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One Step Synthesis of Sapphyrin and N-Confused Porphyrin using Dipyrromethane

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Abstract :

Reaction of dipyrromethane in trifluoroacetic acid produces sapphyrin while the same reaction in toluene p-sulfonic acid gave N-confused porphyrin. © 1998 Elsevier Science Ltd. All rights reserved.

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Research on expanded porphyrins in general and sapphyrins in particular has received considerable attention in recent years because of their diverse applications.[1] Synthetic methods available in the literature for the synthesis of sapphyrins include; a traditional [3+2] acid catalysed MacDonald type condensation between the appropriate precursors,[2,3,4] reaction of diformylbipyrrole with benzaldehyde and pyrrole under Lindsey's conditions[5] and an acid catalysed condensation of a,c-biladienes with pyrrole-2-carboxaldehydes.[6] Recently, a meso substituted sapphyrin was isolated as a side product in 1% yield in a Rothemund reaction of benzaldehyde and pyrrole.[7] In all these reactions, at least two precursors are required for the condensation under different conditions. Herein, we wish to report a novel synthetic method in which the only precursor, the dipyrromethane,

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Scheme - 1

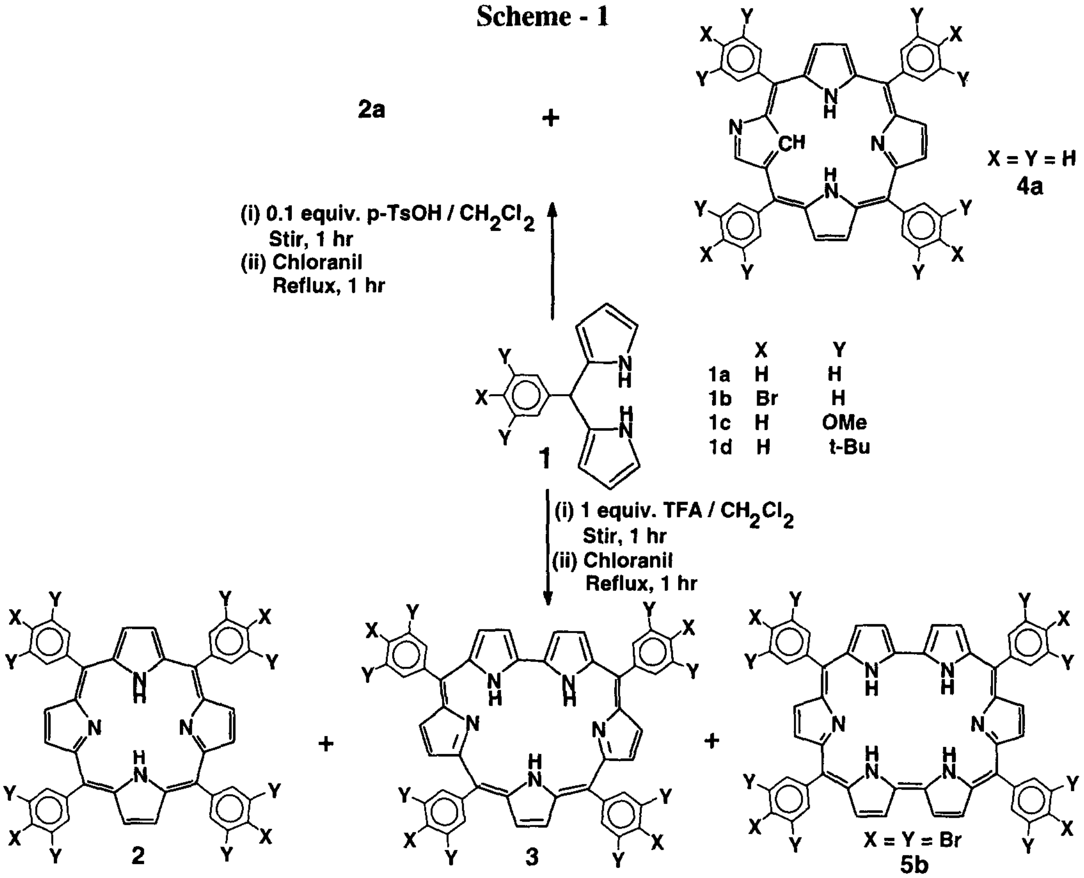

Table - 1

Compound No.	Substituent		Isolated Yields in %	
	X	Y	TFA (1 equiv.)	p-TsOH (0.1equiv)
2a	H	H	2.0, (3.0)[a], (9.5)[b]	9.5, (1.0)[c]
2b	Br	H	3.5	-
2c	H	OMe	2.5	-
2d	H	t-Bu	2.0	-
3a	H	H	11.0, (3)[b]	-
3b	Br	H	7.0	-
3c	H	OMe	9.0	-
3d	H	t-Bu	6.0	-
4a	H	H	-	7.0, (4)[c]

[a] TFA (0.1 equiv.); [b] TFA (2 equiv.); [c] p-TsOH (1 equiv.)

in presence of appropriate acid catalysts, condenses to give not only sapphyrin but also N-confused porphyrin in moderate yield (Scheme - 1).

Dipyrromethane **1a**, synthesised following Lindsey's procedure,[8] on reaction in dry dichloromethane containing 1 equivalent of TFA, followed by chloranil oxidation gave **3a** as major product in addition to **2a**. The product distribution and the isolated yields were dependent on the nature of the acid catalyst and its concentration (Table -1). For example **2a** was isolated in 3% yield using 0.1 equivalent of TFA while **2a** and **3a** were formed in 9.5% and 3% yields respectively using 2 equivalents of TFA which is due to different extents of acidolysis under the reaction conditions. Substituted dipyrromethanes **1b**, **1c** and **1d** also show a similar behaviour in TFA and the yields were dependent on the steric bulk of the substituent .

No sapphyrin was formed when the acid catalyst was changed to toluene p-sulfonic acid. However, using 0.1 equivalent of p-TsOH, the N-confused porphyrin[9,10] **4a** and the normal porphyrin **2a** were isolated in 7% and 9.5% yields respectively. On increasing the amount of p-TsOH to 1 equivalent, the major product was **4a** and **2a** was the minor product. The substituted dipyrromethanes also gave N-confused porphyrins in less than 1% yield. Reaction of **1a** in dry dichloromethane containing $BF_3.OEt_2$ as the catalyst gave only **2a** and polymeric products. When HBr was the catalyst only **2a** was formed. An additional product was isolated in less than 1% yield on reaction of **1b** in 1 equivalent of TFA. On the basis of UV-visible, FAB mass and elemental analysis this was identified as **5b** an analogue of rubyrin reported by Sessler et al.[11] However, the room temperature NMR spectra show only broad lines presumably due to the rotation of the pyrrole rings. This was confirmed by recording the spectra at low temperature. It is pertinent to point out here that for compounds **3a** - **3d**, the pyrrole ring opposite to bipyrrole unit is inverted and on protonation the ring flip takes place, consistent with the observation of Latos-Grazynski and coworkers.[7]

In summary, the synthetic method reported here allows synthesis of sapphyrins containing sterically bulky groups and N-confused porphyrins using a single precursor. Furthermore, the method avoids the difficult synthesis of precursors like diformyl bipyrrole, tripyrrane and biladienes, thus drastically reducing number of steps.

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References :

[1] Jasat A, Dolphin D. Chem. Rev. 1997;97:2267-2340.

[2] Bauer V.J, Clive D.R, Dolphin D, Paine J.B III, Harris F.L, King M.M, Loder J, Wang S.W.C, Woodward R.B. J. Am. Chem. Soc. 1983;105:6429-6436.

[3] Sessler J.L, Cyr M.J, Lynch V, McGhee E, Ibers J.A, J. Am. Chem. Soc. 1990;112: 2810-2813.

[4] Bruckner C, Sternberg E.D, Boyle R.W, D. Dolphin, J. Chem. Soc. Chem. Commun. 1997;1689-1690.

[5] Sessler J.L, Lisowski J, Boudreaux K.A, Lynch V, Barry J, Kodadek T.J, J. Org. Chem. 1995;60:5975-5978.

[6] Paolesse R, Licoccia S, Spangnoli M, Boschi T, Khoury R.G, Smith K.M. J. Org. Chem. 1997;62:5133-5137.

[7] Chmielewski P.J, Latos-Grazynski L, Rachlewicz K, Chem.Eur.J. 1995;1: 68-73.

[8] Lee C.H, Lindsey J.S. Tetrahedron 1994;50:11427-11440.

[9] Chmielewski P.J, Latos-Grazynski L, Rachlewicz K, Glowiak T. Angew. Chem. Int. Ed. Engl. 1994;33:779-781.

[10] Furuta H, Asano T, Ogawa T. J. Am. Chem. Soc. 1994;116:767-768.

[11] Sessler J.L, Morishma T, Lynch V. Angew. Chem. Int. Ed. Engl. 1991;30: 977-979.

Selected spectroscopic data for :

3b : ^{1}HNMR (300 MHz, $CDCl_3$) δ : 11.60 (br, s, 1H); 10.08 (d, 2H, J=6Hz); 9.13 (d, 2H, J=6Hz); 9.035 (d, 2H, J=3Hz); 8.94 (d, 2H, J=6Hz); 8.17 - 8.25 (m, 8H); 7.97 - 8.03 (m, 8H); -1.21 (s, 2H); UV-VIS : (CH_2Cl_2) : λ_{max} (nm) (ε) : 493 (80084); 520(55383); 640 (6920); 700 (10830); 723.18 (sh); 796 (6040); **3b.2H^{++}**: ^{1}HNMR (300 MHz, $CDCl_3$ /HCl) δ : 10.33 (d, 2H, J=6Hz); 9.555(d, 2H, J=3Hz); 9.17 (d, 2H, J=6Hz); 8.97 (d, 2H, J=6Hz); 8.86 (s, 2H); 8.615 (d, 4H, J=9Hz); 8.505 (d, 4H, J=9Hz); 8.235 (d, 4H, J=9Hz); 8.165 (d, 4H, J=9Hz); -2.55 (s, 2H); -2.64 (s, 1H); -3.14 (s, 2H); UV-VIS : (CH_2Cl_2/TFA) : λ_{max} (nm) (ε) : 492 (109104); 674 (2995); 738 (7786); 791.11 (14632); Anal. Calcd. for $C_{48}H_{29}N_5Br_4$: C, 57.92; H, 2.94; N, 7.04; Found : C, 57.87; H, 2.98; N, 7.10.

5b : UV-VIS : (CH_2Cl_2) : λ_{max} (nm) (ε) : 419 (20283); 558 (88749); 721 (8527); 796 (13118); 952 (4995); UV-VIS : (CH_2Cl_2/TFA) : λ_{max} (nm) (ε) : 578 (177043); 795 (11958); 879 (sh); 922 (27548); Anal. Calcd. for $C_{52}H_{32}N_6Br_4$: C, 58.90; H, 3.04; N, 7.92; Found : C, 58.83; H, 3.09; N, 7.86.