



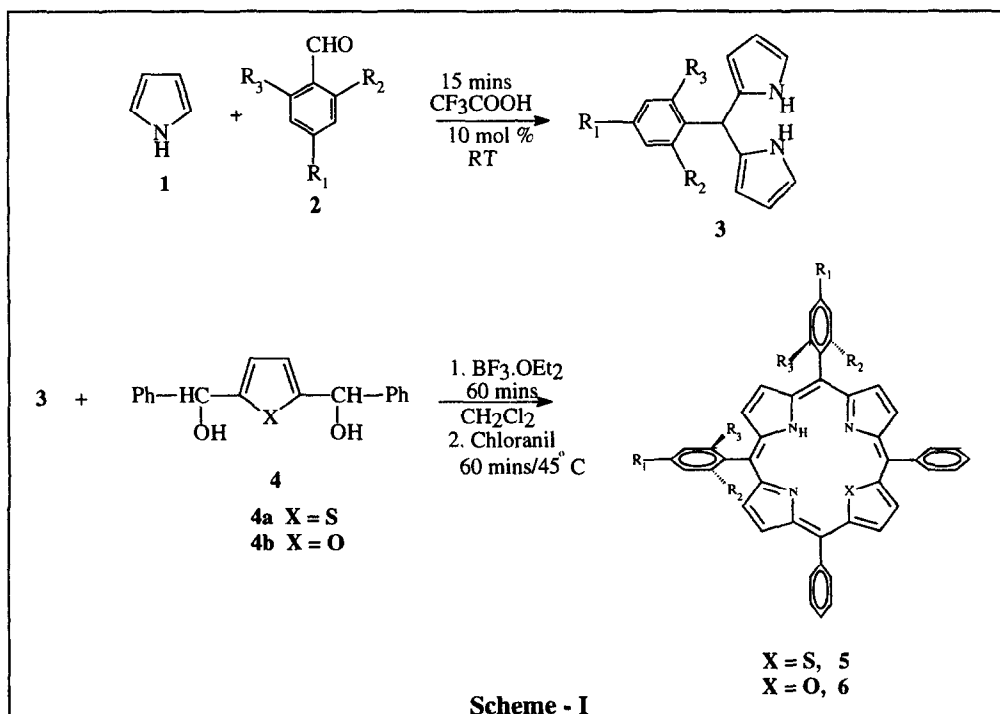
Improved Synthesis of Meso substituted 21-Oxa and 21-Thia Tetra Phenyl Porphyrins

Alagar Srinivasan, Bashyam Sridevi, Mereddy Venkat Ram Reddy, Seenichamy Jeyaprakash Narayanan and Tavarekere K. Chandrashekar*

Department of Chemistry, Indian Institute of Technology,
Kanpur, 208 016, INDIA

Abstract: An efficient method for the exclusive formation of 21-Oxa and 21-Thia tetra phenyl porphyrins in high yields by condensation of dipyrromethane and furan or thiophene diols is described. © 1997 Elsevier Science Ltd.

Core modified tetraaryl porphyrins containing hetero atoms are receiving attention in recent years¹. Core modification results in altered electronic structure leading to interesting optical^{1b}, photochemical^{2,3} and electrochemical^{1,3} properties. Synthetic methods available presently for the preparation of such compounds makes use of acid catalysed condensation of thiophene or furan diols with pyrrole and benzaldehyde⁴.



Formation of mixture of compounds, tedious chromatographic separation and low yield prevents wide applicability of this method. Recently Lee et al. came up with a better method using a 3+1 condensation of modified tripyrrin derivative with the corresponding 2,5 bis (α -hydroxyl methyl) substituted pyrrole, furan or thiophene in presence of Lewis acid catalysts⁵. A variety of core modified porphyrins were synthesized with varying yields of about 5-9%. This communication reports an high yield synthesis (8-21%) of title compounds using a variety of meso substituted dipyrromethanes developed by Lindsey⁶ and others⁷ with the corresponding thiophene or furan diols. Scheme-I summarises the synthetic details employed in the present study.

Table

Compound	R ₁	R ₂	R ₃	Yield of 3 (%)	Yield of 5 or 6 (%)
5a	H	H	H	49	17
5b	Me	H	H	75	21
5c	Br	H	H	52	17
5d	OMe	H	H	68	14
5e	H	Br	H	55	16
5f	Me	Me	Me	55	8
6a	H	H	H		10
6b	Me	H	H		15
6c	Br	H	H		14
6d	OMe	H	H		14

Reaction of pyrrole with the substituted aldehydes gave the corresponding dipyrromethane **3**. The yields of **3** were dependent on the nature of substituent on the starting aldehyde (Table). Treatment of **3** with **4** under Lindsey conditions followed by oxidation with chloranil resulted in the formation of **5** or **6** as the major product⁸ (Table). In each case about 1-2% of meso tetraphenyl porphyrin (TPP) was obtained as the side product. The lowest yield for mesityl derivative probably reflects steric hindrance of the bulky methyl substituents. It is noteworthy that in all the condensation reaction a single desired product was obtained except a small amount of TPP and hence the purification on column became very simple and less time consuming. The exclusive formation of **5** and **6** under the reaction conditions clearly suggests the acidolysis

of dipyrromethane similar to the observations of Lindsey et al⁶. **5** and **6** have been characterized by UV-Visible, ¹H NMR, FAB Mass and Emission spectroscopy⁹. Addition of a dilute solution of Trifluoro acetic acid (TFA) in dichloromethane to **5** and **6** leads to protonation of pyrrole nitrogens forming the corresponding dications. The dications of both **5** and **6** show characteristic redshifts both in absorption and emission spectra due to the resonance interaction between the β pyrrole hydrogens and the meso phenyl substituent which is typical of meso substituted porphyrins². The strength of this interaction is reflected in the magnitude of these shifts. Furthermore, **6** seems to be very sensitive to protonation. On silica TLC plates, which is slightly acidic, it turns green upon elution suggesting the formation of dication. Attempted synthesis of mixed mono oxa, mono thia derivative using one equivalents of **3**, **4a** and **4b** resulted in the exclusive formation of **6** with very little **5** indicating higher reactivity of **4b** relative to **4a**.

In summary, the obvious advantages of the present method is its wide applicability in synthesising exclusively meso substituted core modified porphyrins with only one hetero atom with high yield and the problems associated with separation of mixture of compounds is eliminated.

Acknowledgements:

This work was supported by a grant from the Department of Science & technology (DST) and Council of Scientific and Industrial Research (CSIR), Govt. of India, New Delhi.

References and Notes :

- (a). Latos-Grazynski, L.; Oacholska, E.; Chmielewski, P.J.; Olmstead, M.M.; Balch, A.L.; *Angew. Chem. Int. Edn.Engl.*, **1995**, 34, 2252 - 2254.
(b). Pandian, R.P.; Chandrashekar, T.K.; *Inorg. Chem.*, **1994**, 33, 3317 - 3324.
- Ravikanth, M.; Chandrashekar, T.K., *Structure & Bonding* , **1995**, 82, 105.
- Pandian, R.P.; Chandrashekar, T.K.; Van Willigan, H.; *Chem. Phys.Lett.*, **1993**, 202, 127.
- (a). Latos-Grazynski, L.; Lisowski, J.; Olmstead, M.M.; Balch, A.L.; *J. Am. Chem. Soc.*, **1987**, 109, 4428 - 4429 .
(b). Ulman, A.; Manassen, J.; *J. Chem. Soc. Perkin Trans. I.*, **1979**, 1066 - 1069.
- Phil-Yean Heo; Koo Shin; Chang-Hee Lee, *Tetrahedron Lett.*, **1996**, 37, 197 - 200.
- Chang-Hee Lee; Lindsey, J.L.; *Tetrahedron*, **1994**, 50, 11427 - 11440.
- (a). Vigmond, S.J.; Chang, M.C.; Kallury, K.M.R.; *Tetrahedron Lett.*, **1994**, 35, 2455 - 2458.
(b). Mizutani, T.; Ema, T.; Tamita, T.; kuroda, Y.; Ogoshi, H.; *J. Am. Chem. Soc.* , **1994**, 116, 4240 - 4250 .

8. A typical procedure for the condensation involves stirring of dipyrromethane (1.25 mmol) and diol (1.0 mmol) in dry dichloromethane and in nitrogen atmosphere for 15 minutes at room temperature. A 10 mol % of 2.5M freshly distilled $\text{BF}_3 \cdot \text{Et}_2\text{O}$ solution of dichloromethane was added to the above mixture. The solution immediately turned dark and the stirring was continued for further one hour. The resulting solution was opened to air and chloranil (1.1 mmol) was added and the mixture was heated to reflux in a preheated oil bath at 45° C. After removal of the solvent the crude product was purified by column chromatography using silica gel (100 - 200 mesh) and elution with petroleum ether (60°-80° C) and dichloromethane. Meso tetraphenyl porphyrin came first as a pink band followed by the dark band of the desired product.

9. Spectroscopic data for the selected compounds are given below :

(4a) : $^1\text{H NMR}$: (80 MHz, CDCl_3): δ = 1.17 (s, 2H), 5.14 (s, 2H), 6.06 (s, 2H), 75 (m, 10 H).

(4b) : $^1\text{H NMR}$: (80 MHz, CDCl_3): δ = 3.25 (6s, 2H), 5.87 (s, 2H), 6.01 (s, 2H), 7.45 (m, 10 H).

(5a) : $\text{C}_{44}\text{H}_{29}\text{N}_3\text{S}_1$: FAB Mass: m/z 633 (100 %), $^1\text{H NMR}$: (300 MHz, CDCl_3) : δ = 9.63 (s, 2H), 8.96 (d, 2H, $J=2.16$ Hz), 8.70 (q, 4 H, $J=4.5$ Hz), 8.32 (m, 8H), 7.64 (m, 12H); UV-Vis (CHCl_3): λ nm ($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$): Soret 429 (18.7), Q-bands 513 (1.71), 547(0.44), 618 (0.19), 675 (0.30); Dication : (excess TFA in CHCl_3) : UV-Vis: (CHCl_3) : λ nm Soret 456, Q-bands 699; Emission maxima in CH_2Cl_2 : λ (nm): 678, 760, Dication (excess TFA in CH_2Cl_2) : λ (nm): 751; Anal. calcd. for $\text{C}_{44}\text{H}_{29}\text{N}_3\text{S}$: C, 83.65; H, 4.63; N, 6.65; S, 5.07; Found : C, 83.71; H, 4.52; N, 6.83; S, 5.36.

(6b) : $\text{C}_{44}\text{H}_{29}\text{N}_3\text{O}_1$: FAB Mass: m/z 645 (100 %); $^1\text{H NMR}$: (300 MHz, CDCl_3) : δ = 9.163 (s, 2H), 8.899 (s, 2H), 8.626 (d, 2H), 8.522 (d, 2H, $J=4.2$ Hz), 8.176 (m, 4H), 8.055 (d, 4H, $J=7.7$ Hz), 7.770 (m, 6H), 7.563 (d, 4H, $J=7.7$ Hz), -1.65 (s, 1H); UV-Vis: (CH_2Cl_2): λ nm ($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$): Soret 420 (19.6), Q-bands 509 (1.91), 541 (0.51), 571 (0.33), 611 (0.38), 672 (0.40), Dication : (excess TFA in CH_2Cl_2) : UV-Vis: (CH_2Cl_2): λ (nm) Soret 441, Q-bands 630, 663; Emission maxima in CH_2Cl_2 : λ (nm): 608, 660, Dication : (excess TFA in CH_2Cl_2) : λ (nm): 680; Anal. calcd. for $\text{C}_{44}\text{H}_{29}\text{N}_3\text{O}$: C, 85.82; H, 5.17; N, 6.53; Found : C, 86.01; H, 5.28; N, 6.71.

(Received in UK 10 March 1997; revised 18 April 1997; accepted 25 April 1997)