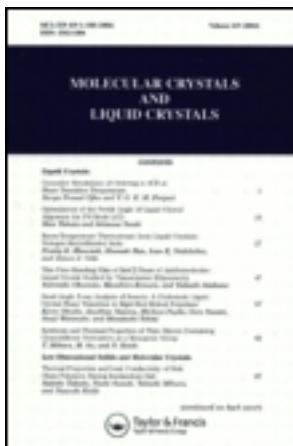


This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 21 February 2013, At: 10:49
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH,
UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
<http://www.tandfonline.com/loi/gmcl16>

Structure and Solid Hydrolysis of 3, 1-Benzoxazin-4-Ones

Jacques Vicens ^a , Claude Decoret ^a , Christine Gaget ^a , Margareth C. Etter ^b & Lou A. Errede ^b

^a Laboratoire de Chimie Industrielle -ERA 600 du C.N.R.S. Université Claude Bernard, LYON I, 43, boulevard du 11 novembre 1918, 69622, Villeurbanne, FRANCE

^b 3M Central Research Laboratories, St Paul, Minnesota, 55101, U.S.A.

Version of record first published: 17 Oct 2011.

To cite this article: Jacques Vicens , Claude Decoret , Christine Gaget , Margareth C. Etter & Lou A. Errede (1983): Structure and Solid Hydrolysis of 3, 1-Benzoxazin-4-Ones, Molecular Crystals and Liquid Crystals, 96:1, 39-43

To link to this article: <http://dx.doi.org/10.1080/00268948308074689>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, 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.

STRUCTURE AND SOLID HYDROLYSIS OF 3,1-BENZOXAZIN-4-ONES

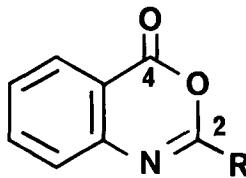
JACQUES VICENS, CLAUDE DECORET, CHRISTINE GAGET
Laboratoire de Chimie Industrielle -ERA 600 du C.N.R.S.
Université Claude Bernard - LYON I, 43, boulevard du
11 novembre 1918 - 69622 - Villeurbanne - FRANCE

MARGARETH C. ETTER, LOU A. ERREDE
3M Central Research Laboratories, St Paul Minnesota
55101 U.S.A.

Abstract Solid hydrolysis of 2-substituted 3,1-benzoxazin-4-ones are presented. 18 O experiments with labelled water and hydrolysis in acidic conditions show the reaction occurs on $>\text{C}=\text{N}-$ function. A protonated intermediate for the reaction is proposed. Theoretical calculations are in agreement with the assumed intermediate.

INTRODUCTION

3,1-Benzoxazin-4-ones are molecules presenting in their framework $>\text{C}=\text{N}-$ and $>\text{C}=\text{O}$ groups on C-2 and C-4 positions.



These nucleophilic sites are in some part implicated in hydrolysis mechanisms during enzyme reactions¹.

The solid-gas hydrolysis of powders² and single crystals³ of acetyl anthranyl¹ has been described. The reaction is anisotropic, beginning at the crystal ends (100) face and moving in the a direction⁵. The results were rationalized in terms of water molecules penetrating in the crystal structure

through hydrophilic planes parallel to (001) in order to reach the nucleophilic centers $>\text{C}=\text{N}-$ and/or $>\text{C}=\text{O}$ ³.

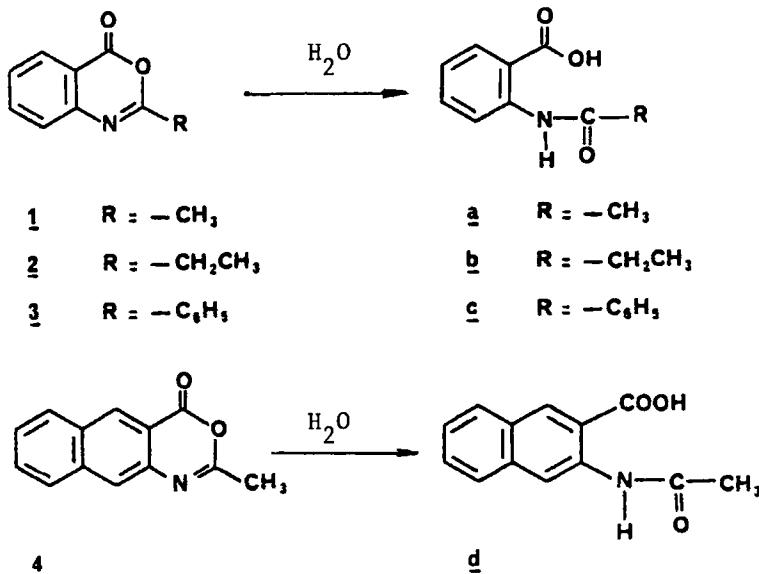


FIGURE 1

In order to gain further insights about the mechanism of the reaction we studied the hydrolysis in the solid state of acetyl anthranyl 1 and the parent compounds 2,3 and 4 into the hydrolysed products a, b, c and d respectively (figure 1).

OXYGEN-18 HYDROLYSIS

Oxygen-18 enriched water (98%), H_2O^* , was reacted with 1 and 2 as a solid-gas reaction, as a suspension, as a homogeneous mixture in $\text{THF} - \text{H}_2\text{O}^*$ and as a two phases system $\text{CHCl}_3 - \text{H}_2\text{O}^*$. Mass spectrometry analysis as in reference⁴ showed oxygen-18 is mostly incorporated as $\text{NH}-\overset{18}{\text{O}}-\text{C}-\text{R}$ in the final labelled products a and b. This clearly shows the hydrolysis to occur at C-2 position.

ACIDIC HYDROLYSIS IN THE SOLID STATE

When microcrystals of 1 are exposed to air saturated with water vapor, reaction is complete after 160 hours. When the air is saturated with water vapor containing HCl (36% HCl- H_2O as liquid) a is obtained in quantitative yields after 5 hours. Figure 2 shows the effect of the concentration of HCl in water on the solid hydrolysis rates of powdered 1.

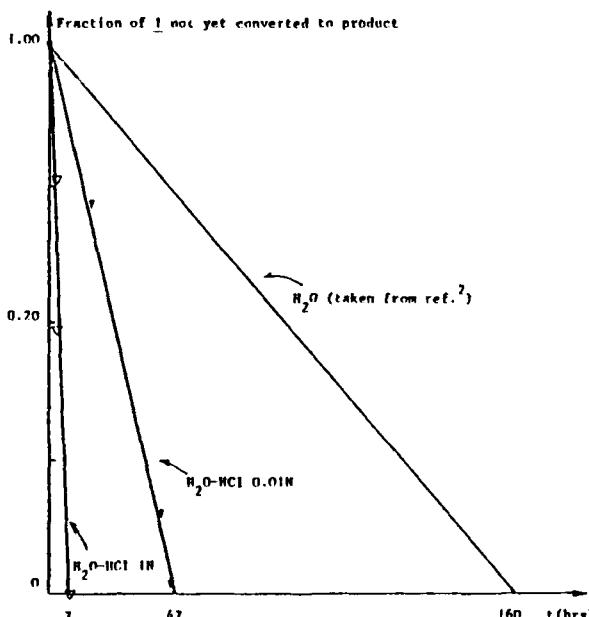


FIGURE 2. Reaction of powdered 2-methyl-3,1-benzoxazin-4-one 1 with H_2O and $H_2O - HCl$ vapors.

When microcrystals of 3 or 4 are exposed to air saturated with water vapor no reaction is observed. However when the air is saturated with water vapor containing HCl (36% HCl- H_2O as liquid) c or d are obtained as the only products after a few days. Hydrolysis of 3 and 4 in H_2O , in $THF - H_2O$ and in $CHCl_3 - H_2O$ take place after one week. This was consistent with an acidic activation of the solid state reaction of 1, 3 and 4.

All the observed results can be interpreted in the following manner : in the crystal of 1 the carbonyl oxygen atoms associate about the screw axis and no close intermolecular contacts are found³. There is no hydrogen bonding within the crystalline structure of 1³.

In the presence of H_2O , the molecules hydrogen bond by preferential protonation of the basic nitrogen atom, thereby rapidly incorporating water into the lattice. Such an interaction assists the water molecules in the reaction at $\text{a} > \text{C}=\text{N}-$ group as proposed for "neutral" and "acidic" hydrolysis²⁻⁴.

CNDO/2 CALCULATIONS

The variation of the reactivity of C-2 position in different conditions was evaluated by preliminary calculations based on CNDO/2 methods on molecules 1 and 3 and on the N-protonated corresponding ions 1-H and 3-H (table 1).

TABLE 1 CNDO/2 Calculations on 1 and 3 and on the N-protonated 1-H and 3-H.

TOTAL CHARGES	<u>1</u>	C-2	3.669	<u>3</u>	C-2	3.708
		C-4	3.603		C-4	3.601
LUMO COEFFICIENTS	<u>1-H</u>	C-2	3.579	<u>3-H</u>	C-2	3.618
		C-4	3.602		C-4	3.599
	<u>1</u>	ϵ = 0.088		<u>3</u>	ϵ = 0.064	
		C-2 0.352			C-2 0.413	
	<u>1-H</u>	ϵ = -0.136		<u>3-H</u>	ϵ = -0.142	
		C-2 0.706			C-2 0.621	
		C-4 0.068			C-4 0.022	

Total charges in 1 show that C-4 is more electropositive than C-2. In total charges of 1-H one can see the electropositivity of C-2 to increase in such a manner that its value becomes higher than C-4. This feature is in agreement with preferential attack of water molecules on the C-2 position in the protonated intermediate. A similar increase of the electropositivity of C-2 is noticed in total charges of 3 and 3-H. It is seen that the LUMO coefficients of the C-2 positions are more reactive than C-4 in all the cases. One can also notice that in protonated systems 1-H and 3-H, the reactivity of C-2 positions are drastically enhanced by comparison with 1 and 3. From these observations it is also concluded the N-protonated molecules are the reactive intermediates. Experimental and theoretical work is in progress on 3,1-benzoxazin-4-one and other molecules presenting $>\text{C}=\text{N}-$ and $>\text{C}=\text{O}$ functions.

REFERENCES

1. D.J. Crenin and A.F. Hegarty, J. Chem. Soc., Perkin Trans. 2, 208 (1978).
2. L.A. Errede, P.D. Martinucci and J.J. Mc Brady, J. Org. Chem., 45, 3009 (1970).
3. M.C. Etter, L.A. Errede and J. Vicens, Cryst. Str. Com. in press.
4. A. Williams and G. Salvadori, J. Chem. Soc., B 1971, 1105 (1971).