Syntheses, Structure, Properties and Chemistry of 1,1-Di(pyrrolyl)ethenes
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Reaction of a 2-unsubstituted pyrrole with acetic anhydride and stannic chloride unexpectedly promotes self-condensation to give symmetrical di(pyrrolyl)ethene as a side-product in 6–10% yield, but overall yields of these 1,1-di(pyrrolyl)ethenes can be improved to 66% using a rational alternate route; structure and chemistry of 1,1-di(pyrrolyl)ethenes 2 are discussed.

The synthesis, chemistry and spectroscopy of 1,2-di(pyrrolyl)ethenes 1 were discussed, in detail, by Hayes et al.1 in 1965. Though BF2 complexes have been reported,2 the isomeric 1,1-di(pyrrolyl)ethenes 2, have never been described, even though an intriguing tautomeric equilibrium with 5-methyl-dipyrromethene 3 is possible.

Attempted Friedel–Crafts acylation of benzyl 3,4-dimethylpyrrole-2-carboxylate 4 using acetic anhydride and tin(iv) chloride afforded the expected 2-acetylpyrrole 5 (86% yield), along with a minor, less polar product (6–12% yield).† 1H, 13C NMR, mass spectrometry, elemental analyses, and single crystal X-ray† studies showed the minor product to be 1,1-di(pyrrolyl)ethene 6. Fig. 1 shows that 6 is not completely planar (the two pyrrole rings are twisted against each other by 54.9°), providing a rationale for the absence of the (coloured) 5-methyldipyrromethene tautomer 3.

When colourless 6, in CH2Cl2, was treated with an excess of TFA in CH2Cl2 a pronounced red shift from 303 (ε 35 100) to 522 nm (ε 71 600) was observed for the salt 7 (Fig. 2). Also apparent in 7 was a three proton peak in the NMR spectrum, at δ 3.05, corresponding to the 5-methyl. When CF3CO2D was used, rapid disappearance of the 5-methyl group at δ 3.05 was observed in the proton NMR spectrum, indicating participation of the acid–base equilibrium 6 ⇌ 7. Attempts to isolate 7 have so far failed. Upon treatment with proteic solvents such as methanol or water, dipyrromethene 7 immediately reverted to the 6 as indicated by the disappearance of the red colour and by 1H NMR spectroscopy. Presumably, the increased steric interactions experienced by the meso-substituted 7 are relieved by the formation of the nonplanar (Fig. 1), thermodynamically stable 6 (Scheme 1).

Yields in the synthesis of 1,1-di(pyrrolyl)ethenes were improved as follows. Acid catalysed condensation of 2-unsubstituted pyrrole 4 with chloroacetaldehyde diethyl acetal (Aldrich) using an excess of Montmorillonite K-10 clay and 15 equiv. of TFA in CH2Cl2 gave the desired 5-(chloromethyl)-

![Scheme 1 Reagents and conditions: i, Ac2O, SnCl4; ii, POCl3, DMF then hydrolysis; iii, CH2-NMe2+I−](image)

![Fig. 1 X-Ray structure of 6. Important bond length (Å) and angles (°): C(5)–C(51) 1.333(6); C(4)–C(5)–C(6) 118.0(3); C(4)–C(5)–C(51) 122.2(4); C(51)–C(5)–C(6) 119.8(4)](image)

![Fig. 2 Optical spectra, in CH2Cl2 of 6 (a) under neutral conditions (b) in presence of TFA (i.e. structure 7)](image)
dipyrrromethane 8 in 75–91% yields. Treatment of 8 with 1.3 equiv. of DBU in CH₂Cl₂ yielded the desired 6 in 66% yield after purification. Regardless of the conditions employed in the elimination reaction to form 6, two minor fluorescent byproducts were always formed, and these were characterized by ¹H NMR spectroscopy and HRMS as the cis- and trans-1,2-di(pyrrolyl)ethenes 9 and 10, respectively. A proposed mechanism for their formation is shown in Scheme 2. Use of large excesses of base (e.g. up to 10 equiv.) for the elimination caused 9 and 10 to become major products. No ethylene dimers were ever formed in acidic media.

The vinyl group at the 5-position of dipyrrromethanes appears to be highly reactive. For example, treatment of 6 with the Vilsmeier reagent from POCl₃ in DMF yielded the di(pyrrolyl)acrolein 6a in 90% yield after intermediate imine hydrolysis. When 6 was treated with a large excess of dimethyl(methylene)ammonium iodide, 90–95% yields of the corresponding 1,1-di(pyrrolyl)-3-(dimethylamino)propane product 6b were obtained. 1,1-Di(pyrrolyl)ethenes are also useful intermediates for the synthesis of meso-substituted porphyrins. For example, condensation of the 5-methyldipyrrromethane-1,9-dicarboxylic acid 6d (obtained by saponification of the diethyl-1,9-dicarboxylate, 6c) with the 1,9-diformyldipyrrromethane 11 under modified MacDonald conditions gave the meso-methylporphyrin 12 in 13% yield, compared with a 28% yield using the corresponding 5-methyldipyrrromethane (obtained by catalytic hydrogenation of 6).

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Footnotes
† A similar acylation reaction in the indole series has also been observed to afford rosindoles existing in the methyl-methene (not 1,1-ethene disubstituted) form.‡ Crystal data for 6: Yellow blocks; C₃₀H₃₀N₂O₄, monoclinic P2₁/c; Z = 4; T = 130 K, Mo-Kα. a = 13.690(7), b = 12.209(5), c = 14.952(6) Å, β = 91.14(4)°. V = 2699(2) Å³; 2719 observed reflections with F > 5.0 o(F); all non-hydrogen atoms refined with anisotropic thermal parameters; R = 0.063. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References