

CATALYTIC OXIDATION OF FURAN AND HYDROFURAN COMPOUNDS.

7.* PRODUCTION OF 2(5H)-FURANONE BY OXIDATION OF FURFURAL WITH HYDROGEN PEROXIDE AND SOME OF ITS TRANSFORMATIONS IN AQUEOUS SOLUTIONS

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Data on the synthesis of 2(5H)-furanone by the oxidation of furfural with aqueous hydrogen peroxide under the conditions of autocatalysis by the accumulating acids and also in the presence of catalytic amounts of Cr(VI) and Mo(VI) compounds are presented. Some transformations of 2(5H)-furanone in aqueous solutions are studied: Hydrolysis, oxidation by potassium permanganate, complex formation with the ions of certain d-metals.

Keywords: 2(5H)-furanone, hydrolysis, complexation, oxidation.

2(2H)-Furanone (**1**), the parent of the class of 2-butenolides, is a valuable reagent in fine organic synthesis [2]. Moreover, in compositions with dicarboxylic acids it is used as a stimulator of the growth of plants (grapes, vegetables, corn, cotton, etc.) and also as a medical agent in fish farming, as a wood antiseptic, and a plasticizer [3-6].

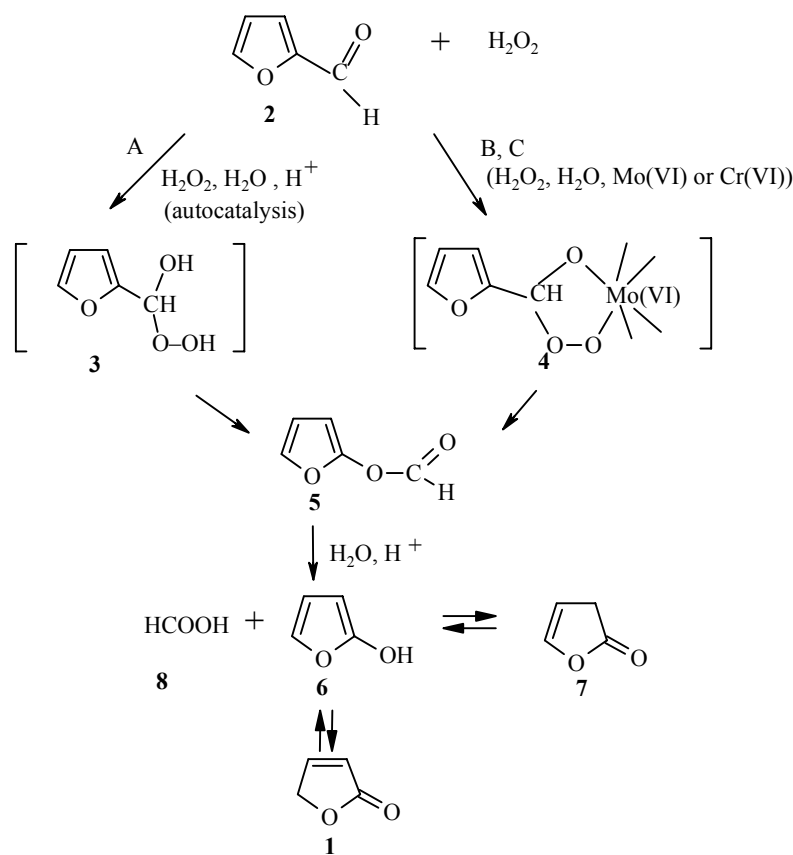
Most methods for the production of furanone **1** are based on the use of substituted butanoic acids, butanolides, and ethers of hydroxyfuran as starting compounds. Thus, it is formed when dihydroxy-, dichloro-, dibromo-, or hydroxychlorobutyric acids are heated [7-14]. A series of methods are based on the transformations of α -bromo- or α -hydroxybutyrolactones when heated in the presence of acids or amines [15-17]. Methods are also known for the production of furanone **1** by pyrolysis of 2,5-diacetoxy-2,5-dihydrofuran and acid hydrolysis of 2-acetoxy- or 2-methoxyfuran [18-21], by catalytic oxidation of vinylacetic acid with molecular oxygen followed by cyclization of the product [22], by reduction and thermolysis of the adduct of furan with maleic anhydride [23], by photolysis of diazobutyrolactone [24], and others. All the above methods are multistage processes and involve the use of difficultly obtainable and in a number of cases toxic starting materials.

* For Communication 6, see [1].

We found that furanone **1** is formed with yields of 35-40% together with other products during the reaction of the readily obtainable furfural **2** with aqueous hydrogen peroxide [25, 26]. In a more recent paper the production of lactone **1** with a yield of 37% by the reaction of furfural with 30% hydrogen peroxide in the two-phase water-dichloroethane system in the presence of sodium sulfate was described [27]. Further study of the possibilities of producing furanone **1** by peroxide oxidation of furfural **2** is therefore of undoubted interest.

In the present paper we present the results of an investigation on the oxidation of furfural **2** by aqueous hydrogen peroxide under the conditions of autocatalysis by the acids that accumulate [25, 28] (method A) and also in the presence of compounds of Mo(VI) (method B) or Cr(VI) (method C). They have made it possible to develop new comparatively simple methods for the production of furanone **1**.

Scheme 1



The course of the process was monitored by UV spectrophotometry (by the consumption of aldehyde **2**), titrimetry, and TLC (the formation of peroxy compounds and acids). The composition of the reaction products was determined by TLC and HPLC (using authentic samples).

The composition of the oxidation products was established to depend on the conditions of the process. In the case of oxidation according to path A (scheme 1) the highest yields of the product **1** (35-40%) were obtained with a 1:22 molar ratio of aldehyde **2** and hydrogen peroxide at 70-98°C and using 15% aqueous hydrogen peroxide. The reaction was continued until the initial aldehyde **2** had been completely used up and the residual peroxides had decomposed (approximately 4-5 h). Under the indicated conditions succinic acid was obtained with a yield of 35-40% in addition to furanone **1**. As well as the main products the reaction mixture contained the cyclic and open forms of *cis*- β -formylacrylic acid, fumaric acid, and maleic acid. The latter dissolves well in furanone **1**, and this hindered its isolation in the pure form.

In order to exclude the formation of maleic acid, which interferes with the isolation of furanone **1**, we used compounds of Mo(VI) or Cr(VI) as catalysts (scheme 1, paths B and C respectively). In the presence of these catalysts (Ct) maleic acid is formed in trace quantities, which simplifies the isolation of furanone **1** and secures a high degree of purity. Moreover, the use of the catalyst made it possible to reduce the duration of decomposition of the peroxy compounds and, consequently, the whole process.

The oxidation of furfural in the presence of sodium molybdate (path B) was conducted with a (2)–H₂O₂–Ct molar ratio of 1:3.5:0.05 at 60°C with 30% hydrogen peroxide. Under these conditions furanone **1** was obtained with a yield of 30-35%, the yield of succinic acid was reduced to 20%, and the products did not contain maleic acid. Tartaric and malic acids were also formed in amounts comparable with those of succinic acid. The process took ~5 h. Oxidation in the presence of potassium bichromate (path C) was realized with 38% hydrogen peroxide in molar ratio (2)–H₂O₂–Ct 1:5.4:0.025 at 60°C. Here, together with the desired product **1** (yield 25-30%), the reaction mixture also contained tartaric, malic, succinic, and *cis*-β-formylacrylic acids with an overall yield of 45-50%. The process took approximately 12 h.

During study of the mechanism of the transformations described above by the indicated methods it was established that compound **1** is formed through peroxide products of one type. The main difference lies in the fact that during autocatalysis by the formed acids the process takes place through the hydroxyhydroperoxide of furfural **3** (Scheme 1, path A), which had been previously isolated from the reaction mixture and studied [25]. In the presence of the Mo(VI) and Cr(VI) compounds it takes place through adducts with supposed structure **4** (Scheme 1, paths B and C), which were detected by chromatography. We assume that ozonides **4** are transformed as a result of Baeyer–Villiger rearrangement by analogy with peroxide **3** into 2-formyloxyfuran **5**. The latter is hydrolyzed with the formation of a mixture of 2-hydroxyfuran **6** and its tautomers **1** and **7**, which were detected in the reaction mixture by GLC and chromato-mass spectrometry. The most stable of the indicated products is furanone **1**, which was isolated in the pure form [25, 26]. At the same time, other substances are produced as a result of oxidative and hydrolytic transformations of compounds **6** and **7** catalyzed by formic acid **8** that is formed. The acid **8** is the first acid product of the reaction of furfural with hydrogen peroxide. Its catalytic role in the process has been demonstrated kinetically [25].

Furanone **1** that we obtained by the methods described above is a colorless liquid soluble in water, benzene, ether, ethanol, and chloroform and insoluble in carbon tetrachloride.

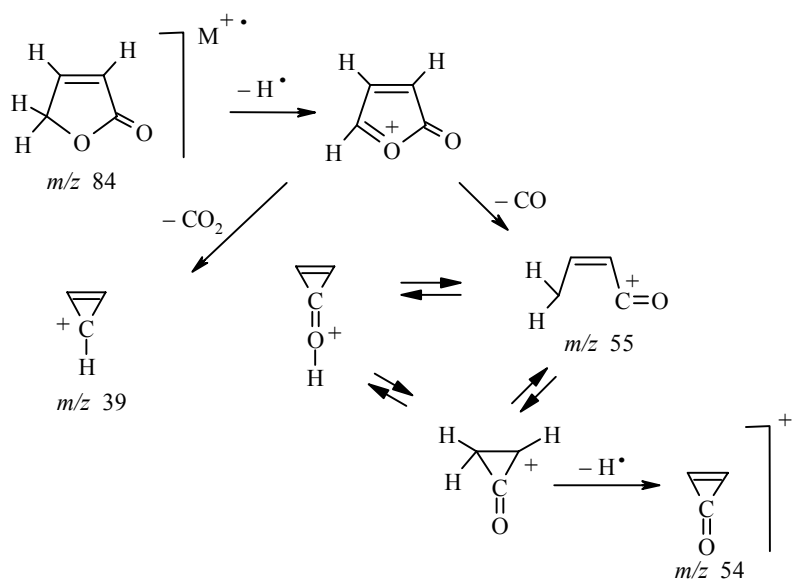
The UV spectrum of furanone **1**, recorded in the range of 185-300 nm at 20°C in aqueous solution at pH 6.5-7.0, has a maximum at 207 nm, irrespective of the concentration. The nature of the spectrum and the values of the optical density of solutions of lactone **1** do not change with time, indicating that it is stable under the given conditions. The molar extinction coefficient is in the order of 10⁴ l/mol·cm. In the range of concentrations 1-13·10⁻⁵ M a linear relation is observed between the optical density and the concentration of furanone **1**. It is approximated by equation: $y = 0.889x + 0.053$, which makes it possible to determine its content in aqueous solutions from the variation of the optical density at wavelength of 207 nm.

A molecular ion with M⁺ 84 is formed at the dissociation of furanone **1** under electron impact. As a result of the removal of an H atom and CO molecule from it the most intense ion with *m/z* 55 appears, and its dissociation with the ejection of an H atom and CO₂ molecule leads to the appearance of an ion with *m/z* 39 (Scheme 2).

The presence of several reaction centers in the molecule of furanone **1** and its unique ability to dissolve both in water and in most organic solvents put this compound in the series of prospective reagents for organic synthesis.

In connection with this it is important to obtain data on the stability of lactone **1** in aqueous solutions at various pH values and also on some of its reactions in aqueous solutions that may be useful for the analytical determination of this lactone.

Scheme 2



The hydrolysis of lactone **1** under various conditions was studied by the UV spectroscopic method described above. Analysis of the UV spectra of acidic solutions of furanone **1** (pH 2-3, c $2 \cdot 10^{-5}$ M) kept at room temperature for up to 30 days and also after boiling for 30 min showed that they remained identical to the spectrum of its neutral aqueous solution (an absorption maximum at 207 nm). This fact demonstrates the high stability of lactone **1** in acidic media. A different picture is observed for its aqueous solutions at pH > 7.

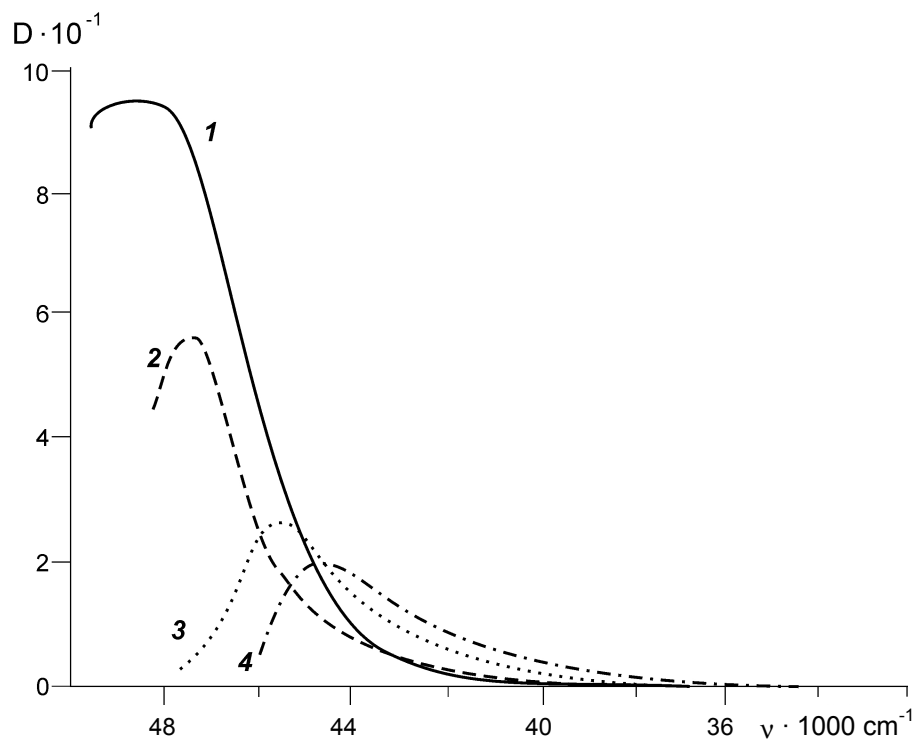
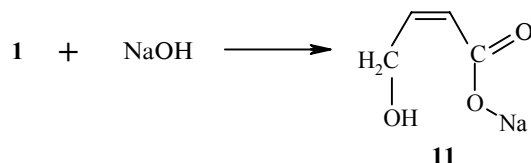


Fig. 1. The UV spectra of furanone **1** in solutions of alkali with various concentrations at given value of $[1] = 1 \cdot 10^{-4} \text{ mol/dm}^3$: 1) in water; 2) in 0.01 N NaOH; 3) in 0.1 N NaOH; 4) in 0.5 N NaOH.

Analysis of the UV spectra of solutions of lactone **1** (pH 7.8-12, $c (2-8) \cdot 10^{-5}$ M), recorded at various times after preparation, showed that its content is greatly reduced. Even at pH 7.8 after 24 h furanone **1** was already absent in the reaction medium. It is noteworthy that the absorption maximum in the UV spectrum of the alkaline solution of lactone **1** is shifted toward the long-wave region compared with its neutral solution, and the shift is larger, the higher the concentration of alkali (Fig. 1). The presented data indicate a decrease in the stability of furanone **1** in media with $\text{pH} > 7$, and this is probably explained by the formation of a salt of 4-hydroxy-2-butenic acid (**11**):

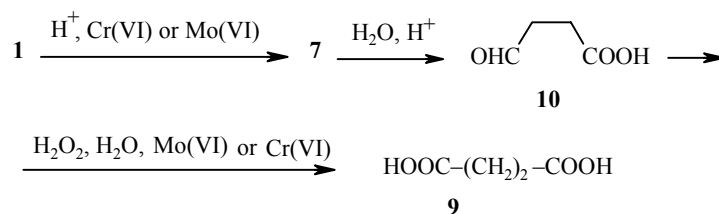


The results of the spectral investigations of the stability of lactone **1** agree with data on its hydrolytic transformation into salt **11** in the presence of alkali, which we obtained by back titration [29]. In alkaline solutions, depending on the concentration of furanone **1** and alkali, it goes to 30-70% in 30 min.

The possibility of oxidizing furanone **1** under the conditions of the peroxide oxidation of furfural **2** in the presence of compounds of Mo(VI) and Cr(VI) was studied. These data were of independent interest and also made it possible to form an opinion about the transformations of lactone **1** during oxidation of furfural **2**.

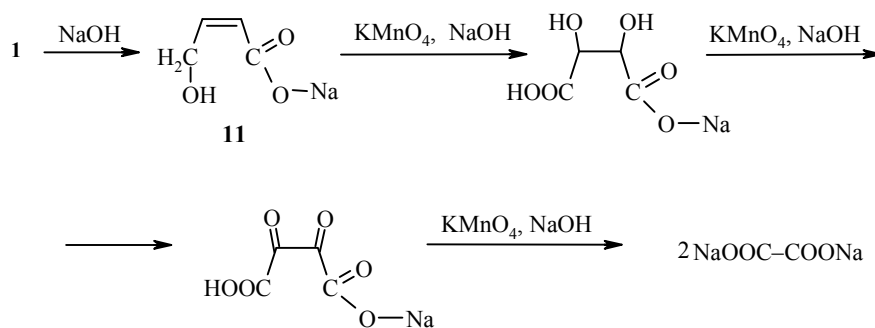
The reaction of furanone **1** with hydrogen peroxide in the presence of Mo(VI) and Cr(VI) compounds was conducted at pH 1-2, 60°C, and molar ratio (1)–H₂O₂–Cr–HCOOH 1:3.5:0.05:1. Lactone **1** was extremely stable under these conditions; after 50 h the degree of its transformation amounted to not more than 50%, which made it possible to isolate it in the form of the target product at oxidation of furfural with hydrogen peroxide under analogous conditions.

Preferential conversion into succinic acid **9** is common to the reaction of furanone **1** with hydrogen peroxide in the presence of both sodium molybdate and potassium bichromate (data from HPLC). In the case of use of potassium bichromate small amounts of oxalic, maleic, and fumaric acids were also formed, and with sodium molybdate malic, tartaric, and malonic acids, identified by HPLC, were formed. The formation of acid **9** during catalytic oxidation of lactone **1** may be due to the following transformations:



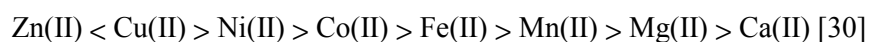
In this process the equilibrium is displaced toward the isomeric lactone **7**, which is hydrolyzed to the aldehyde of succinic acid **10**, and this is oxidized irreversibly to acid **9**.

The oxidation of furanone **1** by potassium permanganate in aqueous acidic, neutral, and alkaline solutions at room temperature was also studied. A large excess of potassium permanganate and acid or alkali was used in the reaction. According to GLC, lactone **1** was stable in acidic and neutral media. In an alkaline medium with high pH values (~12) vigorous oxidation occurred. The actual consumption of potassium permanganate expended on the reaction was determined by back titration of the excess of unreacted potassium permanganate with sodium thiosulfate. It was established that 12 mol of potassium permanganate are used for 1 mol of furanone **1**. This fact and also the data presented above on the alkaline hydrolysis of compound **1** made it possible to represent its transformation by the following scheme:



According to the scheme, in an alkaline medium it is not furanone **1** that undergoes oxidation but its hydrolysis product – salt **11**, which as shown above is readily formed from lactone **1** in the presence of an excess of alkali. In an acidic medium, however, the lactone ring is stable, and oxidation of the double bond by potassium permanganate does not occur obviously on account of decrease of its electron-donating activity resulting from conjugation with the electron-withdrawing ester group.

We studied the complexation of furanone **1** with copper and cobalt acetates. According to Irving's rule, for the majority of oxygen- and nitrogen-containing ligands, irrespective of their nature, the following order of thermodynamic stability of the complexes is observed at the formation of complexes with equally-charged ions:

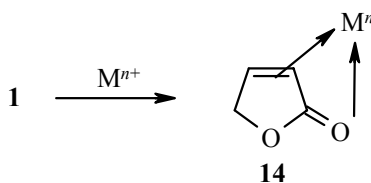


In this series the Cu(II) ions form the most stable complexes, usually colored, and this is convenient for use of control of the complexation process.

During the reaction of furanone **1** and copper or cobalt salts in water–alcohol solutions brown crystalline products are formed. The participation of furanone **1** in complexation was confirmed by the data from the IR spectra of the products, in which a shift of the band for the carbonyl group by 30–40 cm^{-1} toward the low-frequency region (1740–1750 cm^{-1}), characteristic of complexation, was observed [31].

Calculations on the basis of the derivatograms of the complexes of lactone **1** with the copper salt showed that the Cu(II) ion in the obtained compound is attached to one molecule of furanone **1** and first-sphere water according to the formula $[\text{Cu}(\text{H}_2\text{O})_3\text{C}_4\text{H}_4\text{O}_2](\text{CH}_3\text{COO})_2^-$ (**12**). The complex of furanone **1** with the cobalt salt has the composition $[\text{Co}(\text{H}_2\text{O})_2\text{C}_4\text{H}_4\text{O}_2](\text{CH}_3\text{COO})_2$ (**13**).

The structure of the obtained products agrees with the known data that the localization center of the coordination bond in the complexes of organic acids and esters is the oxygen atom of the carbonyl group [32]. Here, irrespective of the hardness or softness of the acids, the volume and nature of the radicals, and also the electronic effects that they cause, in the IR spectra of the complexes a decrease (compared with the free ligands of the molecules of acids and esters) is always observed in the frequency of the carbonyl stretching vibrations. This provides convincing evidence for the formation of a metal–carbonyl oxygen bond. On the other hand the C=C double bond in the molecule of furanone **1** can also take part in complexation. In view of the presented data the following structure **14** can be proposed for the adduct of compound **1** with a *d*-metal ion:



EXPERIMENTAL

The purity of furanone **1** was determined by GLC on a Chrom-5 chromatograph (glass column, 2.5 m × 4 mm, 15% of PMFS on Chromaton N-AWD MCS, grain size 0.250-0.315 mm, carrier gas nitrogen, 30 ml/min, column temperature 140°C, detector temperature 180°C, evaporator temperature 240°C). The sample volume was 0.4 µl, sensitivity $128 \cdot 10^{-10}$, chart speed 1.5 cm/min. According to GLC the mass fraction of furanone **1** amounted to 98.78. The IR spectrum of furanone **1** was recorded on a Specord IR-75 instrument in the region of 4000-650 cm^{-1} (thin layer, sodium chloride prism). The IR spectra of complexes **12** and **13** and also of lactone **1** for comparison were obtained on an UR-20 spectrophotometer (in vaseline oil). The UV spectra of furanone **1** and of the reaction mixtures were recorded on a Specord UV-Vis spectrophotometer. The mass spectra were obtained on a Hitachi M-80B instrument with an INNOWAX quartz capillary column (PEG 20 M), 50 m × 0.2 mm. The carrier gas was helium. The ^1H NMR spectra were recorded on a Varian T-60 spectrometer (60 MHz).

Carboxylic acids were determined quantitatively by modified reverse phase HPLC using an RIDK-101 detector. The reaction mixtures containing oxalic, tartaric, malonic, malic, and succinic acids were separated on an HPP 4001 chromatograph (Czech) with two successive glass columns filled with Separon SC-X C-18 (150 mm × 3.3 mm). The consumption rate of the mobile phase (an aqueous suspension of acetic acid) amounted to 0.3 cm^3/min . The sample volume was 10 µl. The analysis took 20 min. The retention times of acids in the model mixture were: Tartaric 8.25, malic 9.45, malonic 10.25, succinic 14.33 min.

Production of 2(5H)-Furanone (1) by Oxidation of Furfural with Hydrogen Peroxide. A. Under Conditions of Autocatalysis by the Accumulated Acids. Mixture of furfural **2** (168 ml, 2 mol) and 15% solution of hydrogen peroxide (1000 g, 4.6 mol) was stirred in a three-necked flask, immersed in a thermostat and provided with a stirrer and a reflux condenser, at 70°C until 85-90% of compound **2** (according to GLC) had been consumed. The thermostat was then stopped, and the reaction mass was brought to boiling at 96-98°C and boiled for 60-80 min, after which its temperature began to fall spontaneously. The oxidate was cooled to room temperature and evaporated under vacuum. The crystalline succinic acid was separated from the concentrate by vacuum filtration. (The yield of the crude acid was 30-33% on the mass of aldehyde **2**.) According to chromatography and titrimetry, the filtrate contained 35-40% of furanone **1**, 45-50% of organic $\text{C}_1\text{-C}_4$ acids, and 10-15% of water. The product **1** was extracted from the filtrate with chloroform (5 × 50 ml). The extract was dried over sodium sulfate, and furanone **1** was separated by vacuum distillation from the residue after removal of chloroform; bp 90-92°C (12-13 mm Hg). Yield 25-30% (on the mass of furfural **2**). IR spectrum, ν , cm^{-1} : 1744, 1782 (C=O group of butenolides), 1050-1200 (–C–O–C–). ^1H NMR spectrum, δ , ppm, J (Hz): 4.95 (2H, t, $J = 1.2$, CH_2); 6.15 (1H, d, $J = 6$, 4-H); 7.85 (1H, d, $J = 6$, 5-H).

B. In the Presence of Sodium Molybdate. The oxidation was carried out in apparatus similar to that described in method A. In the flask we placed furfural **2** (50 ml, 0.6 mol), and with stirring we added in 3-5 portions (over 20-30 min) previously prepared solution of sodium molybdate (7.6 g, 0.03 mol) in 30% hydrogen peroxide (215 ml, 2.1 mol). The flask was cooled with water for 1 h (temperature of reaction medium 60°C), and the process was then continued in a thermostat (60°C) until the peroxy compounds had been completely used up (according to titrimetry and TLC). The oxidate was then cooled to room temperature and treated as described in method A. The yield of the technical grade succinic acid amounted to 20%. Yield of furanone **1** 30-35%.

B. In the Presence of Potassium Bichromate. In the flask (see method A) we placed furfural **2** (6.96 g, 0.072 mol) and water (6.4 ml). We then added potassium bichromate (0.528 g, 0.0018 mol) and in small portions over 30 min at 20°C 38% solution of hydrogen peroxide (25 ml, 0.391 mol). The temperature of the reaction mixture in the thermostat was then brought to 60°C. The reaction was carried out at this temperature for 8 h until the peroxy compounds had been completely used up (according to titrimetry and TLC). The oxidate was then cooled to room temperature and evaporated under vacuum. The residue was extracted with chloroform, the residue after removal of chloroform was distilled under vacuum, and furanone **1** was obtained. Yield 27-30%.

Oxidation of 2(5H)-Furanone (1) with Hydrogen Peroxide in the Presence of Potassium Bichromate. The reaction was carried out in the apparatus similar to that described in method A. To mixture of furanone **1** (5.1 ml, 0.072 mol), water (6.4 ml), potassium bichromate (0.647 g, 0.0018 mol), and formic acid (2.72 ml, 0.072 mol) 30% aqueous hydrogen peroxide (25 ml, 0.252 mol) was added in small portions over 30 min under stirring at 20°C. The temperature of the reaction mixture was then brought to 60°C. The reaction was then continued for more than 48 h at 60°C until peroxy compounds had been completely used up (according to titrimetry and TLC). The composition of the products from the oxidation of furanone **1** was determined by HPLC.

Oxidation of 2(5H)-Furanone (1) with Hydrogen Peroxide in the Presence of Sodium Molybdate. The reaction was carried out by the method described above, but previously prepared solution of sodium molybdate (0.87 g, $3.6 \cdot 10^{-3}$ mol) in 30% solution of hydrogen peroxide (25.2 ml, 0.0252 mol) was used instead of potassium bichromate. We placed furanone **1** (5.1 ml, 0.07 mol) and formic acid (2.72 ml, 0.072 mol) in the flask together with the other reagents. The reaction was continued for more than 48 h until peroxy compounds had been completely used up. The composition of the products was determined by HPLC.

Synthesis of Complexes 12 and 13. To solution of salt $(\text{MeCOO})_2\text{Cu} \cdot \text{H}_2\text{O}$ (analytical grade) (1.12 g, 0.0056 mol) in ethanol (10 ml) we added furanone **1** (1.89 g, 0.0225 mol) in ethanol (10 ml). The reaction mixture was boiled for 1 h with a reflux condenser, and the precipitate was filtered off and washed on the filter with ethanol and ether. We obtained 0.27 g (15% on the initial lactone **1**) of complex **12**. IR spectrum, ν , cm^{-1} : 3600-3200 (broad diffuse band), 1751, 1742, 1710, 1580, 1570, 1370.

Complex **13** was obtained similarly from furanone **1** and salt $(\text{MeCOO})_2\text{Co} \cdot \text{H}_2\text{O}$. Yield 82% (on the initial lactone **1**). IR spectrum, ν , cm^{-1} : 3352, 3144, 1744, 1688, 1568, 1496, 1392.

Complexes **12** and **13** were analyzed for the metal content by atomic absorption spectrophotometry [33], and the crystallization water was determined by derivatography [34]. The derivatograms of the complexes were recorded on a Paulik–Paulik–Erdey derivatograph in the range of 20-500°C in air (standard Al_2O_3 , corundum crucible).

Stability of 2(5H)-Furanone (1) in an Acidic Medium. Solution of lactone **1** in water (c $2 \cdot 10^{-5}$ M) was kept at pH 2-3 (created by the addition of sulfuric acid) at 20-25°C for 30 days or boiled for 30 min, after which its UV spectrum was recorded. The UV spectra were identical with the spectrum of a neutral solution of furanone **1** of the same concentration.

Hydrolysis of 2(5H)-Furanone (1) in an Alkaline Medium. Solution of lactone **1** (c $2 \cdot 10^{-5}$ M) in 0.01-1.0 N sodium hydroxide was kept for 30 min, 1, 3, 8, and 12 h, after which its UV spectrum was recorded and compared with the spectrum of a solution of sodium hydroxide of the same concentration.

Oxidation of 2(5H)-Furanone (1) with Potassium Permanganate in a Strongly Alkaline Medium. To furanone **1** (0.05 ml, $6.8 \cdot 10^{-4}$ mol) we added 5 N sodium hydroxide (10 ml) to pH 12. After 15 min we added 1 N potassium permanganate (40 ml, 0.04 mol). The obtained green solution was stirred for 30 min, and 5 N sulfuric acid (20 ml) was added. (Here the solution became violet colored.) When the release of gas had stopped we added 2 N potassium iodide (25 ml, 0.05 mol) to determine the unreacted potassium permanganate. The released iodine was titrated with 5 N sodium thiosulfate to a cloudy solution resulting from the formation of sulfur.

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