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SYNTHESIS OF 2,9-DIAZAPHENANTHRENE AND PERLOLIDINE THROUGH A PYRIDYNE CYCLISATION REACTION[1]

S.V. Kessar, Y.P. Gupta, P.S. Pahwa and Paramjit Singh
(Department of Chemistry, Panjab University, Chandigarh-14, India)

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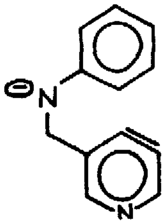
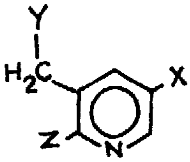
We have reported[2] that the phenanthridine ring system can be easily built through an intramolecular reaction of a benzyne with an aromatic ring activated by a negatively charged appended nitrogen atom. Extension of this procedure to pyridyne intermediates (I) would considerably enlarge the number of heterocyclic systems available through this novel reaction. However, here incursion by AE processes and poor selectivity of pyridynes[3] could be detrimental to the desired cyclisation. Nevertheless, experimentally it has been found to proceed in a satisfactory manner.



I



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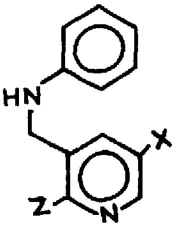

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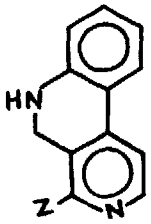

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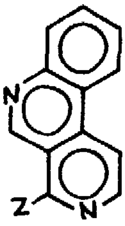

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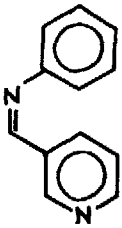

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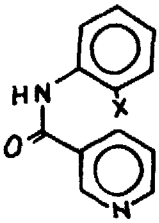

VII

The bromo compound IIIa[*] (X=Br, Z=H, b.p. 210-211°/5 mm) was prepared by reaction of IIa hydrochloride[4] (X = Br, Z=H, Y=Cl) with aniline in ethanol. Its treatment with KNH_2 (6 mole) in liquid ammonia afforded IVa (Z=H, m.p. 89-91°, 80 %) which on stirring with MnO_2 in chloroform gave Va (Z=H, m.p. 141-143°; Lit.[5] m.p. 140-142°) quantitatively. The above procedure is very simple as compared to the only earlier known synthesis of this system[5]. Our attempts to devise an alternate short route to it through photocyclisation (125 W mercury lamp, pyrex or quartz filter) of VI (in conc. H_2SO_4) or VII (X = H, Cl, Br, I; in benzene : methanol) were unsuccessful.

For the synthesis of the alkaloid perlolidine[6] (Vc, Z = OH), the dibromo compound IIb[7] (X = Z = Br, Y = H) was obtained, in a regiospecific manner, from 2-amino-3-methylpyridine by bromination in ethanol followed by diazotisation and treatment with Br_2/HBr. Its reaction with NBS afforded the tribromide IIc (X=Y=Z=Br) which with aniline gave IIIb(X=Z=Br, m.p.108-110°). The bromine ortho to the nitrogen atom in IIIb could be selectively replaced by heating (140°) with ϕ-CH_2ONa in benzyl alcohol. The obtained IIIc (X=Br, Z= ϕ-CH_2O, m.p. 105-106°) was cyclised with KNH_2/NH_3 to IVb (Z = ϕ-CH_2O).This compound was aromatised to get Vb (Z = ϕ-CH_2O, m.p. 134-136°, 70 % from IIIc) which on debenzylation, with refluxing 10 % HCl, cleanly gave perlolidine [Vc, m.p. 338-339°(d); Lit.[6c] m.p. 337-341°(d); UV (in 95 % C_2H_5OH, 0.01N NaOH and 0.01N HCl) and mass spectrum were also identical with the literature values[6c]].

REFERENCES AND FOOT-NOTES

[*] Satisfactory analyses have been obtained for all the unknown compounds described in this communication.

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