

## NOTE

**Microwave-Assisted Synthesis of Metalloporphyrins**

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A clean and eco-friendly microwave-assisted metallation of different free base 5,10,15,20-tetraarylporphyrins (TAP) in 84 to 92% yields is described under dry reaction conditions.

**Key Words:** Microwave, Metalloporphyrins, Dry reaction condition.

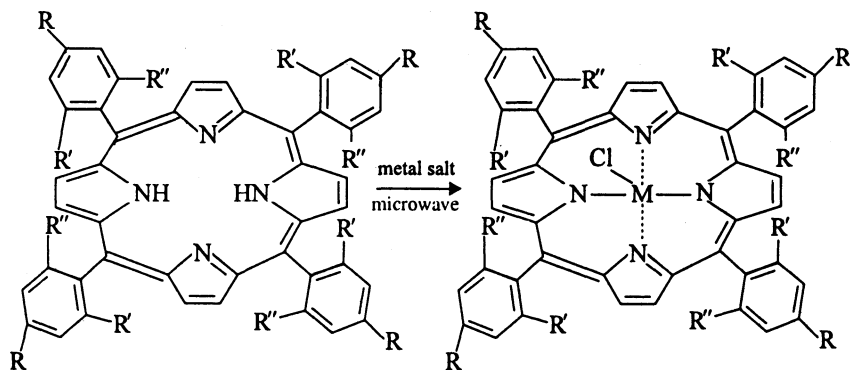
Microwave activation as a non-conventional energy source has become a very popular and useful technology in organic chemistry<sup>1-6</sup>. The acceleration of reactions by microwave exposure results from material-wave interactions leading to thermal effects and non-purely thermal effects<sup>6</sup>. The use of 'dry reaction mixtures' is an option in microwave chemistry because the heating effect utilized in microwave-assisted organic transformations is due to dielectric polarization. The dry reaction condition has the advantage that solvent evaporation and/or unwanted pressure increases in a sealed tube are avoided.

The metalloporphyrin complexes are widely used to mimic the cytochrome P450 which are membrane bound heme enzymes and catalyzes chemical reactions, such as hydroxylation, N-, O- or S-demethylation, dealkylation, epoxidation, etc<sup>7</sup>. The synthesis of metalloporphyrins has been reported by refluxing the porphyrin with metal salt in various solvents such as dimethylformamide, acetonitrile, tetrahydrofuran, etc.<sup>8-10</sup> The disadvantages of the above methods are the requirements of the large amounts of the solvents that have their limitations towards environment<sup>11</sup> and utilization of 4–5 times excess quantity of metal salt<sup>8-10</sup>. Hence, in continuation of our interest to develop environmentally safe methods<sup>12</sup>, we report a simple and facile method for the synthesis of metalloporphyrins under microwave irradiation in solvent-free condition.

The porphyrins used in this study have been prepared by known literature procedures<sup>12, 13</sup>. The process in its entirety involves a simple mixing of porphyrin with metal salt and irradiating in an unmodified household microwave oven for 3 min with the interval of 1 min to afford the corresponding metalloporphyrins in 84–92% yields (Scheme-1, Table-1). Though there is not much enhancement

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in the yields in comparison to the conventional heating method<sup>8-10</sup>, as expected from microwave, but the method reduces the reaction time and quantity of metal salt. The formation of metalloporphyrins has been confirmed spectrophotometrically and on comparison with authentic samples, prepared by conventional methods<sup>8-10</sup>, on TLC. On the formation of a metalloporphyrin, in most of the cases, the four-banded spectrum collapses into an essentially two-banded one in visible region, whereas the soret may remain in the usual range or shifted to higher or lower energy depending upon the metal used<sup>14</sup>.



1. R = R' = R'' = H;      2. R = H, R' = R'' = Cl;  
 3. R = H, R' = R'' = OH;    4. R = H, R' = R'' = OCH<sub>3</sub>  
 a. FeCl<sub>2</sub>·4H<sub>2</sub>O    b. MnCl<sub>2</sub>·4H<sub>2</sub>O

Scheme-1

TABLE-1  
 YIELDS AND UV-VISIBLE SPECTROSCOPIC DATA OF METALLOPORPHYRINS PREPARED

Entry	Product	Yield* (%)	UV-Vis (CHCl <sub>3</sub> ) λ <sub>max</sub> nm (ε <sub>max</sub> mM)
1a	TPPFe(III)Cl	92	416 (111.0), 510 (14.1), 576 (3.1), 657 (2.1)
2a	Cl <sub>8</sub> TPPFe(III)Cl	92	418 (72.0), 509 (8.3), 584 (3.3), 642 (2.3)
3a	(OH) <sub>6</sub> TPPFe(III)Cl	84	414 (71.0), 503 (6.2), 580 (1.1), 640 (0.7)
4a	(CH <sub>3</sub> O) <sub>6</sub> TPPFe(III)Cl	89	413 (51.4), 508 (4.5), 577 (1.3), 644 (1.1)
1b	TPPMn(III)Cl	90	479 (47.3), 528 (3.5), 575 (2.1), 618 (1.9)
2b	Cl <sub>8</sub> TPPMn(III)Cl	92	478 (69.0), 522 (4.4), 580 (8.6), 616 (2.8)
3b	(OH) <sub>6</sub> TPPMn(III)Cl	88	479 (70.1), 525 (4.5), 588 (7.6), 618 (3.0)
4b	(CH <sub>3</sub> O) <sub>6</sub> TPPMn(III)Cl	91	476 (62.0), 520 (4.1), 581 (1.7), 617 (0.9)

\*Isolated Yield

In conclusion, a simple, convenient and eco-friendly method for the synthesis of metalloporphyrins has been achieved under microwave irradiation in solvent-free condition.

In a typical procedure, 5,10,15,20-tetraphenylporphyrin (TPP) (1a) (0.308 g, 0.5 mmol) and FeCl<sub>2</sub>·4H<sub>2</sub>O (0.139 g, 0.7 mmol) was thoroughly ground and

subjected to microwave irradiation in a borosil beaker (25 mL) for 3 min with an interval after every 1 min. The temperature inside the beaker was found to be 100–110°C after removing it from the microwave oven. The reaction mixture was allowed to cool to room temperature and extracted with chloroform. The solution was concentrated and chromatographed using neutral alumina as adsorbent and chloroform as eluent. The first fraction was free base TPP and the second fraction was the desired 5,10,15,20-tetraphenylporphyrinato iron(III) chloride (TPPFe(III)Cl) (2a).

### ACKNOWLEDGEMENTS

Ram Singh is thankful to DBT, New Delhi and Geetanjali is thankful to CSIR, New Delhi, India for financial support.

### REFERENCES

1. R.S. Varma, *Pure Appl. Chem.*, **73**, 193 (2001).
2. A. Loupy, L. Perreux, M. Liagre, K. Burle and M. Moneuse, *Pure Appl. Chem.*, **73**, 161 (2001).
3. J.H. Clark, *Pure Appl. Chem.*, **73**, 103 (2001).
4. S.A. Galema, *Chem. Soc. Rev.*, **26**, 233 (1997).
5. S. Caddick, *Tetrahedron*, **51**, 10403 (1995).
6. L. Perreux and A. Loupy, *Tetrahedron*, **57**, 9199 (2001).
7. A.I. Archakov and G.I. Bachmanova, *The Cytochrome P450 and Active Oxygen*, Taylor and Francis, London-New York-Philadelphia, p. 105 (1990).
8. S.M.S. Chauhan, M. Gupta, A. Gulati and P.N.H. Nizar, *Indian J. Chem.*, **35B**, 1267 (1996).
9. M.D. Assis and J.R.L. Smith, *J. Chem. Soc. Perkin Trans. II*, 2221 (1998).
10. E. Tsuchida, T. Komatsu, E. Hasegawa and H. Nishide, *J. Chem. Soc. Dalton Trans.*, 2713 (1990).
11. A.I. Vogel, *A Textbook of Practical Organic Chemistry*, 4th Edn., Longman Group Limited, London (1978).
12. S.M.S. Chauhan, R. Singh and A. Gulati, *Indian J. Heterocycl. Chem.*, **9**, 231 (2000).
13. S.M.S. Chauhan, B.B. Sahoo, and K.A. Srinivas, *Synth. Commun.*, **31**, 33 (2001).
14. J.W. Buchler, in: D. Dolphin (Eds.), *The Porphyrins Academic Press, New York-San Francisco-London*, Vol. 1, pp. 390–483 (1978).

(Received: 7 November 2003; Accepted: 29 December 2004)

AJC-3578