quantity of IBX; meanwhile, the yield did not distinctly improve when using more IBX.



Scheme 1. Synthesis of *meso*-tetraarylporphyrins.

Table 1. Study of the quantity of CH_2Cl_2[a]

Entry	CH_2Cl_2 (ml)	Time (min)		Yield (%)[b]
		Step 1	Step 2	
1	2.5	30	100	21
2	5	35	120	28
3	10	40	180	43
4	15	50	240	58
5	20	60	260	54
6	25	65	280	53
7	40	120	300	50

[a]Reactions were performed with 1 mmol pyrrole, 1 mmol benzaldehyde, and 0.025 mmol iodine at rt. After step 1 was completed, 1 mmol IBX was added to the solution and refluxed at 39°C.
[b]Isolated yields.

To investigate the applicable scope of our method, we have researched a series of benzaldehyde substrates (Table 3), including a variety of *ortho, meta*, and *para* positions, both electron donating and withdrawing. Various aldehyde substrates can successfully participate in this two-step, one-flask process, and an increase in steric hindrance and the existence of electron-withdrawing groups at the benzaldehyde brings on a general decrease in the yields of porphyrin formation.

Table 2. Study of the quantity of IBX[a]

Entry	IBX (mmol)	Step 2 time (h)	Yield (%)[c]
1	0.5	8	45
2	0.75	5	49
3	1	4	58
4	1.2	3	58
5	1.5	2.6	59
6[b]	1	14	38

[a]Reactions were performed with 1 mmol pyrrole, 1 mmol benzaldehyde, and 0.025 mmol iodine in 15 ml CH_2Cl_2 at rt. After step 1 was completed, IBX was added.
[b]The reaction temperature is room temperature.
[c]Isolated yields.

Table 3. Synthesis of various *meso*-tetraarylporphyrins using a one-pot, two-step method

Entry	PhCHO[a]	Time (h)	Yield (%)[b]
1	H	5	58
2	*p*-MeO	5	63
3	*p*-Me	3.5	60
4	*p*-Cl	5.5	49
5	*p*-F	6	25
6	*m*-MeO	6	48
7	*m*-Br	6	31
8	*m*-Me	3.5	56
9	*m*-NO_2	7	30
10	*o*-MeO	5	28
11	*o*-Br	6	38
12	*o*-Cl	6	40

[a]Reactions were performed with 1 mmol benzaldehyde, 1 mmol pyrrole, and 0.025 mmol iodine in 15 ml CH_2Cl_2 at rt. After step 1 was completed, 1 mmol IBX was added to the solution and refluxed at 39°C.
[b]Isolated yields.

In conclusion, we have developed a practical and novel procedure for the synthesis of *meso*-tetraarylporphyrins in the presence of a catalytic amount of I_2 under IBX oxidation. Our method has the advantages of facile workup, inexpensive and easily available catalyst, small solvent quantity, nontoxic oxidant, and ease of purification.

EXPERIMENTAL

CH_2Cl_2 was distilled from $CaCl_2$. Pyrrole and benzaldehyde were distilled before use; substituted benzaldehydes were used as obtained. ^{1}H NMR spectra were recorded on a Bruker AC-400 NMR spectrometer in solutions of $CDCl_3$ using tetramethylsilane (TMS) a as the internal standard. The ultraviolet–visible spectra was obtained on a T9 UV-vis spectrophotometer.

Typical Procedure

A standard reaction was performed in a 50-ml, one-necked, round-bottomed flask equipped with magnetic stirrer. The flask was charged with 15 ml of distilled CH_2Cl_2, benzaldehyde (1 mmol, 0.106 g), and I_2

(0.025 mmol, 0.0063 g). The resulting solution was stirred for 5 min at room temperature (20°C). Then pyrrole (1 mmol, 0.067 g) was added. The mixture was completed after 50 min of continuous stirring. Afterward, IBX (1 mmol, 0.280 g) was added, and the reaction mixture was refluxed for 4 h at 39°C, cooled, and filtered. The filtrate was concentrated by rotary evaporation and purified by column chromatography (silica gel; CH_2Cl_2/petroleum ether 1:1) to give (**1**) in 58% yield.

Data

5,10,15,20-Tetraphenylporphyrin (**1**)

This compound was obtained as purple crystals, mp > 300°C; ^{1}H NMR (400 MHz, $CDCl_3$): −2.74 (br. s, 2NH), 7.79 (m, 12Ar-H), 8.23 (d, 8Ar-H, $J = 1.6$ Hz), 8.87 (s, 8-pyrrole-H). Anal. calcd. for $C_{44}H_{30}N_4$: C, 85.97; H, 4.92; N, 9.11. Found: C, 85.79; H, 5.01; N, 8.92. UV-vis (CH_2Cl_2; log ε) λ_{max} (nm): 424 (5.58), 514 (4.80), 549 (4.33), 590 (4.12), 645 (4.08).

5,10,15,20-Tetrakis(*p*-methoxyphenyl)porphyrin (**2**)

This compound was obtained as purple crystals, mp > 300°C; ^{1}H NMR (400 MHz, $CDCl_3$). −2.73 (br. s, 2NH), 4.13 (s, 12MeO-H), 7.31 (d, 8Ar-H, $J = 8.8$ Hz), 8.15 (d, 8Ar-H, $J = 8.4$ Hz), 8.89 (s, 8-pyrrole-H). Anal. calcd. for $C_{48}H_{38}N_4O_4$: C, 78.45; H, 5.21; N, 7.62. Found: C, 78.43; H, 5.19; N, 7.60. UV-vis (CH_2Cl_2; log ε) λ_{max} (nm): 426 (5.61), 518 (4.83), 555 (4.63), 595 (4.33), 650 (4.21).

5,10,15,20-Tetrakis(*p*-methylphenyl)porphyrin (**3**)

This compound was obtained as purple crystals, mp > 300°C; ^{1}H NMR (400 MHz, $CDCl_3$): −2.75 (br. s, 2NH), 2.73 (s, 12Me-H), 7.57 (d, 8Ar-H, $J = 7.6$ Hz), 8.12 (d, 8Ar-H, $J = 8.0$ Hz), 8.88 (s, 8-pyrrole-H). Anal. calcd. for $C_{48}H_{38}N_4$: C, 85.94; H, 5.71; N, 8.35. Found: C, 85.70; H, 5.74; N, 8.21. UV-vis (CH_2Cl_2; log ε) λ_{max} (nm): 422 (5.59), 516 (4.81), 551 (4.48), 591 (4.29), 647 (4.13).

5,10,15,20-Tetrakis(*p*-chlorophenyl)porphyrin (**4**)

This compound was obtained as purple crystals, mp > 300°C; ^{1}H NMR (400 MHz, $CDCl_3$): −2.83 (br. s, 2NH), 7.77 (d, 8Ar-H), 8.15 (d,

8Ar-H, $J = 8.4$ Hz), 8.87 (s, 8-pyrrole-H). Anal. calcd. for $C_{44}H_{26}Cl_4N_4$: C, 70.23; H, 3.48; N, 7.45. Found: C, 70.20; H, 3.61; N, 7.46. UV-vis (CH_2Cl_2; log ε) λ_{max} (nm): 424 (5.58), 515 (4.86), 549 (4.45), 590 (4.25), 645 (4.15).

5,10,15,20-Tetrakis(*p*-fluorophenyl)porphyrin (**5**)

This compound was obtained as purple crystals, mp > 300°C; ^{1}H NMR (400 MHz, $CDCl_3$): −2.85 (br. s, 2NH), 7.76 (d, 8Ar-H, $J = 8.4$ Hz), 8.18 (d, 8Ar-H, $J = 8.4$ Hz), 8.86 (s, 8-pyrrole-H). Anal. calcd. for $C_{44}H_{26}F_4N_4$: C, 76.96; H, 3.82; N, 8.16. Found: C, 76.85; H, 3.80; N, 3.91. UV-vis (CH_2Cl_2; log ε) λ_{max} (nm): 424 (5.56), 514 (4.83), 589 (4.24), 644 (4.01).

5,10,15,20-Tetrakis(*m*-methoxyphenyl)porphyrin (**6**)

This compound was obtained as purple crystals, mp > 300°C; ^{1}H NMR (400 MHz, $CDCl_3$): −2.77 (br. s, 2NH), 4.01 (s, 12MeO-H), 7.35–7.85 (m, 16Ar-H), 8.91 (s, 8-pyrrole-H). Anal. calcd. for $C_{48}H_{38}N_4O_4$: C, 78.45; H, 5.21; N, 7.62. Found: C, 78.37; H, 5.24; N, 7.65. UV-vis (CH_2Cl_2; log ε) λ_{max} (nm): 423 (5.60), 514 (4.27), 548 (4.09), 589 (3.94), 644 (3.83).

5,10,15,20-Tetrakis(*m*-bromophenyl)porphyrin (**7**)

This compound was obtained as purple crystals, mp > 300°C; ^{1}H NMR (400 MHz, $CDCl_3$). −2.87 (br. s, 2NH), 7.97–7.99 (m, 12Ar-H), 8.40 (s, 4Ar-H), 8.88 (s, 8-pyrrole-H). Anal. calcd. for $C_{44}H_{26}Br_4N_4$: C, 56.81; H, 2.82; N, 6.02. Found: C, 56.89; H, 2.83; N, 5.94. UV-vis (CH_2Cl_2; log ε) λ_{max} (nm): 424 (5.61), 515 (4.32), 548 (4.04), 591 (3.98), 645 (3.82).

5,10,15,20-Tetrakis(*m*-methylphenyl)porphyrin (**8**)

This compound was obtained as purple crystals, mp > 300°C; ^{1}H NMR (400 MHz, $CDCl_3$): −2.75 (br. s, 2NH), 2.84 (s, 12Me-H), 7.60–7.92 (m, 16Ar-H), 8.87 (s, 8-pyrrole-H). Anal. calcd. for $C_{48}H_{38}N_4$: C, 85.94; H, 5.71; N, 8.35. Found: C, 85.78; H, 5.72; N, 8.18. UV-vis (CH_2Cl_2; log ε) λ_{max} (nm): 424 (5.58), 515 (4.39), 549 (4.16), 590 (4.03), 645 (3.95).

5,10,15,20-Tetrakis(*m*-nitrophenyl)porphyrin (**9**)

This compound was obtained as purple crystals, mp > 300°C; ^{1}H NMR (400 MHz, $CDCl_3$): −2.82 (br. s, 2NH), 8.57–8.75 (m, 16Ar-H), 9.103 (s, 8-pyrrole-H). Anal. calcd. for $C_{44}H_{26}N_8O_8$: C, 66.52; H, 3.25; N, 14.28. Found: C, 66.38; H, 3.27; N, 14.22. UV-vis (CH_2Cl_2; log ε) λ_{max} (nm): 425 (5.60), 516 (4.40), 549 (4.09), 592 (4.01), 645 (3.93).

5,10,15,20-Tetrakis(*o*-methoxyphenyl)porphyrin (**10**)

This compound was obtained as purple crystals, mp > 300°C; ^{1}H NMR (400 MHz, $CDCl_3$): −2.59 (br. s, 2NH), 3.57–3.64 (m, 12MeO-H), 7.33–7.36 (m, 8Ar-H), 7.75–7.79 (m, 8Ar-H), 8.74 (s, 8-pyrrole-H). Anal. calcd. for $C_{48}H_{38}N_4O_4$: C, 78.45; H, 5.21; N, 7.62. Found: C, 78.39; H, 5.11; N, 7.49. UV-vis (CH_2Cl_2; log ε) λ_{max} (nm): 426 (5.58), 513 (4.37), 546 (4.19), 589 (4.12), 643 (4.05).

5,10,15,20-Tetrakis(*o*-bromophenyl)porphyrin (**11**)

This compound was obtained as purple crystals, mp > 300°C; ^{1}H NMR (400 MHz, $CDCl_3$): −2.59 (br. s, 2NH), 7.66–7.70 (m, 12Ar-H), 8.04–8.06 (m, 4Ar-H), 8.69 (s, 8-pyrrole-H). Anal. calcd. for $C_{44}H_{26}Br_4N_4$: C, 56.81; H, 2.82; N, 6.02. Found: C, 56.93; H, 2.72; N, 6.10. UV-vis (CH_2Cl_2; log ε) λ_{max} (nm): 426 (5.53), 513 (4.31), 544 (4.05), 589 (3.96), 643 (3.76).

5,10,15,20-Tetrakis(*o*-chlorophenyl)porphyrin (**12**)

This compound was obtained as purple crystals, mp > 300°C; ^{1}H NMR (400 MHz, $CDCl_3$): −2.63 (br. s, 2NH), 7.67–7.86 (m, 12Ar-H), 8.14–8.19 (m, 4Ar-H), 8.72 (s, 8-pyrrole-H). Anal. calcd. for $C_{44}H_{26}Cl_4N_4$: C, 70.23; H, 3.48; N, 7.45. Found: C, 70.31; H, 3.49; N, 7.37. UV-vis (CH_2Cl_2; log ε) λ_{max} (nm): 426 (5.57), 512 (4.29), 543 (4.08), 587 (3.95), 641 (3.87).

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