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A SYNTHESIS OF 4,7-DIHYDRO-1H-DIPYRROLO[3,2-b:2',3'-d]PYRROLE AND 4,7-DIHYDRO-4H-THIENO[3,2-b]PYRROLO[2,3-d]PYRROLE SYSTEMS

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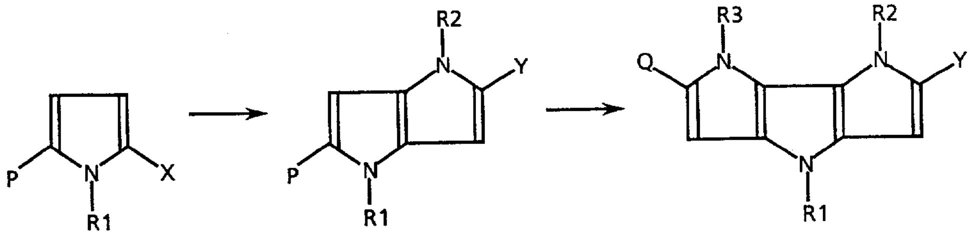
Summary: The titled two systems (**3** and **6**), both new members of linearly fused heteroaromatics, were prepared using pyrrolo-annulation reaction: condensation of an aromatic aldehyde with azidoacetate followed by thermolysis of the resulting azidoacrylate.

Heteroaromatics such as pyrrole and thiophene are promising starting materials for the production of electroconductive polymers (1). Recently a linearly condensed pyrrole, 1,4-dihydro-1H-pyrrolo[3,2-b]pyrrole (**2a** or **2b**: P = Y = H, R1 = R2 = Me or H), was prepared (2) and electrochemically polymerized (3). We wish to record here a synthesis of a higher homologue of **2a**, dihydrodipyrrolo-pyrrole (**3a**: Q = Y = H, R1 = R2 = R3 = Me) (4) and its monothio-analogue, dihydrothieno-pyrrolo-pyrrole (**6a**: R1 = R2 = Me, Z = H) (5).

Pyrrolo-annulation has been applied to the synthesis of pyrrolo-pyrrole skeleton (6). Thus, reaction of N-methylpyrrole-2-carboxaldehyde (**1a**: P = H, R1 = Me, X = CHO) with ethyl azidoacetate gives an azidoacrylate (**1b**: P = H, R1 = Me, X = CH=C(N_3)COOEt), whose pyrolysis affords a dihydropyrrolo-pyrrole-carboxylate (**2c**: P = H, R1 = Me, R2 = H, Y = COOEt) (7).

We tried to introduce a formyl group to the bicyclic ester **2c**. Although Vilsmeyer reaction of **2d** (P = H, R1 = R2 = Me, Y = COOEt) gave a mixture of α- and β-formylated products, the same reaction of the azidoacrylate **1b** furnished only α-formylated product (**1c**: P = CHO, R1 = Me, X = CH=C(N_3)COOEt) in 62% yield. Thermolysis of **1c** gave the desired aldehyde (**2e**: P = CHO, R1 = Me, R2 = H, Y = COOEt) in 61% yield.

Pyrrolo-annulation of the N-methylated aldehyde (**2f**: P = CHO, R1 = R2 = Me, Y = COOEt) gave a tricyclic diester (**3b**: Q = Y = COOEt, R1 = R2 = Me, R3 = H) in 40% yield. Alkaline hydrolysis of the N-methylated diester (**3c**: Q = Y = COOEt, R1 = R2 = R3 = Me) followed by acidification afforded a decarboxylated product (**3a**: Q = Y = H, R1 = R2 = R3 = Me) in 34% yield. Aromatic nature of **3a** was established by NMR spectroscopy (8).



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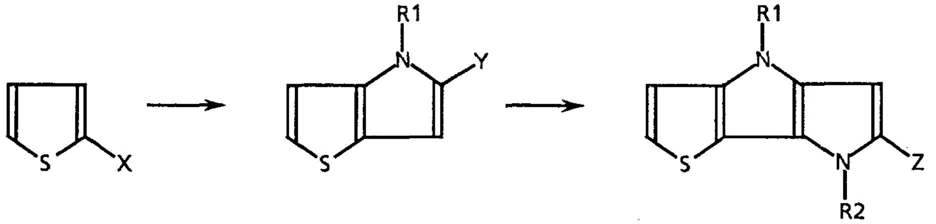
In the same way (6), pyrrolo-annulation of thiophene-2-carboxaldehyde (**4a**: X = CHO) gives dihydrothieno-pyrrole-carboxylate (**5a**: R1 = H, Y = COOEt). In this case, the requisite α-formyl compound was prepared as follows. Reduction of the N-methylated ester (**5b**: R1 = Me, Y = COOEt) with an excess of DIBAL-H gave an alcohol (**5c**: R1 = Me, Y = CH_2OH) whose oxidation with nickel peroxide provided an aldehyde (**5d**: R1 = Me, Y = CHO) in 71% overall yield.

Pyrrolo-annulation of the aldehyde **5d** gave a tricyclic ester (**6b**: R1 = Me, R2 = H, Z = COOEt) in 49% yield. N-Methylation of the ester **6b** followed by hydrolysis gave an acid (**6c**: R1 = R2 = Me, Z = COOH) in 77% yield. Decarboxylation of **6c** was accomplished by heating in quinoline in the presence of copper powder to afford the parent compound (**6a**: R1 = R2 = Me, Z = H) in 59% yield. The NMR spectra of **6a** supported the aromatic structure (9). X-Ray crystallography and electrochemistry of the new tricycles (**3** and **6**) will be reported elsewhere.



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7. When the reaction was conducted at -20°C, the yield of the azidoacrylate **1b**, originally 12% (ref. 6a), was improved to 80%.
8. Spectroscopic data for **3a**, mp 144-147°C, were as follows. MS: m/e 187 (M^+); IR (KBr): ν 3450, 2920, 1510, 1408 and 1358 cm^{-1}; ^1H-NMR (90 MHz, $CDCl_3$, TMS): δ 3.59 (3H, s), 3.84 (6H, s), 5.95 (2H, d, J = 2.70 Hz) and 6.43 (2H, d, J = 2.70 Hz) ppm; UV (EtOH): λ_{max} (ε) 350 (24000) nm.
9. Spectroscopic data for **6a**, mp 91-92°C, were as follows. MS: m/e 190 (M^+); IR (KBr): ν 3440, 3100, 2924, 1516 and 1340 cm^{-1}; ^1H-NMR (90 MHz, $CDCl_3$, TMS): δ 3.75 (3H, s), 3.82 (3H, s), 6.01 (1H, d, J = 2.64 Hz), 6.60 (1H, d, J = 2.64 Hz) and 6.95 (2H, s) ppm; UV (EtOH): λ_{max} (ε) 305 (16000) nm.

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