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Condensation of 3,3'-Diethyl-4,4'-Dimethyl-2,2'-Dipyrrylmethane with Substituted Benzaldehydes

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Abstract *The condensation of dipyrrylmethane **1b** with o-nitrobenzaldehyde furnishes upon oxidation with chloranil, 5,15-di(o-nitrophenyl) porphyrin **4b** in 45% yield and condensation of the same dipyrrylmethane with 2,6-dinitro or 2,6-diacetamido benzaldehyde affords unexpectedly octaalkylporphyrin **5** (15-20% yield) and monoaryl porphyrin **6** (2% yield)*

Synthesis of 5,15-diarylporphyrins from dipyrrylmethanes can be achieved by different ways but two main procedures are known The first one involves the condensation of a dipyrrylmethane **1** with benzaldehyde **2** [1] and the second one draws in as participants an aryldipyrrylmethane and a "one carbon unit", either formic acid or trimethyl orthoformate [2] In the case of the first procedure, condensation of **1a** with **2a** in the presence of *p*-TsOH in MeOH produced, as a major product with a 60% yield the porphyrinogen **3a** which was treated with DDQ in THF to give quantitatively the porphyrin **4a** [1b] In contrast, condensation of **1b** with **2a** using approximatively the same conditions afforded the porphyrinogen **3b** in 27% yield and the porphyrin **4b** after *o*-chloranil oxidation [1d] Higher yields of 5,15-diarylporphyrins have been obtained recently by condensation of dipyrrylmethane **1c** dissolved in CH_2Cl_2 and CF_3CO_2H at room temperature with a variety of aromatic aldehydes after oxidation with chloranil (for example **4c** 73% yield) [1j]

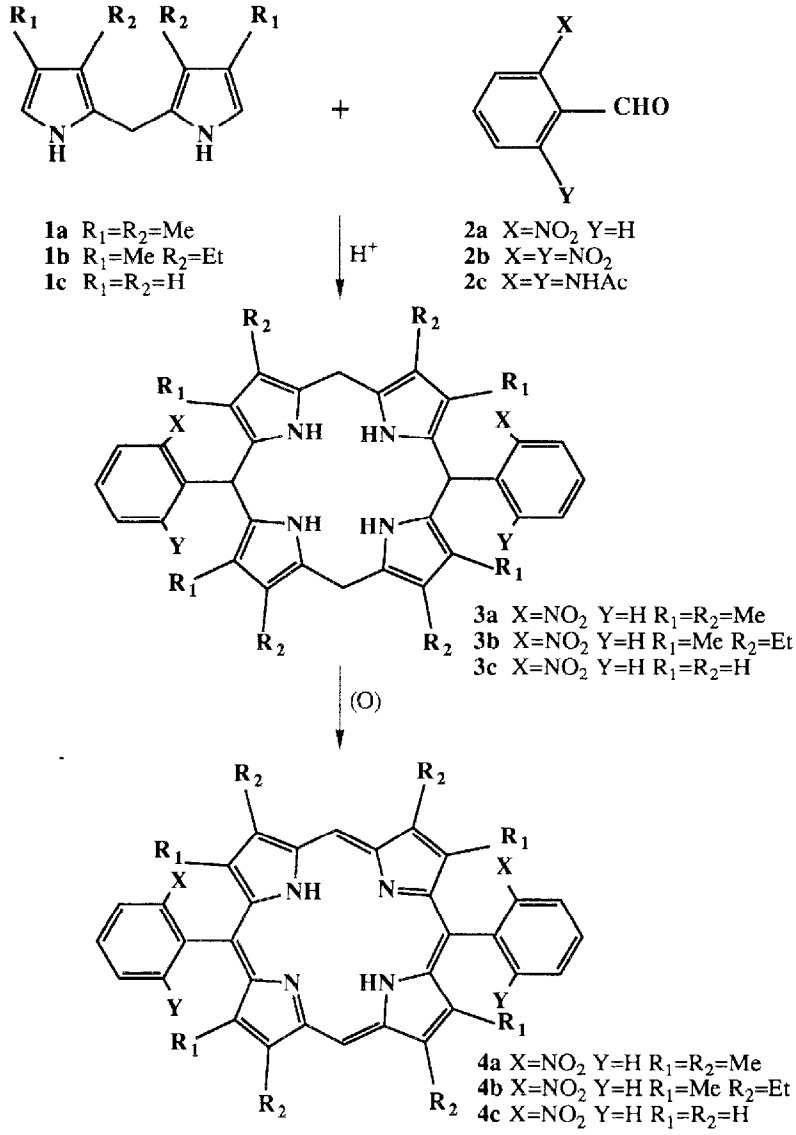
We now report the unexpected obtention of porphyrins **5** and **6** by the condensation of a dipyrrylmethane with 2,6-disubstituted benzaldehydes **2** as well as the preparation of porphyrin **4b** with an improved yield using the same experimental conditions by condensation of dipyrrylmethane with *o*-nitrobenzaldehyde (eq 1)

Condensation of 2,6-diacetamido benzaldehyde [2e] **2c** with dipyrrylmethane **1b** in MeOH (c=85mM) in the presence of *p*-toluenesulfonic acid during 20h at room temperature followed by oxidation with *p*-chloranil yields after flash silicagel chromatography the octaalkylporphyrin **5** (10-15%), the monoarylporphyrin **6b** (2%) and the starting aldehyde **2c** (55%) (eq 2) The same reaction with 2,6-dinitrobenzaldehyde **2b** and dipyrrylmethane **1b** gives the octaalkylporphyrin **5** (15-20%), the monoarylporphyrin **6a** (2%) and the starting aldehyde **2b** (60%) It is worthy to note that we were able to separate 1,3-dinitrobenzene (18% yield), the formation of which could explain why no bis-arylporphyrin **4d** has been detected [3,4] This result definitively proves the fate of the aldehydic proton which is transformed into the *meso* carbon and can also explain the formation of **5** as an unique isomer without contamination of the other three etioporphyrin isomers [6] In other words, the dipyrrylmethane **1b** does not give a pyrrolic derivative in this acidic medium used for the preparation of the porphyrinogen Indeed, it

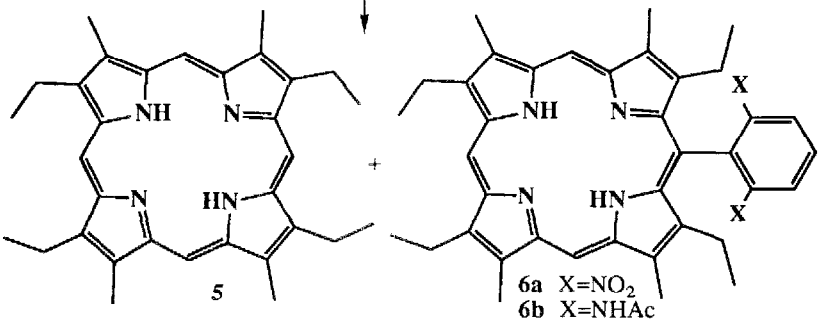
is known that acid-catalyzed monopyrrole tetramerizations yield all four primary type-isomers (moreover the same group claims that regularly substituted isomers must be prepared from dipyrroles) [6] In the case of monoarylporphyrin **6a** or **6b**, it is clear that if we had obtained etioporphyrin type-isomers, ^{1}H NMR spectra of the individual isomers would have been different

We also would like to point out that the condensation of *o*-nitrobenzaldehyde **2a** with the same dipyrrylmethane **1b** (c=6mM) in CH_2Cl_2 in the presence of CF_3CO_2H followed by oxidation with *p*-chloranil using the dilution conditions described in the literature [1j] gives porphyrin **4b** (45% yield) this represents to our knowledge a great improvement in yield with respect to other published procedures [1d]

(eq 1)



(eq 2) **1b** + **2b or 2c** → **4d** X=Y=NO_2 R_1=Me R_2=Et; **4e** X=Y=NHAc R_1=Me R_2=Et



5 **6a** X=NO_2 **6b** X=NHAc

In conclusion, we showed that if benzaldehyde is disubstituted by two nitro or two acetamido groups at the *ortho* positions, condensation of these aldehydes with 3,4-dialkylpyrroles gives octaalkylporphyrin **5** and mono arylporphyrin **6** with no detection of 5,15-diarylporphyrins Isolation of 1,3-dinitrobenzene from the reaction mixture between the aldehyde **2b** and dipyrrylmethane **1b** explains the origin of the *meso* carbon [7]

***4b** MS 721 (M+1), 360, 312 , RMN ^{1}H ($CDCl_3$) 10 13 (s, 2H meso) , 8 34 (d, 2H, J=7 4) , 7 99 (d, 2H, J=7 4) , 7,90 (t, 2H, J=7 4) , 7 85 (t 2H, J=7 4) , 3 92 (m, 8H, CH_2-CH_3) , 2 39 (s, 12H, Me) , 1 68 (t, 12H, J=7 0, CH_2-CH_3) , -2 43 (s, 2H, NH) , ^{13}C 12 44 and 15 95 (Me) , 19 92 (CH_2) , 98 07 (C meso) , 113 54 (C meso) , 124 95 (Ar,C-3') , 131 50 (Ar,C-4') , 132 41 and 132 96 (Cβ pyrr) , 133 16 (Ar,C-5') , 138 21 (Ar,C-6') , 141 34 and 141 89 (Cα pyrr) 143 20 and 152 27 (Ar,C-1' and C-2') , UV-vis (CH_2Cl_2) 407, 509, 535, 576, 628 nm

6a MS 645 (M+1) , RMN ^{1}H ($CDCl_3$ εCF_3CO_2D) 10 44 (s, 2H meso) , 10 36 (s, 1H meso) , 8 60 (d, 2H, J=8 0) , 8 35 (t, 1H, J=8 0) , 4 03 (q, 4H, J=7 8 CH_2CH_3) and 3 85 (m, 4H, CH_2CH_3) , 3 55 (s, 6H, Me) , 2 40 (s, 6H, Me) , 1 60 and 1 48 (t, 2x6H, J=7 6Hz CH_2CH_3), -2 40 (s, 1H, NH) , -3 05 (s, 1H, NH) , UV-vis (CH_2Cl_2) 399, 504, 538, 573, 626

6b MS 669 (M+1) , RMN ^{1}H ($CDCl_3$) 10 24 (s, 2H meso) 10 09 (s, 1H meso) , 8 54 (d, 2H, J=8 2) , 7 86 (t, 1H, J=8 2) , 6 43 (s, 2H, NHAr) , 4 09 (m, 8H CH_2-CH_3) , 3 43 (s, 6H, Me) , 2 59 (s, 6H, Me) , 1 94 and 1 50 (t, 2x6H, J=7 6, CH_2-CH_3) , 1 26 (s, 3H, $COCH_3$) , 1 13 (s, 3H, $COCH_3$) , UV-vis (CH_2Cl_2) 400, 500, 535, 569 622

1,3-Dinitrobenzene RMN ^{1}H ($CDCl_3$) 7 85 (t, 1H) , 8 63 (dd, 2H) , 9 05 (t, 1H) identical to an authentic sample (Aldrich) m p =88-90 °C, m p (mixture with an authentic sample)= 89°C

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3 Note that mixed condensation of pyrrole with benzaldehyde and 2 6 dinitrobenzaldehyde affords only traces of 5-(2,6-dinitrophenyl)-porphyrin I ittle, R G *J Heterocyclic Chem* , **1981**, *18*, 129-133

4 In different reactions, octaalkylporphyrins have been obtained as minor products in the case of the condensation of [bis(5,5'-methoxymethyl)-tetraalkyl-2,2'-dipyrryl]methene, HBr and phenyl-dipyrrylmethane, [1c] and in the case of the condensation of α[*p*-methoxyphenyl-5,5'-bis(hydroxymethyl)-2,2'-dipyrryl]methane and dipyrrylmethane [5]

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7 Note that the condensation of 2,6-dinitro and 2,6-diaminobenzaldehyde with pyrrole gives tetrakis-aryl porphyrins [8,9]

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