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One Pot Synthesis Of Core Modified Expanded Porphyrins

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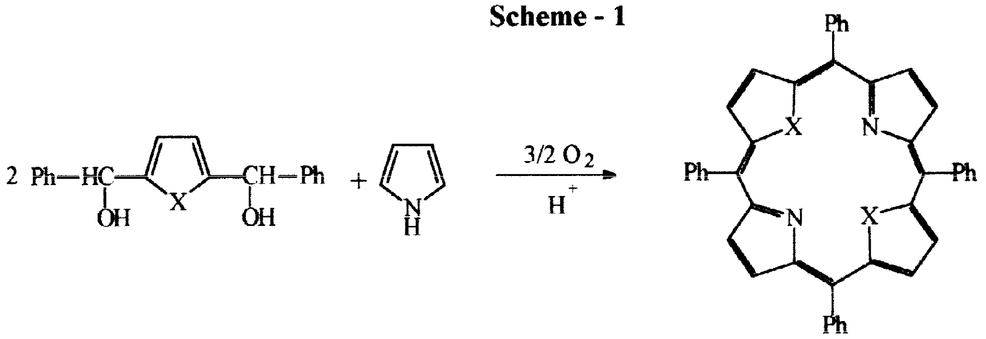
Abstract:
Reaction of various diols with pyrrole in TFA/CH_2Cl_2 leads to formation of core modified expanded porphyrins.

Keywords: Porphyrins and analogues ; Macrocycles ; Oxygen heterocycles ; Selenium heterocycles.

More than twenty years ago Ulman and Manassen reported a general synthetic method (Scheme 1) to synthesize core modified meso tetraphenylporphyrins containing heteroatoms such as S and Se [1-3]. Later, Latos-Grazynski and coworkers with slight modification of this procedure under Lindsey conditions successfully synthesised monothia-, monotellura- and monooxatetraphenylporphyrins [4,5]. Very recently, we have reported the synthesis of core modified expanded porphyrins using a [3+2] MacDonald approach [6] by condensation of modified tripyrrane with bithiophenediols [7]. It was found that the product distribution in this reaction was dependent on the nature of the acid catalyst used. Only sapphyrins were isolated under Lewis acid conditions while protic acid catalysts gave rubyrins and X_2TPP(dithia-, diselena- and dioxatetraphenylporphyrins) in addition to sapphyrins. This observation prompted us to reexamine the Ulman reaction under different protic acid conditions, the results of which are presented in this communication (Scheme 2).

Scheme - 1



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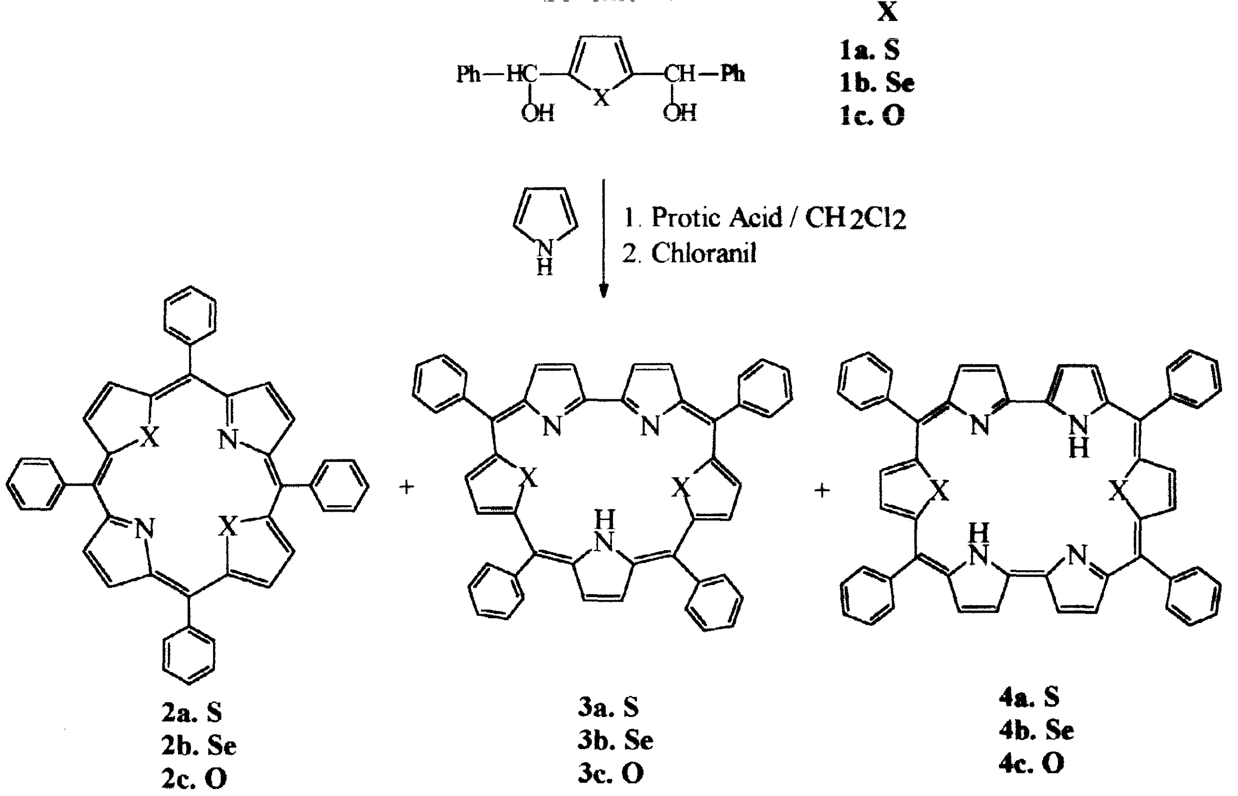
Scheme - 2



Thus the reaction of **1a** with pyrrole in dichloromethane containing 1 equivalent of TFA as the catalyst followed by chloranil oxidation gave **2a**, **3a** and **4a** in 13%, 27% and 9% yield[1].The product distribution and isolated yields were dependent on the nature of the protic acid (**Table**) and of the three protic acids used TFA gave maximum yield of the products relative to p-TsOH and HBr. On the other hand, the reaction of **1c** under similar conditions gave two additional

Table

Compound	Isolated Yield (%)		
	TFA	p-TsOH	HBr
2a	13	14	7
2b	10	6	6
2c	5	3	8
3a	27	6	6
3b	12	5	12
3c	9	8	10
4a	9	9	14
4b	18	7	12
4c	15	8	10

products when TFA was the catalyst in very low yield and these were identified as monooxacorrole and monooxasmaragdyrin based on analytical, FAB mass and ^{1}H NMR data.

The effect of acid catalyst concentration on the product distribution and the yield were also followed using **1a** as the substrate at three concentrations of TFA. **2a** was formed in trace amounts at 0.3 equivalent of TFA while at 2 equivalents of TFA **2a**, **3a** and **4a** were isolated in 16%, 8% and 11% yield respectively. On increasing the concentration of TFA to 3 equivalents more **3a** (15%) was isolated at the expense of **4a** (5%).Recently, Latos-Grazynski and coworkers have reported the synthesis of 26,28-dioxa and dithia sapphyrins by a similar reaction under $BF_3.Et_2O$ catalysis[8].

In conclusion, all the available literature methods to date for the synthesis of core modified expanded porphyrins require sensitive precursors such as tripyrrane and terpyrrane involving multistep synthesis for [3+2] and [4+2] condensations. The simplicity of the present method lies in the fact that using simple diols and commercially available pyrrole, it is possible to synthesise 22π and 26π expanded porphyrins in good yields. Also, the fact that the method works for diols containing three different hetero atoms suggests the generality of the method. Furthermore it has been shown that simple variation in reaction conditions can lead to formation of new macrocycles.

[1] A typical procedure for condensation involves stirring of diol (0.84 mmol) and pyrrole (1.69 mmol) in dry dichloromethane and nitrogen atmosphere for 15 minutes at room temperature. Trifluoroacetic acid (0.84 mmol) was added to the above mixture. The solution immediately turned dark and stirring was continued for further one hour. The resulting solution was exposed to air and chloranil (1.01 mmol) was added and the mixture was heated to reflux in a preheated oilbath at 45° C for an hour. After removal of the solvent the crude product was purified by column chromatography using basic alumina grade III.The first fraction was a dark brown band which moved in dichloromethane and carbon tetrachloride (30:70) and was identified as **2a**. A second, green band identified as **3a** was eluted in dichloromethane and carbon tetrachloride (60:40). The last, pink band which was identified as **4a** was eluted with ethyl acetate and dichloromethane (30:70).

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Spectroscopic data for new compounds.

(3a): FAB MS: m/z: 714(100%)[M^+] , ^{1}HNMR(300 MHz,$CDCl_3$/TFA):δ = -2.18(br s,2H), -2.85 (s, 1H), 8.18(m,8H), 8.23(m,4H), 8.76(m,4H), 8.89(m,4H), 9.17(s,2H), 9.75(d,2H,J=6Hz), 10.12 (d, 2H, J=6Hz), 10.32 (d, 2H, J=6Hz), 10.33 (d, 2H, J=6Hz);UV-Vis(CH_2Cl_2):λnm (ϵx10^{-4}): 470(22.4), 584(1.75), 623(1.07), 730(0.59), 820(1.68).

(3b): FAB MS: m/z: 810(100%)[M^+ for ^{80}Se], ^{1}HNMR(300MHz,$CDCl_3$):δ=-4.4(s,1H),7.6(m,8H), 7.96(m,4H), 8.39(m,4H), 8.49 (m,4H), 8.96(s,2H), 9.36(d,2H,J=6Hz), 10.01(d,2H,J=6Hz), 10.35(d, 2H, J=6Hz) 10.47(d,2H,J=6Hz); UV-Vis(CH_2Cl_2): λnm (ϵx 10^{-4}): 475(30.1), 517(6.4), 592(2.8), 631(1.8), 736(0.7), 823(3.2).

(3c): FAB MS: m/z: 683(100%)[$(M+1)^+$], ^{1}HNMR(300 MHz,$CDCl_3$):δ= -0.75(s,2H), 7.66(m,4H), 7.85(m,8H), 8.31(m,4H), 8.78(d,4H), 8.89(d,2H,J=6Hz), 9.12(d,2H,J=6Hz), 9.54(d,2H,J=6Hz), 9.74(d,2H,J=6Hz); UV-Vis(CH_2Cl_2):λ nm(ϵx10^{-4}): 474(20.11), 581(2.1), 625(1.79), 741(0.59), 838(1.36).

(4a): FAB MS: m/z : 779(100%)[M^+], ^{1}HNMR(300MHz,$CDCl_3$ / HCl):δ= -2.80(br s, 2H), -2.50(br s, 2H), 8.04(m,12H),7.92 (s,4H), 8.82(m,8H), 9.71(s,4H),10.49(s,4H); UV-Vis: (CH_2Cl_2) :λ nm(ϵx10^{-4}): 385(0.16), 532(14.2), 658(1.12), 764(0.9), 1017(1.36).

(4b): FAB MS: m/z : 875(100%)[M^+ for ^{80}Se], ^{1}HNMR(300MHz,$CDCl_3$ / HCl):δ= -1.55(br s,2H),-1.00 (br s,2H), 7.98(m,20H), 8.87(d,4H,J=6Hz), 8.77(d,4H,J=6Hz), 9.58(d,2H,J=6Hz),10.40(d,2H,J=6Hz) ; UV-Vis(CH_2Cl_2):λ nm(ϵx10^{-4}): 530(13.4), 666(1.09), 766(0.62), 849(0.77), 970(1.34).

(4c): FAB MS: m/z : 748(100%)[$(M+1)^+$], ^{1}HNMR(300MHz, $CDCl_3$ / HCl): δ= -2.2(br s, 2H), -1.6(br s, 2H), 7.98(m,12H), 8.51(s, 4H), 8.77(m,8H), 9.61(s,4H), 9.86(s, 4H); UV-Vis(CH_2Cl_2):λ nm(ϵx10^{-4}): 564(4.8), 703(0.7), 771(1.26), 900(0.39), 1041(2.22).