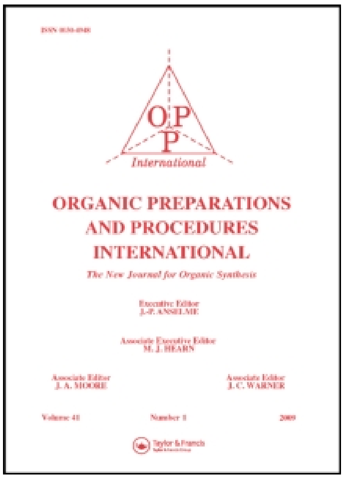

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PYRIDO(3,2-d)-v-TRIAZIN-4(3H)-ONE

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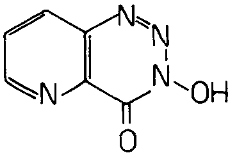
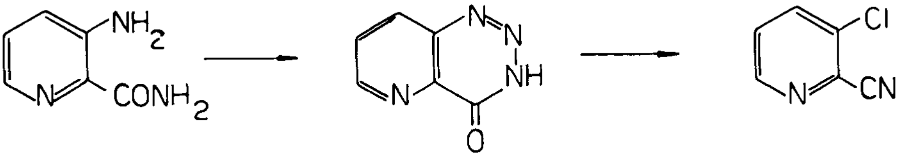
So far, only one derivative of this system has been reported. The compound, a cyclic hydroxamic acid (I), was obtained by action of nitrous acid on 3-aminopicolinhydroxamic acid.[1] The electron densities have been calculated[2] for the parent system, pyrido(3,2-d)-v-triazine, which remains unknown. As a convenient starting material for its preparation pyrido(3,2-d)-v-triazin-4(3H)-one (II) was anticipated. This compound could be prepared in reasonable yield upon treatment of 3-aminopyridine-2-carboxamide with amyl nitrite in glacial acetic acid. The attempted preparation of the



I



II III

corresponding 4-chloro derivative under mild reaction conditions by means of phosphorus pentachloride and phosphorus oxychloride afforded, however, the so far unknown 3-chloro-2-cyanopyridine (III). The formation of (III) may be envisaged as a result of N_2-N_3 bond fission and subsequent replacement of the diazonium group by chlorine and elimination of oxygen to give the cyano function. The instability of this heterocyclic system thus parallels the benzotriazines which frequently display reactions in accordance with their previously described masked diazonium character.[3,4]

Similar attempts to prepare some isomeric pyrido-v-triazinones resulted in the formation of the corresponding pyridones. For example, 2-aminopyridine-3-carboxamide afforded 3-carboxamidopyrid-2(1H)-one.[5]

EXPERIMENTAL [6]

Pyrido(3,2-d)-v-triazin-4(3H)-one.- A solution of 3-aminopyridine-2-carboxamide[7] (0.69 g) in glacial acetic acid (10 ml) was treated with amyl nitrite (0.75 ml). After standing at room temperature the product began to separate from the solution. It was collected (0.62 g) and sublimed for analysis at 200°/0.1 mm. It may be also crystallized from N,N-dimethylformamide and toluene; m.p. 236-238°. MS: $M^+ = 148$. NMR: $\tau = 1.01$ (dd, H_6), 2.08 (dd, H_7), 1.54 (dd, H_8); $J_{6,7} = 4.2$, $J_{7,8} = 8.4$, $J_{6,8} = 1.6$ Hz.

Anal. Calcd for $C_6H_4N_4O$: C, 48.65; H, 2.72; N, 37.83. Found: C, 48.97; H, 3.09; N, 37.48.

3-Chloro-2-cyanopyridine.- A mixture of finely powdered pyrido(3,2-d)-v-triazin-4(3H)one (0.3 g), phosphorus pentachloride (1.0 g) and phosphorus oxychloride (1.0 ml) was heated at 80° for 2 hours. The mixture was poured on ice, the product was filtered off and sublimed at 60°/1 mm (yield 0.1 g); m.p. 83-84°.MS: $M^+ = 138$. NMR: $\tau = 1.86$ (dd, H_4), 2.36 (dd, H_5), 1.41 (dd, H_6); $J_{4,5} = 7.6$, $J_{5,6} = 4.2$, $J_{4,6} = 1.5$ Hz.

Anal. Calcd for $C_6H_3ClN_2$: C, 52.00; H, 2.18; N, 20.21. Found: C, 52.10; H, 2.19; N, 20.25.

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