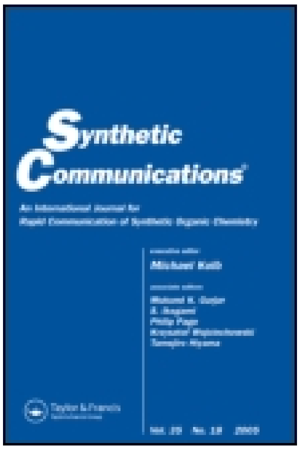


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

MICROWAVE-ASSISTED SYNTHESIS OF 5,10,15,20-TETRAARYL PORPHYRINS

S. M. S. Chauhan [a] , B. B. Sahoo [a] & K. A. Srinivas [a]
[a] Department of Chemistry, University of Delhi, Delhi, 110 007, India

To cite this article: S. M. S. Chauhan , B. B. Sahoo & K. A. Srinivas (2001): MICROWAVE-ASSISTED SYNTHESIS OF 5,10,15,20-TETRAARYL PORPHYRINS, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:1, 33-37

To link to this article: http://dx.doi.org/10.1081/SCC-100000176

SYNTHETIC COMMUNICATIONS, 31(1), 33–37 (2001)

MICROWAVE-ASSISTED SYNTHESIS OF 5,10,15,20-TETRAARYL PORPHYRINS

S. M. S. Chauhan,* B. B. Sahoo, and K. A. Srinivas

Department of Chemistry, University of Delhi,
Delhi 110 007, India

ABSTRACT

Clean and eco-friendly microwave-assisted cyclocondensation of different aryl aldehydes with pyrrole forms 5,10,15,20-tetraaryl porphyrins in 20 to 43% yields in very low amount of propionic acid in one step is presented.

Microwave irradiation is an important tool to improve the selectivity, rate enhancement, and reduction of thermal degradative byproducts in organic synthesis (1,2). Cyclocondensation of aryl aldehydes with pyrrole in propionic acid is an important method for the synthesis of symmetrical 5,10,15,20-tetraaryl porphyrins (3–6) in low yields. The sterically-hindered and electron-withdrawing groups in the phenyl ring of 5,10,15,20-tetraaryl porphyrins have been prepared by BF_3-etherate and DDQ methods in moderate yields (7–13). Although there have been recent advances to improve the synthesis of 5,10,15,20-tetraaryl porphyrins, including solid state and other modifications (14–20), these syntheses suffer from purification problems and low yields. One of the major disadvantages of the above methods is the requirement of large amounts of corrosive, acidic, and

---

*To whom correspondence should be addressed.

environmentally harmful chlorine-containing solvents. Optimal yields are obtained only with 0.01 M concentrations of pyrrole and aldehyde. Microwave-assisted organic synthesis reduces the amount of solvents and time, and leads to high yields. Hence, we report the microwave-assisted synthesis of 5,10,15,20-tetraaryl porphyrins by cyclocondensation of arylaldehydes with pyrrole using a minimum amount of propionic acid in different reaction conditions.

The microwave-assisted cyclocondensation of benzaldehyde and pyrrole in propionic acid (5 ml) for 4 min gave 5,10,15,20-tetraaryl porphyrin in 41% yield. Similarly, the cyclocondensation of arylaldehydes and pyrrole in propionic acid (3–5 ml) gave 5,10,15,20-tetraaryl porphyrins in microwave irradiation for 3 to 5 min. The yields of various porphyrins and their spectroscopic data are presented in Table 1. As shown in Table 1, the MW irradiation method gave a remarkably high yield of 5,10,15,20-tetraaryl porphyrins (**3a–h**), as compared to other high dilution methods. The formation of polymeric by-product depends on the solvent used and the irradiation time. Further, the purification of porphyrins in microwave-assisted synthesis is easier than solution phase synthesis.

Figure 1 represents the effect of time on the formation of porphyrins in microwave-assisted porphyrin synthesis. The high dilution conditions are not required and the chlorin contamination is reduced in microwave-assisted porphyrin synthesis. Thus, microwave-assisted porphyrin synthesis may be developed into eco-friendly methods for the synthesis of different heterocycles.

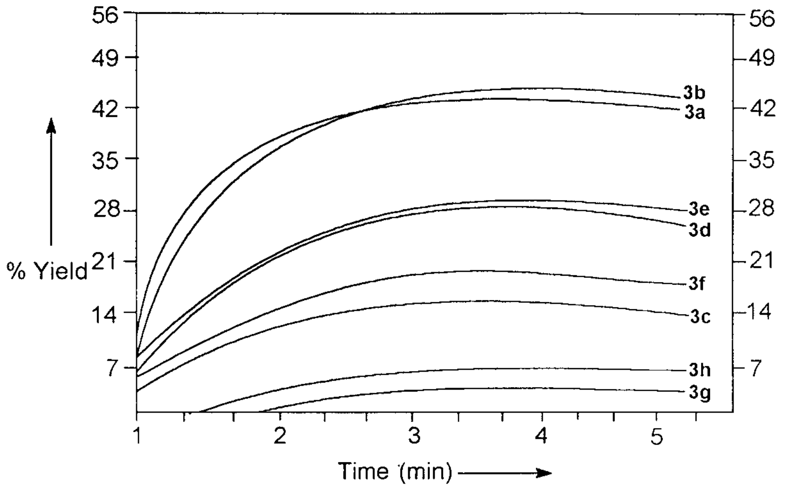
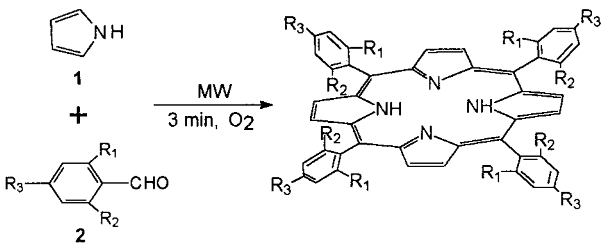


Figure 1. Comparison of maximum yields w.r.t time.

Table 1. 5,10,15,20-Tetraaryl Porphyrin Synthesis in Different Media

		Yield[a] (%)		Spectroscopic Data		
S.N.	POR	Mw[b]/PA (5 ml)	PA[c] (160 ml)	UV-vis (λ_{max}/C_6H_6)	^{1}H NMR δ_H (300 Mz, $CDCl_3$)	^{13}C NMR δ_C (300 Mz, $CDCl_3$)
3a	TPP	41	29	419, 485, 514, 549, 591, 647	−2.80 (2H, brs, NH), 7.72 (12H, m, p & m-Ph), 8.21 (d, 8H, o-Ph), 8.80 (s, 8H, pyrr-H)	120 (C-5, 10, 15 and 20), 126.7, 127.8 (C-β-pyrrolic), 134.6, 139.2 and 142.7
3b	*o*-OMe	43	27	420, 513, 546, 591, 648	−2.62 (2H, brs, NH), 3.55 (s, OMe), 3.58 (s, OMe), 3.51 (s, OMe), 7.3–7.4 (m, Ar), 7.7–7.8 (m, Ar), 7.9–8.1 (m, Ar), 8.7 (s, pyrr-H)	55.9, 111.1, 115.7, 119.5 (C-meso), 129.9, 130.5 (C-β-pyrrolic). The resonance peak of α-carbons was too broad to be detected.
3c	*p*-OMe	15	9	424, 488, 519, 555, 595, 653	−2.77 (2H, brs, NH), 4.20 (12H, s, OMe), 7.30 (8H, d, J = 8.3 Hz, m-Ph), 8.11 (d, 8H, o-Ph), 8.81 (s, 8H, pyrr-H)	56.1, 119.9 (C-5, 10, 15 and 20), 128.5, 133.6 (C-β-pyrrolic), 134.9, 137.0 and 140.4
3d	*o*-NO_2	25	5	420, 513, 546, 591, 648	−2.57 (2H, brs, NH), 7.97–7.99 (m, Ar), 8.25–8.30 (m, Ar), 8.62 (s.pyrr-H)	115.37 (C-5, -10, -15, -20), 124.06, 129.81, 131, 131.20, 136.24, 137.09, 151.96
3e	*p*-NO_2	28	6	421, 485, 515, 549, 591, 649	−2.82 (2H, brs, NH), 7.80 (8H, d, m-Ph), 8.30 (d, J = 8.9 Hz, 8H, o-Ph), 8.87 (s, 8H, pyrr-H)	118.1 (C-5, 10, 15 and 20), 127.5, 131.6 (C-β-pyrrolic), 133.9, 136.9 and 141.1
3f	Me_{12}	19	13	418, 483, 515, 547, 592, 646	−2.51 (2H, brs, NH), 1.85 (24H, s, o-Ph), 2.62 (12H, s, p-Me), 7.27 (8H, s, m-Ph), 8.61 (s, 8H, pyrr-H)	21.8, 31.0, 120.1 (C-5, 10, 15 and 20), 131.5, 133.6 (C-β-pyrrolic), 135.9, 139.6 and 140.3
3g	*o*-Cl	4	Trace*	420, 513, 546, 591, 648	−2.66 (2H, brs, NH), 7.62–7.9 (m, Ar), 8.12–8.30 (m, Ar), 8.70 (s, pyrr-H)	116.8 (C-5, -10, -15, -20), 122.9, 125.4, 129.1, 130.0, 131.0, 135.5, 140.7
3h	*p*-Cl	7	3	419, 512, 543, 589, 656	−2.86 (2H, brs, NH), 7.75 (d, J = 8.2 Hz, *m*-Ph), 8.14 (d, J = 8.2 Hz, *o*-Ph), 8.85 (s, pyrr-H)	119.1 (C-5, -10, -15, -20), 127.2, 131.4 (C-β Pyrr), 134.6, 135.7, 140.5

[a] % yield calculated by weighing the compounds after crystallization.
[b] Aldehyde (0.1 mol), Pyrrole (0.1 mol), Propionic acid (5 ml).
[c] Propionic acid used in the conventional method is 160 ml.
*Detected by UV-visible sectroscopy, PA: Propionic acid.



	R_1	R_2	R_3
3a.	H	H	H
3b.	OMe	H	H
3c.	H	H	OMe
3d.	NO_2	H	H
3e.	H	H	NO_2
3f.	Me	Me	Me
3g.	H	Cl	H
3h.	H	H	Cl

Scheme 1. One step synthesis of *meso*-tetraaryl porphyrin.

EXPERIMENTAL

In a typical procedure, benzaldehyde (or its derivatives) (0.1 mol) and pyrrole (0.1 mol) were added to freshly distilled propionic acid (5 mL) successively. The well-homogenized mixture was irradiated in a microwave oven (domestic, the reaction carried out in a pyrex bottle) for 3 to 5 min by 1-min periods, followed by cooling to room temperature and homogenization. The cooled reaction mixture was diluted with H_2O (50 mL) and extracted in $CHCl_2$(2×50 mL). The dichloromethane layer was separated and evaporated under reduced pressure and the residue was passed through Al_2O_3(Merck aluminium oxide 90, activity II-III, 100 gm) column and eluted with hexane-CH_2Cl_2. The porphyrin fractions were collected and evaporated under vaccum. The nitro porphyrins were purified directly by washing with dichloromethane (3×50 mL), without using column chromatography. The yield(s) of the reaction product was obtained after recrystallization from a mixure of CH_2Cl_2/EtOH, tabulated in Table 1.

ACKNOWLEDGMENTS

We are thankful to Professor R.N. Khanna for providing the microwave oven. We are also thankful to the Department of Science and Technology (DST) and Council of Scientific and Industrial Research (CSIR), New Delhi, India, for financial support.

REFERENCES

1. Caddick, S. Tetrahedron **1995**, *51*, 10403.
2. Loupy, A.; Petit, A.; Hamelin, J.; Texier-Boullet, F.; Jacquault, P.; Mathe, D. Synthesis **1998**, 1213.

3. Adler, A.D.; Longo, F.R.; Shergalis, W.D. J. Am. Chem. Soc. **1964**, *86*, 3145.
4. Adler, A.D.; Longo, F.R.; Finarelli, J.D.; Goldnacher, J.; Assour, J.; Korsakoff, L., J. Org. Chem. **1967**, *32*, 476.
5. Adler, A.D.; Saklar, L.; Longo, F.R.; Finarelli, J.D.; Finurelli, G.M. J. Heterocycl. Chem. **1968**, *5*, 669.
6. Kim, J.B.; Adler, A.D.; Longo, F.R. J. Am. Chem. Soc. **1972**, *94*, 3986.
7. Lindsay, J.S.; Schreiman, I.C. Tetrahedron Lett. **1986**, *27*, 4969.
8. Lindsay, J.S.; Schreiman, I.C.; Hsu, H.C.; Kearney, Marguerettaz, A.M. J. Org. Chem. **1987**, *52*, 827.
9. Lindsay, J.S.; Wagner, R.W. J. Org. Chem. **1989**, *54*, 828.
10. Clezy, P.S. Aus. J. Chem. **1991**, *44*, 1163.
11. Swanson, K.L.; Snow, K.M.; Jeyakumar, D.; Smith, K.M. Tetrahedron **1991**, *47*, 685.
12. Rocha Gonsalaves, A.M.A.; Varejao, M.T.B.; Pereira, M.M. J. Heterocycl. Chem. **1991**, *28*, 685.
13. Drain, C.M.; Gong, X. J. Chem. Soc. Chem. Comm. **1997**, 2117.
14. Li, F.; Yang, K.; Tyhonas, J.S.; MacCrum, K.A.; Lindsay, J.S. Tetrahedron **1997**, *53* (37), 12339.
15. Gradillas, A.; Del Campo, C.; Sinisterra, J.V.; Llama, E.F. J. Chem. Soc. Perkin Transation I. **1995**, 2611.
16. Onaka, M.; Shinoda, T.; Izumi, Y.; Nolen, E. Chemistry Lett. **1993**, 117.
17. Onaka, M.; Shinoda, T.; Izumi, Y.; Nolen, E. Chemistry Lett., **1993**, *34* (16), 2625.
18. Rose, E.; Quelquejeu, M.; Pochet, C.; Julien, N.; Kossanyi, A.; Hamon, L. J. Org. Chem, **1993**, *58*, 5030.
19. Laszlo, P.; Luchetti, J. Chemistry Lett. **1993**, 449.
20. Petit, A.; Loupy, A.; Maillard, Ph.; Momenteau, M. Synthetic Commun. **1992**, *22*, 1137.

Received in the U.K. January 24, 2000

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Downloaded by [University of Haifa Library] at 14:27 29 June 2013

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081SCC100000176