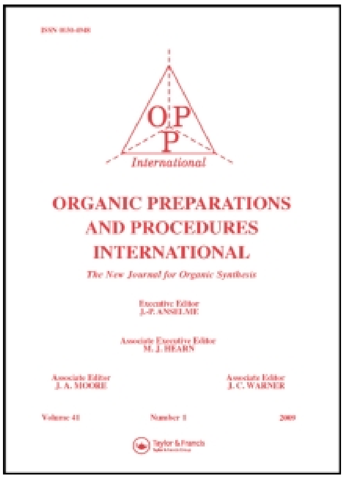

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2,5-BIS-(2-PYRROLYL)-1-PYRROLINES

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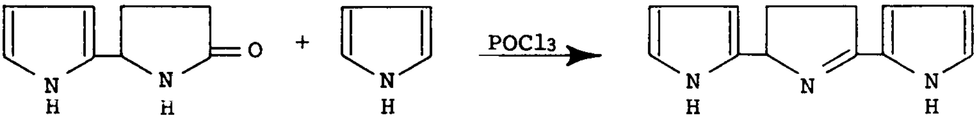

Only two examples of the system of the title compounds are known[1,2]; they give by catalytic dehydrogenation the highly autoxidizable terpyrrole system, to which our studies on pyrroles oxidation have been directed.

The parent compound (R=H) (cited but not isolated nor characterized[2]) was obtained from the reaction of 5-(2-pyrrolyl)-2-pyrrolidinone[3] and pyrrole in the presence of $POCl_3$ (Vilsmeier condensation). Such a sinthesis gave good yields even for $R=CH_3$.

If the number of methyl groups on the pyrrole ring of the 5-(2-pyrrolyl)-2-pyrrolidinone was increased, lower yields were obtained. This probably resulted from extensive self-condensation of the substrates leading to brown, insoluble materials.

The products isolated and herein described showed surprising stability to autoxidation.

Experimental

Melting points were determined by the open capillary method and are uncorrected. Infrared spectra were registered as KBr disks on a Perkin-Elmer Model 137 Infracord spectrophotometer . Ultraviolet spectra were determined with an Unicam SP 500 spectrophotometer. Proton nmr spectra were recorded with a Jeol C-60 HL spectrometer in $CDCl_3$ with TMS as internal standard.

<u>2,5-Bis-(2-pyrrolyl)-1-pyrroline</u> - To a suspension of 0.3 g (2 mmole) of 5-(2-pyrrolyl)-2-pyrrolidinone in THF (1.5 ml) and pyrrole (0.67 g, 10 mmole) freshly distilled $POCl_3$ (0.31 g, 2 mmole) was added during 10 min. with stirring under nitrogen atmosphere. The dark reaction mixture was left at 25° for 1 hr, then poured into a saturated aqueous solution of sodium acetate (100 ml). The mixture was extracted with chloroform, dried ($MgSO_4$) and evaporated. The residue was dissolved in 5 ml of benzene and chromatographed on alumina (alkaline, activity III). Two products were obtained by elution with chloroform; the first was the expected 2,5-bis-(2-pyrrolyl)-1-pyrroline, purified by sublimation at 120° (0.5 mm), obtained as white powder (0.19 g, 48%), mp 140-141°. UV: λ_{max} (0.1N ethanolic HCl) 213 mμ (ε 7700), 321 (20,100) with an inflection at 269 mμ (ε 2660) (lit.[1], 209, 325.5 and 273.5 mμ respectively, for an analogous system); λ_{max} (0.1N ethanolic NaOH) 283 mμ (ε 14,100). IR: strong band at 1610 cm^{-1} (C=N). NMR: (δ) 2-3.3 (m, 4H)(CH_2-CH_2); 5.45 (t, 1H)(C<u>H</u>N=); 6.2-6.9 (m, 6H) (pyrrolic protons).

<u>Anal</u>. Calcd for $C_{12}H_{13}N_3$: C, 72.33; H, 6.58; N, 21.09. Found: C, 72.51; H, 6.61; N, 20.97.

The second product (0.13 g, mp 96-97°), proved to be 2,5--bis-(2-pyrrolyl)-pyrrolidine, identical in all respects (uv, ir and mixture mp) with an authentic sample[4]. It was probably formed from the self-condensation of excess pyrrole in the presence of hydrogen chloride formed during the course of the reaction.

<u>2-(2-Pyrrolyl)-5-(1-methylpyrrol-2-yl)-1-pyrroline</u> - In a similar procedure, 0.33 g (2 mmole) of 5-(1-methylpyrrol-2-yl)--2-pyrrolidinone was reacted with pyrrole and $POCl_3$ in THF. At the end of the addition of $POCl_3$, stirring was continued for 1 hr at 40°. Work up as previously described gave 0.28 g (66%) of a pale yellow solid. Sublimation at 150° (0.5 mm) gave the pure product as a white powder, mp 200°. UV: λ_{max} (0.1N ethanolic HCl) 217 mμ (ε 9000), 268 (4050), 321 (23,300); λ_{max} (0.1N ethanolic NaOH) 283 mμ (15,100). IR: C=N band at 1610 cm^{-1}. NMR: (δ) 2-3.3

(m, 4H)(CH_2CH_2); 3.7 (s, 3H)(CH_3); 5.3 (t, 1H)($C\underline{H}N=$); 6-6.8 (m, 6H)(pyrrolic protons).

Anal. Calcd for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70. Found: C, 73.12; H, 7.15; N, 19.91.

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