

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

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

B. Stanovnik^a; M. Tišler^a

^a Department of Chemistry, University of Ljubljana, Ljubljana, Yugoslavia

To cite this Article Stanovnik, B. and Tišler, M.(1972) 'PYRIDO(3,2-d)-v-TRIAZIN-4(3H)-ONE', *Organic Preparations and Procedures International*, 4: 2, 55 – 57

To link to this Article: DOI: 10.1080/00304947209458261

URL: <http://dx.doi.org/10.1080/00304947209458261>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

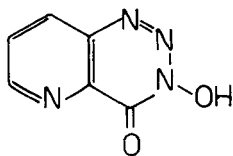
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

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

B. Stanovnik and M. Tišler

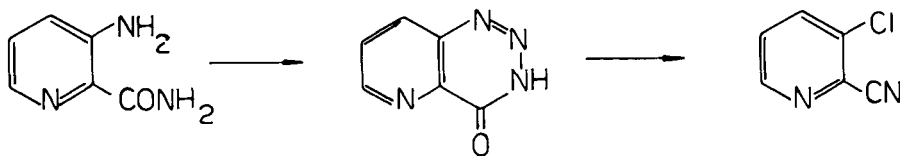
Department of Chemistry, University of Ljubljana,
61000 Ljubljana, Yugoslavia

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 calculated² for the parent system, pyrido(3,2-d)-v-triazine, which remains



I

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



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

EXPERIMENTAL⁶

Pyrido(3,2-d)-v-triazin-4(3H)-one.- A solution of 3-aminopyridine-2-carboxamide⁷ (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 $200^{\circ}/0.1$ mm. It may be also crystallized from *N,N*-dimethylformamide and toluene; m.p. $236-238^{\circ}$. MS: M^+ = 148. NMR: τ = 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 $60^{\circ}/1$ mm (yield 0.1 g); m.p. $83-84^{\circ}$. MS: M^+ = 138. NMR: τ = 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.

REFERENCES

1. D. Harrison, and A.C.B. Smith, *J. Chem. Soc.*, 2157 (1960).
2. S. C. Watt, and J. W. Wesley, *J. Mol. Spectros.*, 19, 25 (1966).
3. J. G. Erickson, P. F. Wiley, and V. P. Wystrach, "The 1, 2, 3- and 1,2,4-Triazines and Pentazines", p. 5, Interscience, New York, 1956.
4. B. Stanovnik, and M. Tišler, *J. Heterocyclic Chem.*, 8, 785 (1971).
5. A. Dornow, *Ber. dtsh. chem. Ges.*, 73, 153 (1940).
6. Melting points were determined on a Kofler melting point apparatus and are corrected. The nmr data were obtained on a dimethylsulfoxide-d₆ solution from a JEOL JNM-C-60 HL spectrometer, using tetramethylsilane as internal standard. Mass spectra were recorded on a CEC 21-110C instrument using direct sample insertion into the ion source.
7. R. K. Robins, and G. H. Hitchings, *J. Amer. Chem. Soc.*, 78, 973 (1956).

(Received December 27, 1971; in revised form March 27, 1972)