## A Novel Ring Cleavage of Pyrrolo[1,2-c]pyrimidines and Indolizines

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RING-OPENING REACTIONS of nitrogen bridgehead compounds have been initiated by both nucleophilic<sup>1</sup> and electrophilic<sup>2</sup> reagents. We now report a novel cleavage of the pyrrole ring in pyrrolo-[1,2-c]pyrimidines and indolizines under mild, neutral conditions.

Reagents: (i)  $H_2$ , Pd-C; (ii)  $N_2H_4$ , Pd-C; (iii) cyclohexene, Pd-C; (iv) Pd-C; (v)  $Pb(OAc)_4$ ; (vi)  $PhCH_2\cdot CN$ ,  $NaNH_2$ .

We have recently described the synthesis and electrophilic substitution reactions of certain pyrrolo[1,2-c]pyrimidines,<sup>3</sup> and, in an attempt to obtain the 7-amino-compounds, we have examined the reduction of the corresponding 7-nitrosoderivatives. Catalytic hydrogenation of 7-nitroso-3,6-diphenylpyrrolo[1,2-c] pyrimidine (I) gave the expected amine (II), but in poor yield, and two further products were also isolated. These were identified as 1-cyano-1-phenyl-2-(6-phenylpyrimidin-4-yl)ethylene (III) and 1-cyano-1-phenyl-2-(6-phenylpyrimidin-4-yl)ethane (IV).

A rapid hydrogenation of the 7-nitroso-compound (I) with hydrazine hydrate and palladiumcharcoal gave solely 7-amino-3,6-diphenylpyrrolo-[1,2-c] pyrimidine (II) [M (mass spec.), 285;  $\nu_{\text{max}}$ (CHCl<sub>3</sub>) 3400 and 3325 (NH<sub>2</sub>), and 1620 cm.<sup>-1</sup>  $(NH_2)$ ;  $\tau$  1·22d, J 1·3 c./sec. (1-H), 1·93—2·10 m and  $2.29-2.60 \,\mathrm{m}$  (10 phenyl protons),  $2.65 \,\mathrm{d}$ , J = 1.3 c./sec. (4-H), 3.48 s (5-H), and 6.58 br sdisappearing on deuteriation  $(NH_2)$ ]. The sole product of a transfer hydrogenation of the 7nitroso-compound (I) with cyclohexene and palladium-charcoal was the cyanoethylene (III) [M (mass spec.), 283;  $v_{max}$  (CHCl<sub>3</sub>) 2225 (C $\equiv$ N), 1610 (C=C), and 910 cm.<sup>-1</sup> (=CH);  $\tau$  0.63 d, J 1.3 c./sec. (2-H), 1·65—1·92 m and 2·22—2·52 m (10 phenyl protons, 4-H and =CH)]. Treatment of the amine (II) with either palladium-charcoal in ethanol or with lead tetra-acetate gave the same nitrile (III). The cyanoethane (IV) [M (mass spec), 285;  $\nu_{\text{max}}$  (CHCl<sub>3</sub>) 2260 cm.<sup>-1</sup> (C $\equiv$ N),  $\tau$  0.73 d, J 1.3 c./sec. (2-H), 1.87—2.03 m and 2·47—2·63 m (10 phenyl protons and 4-H), 5·43 t, J 7.5 c./sec. (CH-CH<sub>2</sub>), 6.67d, J 7.5 c./sec.  $(CH-CH_2)$ ] was prepared by catalytic reduction of the cyanoethylene (III) or by synthesis from 4bromomethyl-6-phenylpyrimidine (VI) and benzyl cyanide.

The corresponding amines and nitriles have been obtained by similar reactions of 6-methyl-7-nitroso-3-phenylpyrrolo[1,2-c]pyrimidine and 3-nitroso-2-phenylindolizine.

We suggest that the reaction probably proceeds via the nitrene (V) which undergoes rapid bond isomerisations to yield the unsaturated nitrile. Similar types of cleavage of o-phenylenediamines with nickel peroxide<sup>4</sup> or 2-aminobenzotriazole with lead tetra-acetate<sup>5</sup> yielded cis-cis-muconitrile. The latter reaction has also been explained in terms of a nitrene intermediate.

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