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- SOLID STATE HYDROLYSIS OF ACETYLANTHRANYL -

- ASSISTANCE BY HYDROGEN BONDING -

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O^{18} and acidic hydrolysis in the solid state of acyl anthranyls are presented. The role of H-bonds in assisting the reactions is discussed.

We have previously reported that acetylanthranyl, 1a (2-methyl-4H-benzoxazin-4-one) reacts with water both in solution and in the solid state to give 2a (1,2). The solution hydrolysis has been shown to proceed by attack of water at the imine center C2 eventhough C4 is expected to be a more electrophilic center (3) (figure 1). This was accounted for by proposing that hydrolysis in solution involves H-bonded arrays of water which protonate the nitrogen and then react at C2. This regiospecificity is caused by H-bonding inducing a more electropositive character at C2 (4) as well as by the steric bulk of the H-bonded array (when the substituent at C2 is bulky, hydrolysis occurs C4). The present study was carried out in order to see what role H-bonds play in the hydrolysis of 1a in the solid-state. Isotopically labelled water vapor was reacted with microcrystalline 1a,b and the products were analysed by mass spectral analysis.

Oxygen-18 hydrolysis. When microcrystals of 1a are exposed to air saturated with O-18 enriched (98%) water, H_2O^*, at room temperature for 15 days, 2a is formed in quantitative yield, as confirmed by tcl and mass spectrometry. A similar set of experiments was done on compound 1b, also giving rise to only one product, 2b. Hydrolysis of 1a as a suspension in H_2O^*, as a homogeneous solution in THF - H_2O^*, and as a two phases system of $CHCl_3$-H_2O^* was also carried out. The results of mass spectral analysis of the products formed in all these experiments are summarized in Table 1. It is clearly seen that in each case O^{18} has been incorporated at the C2 position only.

Acidic hydrolysis in the solid-state. When microcrystals of 1a are exposed to air saturated with water vapor containing HCl (36% HCl-H_2O as a liquid), complete conversion to 1b occurs in only 5 hours (about 30 times faster than in neutral water vapor). We also found that 1c and 1d could be hydrolysed in a gas-solid reaction with aqueous HCl and that reaction was complete after a few days. This contrasts markedly with the solid-gas reactivity of 1c, d with neutral water vapor, in which case no reaction was observed after months. Hydrolysis of 1c, d in water solution, in THF-H_2O and in $CHCl_3$-H_2O takes place in about one week.

Discussion. These experiments show that hydrolysis of acylanthranyl compounds, 1a, b, proceeds with the same regiospecificity in the solid-state as had previously been observed for solution hydrolysis. Previous studies on the single crystal hydrolysis of 1a showed that the rate of diffusion of water through the crystal is fastest along the hydrophilic crystal planes (2). This is indicative of H-bond participation in the diffusion process, possibly occuring in patterns analogous to those observed in the crystal structure of 3 (figure 1), the hydrated form of the N analog of 1a (5). Similar H-bonding arrays could be the actual nucleophilic species in the solid-state hydrolysis reactions. Further work in needed to characterize these arrays and to demonstrate precisely how they influence the mode of attack of water molecules in the solid-state. Nevertheless the fact that the solution and solid-state reactions occur with the same regiospecificity lends support to Errede's proposition that H-bond arrays are also occuring in solution. The solid-state results show reaction rates of acylanthranyls with water are markedly increased in the presence of acids. H-bonds could also be assisting the diffusion of HCl through the lattice, as they did for water vapor. In this case, participation by extended H-bonding arrays, such as N--H--Cl--HOH, is likely, by analogy to the structures of aminoacid monohydrochloride dihydrates (6). Another possibility is that the protons are being transported through the lattice by a Grotthuss mechanism, in which case Cl^- would not have to penetrate the lattice (7). These aspects of proton conduction and the role of H-bond arrays are being pursued further in our studies on related acylanthranyl compounds.

Reactants	Conditions	a^+	b^+	c^+
1a, H_2O^*	Suspension, H_2O^*	4.1	.00114	.0080
1a, H_2O^*	Solution, THF	4.0	.00113	.0081
1a, H_2O^*	Solution, $CHCl_3$	3.4	.0010	.0081
1a, H_2O	Gas-solid	.0061	.0017	.0020
1a, H_2O^*	Gas-solid	4.1	.0051	.0075
1b, H_2O^*	Suspension, H_2O^*	13.72	.0133	.011
1b, H_2O^*	Solution, THF	8.06	<.0001	.0021
1b, H_2O^*	Solution, $CHCl_3$	13.9	.0134	.100
1b, H_2O	Gas-solid	<.0001	<.0001	<.0001
1b, H_2O^*	Gas-solid	6.59	.0055	.0065

[+] Fragmentation intensity ratio, $|(m+2)/e|$ / $|m/e|$ of : a = 2-amidobenzoic acid, b = 2-aminobenzoic acid, c = dehydrated anthranilic acid, as described in reference 3.

Table 1 - Mass spectrometric analysis of hydrolysis products from acylanthranyls.

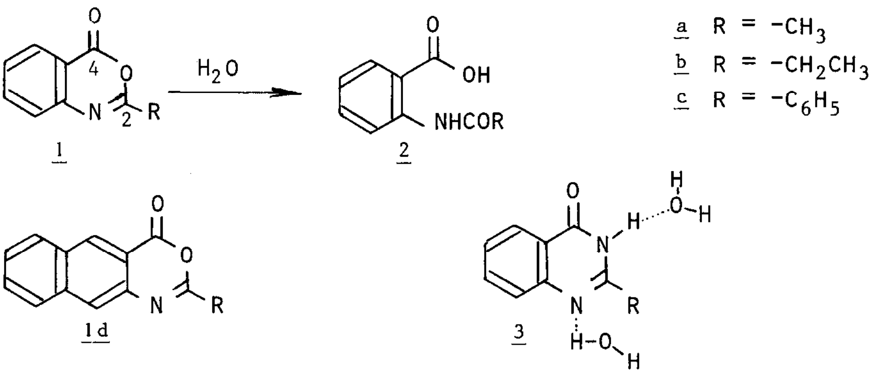

figure 1

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