

# CATALYTIC REACTIONS OF FURAN COMPOUNDS (REVIEW)

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*The literature data on the catalytic synthesis and transformations of furan compounds are correlated. The compositions of the most frequently used catalysts are presented, and the prospects for the more extensive incorporation of metal-complex and interphase catalysis in processes involving the transformation of furan compounds are examined.*

## 1. INTRODUCTION

The synthesis and transformation of furan compounds based on oxidation, hydrogenation, and hydrogenolysis are catalytic processes of the heterogeneous (in most cases) or homogeneous type. Among the most extensively studied representatives of this class, one should cite furfural and derivatives obtained from it, most of which are manufactured in large-tonnage volumes. The corresponding reactions and catalysts have been quite fully described in monographs and collected works published several years ago [1-3]; however, a great deal of interesting data both with respect to the use of catalytic systems and the synthesis of new compounds has been published in the last 10 yr, and this material constitutes the contents of the present review.

At the same time, it seemed appropriate to us to examine reactions involving the synthesis of 2,5-dihydrofuran-2,5-dione, interest in which, despite their half-century history, is not diminishing. Systematic studies of reactions involving the conversion of furan compounds to derivatives of the thiophene, pyrrole, pyran, and pyridine series are continuing; however, they will be discussed in appropriate reviews devoted to these heterocycles.

The noted tendency for the intensified development of small-tonnage processes in the synthesis and application of new metal-complex and interphase catalysts that are distinguished by high monofunctionality, which is particularly valuable from the point of view of increasing the selectivity of the transformations of highly reactive compounds, as most furan derivatives are.

As is the case with respect to classes of other heterocycles, the development of catalytic reactions with the participation of heteroorganic derivatives is also characteristic for oxygen-containing heterocycles, and this opens up a new branch not only in the chemistry of furan but also in catalysis. In this review chief attention was directed to research conducted in this field in the last 5-10 years in the Latvian Institute of Organic Synthesis.

The information regarding the catalytic reactions of compounds of the furan series encompasses the following topics: 1) catalysis in the processes involved in the manufacture of furfural; 2) decarbonylation and hydrogenation catalysts; 3) catalytic oxidation; 4) catalytic alkylation.

## 2. CATALYSIS IN FURFURAL-MANUFACTURING PROCESSES

Furfural, which was discovered by Dobereiner in 1831, is currently a large-tonnage product manufactured from the so-called pentosan-containing raw material. The volume of the manufacture of furfural in western countries in 1984 was

TABLE 1. Raw Materials Used in the Manufacture of Furfural [4]

Type of raw material	Pentosan content, %	Yield of furfural, %	Production vol., thousands of tons/yr
Bagasse	21...23	8,3...9,0	187
Rice husk	18,1	7,2	20
Olive extracts	23,0	3,6	13,8
Almond shells	30,8	6	9,2
Corn stalks	37	11,1 (9,1...10)	9
Black liquor			3

240,000 tons and had a tendency for further growth [4]. The principal raw material that is converted to furfural is bagasse (Table 1). In the territory of the former USSR several years ago  $\approx 60,000$  tons of furfural were manufactured annually by conversion of rice husks, corn stalks, cotton chaff, tan waste, and deciduous trees [5-8].

The production of furfural from plant raw material is based on a consecutive sequence of hydrolysis of pentosans and dehydrodehydrocyclization of pentoses. Mineral and organic acids and salts have been proposed and studied as catalysts to accelerate the process, and research to find catalysts that ensure an increase in the yield of furfural [8-14], which does not exceed 60% of the theoretical value in most operating plants [4, 5], is continuing.

Research on the separate hydrolysis of pentosans and dehydrodehydration of pentoses has shown that the yield of furfural can be increased to 80% [4].

The cost of the raw material amounts to 40% of the expenditure in the prime cost of furfural, and a large part of the production developments in recent years provides for the complex refining of the principal components of the plant raw material. Thus furfural and yeast are obtained as marketable products in several plants as a result of refinement of polysaccharides [6, 7, 9-13]. Bader Engineers Inc. have developed a technological process for the manufacture with the simultaneous production of 1.3 tons of ethanol and 2980 kW of electrical energy for each ton of furfural. As a result, the prime cost of furfural was reduced by more than 50% as compared with the cost of furfural manufactured by the classical Petrole et Chimie procedure [4].

Research to find effective catalysts for the conversion of pentoses and hexoses, respectively, to furfural and hydroxymethylfurfural is under way. A vanadylporphyrin complex fastened in a polyacrylamide gel matrix was used as a catalyst for the dehydrocyclization of D(+)-xylose and D(+)-glucose [14]. It was found that the heterogenized catalyst three to five times higher activity than the homogeneous complex catalyst with a amount of vanadyl groups.

### 3. DECARBONYLATION AND HYDROGENATION

Catalytic processes for the transformation of furfural and catalysts for them have been described both in the above-mentioned monographs and collected works [1-3] and in review papers [15-17]. Research in this area is continuing. Thus for the industrially skillful decarbonylation of furfural using the KDF palladium catalyst another catalyst with a similar composition, viz., KDFS on the Sibunit carbon support, has been proposed; this catalyst is distinguished by decreased porosity, on it the cycle duration was increased, and the conversion of furfural and the selectivity with respect to furan were  $> 90\%$  [18]. The furan obtained in this process undergoes hydrogenation to give tetrahydrofuran.

However, the manufacture of tetrahydrofuran is based chiefly on other forms of raw materials, primarily on the dehydration of butane-1,4-diol, which is obtained by the hydration of butadiene [19]. Studies of the mild oxidation of butadiene in the gas and liquid phases showed that the yield of tetrahydrofuran reached 95-100% in the liquid phase on some catalysts (oxidation with oxygen at a pressure of 0.2-0.3 MPa). Furan was primarily formed as the product of oxidation in the gas phase, but the conversion of the starting compound and the selectivity with respect to furan were low.

A number of experiments on the dehydration of butane-1,4-diol were carried out on oxide catalysts. On tungsten oxide at 250-300°C the yield of tetrahydrofuran was 100% [20]. A high yield of tetrahydrofuran is obtained when various brands of silica gel are used as the catalyst (Table 2) [21].

The hydrogenation of furfural at the carbonyl group is used in the manufacture of furfuryl alcohol, which is used in various areas of the national economy [22, 23]. Despite the fact that this reaction has been investigated for more than 50 years,

TABLE 2. Indexes of the Synthesis of Tetrahydrofuran from Butane-1,4-diol

Silica gel				Reaction condition		Butane-diol conversion, %	Selectivity with respect to tetrahydrofuran, %
type	porosity, %	pore radius, Å	S <sub>sp</sub> , m <sup>2</sup> /g	T, °C	charge, g/cm <sup>3</sup> /h		
KCK N2	72,7	70,0	338	260	3,42	100	100
				300	4,17	100	99,7
				300	11,6	98	99,5
				340	4,17	100	99,5
KSS N3	67,4		552	300	5,39	100	99,3
				420	22,7	100	99,2
KSM	56,4	161	715	300	4,6	100	99,3
				420	19,8	100	99,3

TABLE 3. Catalysts for the Hydrogenation of Furfural at the Formyl Group

Catalyst	Pressure, MPa	T, °C	Literature
Hydrogenation of the formyl group to a carbonyl group			
Modified Raney cobalt and copper	15...18	150...200	[24, 25]
Copper-chromium	In the gas		[26]
Copper-chromium promoted	Decreased	80...140	[27]
Copper-chromium GIPKh-105		200...300	[28]
Rhodium on a polymer		20...30	[29, 30]
Copper-chromium GIPKh-105			[31]
Copper-chromium GIPKh-105			[32]
VNKh-103, VNKh-104, NTK-4			[33]
Hydrogenation of the formyl group to a methyl group			
Copper-chromium GIPKh-105*		200...300	[34—36]
Palladium on supports, KDF		110...200	[37]

\*Hydrogenation of 5-methylfurfural.

studies whose authors present new compositions of catalysts and new data relative to the reaction mechanism are still being published. The catalysts that are most frequently used in this reaction are presented in Table 3. The hydrogenation of furfural on multicomponent Raney catalysts has been studied extensively by representatives of the Kazakh school of catalyst scientists [24, 25]. In practice, a copper—chromium catalyst [26, 27], which is deactivated as a consequence of blocking of the surface by strongly adsorbed furfural, is used in this process.

The structure of the starting compound has a substantial effect on the degree of hydrogenation of the formyl group. Thus furfural is hydrogenated primarily to furfuryl alcohol on a copper—chromium catalyst, while methylfurfural is converted almost quantitatively to 2,5-dimethylfuran [28]. The hydrogenation of a mixture of both furan aldehydes (200°C, overall charge of the aldehydes 800 g/liter/h, hydrogen—aldehyde ratio 3:1) leads to a mixture of the corresponding methylfurans.  $\alpha$ -Methylfuran and dimethylfuran comply with the "chemically pure" qualification after distillation. 2,5-Dimethylfuran is also formed in the hydrogenation of 5-chloromethylfurfural on a 5% Pd/C catalyst [38].

Saturation of the olefinic bond is the chief process in the hydrogenation of  $\alpha,\beta$ -unsaturated furan ketones using copper catalysts (copper chromite, copper oxide, Raney nickel, etc.) [39].

Hydrogenation of the ring, which leads to tetrahydrofuran derivatives, pertains to large-tonnage processes involving the refinement of furfural. Nickel catalysts are traditionally used in these processes, but there have been reports regarding the use also of rhodium complexes, including those fastened in polymers.

The hydrogenation of furan compounds in the heteroring has been investigated in order to create processes for the manufacture of products such as tetrahydrofurfuryl alcohol and tetrahydrofuran (or tetrahydro- $\alpha$ -methylfuran), as well as a number of other furanidine derivatives, including heteroorganic compounds (Table 4).

The hydrogenation of furan ketones on rhodium—polyacrylate catalysts at room temperature and atmospheric pressure takes place only in the ring — ketones of the tetrahydrofuran series are obtained [49]. Saturation of the double bond in the dihydrofuran ring occurs at 90°C and a pressure of 10 MPa in the 2-methyl- and 2,7-dimethyl-3-ethoxycarbonyl-1,6-dioxaspiro[4,4]non-2-ene complex molecules on catalysts (Raney nickel or 5% Pd/C) [50]. Examples of the modification of palladium catalysts by the introduction of rhodium in order to regulate their activity in the hydrogenation of furan compounds

TABLE 4. Catalysts for the Formation of Furan Compounds to Give Tetrahydrofuran Compounds

Compound	Reaction product	Catalyst	Pressure, MPa	T °C	Literature
Furan	Tetrahydrofuran	Metal polymers	Atm.	18...20	[40]
Furfural	Tetrahydrofurfuryl alcohol	Rh and others			
Furfuryl alcohol	Tetrahydrofurfuryl alcohol	Ni/aluminum silicate Ni/Cr <sub>2</sub> O <sub>3</sub>	4,0	130	[41, 42]
2,5- and 2,3-Dihydrofurans	Tetrahydrofuran	Rh complex, heterogeneous Rh/support	0,4	70	[43]
α-Methylfuran	Tetrahydrofuran	Raney Ni	0,4	70	[44]
2-tert-Butylfuran	2-tert-Butyltetrahydrofuran	Raney Ni	0,4	70	[44]
Trimethyl(2-furyl)silane	Trimethyl(2-tetrahydrofuryl)silane	Raney Ni	0,4	70	[44]
Triethyl(2-furyl)germane	Triethyl(2-tetrahydrofuryl)germane	Raney Ni	0,4	70	[44]
Trimethyl(2-furyl)germane	Trimethyl(2-tetrahydrofuryl)germane	1,8% Pd/C	—	150	[44]
Trimethyl-2-(5'-methylfuryl)germane	Trimethyl-2-(5'-methyltetrahydrofuryl)germane	1,8% Pd/C	—	150	[44]
Dimethyldi(2-furyl)germane	Dimethyl(2-furyl)(2-tetrahydrofuryl)germane	Raney Ni Rh(CO)(PPh <sub>3</sub> ) <sub>3</sub>	0,4...1,9 1,9	70 70	[45] [47]
Trimethyl-2-(4,5-dihydrofuryl)silane	Trimethyl(2-tetrahydrofuryl)silane	2.0% Pd/C; 5% Pd/Al <sub>2</sub> O <sub>3</sub>	0,1	25	[47]
Trimethyl-2-(4,5-dihydrofuryl)germane	Triethyl(2-tetrahydrofuryl)germane	2.0% Pd/C; 5% Pd/Al <sub>2</sub> O <sub>3</sub>	0,1	25	[47]
Dimethyl(2-furyl)silane	Dimethyldi(2-tetrahydrofuryl)silane Dimethyl(2-furyl)(2-tetrahydrofuryl)-silane	Pd/C	0,1...1,9	25	[46,47]
Dimethyl-2-(4,5-dihydrofuryl)hydrosilane	Dimethyl(2-tetrahydrofuryl)hydro-silane	5% Pd/Al <sub>2</sub> O <sub>3</sub>	0,1	18...20	[44, 47, 48]

\*After complete transformation, the tetrahydrofuran derivative undergoes rearrangement to 2,2-dimethyl-1-oxa-2-silacyclohexane [44, 47, 48].

are known [51]. Modification of the activity of a nickel catalyst is observed when ammonia is introduced into the reaction medium — in this case the carbonyl group in furfural (rather than the ring itself) is primarily involved, and the chief product is furfurylamine [52, 53].

Not only hydrogenolysis but also ring formation occur under hydrogenation conditions, particularly if the starting molecule contains two or more functional groups at a distance that makes the formation of a five- or six-membered ring possible. 5-Methoxytetrahydrofuran-3-carbaldehyde dimethylacetal was synthesized from 2-dimethoxymethyl-4,4-dimethoxybutanal [54], while 2-isobutyl-4-methyltetrahydropyran was synthesized from 3,7-dimethyl-5-oxooctanal [55].

The use of nickel catalysts modified by ruthenium, in the presence of which in an ammonium medium consecutive reduction of the carbonyl group, saturation of the furan ring, hydrogenolysis, and the formation of pyrrolidylalkanols, has been described in a number of publications [56-58].

In the presence of a promoted, fused, iron catalyst tetrahydrofurfuryl alcohol is converted to piperidine in an atmosphere of hydrogen and ammonia through an intermediate step involving the formation of pentane-1,5-diol and 1-amino-5-pentanol [59].

The formation of sulfur-containing heterocycles such as thiolane occurs on oxide acid-base catalysts by the action of hydrogen sulfide on tetrahydrofuran [60].

TABLE 5. Partial Oxidation of Methylfuran Compounds

Compound	T, °C	Reaction product	Yield, %, on the catalysis*		
			I	II	III
2-Methylfuran	350	5-Methylenefuran-2-(5H)-one(protoanemone)	26	43	30
2-Methyl-5-tert-butylfuran	430	5-tert-Butylfuran-2-carbaldehyde	15	24	
5-Methylfuran-2-carbaldehyde	400	Furan-2,5-dicarbaldehyde	30	35	
2,5-Dimethylfuran	400		60	56	

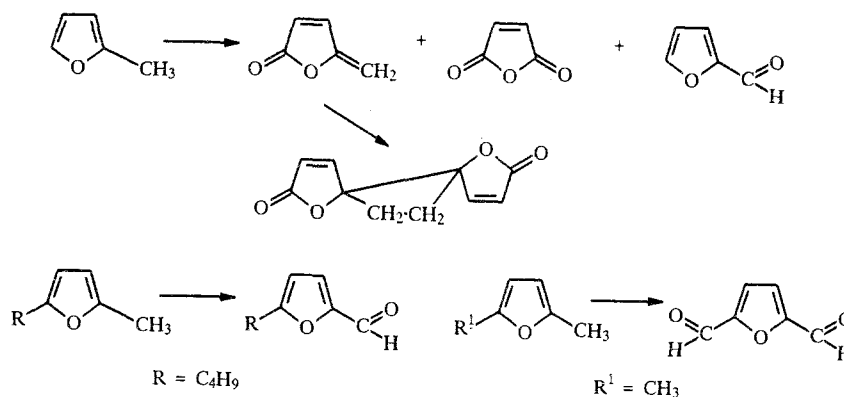
\*Catalysts: I is vanadium pentoxide, II is vanadium molybdenum oxide (V:Mo = 3:1), and III is vanadium molybdenum oxide modified with silver oxide (V:Mo:Ag = 1:1:0.02).

Thus in the transformations of furan compounds catalytic hydrogenation reactions open up rich possibilities in a synthetic respect and deserve the close attention of catalyst theoreticians from the point of view of pinning down the state of the active centers on the surface and the role of hydrogen in the aggregate of reactions that take place on them.

#### 4. OXIDATION

The oxidation of furfural and furan on vanadium oxide catalysts in the gas phase has been studied in order to create a method for the manufacture of maleic anhydride (voluminous material was presented in [2], in which reactions involving the liquid-phase oxidation of furfural and 5-methylfurfural were also described).

In an investigation of the gas-phase oxidation of the simplest furan compounds it was found that, under certain conditions, methyl derivatives of furan can be selectively oxidized at the methyl group [61-65] to give products such as protoanemone and furan-2,5-dicarbaldehyde (Table 5). The formation of protoanemone in the oxidation of 2-methylfuran is due to the dehydrogenating action of vanadium pentoxide on the methyl group, which, by losing one hydrogen atom, changes the electron-density distribution in the ring. As a result, the carbon atom in the ring 5 position undergoes attack.



In the oxidation of 2,5-disubstituted furan derivatives with oxygen the same methyl group from which the hydrogen atom "departed" is attacked, and a mono- or dialdehyde is formed as the product.

The liquid-phase oxidation of furfural with hydrogen peroxide in the presence of vanadium catalysts has been investigated for a number of years under the supervision of L. A. Badovskaya. Furfural, furan, methylfuran, and a number of 2-substituted and 2,5-disubstituted furan compounds were subjected to oxidation in the presence of vanadyl sulfate, vanadium pentoxide, and vanadium complexes. 5-Hydroxy-2(5H)-furanone was obtained in 60% and 65% yields in the presence of vanadyl acetylacetonate, phenanthroline, and 2-hydroxynaphthenate [66, 67]. The introduction into the reaction medium of inhibitors of radical-chain processes in the presence of vanadium phenanthroline or hydroxynaphthenate made it possible

TABLE 6. Yields of Triethylsilyl Ether As a Function of the Catalyst (%)

Catalyst	Reaction time					
	1	2	3	4	5	6
Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl	12	35	55	59	60	55
Rh(PPh <sub>3</sub> ) <sub>3</sub> (CO)H	0	0	—	8	—	12
Rh(PPh <sub>3</sub> ) <sub>3</sub> (CO)Cl	7	30	—	70	—	59
Ru(PPh <sub>3</sub> ) <sub>3</sub> Cl <sub>2</sub>	10	25	—	58	75	73
Ru(PPh <sub>3</sub> ) <sub>2</sub> (CO) <sub>2</sub> Cl <sub>2</sub>	0	0	—	5	—	7
Pd(PPh <sub>3</sub> ) <sub>3</sub> Cl <sub>2</sub>	5	8	—	24	—	27
RhCl <sub>3</sub>	56	—	—	—	—	—
(Et <sub>3</sub> PhCH <sub>2</sub> N)RhCl <sub>4</sub>	43	—	—	—	—	—
Poly-CH <sub>2</sub> PBu <sub>3</sub> (RhCl <sub>4</sub> )	5	—	—	—	—	—

to increase the yield of 5-hydroxy-2(5H)-furanone by another 25%. If, however, the reaction is effected in an aqueous alcohol medium rather than in an aqueous medium, the yield of the desired product reaches 90%.



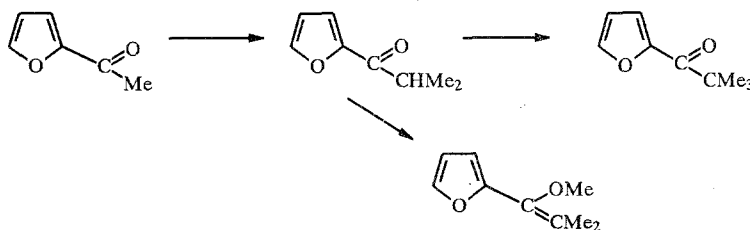
A number of researchers suppose that furan is an intermediate in the manufacture of maleic anhydride from such relatively available and cheap raw materials as C<sub>4</sub>—C<sub>5</sub> hydrocarbons [68-70]. Vanadium phosphates, as well as catalysts promoted by the addition of molybdenum, titanium, and other oxides, have been proposed as catalysts [71-92]. Studies of the transformation of furan under the conditions of oxidation of butane and butenes have been made [93-97]. Despite the fact that the formation of a furanlike structure in the oxidation of benzene has been previously proposed, in recent studies [98-100] it was shown that neither maleic anhydride or other products that accompany it are formed on a reduced vanadium catalyst, and carbon oxides were detected as the only reaction products. Chloro-2,5-dihydrofuranones were obtained by the catalytic oxidation of C<sub>4</sub> chloro hydrocarbons [101-103], as well as by the oxidation of mono- and dichlorobenzenes on a catalyst promoted by vanadium molybdenum oxide [104].



The gas-phase oxidation of C<sub>4</sub> hydrocarbons is currently being used by industry, and, in addition, the production of furan-2,5-dicarbaldehyde and 5-hydroxy-2(5H)-furanone is of practical value. The formation of protoanemonine in the oxidation of 2-methylfuran — a new reaction — is of interest from a theoretical point of view.

## 5. ALKYLATION

The alkylation of furyl ketones by alkyl and benzyl halides in a liquid—solid two-phase system has been accomplished in the presence of an interphase-transfer catalyst [105, 106]. Isopropyl 2-furyl ketone was synthesized in 75% yield when methyl iodide was used as the alkylating agent at room temperature starting from acetylfuran.



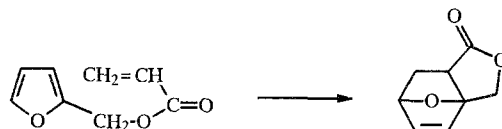
The further reaction of this ketone with methyl iodide was realized only at the boiling point of the reaction mixture — tert-butyl 2-furyl ketone was obtained as the chief product, along with a certain amount of an O-alkylation product. The formation of the corresponding alkyl ketones is observed in the action of ethyl and propyl iodides on acetylfuran, and a

TABLE 7. Yields of Ethers I and II\* in the Hydrosilylation of 5-Methylfurfural As a Function of the Catalyst (%)

Catalys	Reac- tion prod- uct	Reaction time							
		1	2	3	4	5	6	7	8
Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl	I	11	18	27	33	37	42	44	45
	II	12	23	35	32	—	—	—	—
Rh(PPh <sub>3</sub> ) <sub>3</sub> (CO)H	I	—	2	3	3	3	3	—	—
	II	5	30	37	32	—	—	—	—
Rh(PPh <sub>3</sub> ) <sub>3</sub> COCl	I	—	34	39	46	50	54	56	59
	II	27	42	45	47	—	—	—	—
Ru(PPh <sub>3</sub> ) <sub>3</sub> Cl <sub>2</sub>	I	—	7	18	24	30	38	35	35
	II	1	2	—	—	—	—	—	—
Ru(PPh <sub>3</sub> ) <sub>2</sub> (CO) <sub>2</sub> Cl <sub>2</sub>	I	—	2	3	3	2	—	—	—
	II	2	2	3	—	—	—	—	—
Pd(PPh <sub>3</sub> ) <sub>3</sub> Cl <sub>2</sub>	I	—	23	34	55	58	58	48	44
	II	12	29	26	27	—	—	—	—
(Et <sub>3</sub> PhCH <sub>2</sub> N)RhCl <sub>4</sub>	I	85	90	—	—	—	—	—	—
(Bu <sub>4</sub> N) <sub>2</sub> PtCl <sub>6</sub>	I	5	10	—	—	—	—	—	—

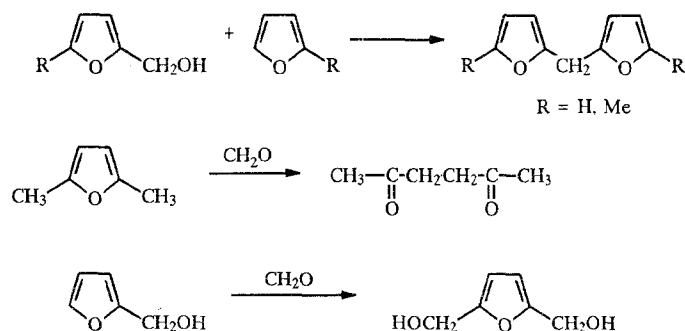
\*The yields of II were determined for the reaction at 100°C.

significant part of the substrate undergoes O-alkylation to give mono-O-alkyl and C,O-dialkyl derivatives. The alkylation of 2-acetylfuran with benzyl bromide under similar conditions takes place regiospecifically to give 2,2-dibenzyl-1-(2-furyl)ethanol in 50% yield. Furfuryl chloride was used as the alkylating agent in a reaction with sodium acrylate in the presence of triethylbenzylammonium chloride as the catalyst in order to synthesize furfuryl acrylate [107], which, in the presence of heterogeneous catalysts (diatomite, for example), undergoes cyclization to give 3a,6-epoxy-3a,6,7,7a-tetrahydro-3H-benzo[c]furan-1-one.



The synthesized allyl and propargyl furfuryl ethers also underwent intramolecular cyclization.

Alkylation at the ring carbon atom by the furfuryl alcohol formed in the first step occurs under the conditions of the hydroxymethylation of furan and methylfuran in the presence of H<sup>+</sup> cation-exchange resins. 2,2'-Difurylmethane and 5,5'-dimethyl-2,2'-difurylmethane were synthesized in this way [108, 109]. Under hydroxymethylation conditions (by the action of aqueous formaldehyde) 2,5-dimethylfuran undergoes hydrolysis to give hexane-2,5-dione. On a slightly acidic cation-exchange resin (carboxylate) furfuryl alcohol is hydroxymethylated at the carbon atom in the 5 position to give furyl-2,5-dicarbinol.



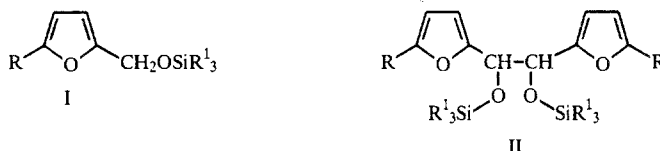
A number of bis(5-methyl-2-furyl)methanes were synthesized by the action of aldehydes on 2-methylfuran in the presence of cation-exchange resins [110].



Macroporous resins that contain sulfono groups, as well as carboxylato groups, have served as cation-exchange resins. It was found that the latter have little effect in the reaction under investigation.

In the presence of metal-complex catalysts furan aldehydes (furfural, 5-methylfurfural, and furan-2,5-dicarbaldehyde) react with triethylsilane to give triethylsilyl ethers of the corresponding furylcarbinols. The indexes of the transformation of furfural by the action of triethylsilane as a function of the metal-complex catalyst (at 25°C and a furfural—triethylsilane—catalyst ratio of 1:1.2:0.001) are presented in Table 6.

On rhodium and palladium complex catalysts at 100°C a mixture of 5-methylfurfural and triethylsilane undergoes not only hydrosilylation but also dehydrocondensation, and difurylethane-1,2-diol bis(triethylsilyl) ether is detected in the reaction products [111, 112].



The dependence of the yields of 5-methyl-2-furylcarbinol triethylsilyl ether (I) and bis(5-methyl-2-furyl)ethane-1,2-diol bis(triethylsilyl) ether (II) in the hydrosilylation of 5-methylfurfural on the metal-complex catalyst under conditions similar to the conditions for the hydrosilylation of furfural is presented in Table 7.

The yields of the corresponding monoethers in the reactions with both furfural and 5-methylfurfural are higher on rhodium catalysts, of which the most effective was the triethylbenzylammonium rhodium tetrachloride complex.

The hydrosilylation of furan-2,5-dicarbaldehyde was accomplished on the Wilkinson catalyst at 130°C. Triethyl(5-formylfuryloxy)silane and 2,5-bis(triethylsiloxymethyl)furan are formed as the reaction products in virtually comparable yields.

The hydrosilylation of furan aldehydes and ketones with dimethylphenylsilane was carried out in a low-polarity solvent at room temperature in the presence of interphase-transfer catalysts (18-crown-6) with added alkali metal fluorides [113].

The use of the principles of interphase catalysis makes it possible, on the basis of such quite labile compounds as derivatives of the furan series, to accomplish complex reactions with good yields of the desired products.

## 6. CONCLUSION

The examined catalytic reactions of furan compounds constitute an illustration of the new synthetic possibilities not only in this series but also in the chemistry of heteroorganic and other classes of organic compounds. The investigation of the reaction of a number of furan derivatives with catalysts and the elucidation of the mechanism of the surface reactions are interesting from the point of view of a more profound understanding of the theoretical concepts regarding the nature of the active centers of catalysts and their ability to be formed as a result of the action of complex multifunctional substrates such as furan derivatives. These problems should become the subject of further discussion.

## REFERENCES

1. I. F. Bel'skii and V. M. Shostakovskii, *Catalysis in the Chemistry of Furan* [in Russian], Nauka, Moscow (1972).
2. M. V. Shimanskaya (Ed.), *Catalytic Reactions of Furan Compounds* [in Russian], Zinatne, Riga (1985).
3. *Catalytic Synthesis and the Transformations of Heterocyclic Compounds. Heterogeneous Catalysis* [in Russian], Zinatne, Riga (1976).
4. L. M. Bova, *Khim. Promysh. Rubezhom*, No. 8, 19 (1988).
5. V. N. Sergeeva and G. É. Domburg, *The Formation of Furfural and Methods to Obtain It* [in Russian], Izd. Akad. Nauk Latv. SSR, Riga (1962).
6. N. S. Maksimenko, *Gidroliz. Lesokhim. Promysh.*, No. 1, 6 (1981).
7. E. F. Morozova, *The Manufacture of Furfural* [in Russian], Lesnaya Promyshlennost', Moscow (1978).
8. V. K. Kuznetsov and S. A. Kuznetsova, *Khim. Drevesiny*, No. 5, 3 (1988).
9. E. F. Morozov, V. M. Shkut, E. P. Shishakov, M. S. Kebich, P. I. Samsonov, and T. G. Mirskova, *Gidroliz. Lesokhim. Promysh.*, No. 7, 23 (1985).



10. M. S. Kebich, V. I. Sobolev, E. F. Morozov, and O. I. Fedorova, *Gidroliz. Lesokhim. Promysh.*, No. 4, 1 (1989).
11. N. A. Vedernikov and I. M. Roze, *Khim. Drevesiny*, No. 2, 81 (1988); No. 3, 85 (1990).
12. N. A. Vedernikov, S. S. Popov, N. A. Trautmane, Z. O. Okonova, and V. A. Zav'yalov, *The Chemistry, Biochemistry, and Applications of Hemicelluloses. Summaries of Papers Presented at the 3rd All-Union Conference [in Russian]*, Riga (1985), p. 80.
13. A. Ya. Butsena and A. Ya. Kul'kevits, *Khim. Drevesiny*, No. 4, 96 (1986).
14. G. P. Potapova, M. I. Alieva, E. I. Kazakova, V. I. Krupenskii, and S. V. Rodionova, *Fifth International Symposium on the Relationship Between Homogeneous and Heterogeneous Catalysis. Summaries of Papers [in Russian]*, Novosibirsk (1986), p. 197.
15. M. V. Shimanskaya, *Izv. Akad. Nauk Latv. SSR*, No. 11, 95 (1989).
16. M. V. Shimanskaya, *Gidroliz. Lesokhim. Promysh.*, No. 5, 4 (1983).
17. V. A. Slavinskaya, R. A. Karakhanov, L. Yu. Brezhnev, I. I. Geiman, A. K. Strautinya, V. M. Ignat'ev, and V. M. Levitin, *Izv. Akad. Nauk Latv. SSR*, No. 1, 85 (1984).
18. N. N. Machalaba, *Gidroliz. Lesokhim. Promysh.*, No. 7, 82 (1989).
19. V. M. Ignat'ev, V. M. Levitin, and I. M. Golubkov, *Gidroliz. Lesokhim. Promysh.*, No. 1, 10 (1989).
20. J. Oshis (Osis), P. Meksh (Mekss), A. Andersons, and M. Shimanskaya (Shimanska), *Fifth International Symposium on Furan Chemistry. Abstracts [in Russian]*, Riga (1988), p. 111.
21. Ya. F. Oshis, P. A. Meksh, and M. V. Shimanskaya, *USSR Author's Certificate No. 1,294,805; Byull. Izobret.*, No. 9, 107 (1987).
22. J. Nowicki and Z. Maciejewski, *Przem. Chem.*, **64**, No. 1, 21 (1985).
23. É. A. Karakhanov and A. G. Dedov, *Catalytic Hydrogenation of Heterocyclic Compounds [in Russian]*, Izd. Moskovsk. Univ., Moscow (1986).
24. M. S. Erzhanova and T. Beisekov, *Fourth All-Union Symposium on Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds. Summaries of Papers [in Russian]*, Riga (1987), p. 123.
25. M. S. Erzhanova, *Development of Research in Catalysis in Kazakhstan [in Russian]*, Part 2, Alma-Ata (1990), p. 190.
26. N. D. Gilchenok, M. S. Borts, Zh. V. Mitrofanov, and V. M. Ignat'ev (Ignatiev), *Fifth International Symposium on Furan Chemistry. Abstracts [in Russian]*, Riga (1988), p. 105.
27. J. Costa, F. Cunill, and J. F. Izquierdo, *An. Quim., Ser. A*, **83**, No. 3, Suppl. 1, 586 (1984).
28. V. V. Stonkus, Zh. G. Yuskovets, and M. V. Shimanskaya, *The Chemistry and Technology of Furan Compounds [in Russian]*, Krasnodar (1988), p. 34.
29. É. A. Karakhanov, E. B. Neimerovets, V. S. Pshezhetskii, and A. G. Dedov, *Khim. Geterotsikl. Soedin.*, No. 3, 303 (1986).
30. É. A. Karakhanov, *Fourth All-Union Symposium on Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds. Summaries of Papers [in Russian]*, Riga (1987), p. 27.
31. V. M. Evgrashin, V. M. Ignat'ev, G. S. Pozharskaya, N. D. Gil'chenok, V. G. Rarog, and M. S. Borts, *Fourth All-Union Symposium on Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds. Summaries of Papers [in Russian]*, Riga (1987), p. 122.
32. V. I. Sushkova and Z. K. Malkova, *Gidroliz. Lesokhim. Promysh.*, No. 6, 24 (1990).
33. N. V. Veber, L. G. Grankina, and V. I. Kuznetsova, *Gidroliz. Lesokhim. Promysh.*, No. 1, 20 (1989).
34. V. V. Stonkus, Zh. G. Yuskovets, and M. V. Shimanskaya, *Khim. Geterotsikl. Soedin.*, No. 11, 1460 (1990).
35. V. V. Stonkus, Zh. G. Yuskovets, V. N. Sokolova, and M. V. Shimanskaya, *USSR Author's Certificate No. 1,362,733; Byull. Izobret.*, No. 43, 72 (1987).
36. V. V. Stonkus, Zh. G. Yuskovets, and M. V. Shimanskaya, *Third All-Union Conference on Chemical Reagents. Summaries of Papers. Organic Reagents [in Russian]*, Vol. 1, Ashkhabad (1989), p. 34.
37. Zh. Yuskovets, V. Stonkus, N. V. Nekrasov, S. I. Kiperman, and M. Shimanskaya (Shimanska), *Fifth International Symposium on Furan Chemistry. Abstracts [in Russian]*, Riga (1988), p. 106.
38. Sumitomo Chem. Co., *Japanese Patent No. 5, 813,575; Chem. Abstr.*, **98**, 198,001r (1983).
39. R. M. Mat'yakubov, K. T. Tuichiev, and A. S. Ismailov, *Fourth Symposium on Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds. Summaries of Papers [in Russian]*, Riga (1987), p. 123.

40. É. A. Karakhanov, E. B. Neimerovets, V. S. Pshezhetskii, and A. G. Dedov, Fifth International Symposium on the Relationship Between Homogeneous and Heterogeneous Catalysis. Summaries of Papers [in Russian], Novosibirsk (1986), p. 116.
41. N. Merat, C. Godawa, and A. Gaset, *J. Mol. Catal.*, **57**, No. 3, 397 (1990).
42. V. N. Baidin, V. M. Ignat'ev, L. P. Erdyakova, D. N. Gil'chenok, G. I. Kiseleva, V. V. Losev, and S. M. Shlenskaya, Fourth All-Union Symposium on Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds. Summaries of Papers [in Russian], Riga (1987), p. 121.
43. K. Felfeldi, M. Laspavik, and M. Bartok, Fifth International Symposium on the Relationship Between Homogeneous and Heterogeneous Catalysis. Summaries of Papers [in Russian], Novosibirsk (1986) (1986), p. 255.
44. É. Ya. Lukevits, Yu. Sh. Gol'dberg, Zh. G. Yuskovets, V. N. Gevorgyan, L. M. Ignatovich, and M. V. Shimanskaya, *The Chemistry and Technology of Furan Compounds* [in Russian], Krasnodar (1987), p. 64.
45. É. Ya. Lukevits, L. M. Ignatova, Zh. G. Yuskovets, L. O. Golender, and M. V. Shimanskaya, *Zh. Obshch. Khim.*, **57**, 1294 (1987).
46. Zh. G. Yuskovets, L. O. Golender, M. V. Shimanskaya, L. M. Ignatovich, and É. Lukevits, Fourth All-Union Symposium on Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds. Summaries of Papers [in Russian], Riga (1987), p. 128.
47. É. Lukevits (Lukevics), V. N. Gevorgyan, Yu. S. Gol'dberg (Goldberg), and M. Shimanskaya (Shymanska), *J. Organomet. Chem.*, **294**, 163 (1985).
48. E. Lukevits (Lukevics), L. Ignatovich, Zh. Yuskovets, L. Golender, and M. Shimanskaya (Shymanska), Seventh Fechem Conference on Organometallic Chemistry. Abstracts, Toledo (1987), p. 163.
49. A. G. Dedov, E. B. Neimerovets, R. A. Karakhanov, D. Biryukova, and V. V. Yakovlev, Fourth All-Union Symposium on Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds. Summaries of Papers [in Russian], Riga (1987), p. 125.
50. L. Yu. Brezhnev, M. M. Vartanyan, and N. P. Karzhavina, Fourth All-Union Symposium on Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds. Summaries of Papers [in Russian], Riga (1987), p. 126.
51. M. K. Kacher, G. E. Mogilevich, and A. G. Pankov, *Fundamental Organic Synthesis and Petroleum Chemistry* [in Russian], No. 33, Yaroslavl (1987), p. 89.
52. Kh. M. Makhamov, V. N. Sanamians, E. S. Svetsitskii, I. Y. Krupina, and I. Kh. Penke, Fifth International Symposium on Furan Chemistry. Abstracts [in Russian], Riga (1988), p. 108.
53. É. Lukevits and M. Shimanskaya, Oxygen-Containing Heterocycles. Summaries of Papers Presented at the All-Union Conference [in Russian], Krasnodar (1990), p. 8.
54. I. N. Klochkova, T. E. Sorokina, and M. V. Noritsina, *The Chemistry and Technology of Furan Compounds* [in Russian], Krasnodar (1988), p. 43.
55. T. G. Nikolaeva, E. A. Karavaeva, and A. P. Kriven'ko, *The Chemistry and Technology of Furan Compounds* [in Russian], Krasnodar (1988), p. 76.
56. M. V. Noritsina, I. N. Klochkova, and N. N. Sorokin, *Khim. Geterotsikl. Soedin.*, No. 2, 177 (1990).
57. G. A. Kliger, L. S. Glebov, O. A. Lesik, and S. M. Loktev, Fifth All-Union Conference on the Mechanism of Catalytic Reactions. Summaries of Papers [in Russian], Moscow (1990), 176 (1990).
58. M. M. Vartanyan, A. V. Khandin, and L. Yu. Brezhnev, *Khim. Geterotsikl. Soedin.*, No. 10, 1428 (1990).
59. V. G. Kharchenko, N. S. Smirnova, V. N. Kravtsova, L. M. Yudovich, and A. D. Shebaldova, *Khim. Geterotsikl. Soedin.*, No. 8, 1011 (1990).
60. I. V. Desyatov, V. N. Yakovleva, and A. V. Mashkina, *React. Kinet. Catal. Lett.*, **41**, No. 1, 97 (1990).
61. I. Iovel' (Iovel), Yu. Gol'dberg (Goldberg), and M. Shimanskaya (Shymanska), *J. Chem. Soc., Chem. Commun.*, Issue 16, 1079 (1990).
62. I. G. Iovel', Yu. Sh. Gol'dberg, R. M. Zolotoyabko, and M. V. Shimanskaya, USSR Author's Certificate No. 1,216,965.
63. I. G. Iovel', M. P. Gavars, A. P. Gaukhman, and M. V. Shimanskaya, USSR Author's Certificate No. 1,342,903; *Byull. Izobret.*, No. 37, 97 (1987).
64. I. G. Iovel' and M. V. Shimanskaya, Fourth All-Union Symposium on Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds. Summaries of Papers [in Russian], Riga (1987), p. 84.

65. I. G. Iovel', Yu. Sh. Gol'dberg, Zh. G. Yuskovets, and M. V. Shimanskaya, Seventh All-Union Conference Devoted to the 100th Birthday of Professor Gustav Vanag. The Chemistry of Dicarboxyl Compounds. Summaries of Papers [in Russian], Riga (1991), p. 97.
66. V. V. Poskonin, L. A. Badovskaya, S. P. Gavrilova, and V. G. Kul'nevich, *Zh. Org. Khim.*, **25**, No. 8, 1701 (1959).
67. V. V. Poskonin, L. A. Badovskaya, and N. A. Vysotskaya, Fifth International Symposium on Furan Chemistry. Abstracts [in Russian], Riga (1988), p. 110.
68. B. L. Moldavskii and Yu. D. Kernos, *Maleic Anhydride and Maleic Acid* [in Russian], Khimiya, Leningrad (1976).
69. *Przem. Chem.*, **69**, No. 4, 191 (1990).
70. *Przem. Chem.*, **69**, No. 9, 432 (1990).
71. N. D. Konovalova, V. A. Zazhigalov, V. M. Belousov, G. A. Komashko, A. I. Pyatnitskaya, and E. Stokh, Fourth All-Union Symposium on Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds. Summaries of Papers [in Russian], Riga (1987), p. 89.
72. V. A. Zazhigalov, N. D. Konovalova, Yu. P. Zaitsev, V. M. Belousov, E. Stokh, Z. Krupa, and E. Khaber, *Ukr. Khim. Zh.*, **53**, No. 11, 1145 (1987).
73. V. A. Zazhigalov, N. D. Konovalova, Yu. P. Zaitsev, V. M. Belousov, E. Stokh, and Z. Krupa, *Fiz. Khim., Mekhanika*, No. 10, 55 (1987).
74. V. A. Zazhigalov, *Catalysis and Catalysts* [in Russian], No. 26, Naukova Dumka, Kiev (1989), p. 12.
75. V. V. Sidorchuk, V. M. Belousov, V. A. Zazhigalov, G. A. Komashko, and A. I. Pyatnitskaya, *Catalysis and Catalysts*, No. 25, Naukova Dumka, Kiev (1987).
76. V. A. Zazhigalov, N. D. Konovalova, and E. Stokh, *Kinet. Katal.*, **29**, No. 2, 419 (1988).
77. V. A. Zazhigalov, V. M. Belousov, G. A. Komashko, A. I. Pyatnitskaya (Pyatnickaya), G. I. Gol'denberg (Goldenberg), and N. D. Konovalova, *React. Kinet. Catal. Lett.*, **37**, No. 1, 71 (1988).
78. V. A. Zazhigalov, V. M. Belousov, N. D. Konovalova, Yu. N. Merkurova, A. I. Pyatnitskaya (Pyatnickaya), and G. A. Komashko, *React. Kinet. Catal. Lett.*, **38**, No. 1, 147 (1989).
79. V. A. Zazhigalov, V. M. Belousov, A. I. Pyatnitskaya (Pyatnickaya), G. A. Komashko, N. D. Konovalova, and G. I. Gol'denberg (Goldenberg), *React. Kinet. Catal. Lett.*, **39**, No. 2, 311 (1989).
80. G. A. Kozlova, A. K. Avetisov, and A. I. Gel'bshtein, Sixth Conference on Oxidative Heterogeneous Catalysis. Summaries of Papers [in Russian], Baku (1988), p. 17.
81. V. I. Gomonai, *Catalysis and Catalysts* [in Russian], No. 26, Naukova Dumka, Kiev (1989), p. 52.
82. G. Centi, F. Trifiro, J. R. Ebner, and V. M. Franchetti, *Chem. Rev.*, **88**, No. 1, 55 (1988).
83. J. W. Johnson, D. C. Johnston, and A. J. Jacobson, *Prep. Catal.* 4. Proceedings of the 4th International Symposium in Louvain la Neuve, September 1-4, 1986, Amsterdam (1987), p. 181.
84. F. Mori, K. Yoshida, M. Yamazaki, and I. Matsuura, *Shokubai*, **29**, No. 6, 490 (1987).
85. V. A. Zazhigalov, G. A. Komashko, A. I. Pyatnitskaya, E. V. Artemov, Yu. N. Merkur'eva, G. I. Gol'denberg, N. D. Konovalova, A. S. Shul'man, A. K. Sinel'nichenko, and N. V. Kirillova, *Catalysis and Catalysts* [in Russian], No. 26, Naukova Dumka, Kiev (1989), p. 85.
86. A. Ramonosona, E. Bordes, and P. Courtine, *J. Solid State Chem.*, **68**, 1 (1987).
87. S. P. S. Kuo and B. L. Yang, *J. Catal.*, **117**, 301 (1989).
88. V. V. Sidorchuk, V. M. Belousov, and L. I. Koval'chuk, *Catalysis and Catalysts* [in Russian], No. 26, Naukova Dumka, Kiev (1989), p. 63.
89. U. Ozkan and G. L. Schrader, *J. Catal.*, **95**, 120 (1985).
90. U. Ozkan and G. L. Schrader, *J. Catal.*, **95**, 137 (1985).
91. U. Ozkan, R. C. Gill, and M. R. Smith, *J. Catal.*, **116**, 171 (1989).
92. R. C. Gill and U. S. Ozkan, *J. Catal.*, **122**, 452 (1990).
93. T. Ono, T. Mukai, H. Miyata, T. Ohno, and F. Hatayama, *Appl. Catal.*, **49**, 273 (1989).
94. N. T. Do and M. Baerns, *Appl. Catal.*, **45**, 1 (1988).
95. N. T. Do and M. Baerns, *Appl. Catal.*, **45**, 9 (1988).
96. U. S. Ozkan, M. R. Smith, and S. A. Driscoli, *J. Catal.*, **123**, 173 (1990).
97. U. Ozkan and G. L. Schrader, *J. Catal.*, **95**, 147 (1985).
98. A. Bielanski, J. Piwowarczyk, and J. Pozniczek, *J. Catal.*, **113**, 334 (1988).
99. A. Inglot, Abstracts of the 1st French-Polish Workshop on Catalysis, Wroclaw (1988), p. 60.

100. A. Inglot, *React. Kinet. Catal. Lett.*, **39**, 323 (1989).
101. T. N. Shakhtakhtinskii, A. Ya. Rozovskii, A. D. Efendiev, and A. D. Agazade, *React. Kinet. Catal. Lett.*, **38**, 79 (1989).
102. A. N. Gulieva and A. D. Agazade, Fifth Conference on Oxidative Heterogeneous Catalysis. Summaries of Papers [in Russian], Baku (1988), p. 41.
103. A. D. Efendiev, A. Ya. Rozovskii, and A. D. Agazade, Sixth Conference on Oxidative Heterogeneous Catalysis. Summaries of Papers [in Russian], Baku (1988), p. 43.
104. I. V. Davidenko, Yu. V. Belokopytov, Yu. I. Pyatnitskii, and A. A. Davydov, Fifth All-Union Conference on the Mechanisms of Catalytic Reactions. Summaries of Papers [in Russian], Moscow (1990), p. 115.
105. Yu. Gol'dberg (Goldberg), E. Abele, J. Popelis, and M. Shimanskaya (Shimanska), Fifth International Symposium on Furan Chemistry. Abstracts [in Russian], Riga (1988), p. 48.
106. É. M. Abele, Yu. Sh. Gol'dberg, Yu. Yu. Popelis, and M. V. Shimanskaya, *Zh. Org. Khim.*, **26**, No. 8, 1784 (1990).
107. G. O. Torosyan, A. A. Akopyan, A. T. Torosyan, and A. T. Babayan, *Khim. Geterotsikl. Soedin.*, No. 4, 457 (1990).
108. I. Iovel' (Iovel), Yu. Gol'dberg (Goldberg), A. Gaukhman, and M. Shimanskaya (Shimanska), Fifth International Symposium on Furan Chemistry. Abstracts [in Russian], Riga (1988), p. 35.
109. I. G. Iovel', Yu. Sh. Gol'dberg, and M. V. Shimanskaya, *Khim. Geterotsikl. Soedin.*, No. 12, 1640 (1991).
110. A. Riad, Z. Mouloungui, M. Delmas, and A. Gaset, *Synth. Commun.*, **19**, No. 18, 3169 (1989).
111. I. G. Iovel', Yu. Sh. Gol'berg, A. P. Gaukhman, M. P. Gavars, M. V. Shimanskaya, and É. Lukevits, *Khim. Geterotsikl. Soedin.*, No. 10, 1372 (1988).
112. I. G. Iovel', Yu. Sh. Gol'dberg, M. V. Shimanskaya, and É. Lukevits, *Khim. Geterotsikl. Soedin.*, No. 1, 31 (1987).
113. Yu. Gol'dberg, E. Abele, M. Shimanskaya (Shymanska), and E. Lukevits (Lukevics), *J. Organomet. Chem.*, **372**, C9 (1989).