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UNUSUAL CONVERSION OF 5-HYDROXY-2(5H)-FURANONE IN AQUEOUS SOLUTION

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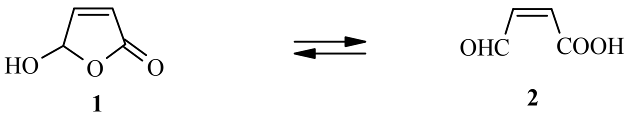
The conversion of 5-hydroxy-2(5H)-furanone into succinic acid in aqueous solution has been detected experimentally for the first time, indicating the possibility of forming and hydrolyzing its previously unknown tautomeric forms. The accelerating effect of increased pH values and temperature on the reaction has been established. A scheme is proposed to form succinic acid from 5-hydroxy-2(5H)-furanone.

Keywords: 5-hydroxy-2(5H)-furanone, succinic acid, solution equilibrium.

5-Hydroxy-2(5H)-furanone (**1**), used in the synthesis of heterocyclic compounds [1-5], is the cyclic form of *cis*-β-formylacrylic acid (**2**) (Scheme 1). At the basis of the mobile equilibrium existing between structures **1** and **2** lies a mechanism of ring-chain tautomerism [6-8]. Previously we developed conditions assisting a shift in this equilibrium in the direction of the cyclic form **1**. This permitted its separation from the mixture with tautomer **2** formed on oxidation of furfural with hydrogen peroxide in the presence of vanadium compounds [1,9,10].

Scheme 1



However recent results obtained on investigating the behavior of hydroxy-furanone **1** in aqueous media have indicated the possibility of carrying out tautomeric–hydrolytic conversions of it under definite conditions more complex than Scheme 1. The formation of succinic acid (**3**) in aqueous solutions of lactol **1** at pH 1-10 has been established by us for the first time.

On heating an aqueous solution of furanone **1** (concentration 1.2 M) at 60°C for 3 h the yield of acid **3** was 3%. On increasing the heating time to 24 h the yield grew to 13%. Increasing the acidity of the medium (by introducing the appropriate quantity of perchloric acid) was the same as reducing the temperature and led to a slowing of the process of forming product **3**. On the other hand, in media of increased basicity (at pH > 8), the reaction suddenly accelerated. Thus at 70-80°C in NaOH solution of pH about 9-10 practically complete conversion of compound **1** into acid **3** was observed in a few minutes.

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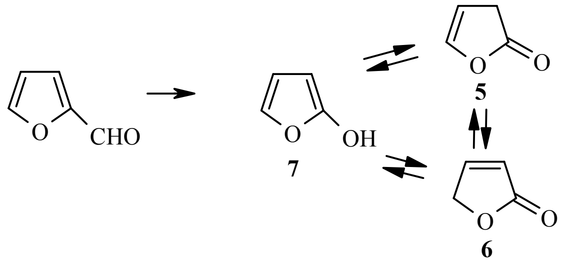
A polarographic investigation was carried out on dilute solutions of furanone **1** (concentration $1 \cdot 10^{-4}$ M, pH 0-4) blown through with nitrogen and maintained for 1 year at room temperature in the absence of oxygen of the air. The results obtained confirmed the acceleration of the conversion of compound **1** into acid **3** on reducing the proton concentration.

Product **3** was isolated from the reaction mixture as the diethyl ester **4**. The spectral and other characteristics of this ester, and of the acid **3** obtained from it by acid hydrolysis, corresponded with the data of standard samples of the compounds indicated.

The results presented above enabled acid **3** to be considered as the final product of previously unknown tautomeric conversions of furanone **1**.

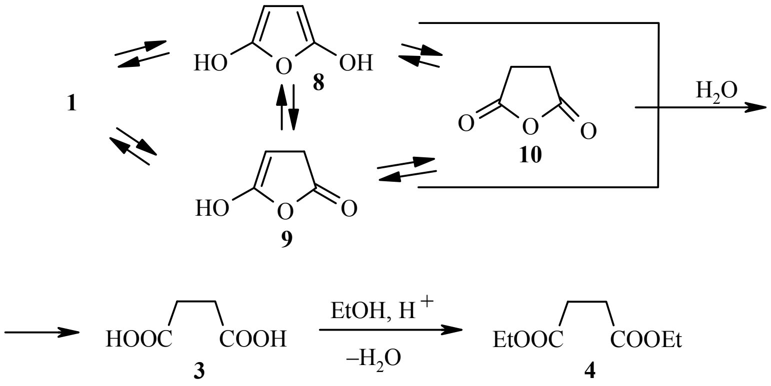
Among the main products of oxidation of furfural with aqueous hydrogen peroxide 2(3H)- and 2(5H)-furanones **5** and **6** were detected by one of us in [11]. Their formation under these conditions is explained by isomerization of the unstable intermediate reaction product, 2-hydroxyfuran (**7**), by a type of keto-enol equilibrium (Scheme 2).

Scheme 2



We propose that a similar mechanism, linked with migration of the proton found at position 5 of the lactone ring and occurring without ring opening, is also possible for hydroxyhydrofuranone **1**. In accordance with this mechanism compound **1** is in equilibrium with extremely unstable tautomeric forms, *viz.* 2,5-dihydroxyfuran (**8**), 5-hydroxy-2(3H)-furanone (**9**), and succinic anhydride (**10**). The last compound is hydrolyzed in aqueous medium with the formation of succinic acid **3** (Scheme 3). The effect described above of acids and bases on the reaction is in agreement with this Scheme.

Scheme 3



The addition of analytical reagents, reacting specifically with anhydrides of dicarboxylic acids ($NH_2OH \cdot HCl + FeCl_3$ [12]) and with enols ($FeCl_3$, ethanol [13]), to furanone **1** or to solutions of it in anhydrous solvents under various conditions (at different temperatures, in the presence of acids or bases, or without them) did not lead to detection of the desired grouping. This result may be explained by the fact that in the absence of water the equilibrium between furanone **1** and its tautomers **8-10** is shifted practically completely in the direction of the first compound. In aqueous medium this equilibrium may be displaced in the direction of the indicated intermediates due to their rapid irreversible conversion into the final product **3**.

The use of the analytical reagents indicated above as traps for tautomers **8-10** proved to be impossible due their rapid competing reaction with the initial substance **1**, leading respectively to the oxime and Fe(III) salt of β-formylacrylic acid.

The succinic acid **3** formed in the peroxide oxidation of furfural is therefore probably the conversion product not only of its known precursors **5** and **7** but also of hydroxyhydrofuranone **1** (through its postulated unstable forms **8** and **9**).

The established possibility of the fairly ready conversion of 5-hydroxy-2(5H)-furanone (**1**) in aqueous media into succinic acid **3** has been taken into consideration by us when planning syntheses based on it.

EXPERIMENTAL

Procedure for Obtaining Succinic Acid (3) from 5-Hydroxy-2(5H)-furanone (1). A solution of furanone **1** (1.0 g, 10 mmol) in water (8.6 ml) was stirred at 60°C for 3-24 h. The reaction mixture was evaporated at reduced pressure. Ethanol (5 ml), chloroform (10 ml), and a small quantity of TsOH were added to the residue, and the mixture was boiled for 10 h with azeotropic distillation of water. The esterification products obtained were analyzed by GLC in a Chrom 4 (Czechoslovakia) instrument with a flame-ionization detector and a glass column (300 × 0.3 cm). Carrier gas was nitrogen at 30 ml/min. The carboxylic acid ethyl esters were determined quantitatively on polymethylphenylsiloxane oil (PPMS-4), (15% on Chromaton N-AW DMCS) at a column temperature of 150°C, evaporator and detector temperatures were 220°C. The time for diethyl ester **4** to emerge was 345-355 sec.

Procedure for Detecting Dicarboxylic Acid Anhydrides in Nonaqueous Solutions of 5-Hydroxy-2(5H)-furanone. A test sample (1-2 drops) of the reaction mixture, obtained by heating aqueous solutions of furanone **1** at various pH values at 60-80°C, was mixed with freshly prepared reagent solution (3-4 drops) containing a 5% alcoholic solution of $FeCl_3$, acidified with HCl, and saturated with $NH_2OH{\cdot}HCl$. The mixture was evaporated and water (several drops) was added to open the anhydride. No change was observed in the color of the mixture in each case.

Procedure for Detecting Enols in Nonaqueous Solutions of 5-Hydroxy-2(5H)-furanone. A 1% alcoholic solution (1-2 drops) of $FeCl_3$ was added to an alcohol solution of the reaction mixture test sample. No change was observed in the color of the solution.

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