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SYNTHESIS OF PERLOLIDINE

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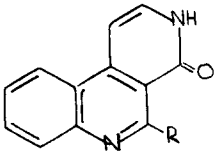
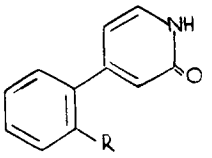
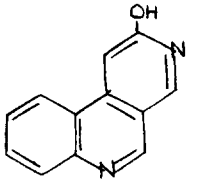
Perlolidine, a minor alkaloid of rye-grass Lolium perenne (1), has been assigned the 2,9-diazaphenanthrene structure (Ia) by Jeffreys, Sim et.al. (2). We have synthesized perlolidine in 45% overall yield utilizing a general method for substituted 2-pyridones developed by Thesing and Müller (3).



Ia (R = H)
Ib (R = Me)



IIa R = NO_2
IIb R = NH_2
IIc R = NHCH=O
IId R = NHAc



III

o-Nitrocinnamaldehyde was condensed with acetamido-pyridinium chloride to give 4-(o-nitrophenyl)-2-pyridone (IIa) in 75% yield, m.p. 211-12°, ν cm^{-1} 2500-3000(NH), 1666(C=O), 1335, 1560 (NO_2). Iron aqueous/ethanol reduced (IIa) to the amine (IIb), m.p. 236-7°, ν cm^{-1} 3400, 3280 (NH), 1660(C=O), which with formic acid treatment afforded the N-formyl derivative (IIc), m.p. 245-7°, ν cm^{-1} 3280(NH), 2500-3000 (NH of pyridone), 1690, 1650

(Amide I and II), 1660(C=O of pyridone). Cyclisation of (IIc) might have given either (Ia) or III), since both the 3 and 5 positions of pyridones readily undergo electrophilic substitution. In fact with a melt of sodium and aluminium chlorides at 200° we obtained only one product in 70% yield, m.p. 332-4° d., identical (mixed m.p., IR and R_f) with an authentic sample of perlolidine kindly provided by Dr E.P. White, (Dept of Agriculture, Ruakura, N.Z.). A similar cyclisation of the acetyl compound (IId), m.p. 264-6° gave the methyl analogue (Ib), m.p. 301-3° d., with similar properties and fluorescence to those of perlolidine.

Satisfactory analyses have been obtained for all compounds.

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