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The Synthesis of 1*H*-Pyrazolo[3,4-*b*]pyridine

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DERIVATIVES of the 1*H*-pyrazolo[3,4-*b*]pyridine system have been known for a number of years.[1] A variety of methods have been used in their syntheses but most workers have used substituted pyrazoles as starting materials. The parent heterocycle does not appear to have been described

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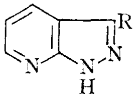
hitherto. We now report the convenient synthesis of the unsubstituted heterocycle, 1*H*-pyrazolo[3,4-*b*]pyridine.

2-Chloro-3-cyanopyridine, prepared from nicotinamide *N*-oxide,[2] was allowed to react with a refluxing solution of ethanol containing two moles of hydrazine hydrate. The product [m.p. 184—185°, λ_{max} (EtOH) 276, 332 mμ (log ϵ, 3·47, 3·44); ν_{max} (KBr disc) 3340, 3210 (NH_2), 3180 (NH), 1640 (NH_2) cm.$^{-1}$] was assigned structure (II) on the basis of its infrared and ultraviolet spectra. The n.m.r. of this compound was consistent with this structure.

Diazotisation of compound (II) followed by treatment of the resultant diazo-salt solution with hypophosphorous acid at 5° led to the isolation of a colourless compound [m.p. 98—99°, λ_{max} (EtOH) 265, 295, 301·5 (infl.) mμ (log ϵ, 3·60, 3·76, 3·68), ν_{max} ($CHCl_3$) 3300 (NH) cm.$^{-1}$] to which structure (I) was assigned on the basis of its infrared and ultraviolet spectra. The n.m.r. of this compound was also consistent with the structure assigned.



(I) R=H
(II) R=NH_2

Using this synthesis we have prepared a number of 1*H*-pyrazolo[3,4-*b*]pyridines subsituted in the 4-, 5-, and 6-positions. The substitution reactions of the parent heterocycle are being investigated.

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[1] *e.g.*, C. Bübaw, *Ber.*, 1910, **43**, 3401; S. Chechi, P. Papini, and M. Ridi, *Gazzetta*, 1955, **85**, 1160; A. Dornow and M. Siebrecht, *Chem. Ber.*, 1960, **93**, 1106; G. M. Badger and R. P. Rao, *Austral. J. Chem.*, 1965, **18**, 1267.

[2] E. C. Taylor and A. J. Crovetti, *J. Org. Chem.*, 1954, **19**, 1633.