THERMAL CYCLODEHYDRATION OF N-BENZOYLANTHRANILIC ACID

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Water is split out to form 2-phenyl-4H-3,l-benzoxazin-4-one when N-benzoylanthranilic acid is heated. A mass spectrometric study of 0^{16} -labeled N-benzoylanthranilic acid and the product of its thermal cyclodehydration showed that the oxygen atoms of the carboxyl and benzoyl groups participate equally probably in splitting out of water.

One of the methods for the synthesis of 4H-3,1-benzoxazin-4-ones is thermal cyclodehydration of N-acylanthranilic acids. Theoretically, an oxygen atom from both the carboxyl group and the benzoyl group may depart with the water that it split out. The absence in the literature of experimental data on this problem makes it impossible to conceive of a more nearly complete mechanism for the reaction.

We have studied the cyclodehydration of 0¹⁸-labeled N-benzoylanthranilic acid:



The change in the percent enrichment that occurs during the reaction, which we determined by a mass spectrometric method, makes it possible to ascertain the site from which the oxygen atom is detached.

The labeled N-benzoylanthranilic acid was obtained by alkaline hydrolysis of 2-phenyl-4H-3,l-benzoxazin-4-one in heavy-oxygen water. Cleavage of the bond at the amide group occurs during the dissociative ionization of N-benzoylanthranilic acid under the influence of electron impact, and fragment ions with m/e* 105 and 137 (rearranged) are formed. The O¹⁸ distribution in the fragments is illustrated by the data in Table 1. It is evident from Table 1 that 79% of the O¹⁸ with which the N-benzoylanthranilic acid is labeled is found in the carboxyl group and 21% is found in the benzoyl group. If one of the oxygen atoms of the carboxyl group departs during thermal splitting out of water, a molecule of the resulting 2phenyl-4H-3,l-benzoxazin-4-one should contain 79.5% less heavy oxygen than the starting molecule. However, if an oxygen of the benzoyl group is split out, the loss should be 20.8%. In general form, the fraction of split-out heavy oxygen (A) depends on the contribution of the carboxyl (k) and benzoyl (1 - k) groups:

$$A = \frac{79.1}{2} k + 20.8(1-k). \tag{1}$$

The enrichment (P) was calculated from the expression

*Here and subsequently the numbers that characterize the ions are the mass-to-charge ratios.

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TABLE 1.	0 ¹⁸ Distribution in the
Fragments	Formed during the Dis-
sociative	Fragmentation of N-
Benzoylant	thranilic Acid

Fragment	Characteristic ion peaks: m, m+2	Rel. en- richment, %
$\begin{array}{c} M+\\ C_6H_5CO+\\ o\text{-}NH_2C_6H_4COOH+\\ C_7H_5NCO+ \end{array}$	241, 243 105, 107 137, 139 119, 121	100 20,8 79,1 38,7

TABLE 2. Heavy-Oxygen Enrichment of 2-Phenyl-4H-3,1-benzoxazin-4-one and N-Benzoylanthranilic Acid

Enrichment, %		Fraction of O ¹⁸ remain-	
N-benzoylanthranilic acid	2-pheny1-4H-3,1-benzoxazin-4-one	tion in % rel. to start. amt.	
$P_{a} = \frac{J'_{243}}{J'_{243} + J_{241}} \ 100$	$P_b = \frac{J'_{225}}{J'_{225} + J_{223}} \ 100$	$\frac{P_b}{P_a} 100$	
$22,2\pm0,1$	$15,4 \pm 0,2$	69,4	

$$P = \frac{l'_{m+2}}{l'_{m+2} + l_m},$$
(2)

where I_m is the intensity of the m-th peak of the ions, I'_{m+2} is the intensity of the (m + 2)-th ion peak after introduction of the isotopic correction

$$I'_{m+2} = I_{m+2} - p \cdot I_m , (3)$$

and $p = I_{m+2}/I_m$ for the O¹⁸-unenriched compound.

It is apparent from Table 2 that 69.4% of the initially contained heavy oxygen is retained in the thermal cyclodehydration of N-benzoylanthranilic acid, and 30.6% is lost (A = 30.6). Dividing by A in Eq. (1), we obtain k = 0.52. In other words, splitting out of oxygen from the carboxyl and benzoyl groups is equally probable in this reaction. This conclusion is also confirmed by the increase in the percentage of 0¹⁸ in the C₆H₅CO fragment (105) obtained in the fragmentation of 2-phenyl-4H-3,1-benzoxazin-4-one with respect to the same fragment formed from N-benzoylanthranilic acid from 20.8 to 39.4%. In this case one should bear in mind that the formation of the $[M - H_20]^+$ ion during the dissociative ionization of N-benzoylanthranilic acid occurs due to primary removal of an oxygen atom from the carboxyl group. This is attested to by the character of the 0¹⁹ distribution in the M⁺ and $[M - H_20]^+$ ions. If one assumes that the degree of enrichment of the M⁺ ion is 100%, the $[M - H_20]^+$ ion turns out to be 58.8% enriched. If the oxygen were split out from the benzoyl group, the enrichment of the $[M - H_20]^+$ ion should have been about 80%.

EXPERIMENTAL

The mass spectra were recorded with an MS-702 mass spectrometer. The ionizing-electron energy was 70 eV, the accelerating voltage was 10 kV, and the electron emission current was 300 μ A. The O¹⁸-labeled N-benzoylanthranilic acid was obtained by the method in [1].

Thermal Cyclodehydration. Approximately 150 μ g of the labeled N-benzoylanthranilic acid was placed in a 1-cm long sealed glass capillary with a diameter of 0.3 mm, and the capillary was heated at 200° for 1 h. It was then opened and placed in the cell for direct introduction into the ion source of the mass spectrometer.

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NUCLEOPHILIC ADDITION TO THE PHENOXAZONIUM CATION

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At the instant of its formation of oxidation of phenoxazine with ferric chloride. the phenoxazonium cation adds arenesulfinate and nitrite ions to give 3-arylsulfonyl- and 3-nitrophenoxazines, respectively. It is shown that the introduction of a second sulfonyl group proceeds more slowly and gives 3,7-di(arylsulfonyl)phenoxazines in low yields. The PMR spectra of the synthesized compounds are examined in comparison with 3-substituted phenothiazines.

Continuing our search for stabilizers and antioxidants of polymeric materials, we undertook the oxidation of phenoxazine with ferric chloride in the presence of arenesulfinate and nitrite ions.

It is known [1, 2] that 1,4-oxazine and 1,4-thiazine systems readily form saltlike structures. The presence of an unstable o-quinoid cation is responsible for their high activity with respect to nucleophilic substitution in the 3 position.



At the instant of its formation in the oxidation of phenoxazine with ferric chloride, the phenoxazonium ion readily adds nitrite and arenesulfinate ions to give I and IIa,b, respectively.

Nitrophenoxazine I was identical to the 3-nitrophenoxazine described in [4], and this confirms incorporation of the substituent in the 3 position. The product (II) of the addition of the arenesulfinate ion is completely similar to the corresponding rearrangement product [3] and can be identified as 3-arylsulfonylphenoxazine. The introduction of a second sulfonyl group proceeds more slowly and gives 3,7-di(arylsulfonyl)phenoxazines (IIIa,b) in low yields.

Characteristic absorption bands of NH (3350-3400 cm⁻¹), NO₂ (1530, 1330 cm⁻¹), and SO₂ (1140-1160 cm⁻¹) groups are present in the IR spectra of the synthesized I, IIa,b, and IIIa,b.

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