Pyrrolo[1,2-*d*]-*as*-triazine. A New Heteroaromatic System

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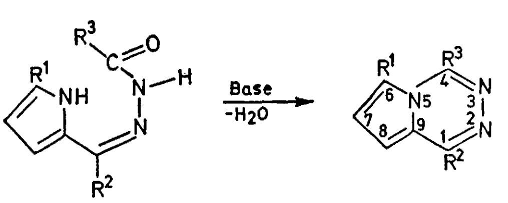
Summary The title compound has been synthesized by base-catalysed cyclodehydration of pyrrole-2-carbaldehyde formylhydrazone.

Pyrrolo[1,2-*d*]-*as*-triazine (Ia) and several methyl substituted derivatives have been synthesized. These compounds are of interest since they represent a resonance stabilized 10π-electron system which is expected to exhibit heteroaromaticity. A derivative of this system, pyrrolo-[1,2-*d*]-*as*-triazin-4(3*H*)-one has been reported recently to exist in the keto-form.[1]

The parent compound (Ia), m.p. 113—114°, was prepared by base-catalysed (Pr^i_2EtN in refluxing xylene) cyclodehydration of (IIa) in 56% yield. The methyl derivatives (Ib—d) were similarly obtained from the appropriate hydrazones. The structure of this new aromatic system is suggested by the i.r., n.m.r., and mass spectra, and elemental analyses of the products {for (Ia), i.r. spectroscopy shows the absence of N–H and C=O; n.m.r.: δ [$(CD_3)_2SO$] 9·45 and 9·15 (each 1H, d, *J* 2·4 Hz; 4- and 1-H, respectively), 7·81 br (1H, 6-H), and 6·80—7·10 (2H, 7- and 8-H); M^+, *m/e* 119 (100%); λ_{max} (95% EtOH) 322 (ϵ 2900), 278 (5550), 268 (6550), 262 (6300), 232sh (31,500), and 223 (37,100) nm}.

The expected substitution product 6-bromopyrrolo[1,2-*d*]-*as*-triazine, m.p. 103—104°, was obtained from the reaction of (Ia) with *N*-bromosuccinimide in dichloromethane at ambient temperature.



(II) (I)

a; $R^1 = R^2 = R^3 = H$
b; $R^1 = R^3 = H, R^2 = Me$
c; $R^1 = R^2 = H, R^3 = Me$
d; $R^1 = Me, R^2 = R^3 = H$

A detailed study of the n.m.r. spectrum and the chemical properties of (Ia) and application of the cyclodehydration of azolecarbaldehyde formylhydrazones to the synthesis of other new 10π-electron heterocycles are currently being investigated.

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[1] C. Jaureguiberry and M. B. Roques, *Comp. rend.*, 1972, **274**, 1703.