

N,N'-LINKED BI(HETEROARYLS) : NEUTRAL SPECIES, CATIONS, AND DICATIONS

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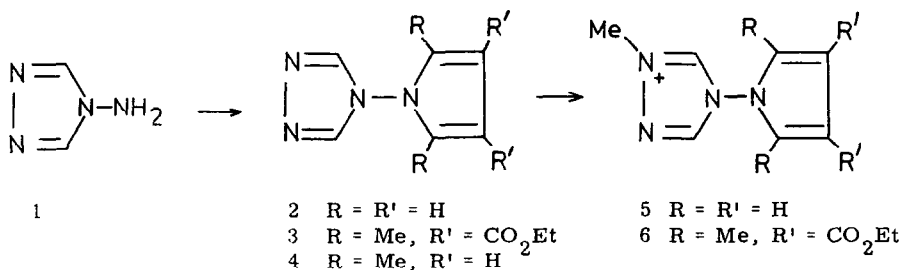
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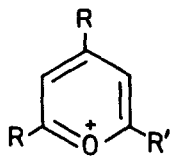
Despite increased interest recently in N-amino heterocycles,^{2,3} there exist relatively few examples of compounds in which two heteroaromatic rings are directly linked by an N-N bond. Several 1,1'-bipyrryls⁴ are known, and isolated examples of a 1,1'-biquinolone⁵ and 1,1'-biimidazoles⁶ and 1,1'-and 2,2'-bisbenzotriazoles.⁷ We now report general routes for the preparation of N,N'-bi(heteroaryls) applicable to mono- and di-cations as well as to neutral species.⁸

4-Amino-1,2,4-triazole 1 reacts with 2,5-diethoxytetrahydrofuran (in AcOH), with 3,4-diethoxycarbonylhexane-2,5-dione (in hot AcOH) and with hexane-2,5-dione (in hot MeOH) to give 1-(1',2',4'-triazol-4'-yl)pyrrole 2 (m. p. 135 - 136°) and the 2,5-dimethyl-3,4-diethoxycarbonyl 3 (m. p. 134 - 136°) and 2,5-dimethyl 4 (m. p. 140 - 142°) analogues, respectively.

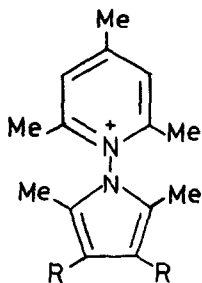
Monocations 5 (m. p. 110 - 112°) and 6 (m. p. 128 - 130°) were obtained as perchlorates by the quaternization of 2 and 3 with methyl fluorosulphonate followed by anion exchange with sodium perchlorate. The further monocations 10 - 16 have been prepared as perchlorates by the reaction of the appropriate pyrylium perchlorate 7, 8 or 9 with N-amino heteroaromatic compounds. In this way 1-amino-2,5-dimethylpyrrole gives 10 (m. p. ca. 170°), 1-amino-2,5-dimethyl-3,4-diethoxycarbonylpyrrole gives 11 (m. p. 139 - 140°), 9-amino-carbazole gives 12 (m. p. 170 - 172°), 4-amino-1,2,4-triazole gives 13 (m. p. 200 - 201°) 14, (m. p. 180 - 282°), or 15 (m. p. 195 - 196°), and 1-amino-2-pyridone gives 16 (m. p. 129 - 130°).

Three dicationic species were prepared from the appropriate monocations 13 - 15 with methyl fluorosulphonate : anion exchange with sodium perchlorate gave the perchlorates of 17 (m. p. 171 - 172°), 18 (m. p. 248 - 250°) and 19 (m. p. 170 - 172°).

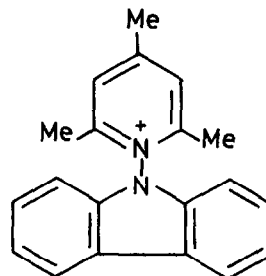




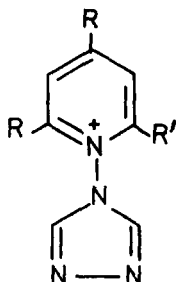
- 7 R = R' = Me
 8 R = R' = Ph
 9 R = Ph, R' = Me



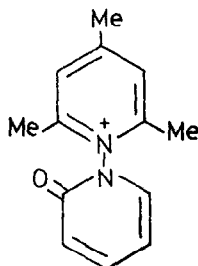
- 10 R = H
 11 R = CO₂Et



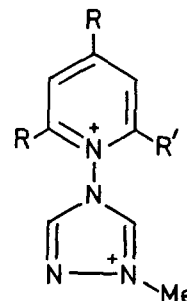
12



- 13 R = R' = Me
 14 R = R' = Ph
 15 R = Ph, R' = Me



16



- 17 R = R' = Me
 18 R = R' = Ph
 19 R = Ph, R' = Me

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- (8) Satisfactory analytical data were obtained for all new compounds reported except for **10** which was characterised by its NMR spectrum. Yields of the neutral species (**2** - **4**) varied 7 - 85%; yields of the monocations (**11** - **16**) were within the range 60 - 90% and the quaternisation also proceeded in satisfactory yield.