

## OXIDATION OF FURANS (REVIEW)

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*Published data and the results of the authors' own investigations on the catalytic oxidation of furan and its homologs under various conditions are reviewed. The mechanisms and the characteristics and composition of the products from the transformations of furans are discussed in relation to the type of oxidizing agent and the reaction conditions. The prospects of using the oxidation processes of furan and its homologs in the synthesis of alkoxy- and dialkoxydihydrofurans, 5-alkoxy-2(5H)-furanones,  $\beta$ -formylacrylic acid, maleic acid, and its dialdehyde are indicated.*

**Keywords:** 2-alkoxy-5-hydroperoxy-2,5-dihydrofuran, 5-alkoxy-2(5H)-furanone, malealdehyde bis(2,4-dinitrophenyl)hydrazone, 5-hydroxy-2(5H)-furanone, 2,5-dihydroxy-2,5-dihydrofuran, 2,5-dimethoxy-2,5-dimethyl-2,5-dihydrofuran, 2,5-dimethylfuran,  $\beta$ -formylacrylic acid 2,4-dinitrophenylhydrazone, diepoxides, 2,5-diethoxy-2,5-dihydrofuran, maleic acid, maleic anhydride, malealdehyde, 2-methylfuran, molecular oxygen, monoepoxides, peracids, hydrogen peroxide, peroxides, fumaric acid, furan, endoperoxides, epoxy lactones, succinic acid, vapor-phase oxidation, photosensitized oxidation.

The oxidation reactions of furans have attracted the attention of researchers over many years. The expediency of a comprehensive study of oxidation processes in furan and its homologs arises from the possibility of obtaining a whole series of prospective compounds for fine organic synthesis and the chemistry of biologically active substances on the basis of these processes. Molecular oxygen or peroxides (peracids and hydrogen peroxide) have been used as oxidizing agents in certain oxidation reactions of furans.

### 1. Oxidation of Furan and its Homologs with Molecular Oxygen

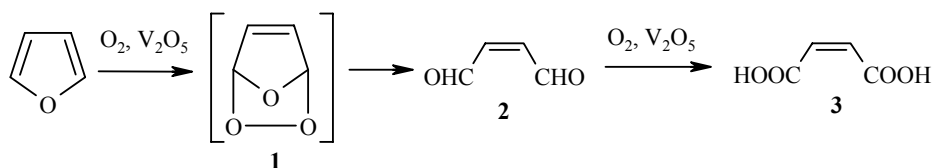
The results of investigations of the processes involved in the vapor-phase oxidation of furans with molecular oxygen are presented in [1-8]. In the opinion of the authors in [1] the oxidation of furan in the presence of vanadium(V) oxide takes place through a stage involving the formation of the endoperoxide **1**, structurally related to ozonides, and malealdehyde (**2**). This is then oxidized to maleic acid (**3**), which is isolated as the main product [1] (Scheme 1).

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Scheme 1

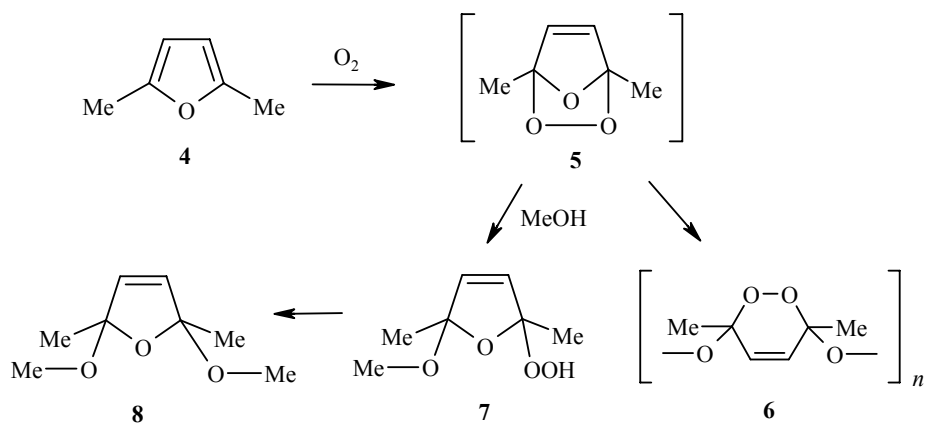


It was shown [2] that the vapor-phase catalytic oxidation of furan homologs with molecular oxygen takes place through the formation of furancarboxylic acids, which are then decarboxylated to furan. The further mechanism of the oxidation of the homologs is similar to the scheme presented above [1].

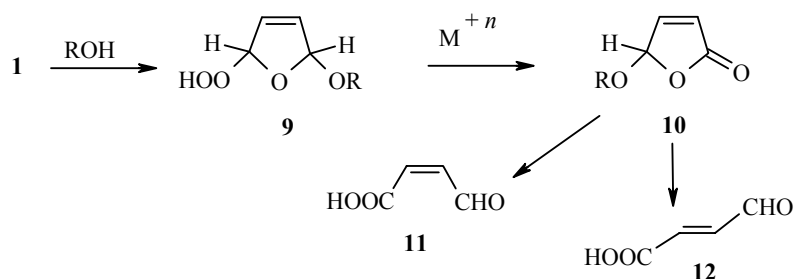
Investigations of the vapor-phase oxidation of furan and its oxidation in the presence of metal-containing catalysts [3-8] showed that the main oxidation products are maleic anhydride and carbon monoxide and dioxide with small amounts of acetic and oxalic acids. It was established that the vapor-phase oxidation of furan, in contrast to its derivatives, is more selective; the yield of maleic anhydride is higher, and complete transformation of the furan is achieved in a shorter period.

The photosensitized oxidation of furan and alkylfurans by molecular oxygen under various conditions has been studied widely [9-24]. The photosensitized oxidation of 2,5-dimethylfuran (4) in absolute methanol with UV irradiation for several days in the presence of eosin was investigated in [9]. In the opinion of the authors the endoperoxide 5 is formed at the initial stages of the reaction. It is converted either into the polymer 6 or changes in reaction with methanol into the hydroperoxide 7, from which 2,5-dimethoxy-2,5-dimethyl-2,5-dihydrofuran (8) is formed [9] (Scheme 2).

Scheme 2



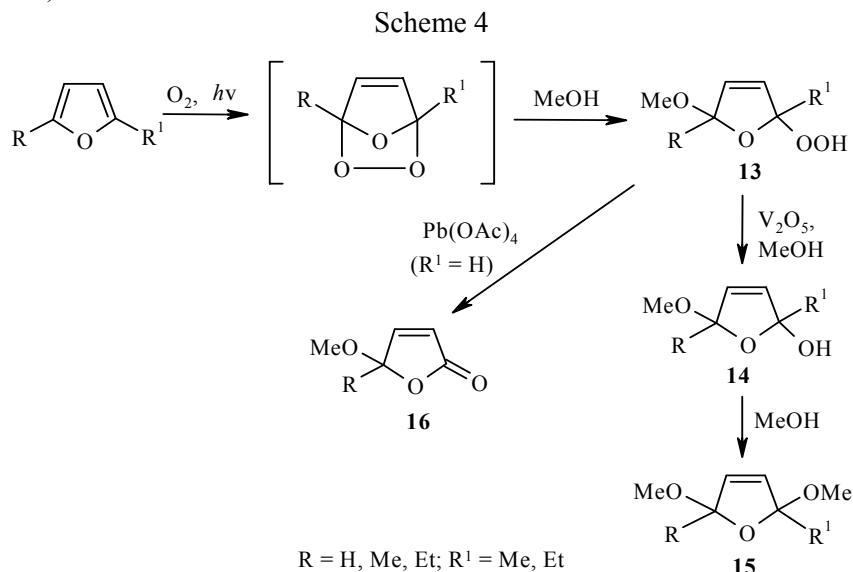
Scheme 3



R = Me, Et; M – metal

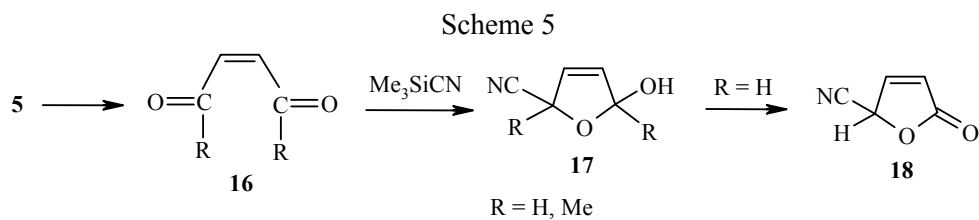
The photochemical oxidation of furan in the presence of other sensitizers (rose Bengal or methylene blue) was studied in [10]. It is assumed that in this case the reaction takes place through the formation of the endoperoxide **1**; this is converted in an alcohol medium into 2-alkoxy-5-hydroperoxy-2,5-dihydrofuran **9**, which changes in the presence of a metal-containing catalyst into 5-alkoxy-2(5H)-furanone **10**. After acid hydrolysis of compound **10** the *cis* and *trans* isomers of  $\beta$ -formylacrylic acid **11** and **12** are formed [10] (Scheme 3).

Investigations of the photosensitized oxygenation of the homologs of furan [11] showed that the photooxidation of various alkylfurans with oxygen in the presence of rose Bengal as sensitizer in methanol takes place, like the oxidation of furan, through an endoperoxide of type **5** and a hydroperoxide of type **13**. The latter is converted by the action of  $\text{Pb}(\text{OAc})_4$  into the furanone **16** and in the presence of  $\text{V}_2\text{O}_5$  changes through the unstable compound **14** into 2,5-dimethoxy-2,5-dihydrofuran **15**, which is formed as a mixture of *cis* and *trans* isomers [11] (Scheme 4).



Thus, the authors of [9-11] revealed that the photosensitized oxidation of furan by oxygen results in the formation of 5-alkoxy-2(5H)-furanones, the *cis* and *trans* isomers of  $\beta$ -formylacrylic acid, and 2,5-dialkyl-2,5-dimethoxy-2,5-dihydrofurans. As known, other methods for the production of 2,5-dialkoxy-2,5-dihydrofurans are based either on the alkoxylation of furan in the presence of bromine [12-14] or on the electrochemical alkoxylation of furan [15-18]. The results of investigations of the photosensitized oxidation of furans by molecular oxygen have made it possible to create new methods for the production of the above-mentioned substances, which are important intermediates of organic synthesis.

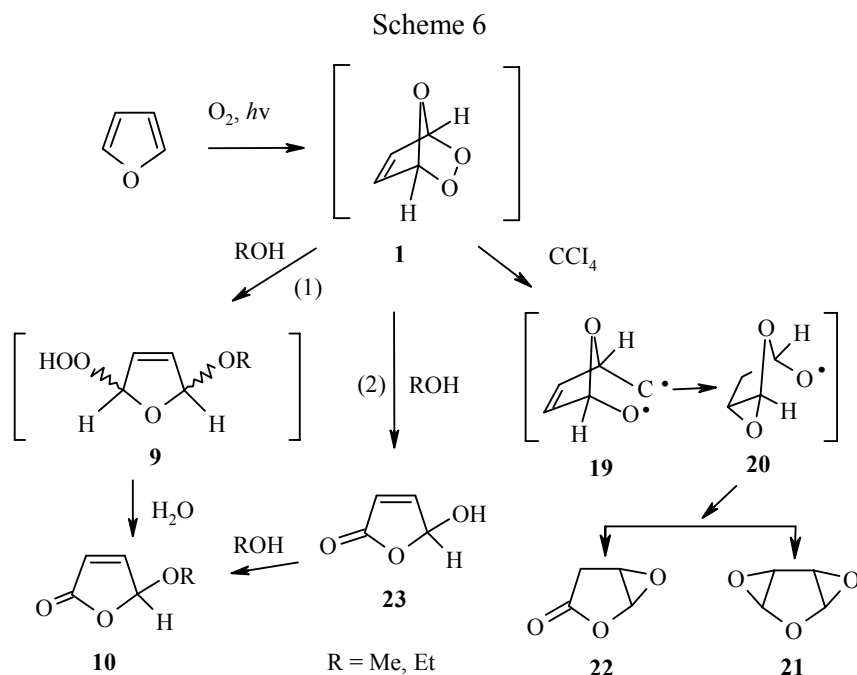
The low-temperature photooxygenation of furan and 2,5-dimethylfuran by molecular oxygen in the presence of  $\text{Me}_2\text{S}$  and  $\text{Me}_3\text{SiCN}$  was described in [19]. The process was realized in methylene chloride at  $-70^\circ\text{C}$ . The authors also mention the formation of endoperoxides of type **5**, transformed into unsaturated dicarbonyl compounds, which give products of type **17**. During the further oxidation of compound **17** ( $\text{R} = \text{H}$ ) 4-cyano-2(5H)-furanone (**18**) was obtained [19] (Scheme 5)



The structure of the endoperoxides of type **5** was confirmed by the data from  $^1\text{H}$  NMR spectroscopy [20, 21]. In addition it was established that more stable dimers are formed from them.

The intermediate products in the oxidation of furans **1** and **5** were isolated for the first time in the individual form and characterized by the authors of [22] as a result of the investigation of the photosensitized oxidation of furan and its homologs by molecular oxygen in the presence of rose Bengal in various solvents.

Here it was shown that the photochemical transformations of furan in the presence of molecular oxygen take place by the mechanism presented in scheme 6 [22].

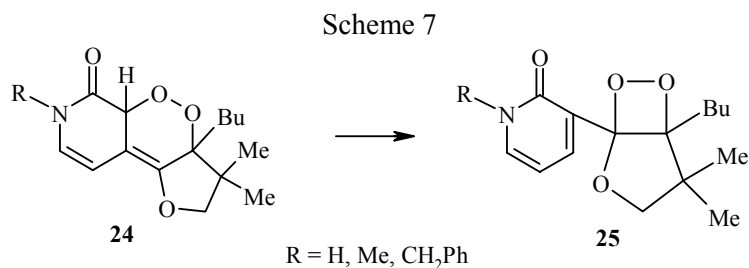


At the initial stage of the process the ozonide **1**, which is only stable at temperatures below  $-15^\circ\text{C}$ , is mainly formed. During slow heating in benzene or petroleum ether it changes into the dimer, which is more stable under normal conditions. It was established that the monosubstituted furan ozonides are less stable and less liable to form dimers than the disubstituted compounds. Further transformations of the ozonide **1** in aprotic solvents ( $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CFCl}_3$ ) are accompanied by homolytic cleavage of the O–O bond and lead to the formation of the extremely unstable intermediates **19** and **20**, which change into the di- and monoepoxides **21** and **22**.

In an alcohol medium the ozonide **1** changes either into 5-hydroxy-2(5H)-furanone **23** or into the *cis* and *trans* isomers of 2-alkoxy-5-hydroperoxy-2,5-dihydrofurans **9**, which are converted into the respective 5-alkoxy-2(5H)-furanones **10**.

The formation and structure of the endoperoxides **1** and **5** were also confirmed during a study of the composition of the products from the photooxidation of furan, 2-methylfuran, and 2,5-dimethylfuran with molecular oxygen over a wide range of temperatures ( $20$ – $360^\circ\text{C}$ ) by mass spectrometry [23].

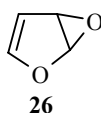
The formation of endoperoxides was also mentioned in one of the recent papers on the 1,4-addition of singlet oxygen [24]. It was established that the singlet oxygenation of 4-(4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran-5-yl)-2-pyridone during irradiation in methylene chloride at  $-78^\circ\text{C}$  in the presence of tetraphenylporphyrin leads to the nonstereospecific 1,4-addition of singlet oxygen to the 1,3-diene system of the initial substrate. The endoperoxides **24** are formed here; when heated in benzene they change into stable 1,2-dioxetanes **25** as a result of isomerization and thermal rearrangement [24] (Scheme 7).



The processes leading to the oxidation of furan and its homologs by molecular oxygen make it possible to obtain a whole series of important and difficultly obtainable compounds. At the same time they are lengthy, laborious, and energy-consuming processes. The reactions involving the peroxide oxidation of furan and its homologs examined below are to some extent free from such disadvantages [25-26].

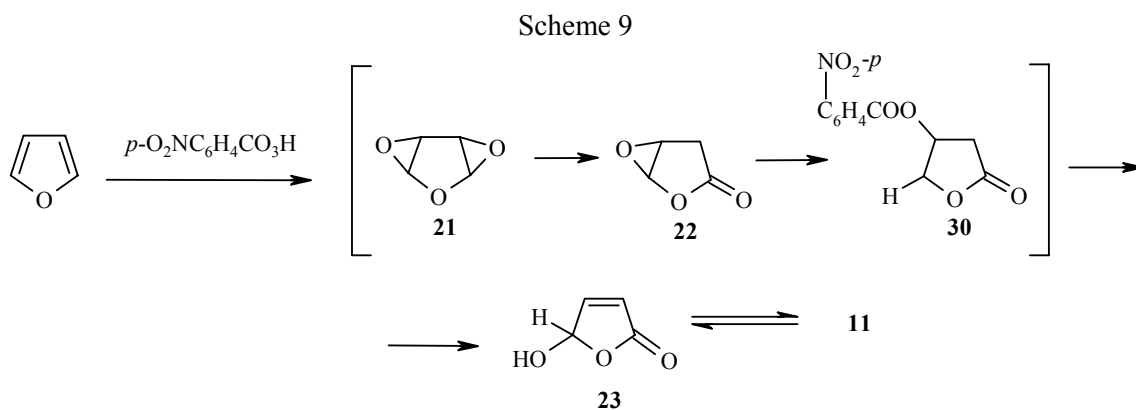
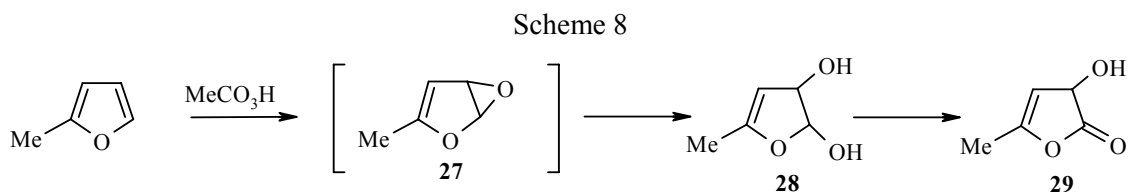
## 2. Oxidation of Furan and its Homologs by Peracids

The oxidation of furans by peracetic and perbenzoic acids was first described in [25]. The authors suggest that the monoepoxide **26** is formed initially during the oxidation of furan.



During oxidation by peracetic acid it is fully polymerized, and during the action of perbenzoic acid it is converted into the diepoxide **21**.

During the oxidation of 2-methylfuran with 70% peracetic acid crystalline substances with supposed structures **28** and **29** are formed together with resinous substances. In the opinion of the investigators they are formed according to scheme 8 [25].



The oxidation of furan by *p*-nitroperbenzoic acid in anhydrous ether was studied by the authors in [26]. *cis*- $\beta$ -Formylacrylic acid **11** was isolated from the products mixture. The authors consider that the formation of the acid **11** in the anhydrous medium also takes place through transformations of the intermediate epoxides **21** and **22** and the ester lactone **30** (Scheme 9).

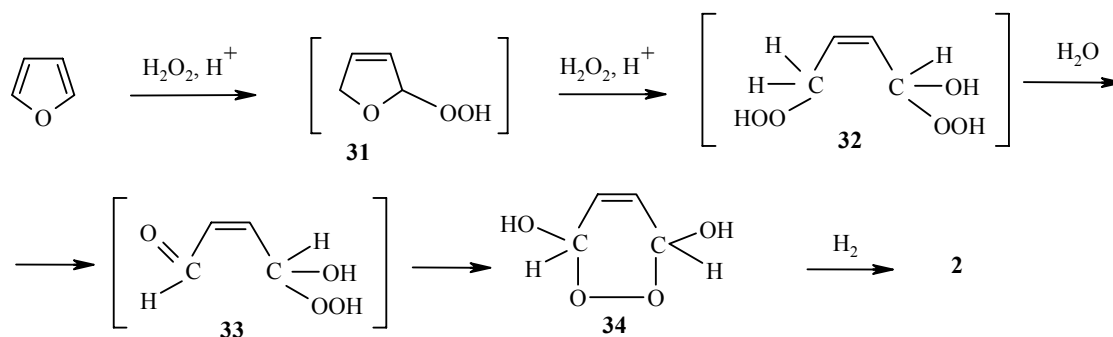
### 3. Oxidation of Furans by Hydrogen Peroxide

The oxidation reactions of furan and its homologs by hydrogen peroxide have been widely investigated [27-56]. They attract the attention of researchers because of the simplicity of execution and by possibility of obtaining a whole series of difficultly obtainable compounds more difficult to synthesize by other methods. Moreover, hydrogen peroxide is extremely useful as oxidizing agent on account of its high reactivity, its accessibility, and the ecological compatibility of the processes involving it [27].

In [28] the photosensitized oxidation of 2,5-dimethylfuran by hydrogen peroxide in methanol was investigated. The authors suggest that the peroxide photooxidation of 2,5-dimethylfuran takes place by a reaction similar to its photosensitized oxidation by molecular oxygen [9] with the formation of the ozonide **5**, which is transformed in the presence of methanol into the hydroperoxide **7** [28] (see Scheme 2).

The reaction of furan with hydrogen peroxide in the presence of sulfuric acid was studied in [29, 30]. It was suggested that this reaction leads to the formation of the unstable intermediate hydroperoxide **31**, which is converted by the action of hydrogen peroxide into the hydroxydihydroperoxide **32**. The latter in turn changes into the hydroxyhydroperoxide **33**, which rearranges to the more stable ozonide **34**. This ozonide was isolated in the individual form by the authors of [29, 30]. During catalytic hydrogenation compound **34** is converted into the malonaldehyde **2** (scheme 10), isolated in the form of the 2,4-dinitrophenylhydrazone [29, 30].

Scheme 10

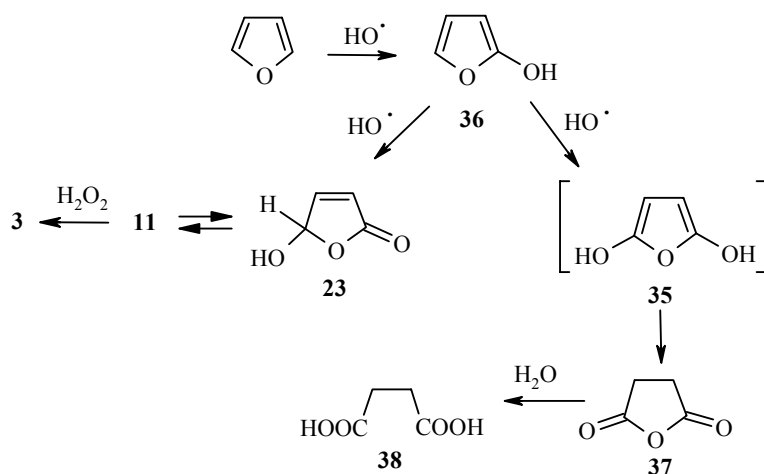


It was established [29, 30] that 2-methylfuran is oxidized to the corresponding keto aldehyde under these conditions.

The oxidation of furan by hydrogen peroxide in the gas phase at 160-170°C was investigated in [31]. Under these conditions a mixture of acids (oxalic, maleic, fumaric) was obtained. In the authors' opinion oxygen formed from the  $\text{H}_2\text{O}_2$  acts as oxidizing agent in this process, and the reaction takes place through the intermediate formation of 2,5-dihydroxyfuran.

It was suggested [32] that the peroxide oxidation of furan under the conditions of [31] is realized by a mechanism of the radical hydroxylation type on account of  $\text{OH}^\cdot$  radicals formed from the hydrogen peroxide. 2-Hydroxyfuran (**36**) is formed here at the intermediate stage and in the course of the oxidation–hydrolysis reactions gives maleic monoaldehyde **11** and succinic anhydride **37**, which are then transformed into the corresponding acids **3** and **38** [32] (Scheme 11). The formation of the products **3**, **23**, and **38** was demonstrated experimentally, and no other arguments in favor of the mechanism in [32] were presented.

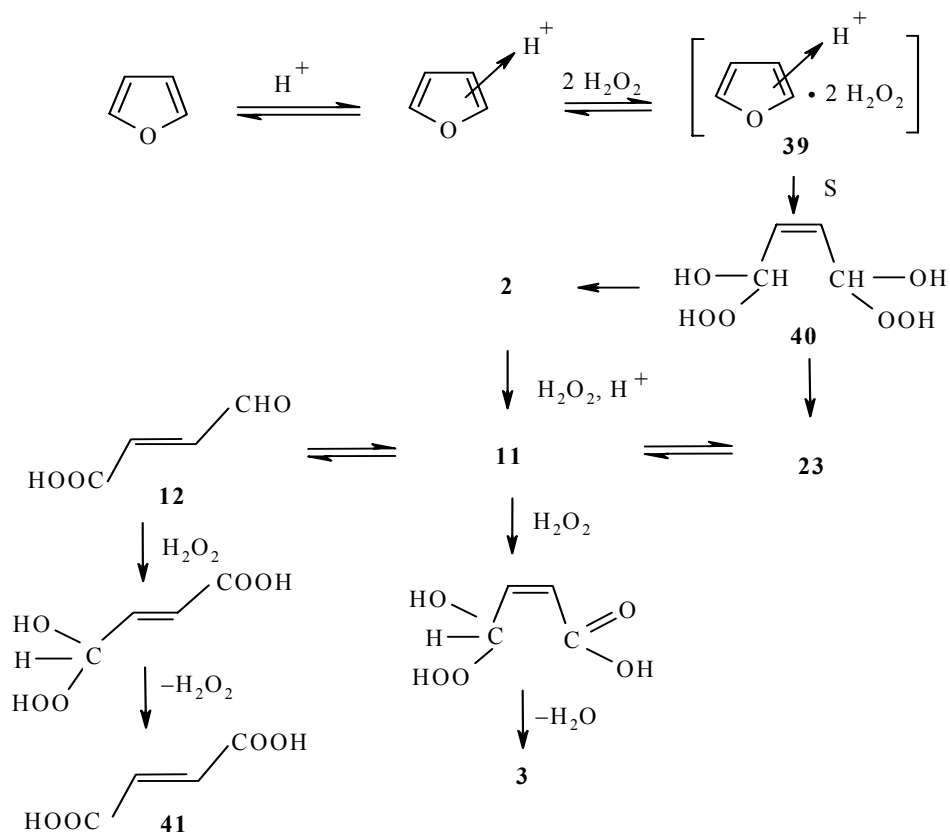
Scheme 11



The formation of the di- and monoaldehydes of maleic acid **2** and **11** in the reaction of furan with  $\text{H}_2\text{O}_2$  under acid catalysis conditions was mentioned in [33, 34].

The oxidation of furan by hydrogen peroxide in the presence of additions of mineral acids was investigated [35]. It was shown that organic peroxides are formed at the first stage of the reaction. Their formation does not require heating or the addition of acids. At the same time the production of carbonyl compounds (malealdehyde **2** and the monoaldehydes **11** and **12**) and organic acids (maleic, fumaric, oxalic)

Scheme 12



requires acid catalysis and heating to 40-100°C. It was established that increase of the concentration of acid in the reaction mixture leads to oxidation of the carbonyl compounds and promotes the accumulation of the dibasic acids. It was found that the nature of the added acid affects the rate of consumption of the furan and the qualitative composition of the obtained dibasic acids.

The effect of the nature of the solvent (water, ethanol, dioxane, tetrahydrofuran, N,N-dimethylformamide, formic acid) on the direction of the reaction in the furan–H<sub>2</sub>O<sub>2</sub> system has also been studied [35]. It was shown that the largest yield of the organic acids is observed in the presence of protophilic solvents and of dioxane in particular. The yield of the carbonyl compounds also depends on the type of solvent; their maximum accumulation is observed during the oxidation of furan in formic acid, and the minimum is observed in water.

The author of [35] suggests that furan is protonated in an acidic medium with the formation of the complex **39**, which then undergoes oxidative cleavage. The hydroperoxide **40** is formed here and is then transformed into the maleic dialdehyde **2**. The latter is oxidized to the *cis* and *trans* isomers of β-formylacrylic acid **11** and **12**, which are then oxidized further to maleic and fumaric acids **3** and **41** [35] (see Scheme 12).

Thus, the author of [35] first proposed an approach to control of the direction of the reaction of furan with H<sub>2</sub>O<sub>2</sub> by changing such factors as temperature, the nature of the solvent, and the type and amount of added acid. This made it possible to develop new methods for the synthesis of β-formylacrylic, maleic, and fumaric acids **11**, **3**, and **41** based on the oxidation of furan with hydrogen peroxide in the presence of HCl and a co-solvent (dioxane, ethanol) at 70-75°C. It was not possible to isolate maleic dialdehyde under these conditions [35].

#### 4. Oxidation of Furans by Hydrogen Peroxide in the Presence of Compounds of Transition Metals

The oxidation of furan by hydrogen peroxide in the presence of OsO<sub>4</sub> in ethanol was realized in [36]. Maleic dialdehyde was obtained as final product.

Subsequently the idea of using compounds of metals with variable valence in the reaction of furan with H<sub>2</sub>O<sub>2</sub> was developed, and comprehensive investigations of these processes were undertaken [37-56]. In [38-40] it was shown that the use of compounds of vanadium(IV, V) as catalysts makes it possible to enhance the oxidation of furans by hydrogen peroxide substantially and to realize it at lower temperatures (60-70°C).

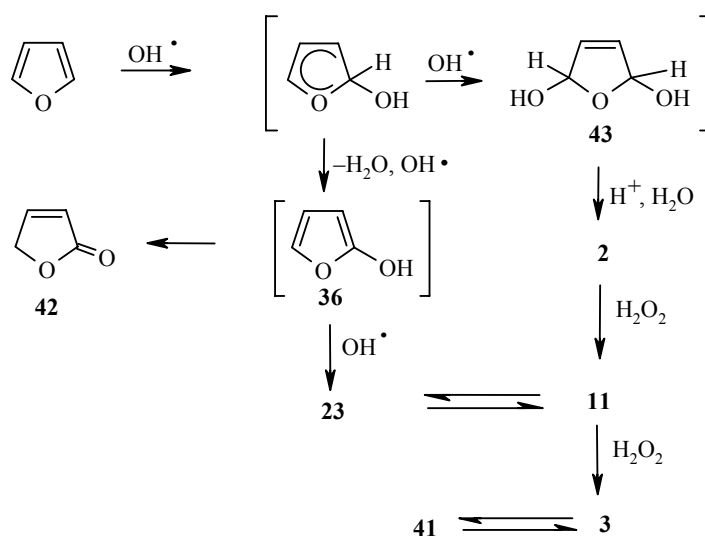
It was established [38, 40] that β-formylacrylic acid in the form of the cyclic tautomer 5-hydroxy-2(5H)-furanone (**23**), 2-(5H)-furanone (**42**), and maleic and fumaric acids **3** and **41** are formed during the oxidation of furan with aqueous hydrogen peroxide. In the opinion of the authors [38, 40] the catalytic oxidation of furan by hydrogen peroxide takes place through the stage of radical hydroxylation at positions 2 and 5 of the furan ring by OH· radicals formed in the vanadium(IV, V)–H<sub>2</sub>O<sub>2</sub> system [41, 42]. This agrees with the results from ESR investigations of the initial stages in the reaction of furan with hydroxyl radicals generated from Fenton's reagent (FeSO<sub>4</sub>–H<sub>2</sub>O<sub>2</sub>) [43, 44]. The authors [38, 40] assume that the main reaction products are formed through the hypothetical 2,5-dihydroxy-2,5-dihydrofuran (**43**) and the product of its opening – the dialdehyde **2** (Scheme 13). It was not possible to isolate the latter on account of its low stability [38].

In our researches [45-56] we studied the oxidation of furan and 2-methylfuran with hydrogen peroxide in aqueous–organic media in the presence of compounds of vanadium(IV, V) at lower temperatures (20-25°C).

Here some features of the oxidation of furan in homogeneous aqueous–organic media in the presence of water-miscible solvents [45-52] and in heterogeneous aqueous–organic media under the conditions of phase-transfer catalysis [46, 53] were revealed. In the last case phase-transfer and vanadium catalysts were used simultaneously. It was established that the composition and yields of the products from the peroxide oxidation of furan [45, 55] and 2-methylfuran [56] depend substantially on the nature of the organic solvent, the types of vanadium and phase-transfer catalyst, and the molar ratio of the reagents [45-56].



Scheme 13



During the oxidation of furan and 2-methylfuran in homogeneous aqueous–organic media the largest yields of the main products **6**, **11**, **23**, and **44** are obtained in aqueous–organic media in the presence of VOSO<sub>4</sub> or VOCl<sub>2</sub> as catalysts with the furan (2-methylfuran), H<sub>2</sub>O<sub>2</sub>, aliphatic alcohol, and vanadium catalyst in molar ratios of 1:2:12:0.02.

During the oxidation of furan in heterogeneous aqueous–organic media the largest yields of the main products **2**, **11**, **23**, and **42** are obtained in the presence of tridecylmethylammonium chloride (TDMAC) as phase-transfer catalyst and the VOCl<sub>2</sub> vanadium catalyst with the furan, H<sub>2</sub>O<sub>2</sub>, vanadium catalyst, and TDMAC in molar ratios of 1:2:0.02:0.04.

A new method was developed for the production of 2,5-dialkoxy-2,5-dihydrofurans based on the oxidation of furan with hydrogen peroxide in the presence of vanadium compounds in aqueous–alcohol media at 20°C [47, 50, 51]. This method makes it possible to use widely available low-toxicity chemical raw material, is highly efficient, and is simple in execution compared with existing methods of electrochemical alkoxylation and sensitized photochemical oxygenation of furans [15-17].

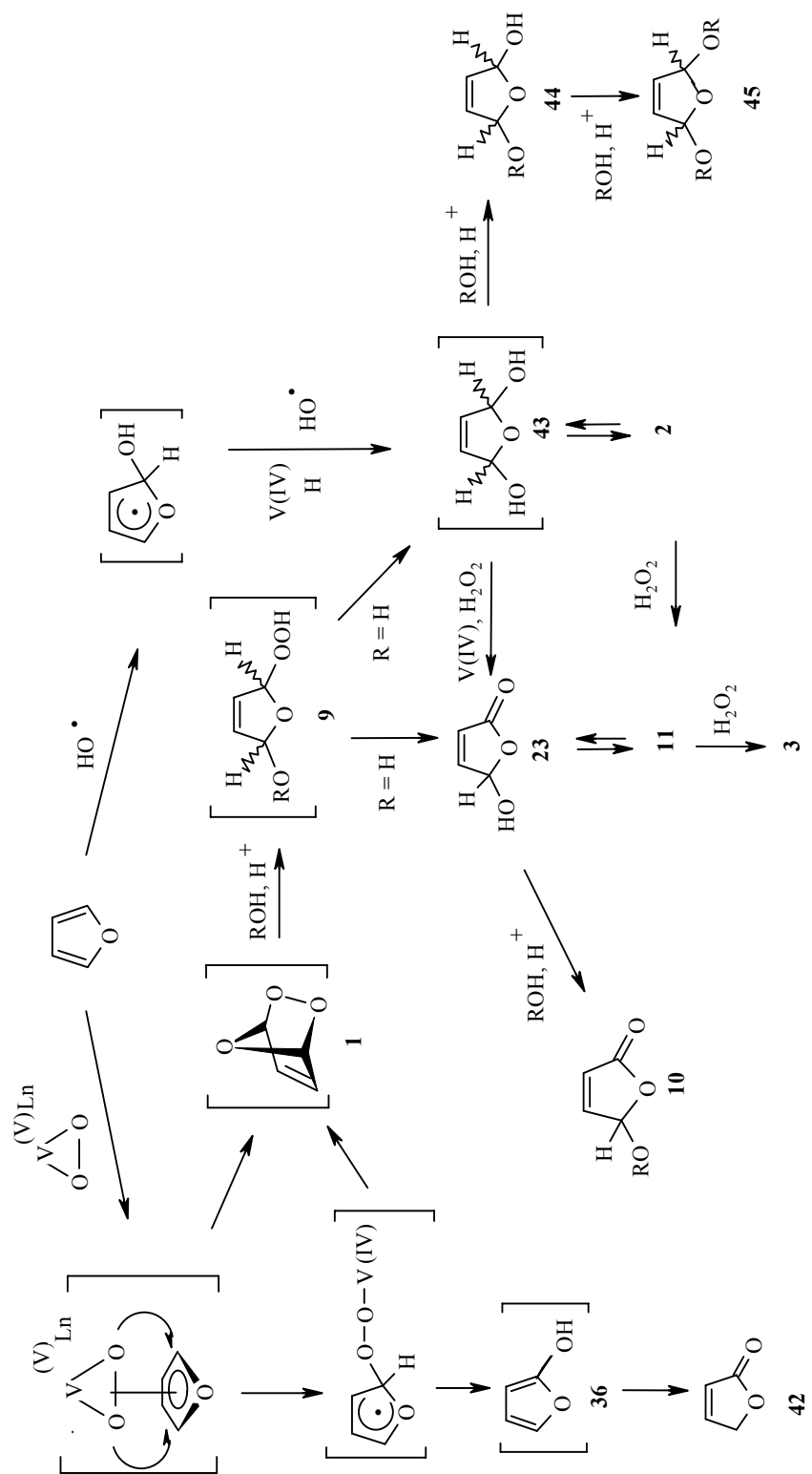
Methods for the production of 5-ethoxy-2(5H)-furanone, the 2,4-dinitrophenylhydrazone of β-formylacrylic acid, and the bis(2,4-dinitrophenyl)hydrazone of malealdehyde were upgraded [46, 50-53].

It was shown by chromato-mass spectrometry that the intermediate compounds 2,5-dihydroxy-2,5-dihydrofuran (**43**), 5-ethoxy-2-hydroxy-2,5-dihydrofuran (**44**), and 2-hydroxyfuran (**36**) are formed during the oxidation of furan by hydrogen peroxide in the presence of vanadium catalysts. These substances were isolated in the form of the stable derivatives **10**, **23**, **42**, and **45** [50-53].

A scheme, supported by the data from physicochemical methods of analysis of the reaction products, was proposed for the mechanism of the peroxide oxidation of furan. It involves the formation of endoperoxides of furan **1**, 2-hydroxyfuran (**36**), organic peroxides **9**, and 2,5-dihydroxy-2,5-dihydrofuran (**43**) as key intermediate compounds [46, 51] (Scheme 14).

In the authors' opinion [51] a major role in the oxidative transformations of furan under the adopted conditions is played by the peroxo complexes of vanadium and the hydroxyl radicals formed during the reaction of hydrogen peroxide with the vanadium compounds with significantly greater oxidizing power than H<sub>2</sub>O<sub>2</sub> [41, 42]. The main reaction products are formed through the endoperoxides of furan **1**, organic peroxides **9**, 2-hydroxyfuran (**36**), and 2,5-dihydroxy-2,5-dihydrofuran (**43**). Investigations of the processes involved in the catalytic peroxide oxidation of furans are continuing [56].

Scheme 14



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