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

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

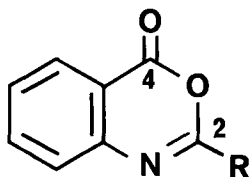
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Abstract Solid hydrolysis of 2-substitued 3,1-benzoxazin-4-ones are presented. O^{18} experiments with labelled water and hydrolysis in acidic conditions show the reaction occurs on $>C=N-$ function. A protonated intermediate for the reaction is proposed.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

INTRODUCTION

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

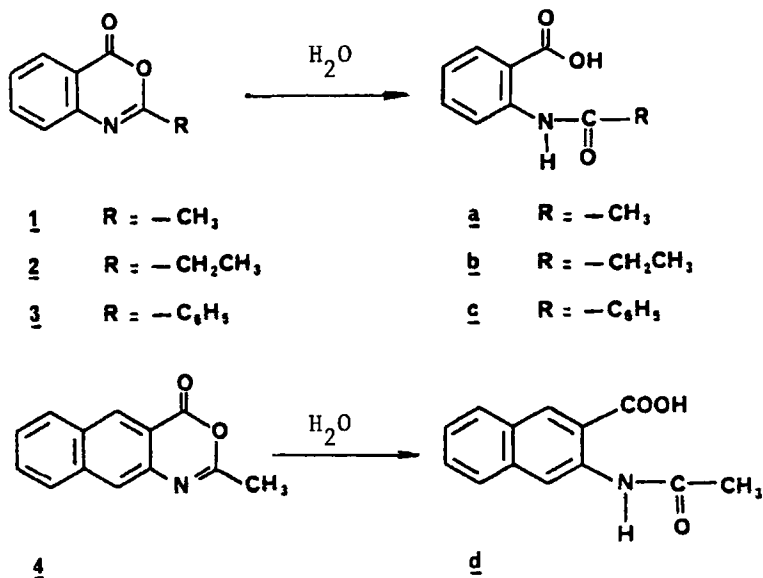


FIGURE 1

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 $\text{NH}-\overset{\text{O}^*}{\text{C}}-\text{R}$ 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-H₂O 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.

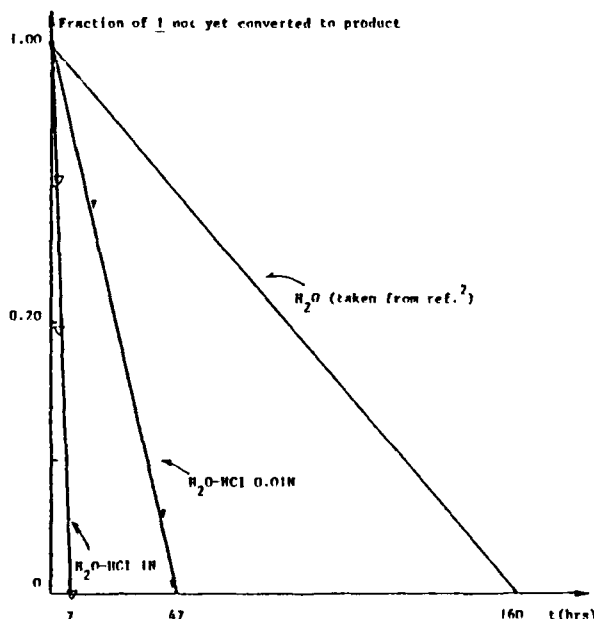


FIGURE 2. Reaction of powdered 2-methyl-3,1-benzoxazin-4-one 1 with H₂O and H₂O - HCl vapors.

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 - H₂O as liquid) c or d are obtained as the only products after few days. Hydrolysis of 3 and 4 in H₂O, in THF - H₂O and in CHCl₃ - H₂O 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 H₂O, 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 a>C=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
	<u>1-H</u>	C-2	3.579	<u>3-H</u>	C-2	3.618
		C-4	3.602		C-4	3.599
LUMO COEFFICIENTS	<u>1</u>	ϵ	= 0.088	<u>3</u>	ϵ	= 0.064
		C-2	0.352		C-2	0.413
		C-4	0.282		C-4	0.131
	<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 $>C=N-$ and $>C=O$ functions.

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