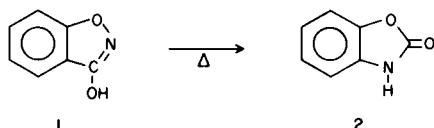


Thermal Conversion of 3-Hydroxy-1,2-benzisoxazole to Benzoxazolinone

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During the course of a study whose goal is to compare the mass spectral behavior of several heterocyclic systems with their thermal and photochemical behavior, we have observed the clean thermal conversion of the 3-hydroxy-1,2-benzisoxazole ring system (**1**) to the isomeric benzoxazolinone ring system (**2**).



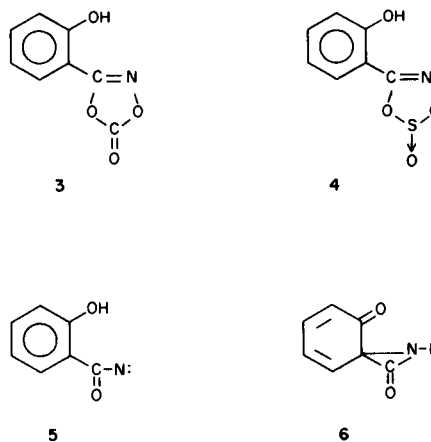
Authentic **1** and several of its derivatives have only recently become available (2), despite earlier reports (3) of their synthesis. A sample of **1** prepared from **4** according to Böhshagen (2) exhibited spectral properties much like those reported: no infrared carbonyl absorption, strong -OH and C=N absorptions at 3000-2500 and 1615 cm^{-1} , respectively, and aryl proton nmr resonances at 7.2-7.9 ppm. When a sample of **1** was sublimed under high vacuum into a 7 in. pyrex pyrolysis column packed with glass beads heated to 450°, **2** was obtained directly from the column in essentially quantitative yields and > 95% purity. Compound **2** is clearly differentiated from **1** by melting point, a C=O stretch at 1740-1780 cm^{-1} (doublet, as potassium bromide pellet) and aromatic proton resonance at 7.12 ppm (singlet). Either spectroscopic method can be used to analyze mixtures of **1** and **2**. The temperature dependence on percent conversion is shown in the Table.

TABLE

Effect of Temperature on Percent Conversion of **1** \rightarrow **2**

Temp ($^{\circ}\text{C}$)	% 2 formed (by nmr integration)
240-250°	0
340-350°	50
440-450°	> 95

The mechanism of this transformation may be related to that suggested for the degradation of 3-(2-hydroxyphenyl)- Δ^2 -1,4,2-dioxazolinone (**3**) which also produces **2** via a postulated nitrene **5** (**4**).



Alternatively, the mechanistic pathway may parallel that proposed for thermal isomerization of 4-isoxazolines (**5**) and *N*-arylisoxazoline-3-ones (**6**) which would suggest **6** as an intermediate. We are actively pursuing studies designed to elucidate the mechanism for the conversion **1** \rightarrow **2** as well as to define the scope and limitations of the reaction.

EXPERIMENTAL

The pyrolysis of 3-hydroxy-1,2-benzisoxazole (**1**) was carried out by subliming 50-100 mg. of **1** into a Pyrex tube (180 mm x 26 mm. O.D.), which was packed with 5 mm. Pyrex beads and heated at various temperatures (see Table) with an electric tube furnace. The temperature of the furnace was measured with a thermocouple connected to a potentiometer. A pressure of 0.10 mm of Hg was maintained during the pyrolysis. The products were condensed in a U-tube immersed in liquid nitrogen and were removed after the pyrolysis by washing the trap with ether. The ether was evaporated at reduced pressure, leaving a crystalline residue which was analyzed by infrared and nmr techniques.

3-Hydroxy-1,2-benzisoxazole, (1).

This compound was prepared according to Böshagen (2) from 4-(2-hydroxyphenyl)- Δ^3 -1,2,5,3-thiadioxazolin-S-oxide (4) and triethylamine. Since 4 decomposes readily in the presence of water, an alternate method (4) of synthesizing 1 was also utilized.

A solution of 5 g. of salicylhydroxamic acid in 50 ml. dry tetrahydrofuran was placed in a 3-necked 100 ml. flask equipped with a condenser, gas-dispersion tube, and stirrer. The solution was heated to refluxing temperature and phosgene gas was bubbled slowly into the stirred solution for 2.5 hours. Stirring was continued for another 2 hours at room temperature. The tetrahydrofuran was then removed on a rotary evaporator, and the solid residue was recrystallized from a hexane-ethyl acetate solution to yield 5 g. (85%) of 3.

Four g. of 3 was dissolved in 20 ml. of dry dioxane, and 6.77 g. of triethylamine was added dropwise to the stirred solution which was maintained at a constant temperature of $\sim 20^\circ$. The reaction mixture was poured into 70 ml. of water, neutralized with 2 N HCl, and placed in the refrigerator. The crystals which formed were filtered, washed with water, and dried under vacuum overnight. The yield was 2.5 g. (83%), m.p. 144-145°.

2-Benzoxazolinone (2).

This compound was prepared independently from *o*-aminophenol and urea as described in reference (7).

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