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FURAN AND ITS DERIVATIVES IN THE SYNTHESIS OF OTHER HETEROCYCLES (REVIEW)

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Data on methods of transforming furans into heterocycles containing oxygen, nitrogen, sulfur, and selenium are discussed and summarized.

The chemistry of furan is one of the most widely studied regions of organic chemistry. At the present time extensive data have accumulated on the synthesis of furan compounds and their chemical characteristics, and this is reflected in the monographs [1-5].

An important property of furans is their ability to change into other O-, N-, S-, and Se-containing heterocyclic compounds, and this often makes them an irreplaceable raw material source in organic synthesis. Data on this subject have been partly covered in monographs and reviews [6-9].

The aim of the present review is to analyze and summarize data on the transformation of furans into the above-mentioned heterocycles as a result of ring cleavage.

1. TRANSFORMATION OF FURANS AND TETRAHYDROFURANS INTO OTHER HETEROCYCLES UNDER THE CONDITIONS OF CATALYTIC DEHYDRATION

1.1. Yur'ev Conversion of Heterocycles

A classical transformation of furan is the catalytic conversion of this heterocycle into the heterocyclic analogs pyrrole, thiophene, and selenophene, which was discovered in 1935 by Yur'ev and was more recently extended to tetrahydrofuran. The method is based on the simultaneous catalytic dehydration of the reactants on the surface of highly active oxide catalysts at 350-500°C.

The reaction is successful between furan and various nucleophiles (ammonia, amines, hydrogen sulfide, and selenide). The introduction of a substituent at position 2 of the ring and also increase in the number of carbon atoms greatly reduce the yield of the pyrroles and prevent the production of thiophenes and selenophenes. Yur'ev only achieved the catalytic transformation of functional derivatives of the furan series to nitrogen-containing heterocycles. The possibility of exchanging the oxygen of tetrahydrofuran derivatives was demonstrated in the case of butyrolactone (by nitrogen and sulfur) and tetrahydrofuryl alcohol, while the latter undergoes isomerization from the five-membered ring to a six-membered ring during the reaction. Yur'ev studied aluminum, thorium, and chromium oxides as active dehydration catalysts. The yields of the required products did not exceed 40%. The results from comprehensive study of the reaction were set out in [10, 11].

Subsequent developments of the Yur'ev reaction involved either enlargement of the range of products obtained from furan (mainly nitrogen-containing heterocycles) or searches for the new dehydration catalysts required in the development of conditions for the technological synthesis of pyrrole, pyrrolidine, thiophene, and thiophane. Thus, the catalysts employed included aluminum oxide modified by various additives (molybdenum and vanadium oxides [12], boric acid [13], a mixture of manganese and cobalt chlorides with potassium and lithium chlorides [14], hydrofluoric acid and cobalt chloride [15, 16], sodium tungstate [17], potassium phosphotungstate [18], silicic acid [19], sodium oxide [20]).

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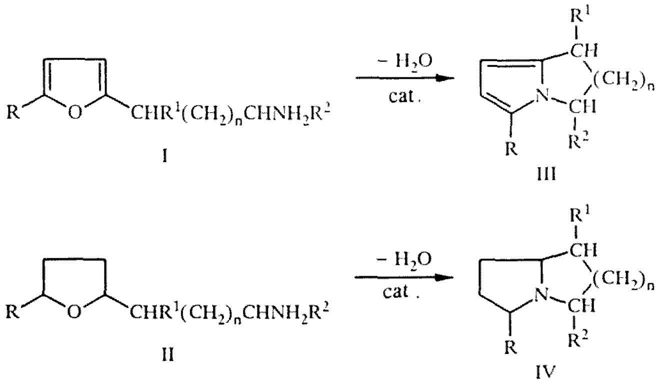
Aluminosilicates [21-24] and zeolites [25-27] were also used in the heteroexchange reactions. The aluminosilicates were modified with cadmium, tin, boron, magnesium [28], and calcium [29] compounds; zeolites X and Y were modified with calcium, cobalt, copper, nickel, and manganese ions [30]. Zeolite L in the hydrogen form was also used [31]. By using the modified catalysts it was possible to raise the selectivity of the process to 90%, the conversion of the initial furan and tetrahydrofuran to 80%, and the yield of the required products to 60-90%.

The mechanism of the Yur'ev conversion of heterocycles includes initial hydrogenolysis of the furan or tetrahydrofuran ring at the C–O bond with the addition of the elements of ammonia, amines, hydrogen sulfide, or hydrogen selenide and dehydration of the intermediate bifunctional acyclic compound followed by cyclization at the new heteroatom. To obtain evidence for such a mechanism Yur'ev realized the synthesis of the respective nitrogen- and sulfur-containing heterocycles from 1,4-butanediol and ammonia or hydrogen sulfide and also the cyclization of 4-aminobutanol. The investigations showed that the reaction was catalytic and did not take place under the influence of high temperature alone.

More recently Topchieva carried out investigations into the transformations of furan and tetrahydrofuran into thiophene at the sodium and lithium forms of faujasite zeolites [25, 32]. The data on the catalytic activity of the zeolites were compared with the results from the IR spectra of the reactants and the transformation products in the adsorbed state and confirmed the accuracy of the mechanism proposed for the Yur'ev reaction.

1.2. Catalytic Synthesis of 1-Azabicycles

Furan and tetrahydrofuran amines are transformed into 1-azabicycles as a result of catalytic dehydration in the gas phase. This intramolecular form of the Yur'ev reaction was first described in 1947 [33] and was investigated systematically by Ponomarev and Skvortsov [32-42]. A wide range of amines of the furan series (I, II) enters into the reaction [42-44]:



R, R^1, R^2: H, Alk, Ar; $n = 0, 1, 2, 3$

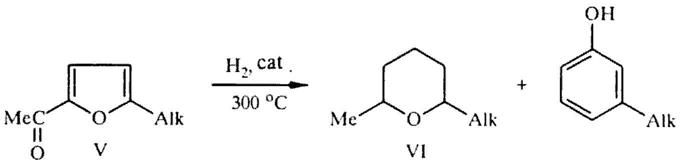
The most important factors influencing the reaction path are the structure of the initial amines and the choice of catalyst. The possibility of the formation of five-, six-, seven-membered rings condensed with the pyrrole or pyrrolidine rings at the C–N bond depends on the mutual positions of the ring and the amino group. The investigated catalysts were γ-Al_2O_3, Al_2O_3 promoted with 5% of ThO_2, and the mixed catalyst γ-Al_2O_3 (80%)–ZrO_2 (20%). The best results were obtained with γ-Al_2O_3 at 330-380°C. The yields of the products (III, IV) did not exceed 40-65%.

2. TRANSFORMATION OF FURANS INTO OXYGEN- AND NITROGEN-CONTAINING HETEROCYCLES UNDER THE CONDITIONS OF CATALYTIC HYDROGENATION

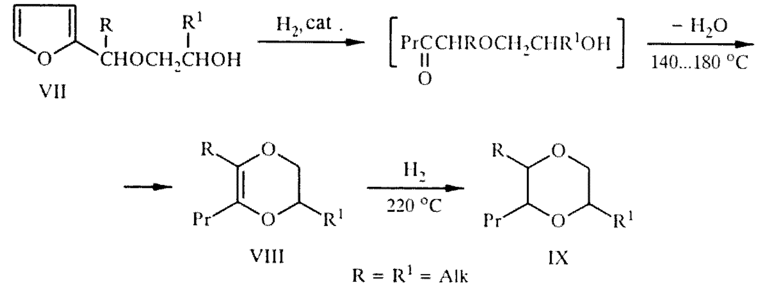
An important position among the catalytic methods for the transformation of furan compounds is taken by their hydrogenation, combined with hydrogenolysis or hydrolysis of the ring.

2.1. Synthesis of Oxygen- and Nitrogen-Containing Heterocycles by the Hydrogenolysis of Furans

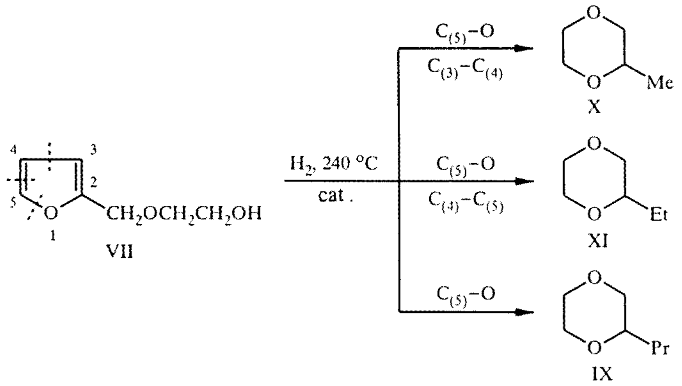
Under the conditions of catalytic hydrogenation in a stream of hydrogen at 200-300°C in the presence of group VIII metals, deposited on carbon, 2-alkyl-5-acylfurans (V) are converted into the homologs of tetrahydropyran (VI), in addition to which phenols are also formed. Here the furans (V) undergo hydrogenolysis of the ring with the formation of δ-ketones, which are transformed under the reaction conditions into the products (VI) through the diols [45-47]:



At the Pt/C catalyst under analogous conditions 2-(4-hydroxy-2-oxoalkyl)furans are converted into the homologs of dioxene (VIII) and dioxane (IX). This transformation can be realized selectively by varying the temperature [48].

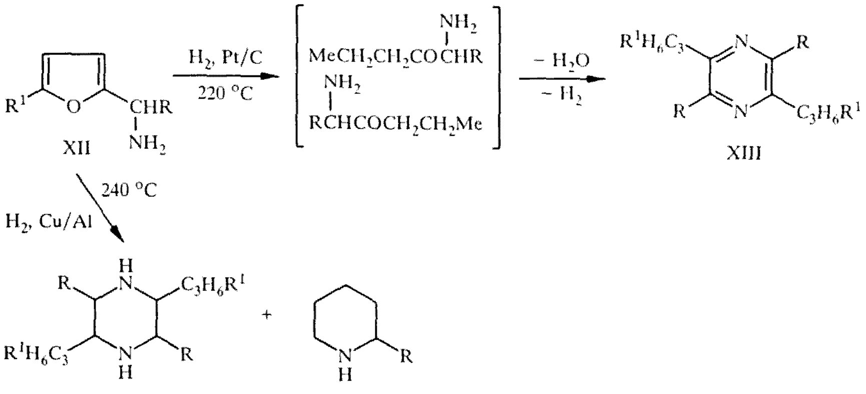


If the process is conducted at Raney nickel catalyst, hydrogenolysis of the furan ring at the $C_{(5)}-O$, $C_{(5)}-C_{(4)}$, and $C_{(4)}-C_{(3)}$ bonds occurs. This makes it possible to synthesize the three homologs of dioxane (IX) (R = R^1 = H), (X), and (XI) from compound (VII) (R = R^1 = H) [49]:



The possibility of catalytic synthesis of the amines was examined in detail in the monographs [6, 50], and we will therefore only point out its principal characteristics: Heteroaromatic compounds (250-300°C) or their saturated analogs (200-400°C) can be obtained, depending on the temperature; the structure of the products is determined by the position of the amino group in the aminoalkyl substituent and by the relative resistance of the C–O bonds in the furan ring to hydrogenolysis.

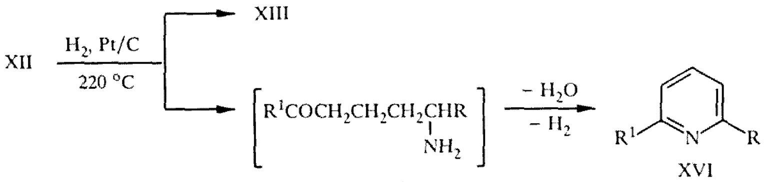
During hydrogenation over Pt/C in a flow-type system (hydrogen at atmospheric pressure, 220°C) furan amines containing the amino group at the α-carbon atom are capable of being transformed into the homologs of pyrazine (XIII). The hydrogenation of the amines over a Raney-type copper catalyst by a flow-type method (hydrogen pressure 5 MPa, 230-250°C) leads to a 4:1 mixture of the respective homologs of piperazine (XIV) and piperidine (XV) [51]:



R = H, Alk; R^1 = H

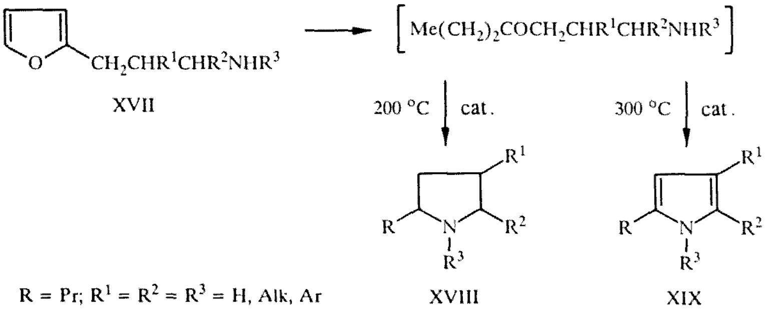
The formation of the pyrazines and piperazines is due to hydrogenolysis of the $C_{(5)}-O$ bond of the furan ring and cyclodehydration of two molecules of the intermediate α-amino ketones.

In the case of 5-alkyl-2-furfurylamines (XII) (R^1 = Alk) hydrogenolysis of the furan ring takes place at the $C_{(2)}-O$ and $C_{(5)}-O$ bonds, and this leads to the formation of the homologs of pyridine (XVI) and pyrazine (XIII):



R = H, Alk; R^1 = Alk

The hydrogenolysis of the furan amines (XVII) containing the amino group at the γ-carbon atom of the side chain has been investigated most fully [52-56]. Various homologs of pyrrolidine (XVIII) and pyrrole (XIX) were obtained:



R = Pr; R^1 = R^2 = R^3 = H, Alk, Ar

The process was conducted in the presence of platinum, palladium, rhodium, and osmium, deposited on carbon or asbestos, and also Raney-type palladium, nickel, and copper catalysts. The Pt/C and Raney-type palladium and copper catalysts exhibited the highest activity.

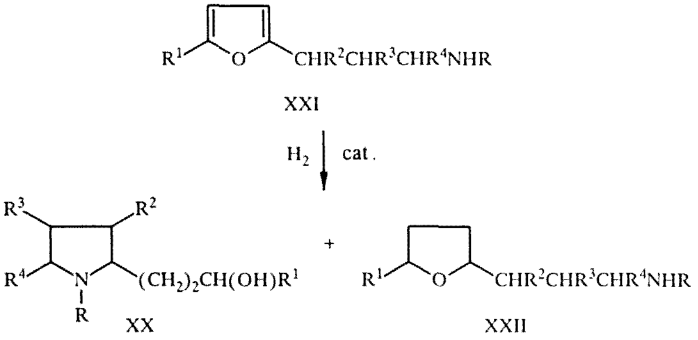
The structure of the obtained pyrrole and pyrrolidine analogs is determined by the structure of the side amino group in the chain and by the type of hydrogenolysis of the furan ring only at the $C_{(5)}-O$ or at the $C_{(4)}-C_{(5)}$ or $C_{(3)}-C_{(4)}$ bonds. The latter takes place when the reaction is conducted at Raney nickel and makes it possible to obtain three homologs each of pyrrole (XIX) and pyrrolidine (XVIII), where R = C_3H_7, C_2H_5, or CH_3, from compounds (XVII) [57].

2.2. Synthesis of Azaheterocycles by Intramolecular Hydroamination of Furan Compounds

The transformation of furan amines into five-membered nitrogen-containing heterocycles takes place during their catalytic hydrogenation at heterogeneous catalysts in the liquid phase in an acidic medium. The process involves the cleavage of the furan ring under the conditions of hydrolysis. Reactions of this type are characteristic of amines containing a functional group at the γ-carbon atom of the side chain. The azacyclization process is regarded as the result of intramolecular hydroamination of the intermediately formed aminocarbonyl compounds, containing favorably located groups.

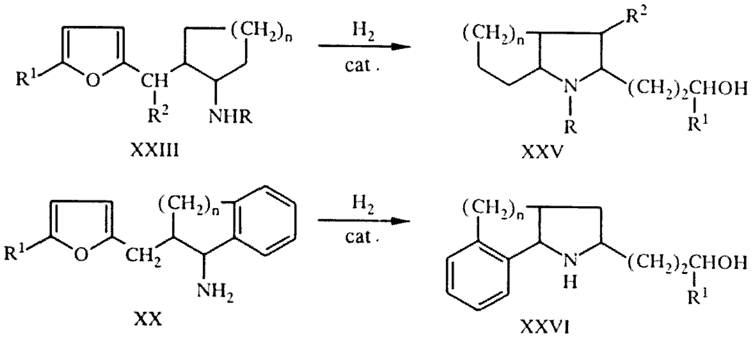
Such a process was realized for the first time by Sorm [58]: α-propylpyrrolidine was obtained with a 17% yield as a result of the hydrogenation of 3-aminopropane at platinum dioxide in a hydrochloric acid solution at 20°C and a hydrogen pressure of 5 MPa.

Systematic investigations into the intramolecular hydroamination of furan compounds in the liquid phase were carried out by Ponomarev, Kriven'ko, and Noritsina [59-64]. They developed a method for the production of various alcohols of the pyrrolidine series (XX) by the hydrogenation of primary and secondary amines and diamines (XXI) in acidic aqueous solutions (pH 4-5) at 80-100°C and a hydrogen pressure of 5-10 MPa in the presence of heterogeneous catalysts based on metals of group VIII. Here the corresponding derivatives of tetrahydropyran (XXII) are formed together with the required alcohols (XX).



R = H, Alk, Ar, $(CH_2)_3NH_2$, $(CH_2)_2OH$; R^1 = H, Me; $R^2 = R^3$ = H, Alk; R^4 = H, Alk, Ar

From furfuryl-substituted acyclic amines (XXIII, XXIV) under the indicated conditions polycyclic alcohols in the form of derivatives of 2,3-trimethylenepyrrolidine, octahydroindole, benzo[c]octahydroindole, and indanopyrrolidine (XXV, XXVI) were synthesized [64-66]:



$R = R^1 = R^2$ = H, Alk; n = 1, 2

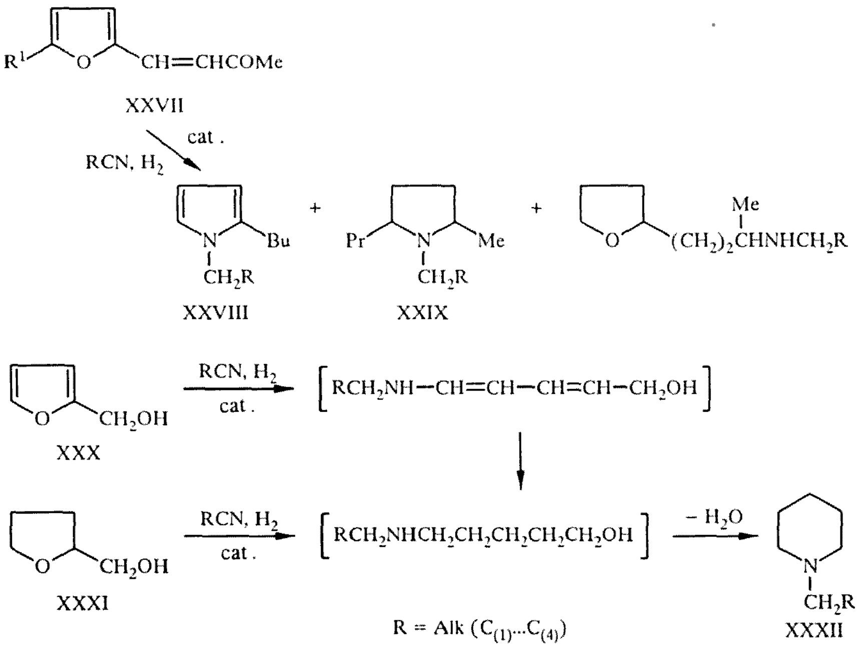
Pyrrolidylalkanols are formed as a result of hydrolytic cleavage of the furan ring followed by azaheterocyclization of the aminodicarbonyl intermediate, as was demonstrated in a number of cases by the isolation of the corresponding aminodiols [67] and by experiments on hydrogenation in heavy water [68]. It was established that the product yield depended on the reaction conditions, the nature of the employed catalysts, and the structure of the initial amines.

By the use of such catalysts as Raney-type cobalt, Raney nickel and cobalt promoted by 2% acetic acid, and also Pd/C, nickel boride, nickel–ruthenium, and industrial nickel–potassium catalysts it was possible to obtain alcohols of the pyrrolidine series with yields of up to 80% [64, 69-72].

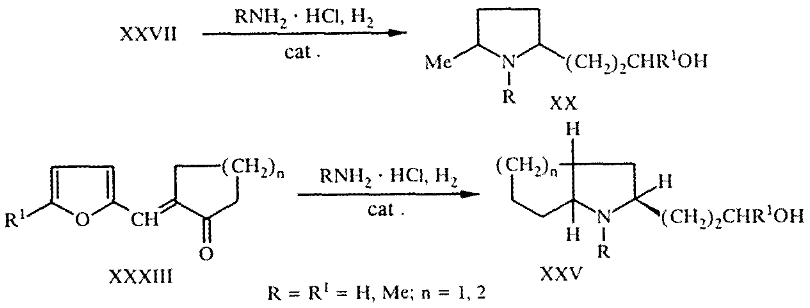
2.3. Synthesis of Azaheterocycles by the Hydroamination of Furan Hydroxy and Oxo Compounds

Investigations into the direct transformation of furan alcohols and unsaturated ketones into five- and six-membered azaheterocycles under the conditions of reductive amination are of interest.

Under the conditions of vapor-phase hydroamination with aliphatic nitriles furfurylideneacetone (XXVII) (R^1 = H) is converted into N-substituted pyrroles (XXVIII) and pyrrolidines (XXIX) [73, 74], while furfuryl (XXX) and tetrahydrofurfuryl (XXXI) alcohols are converted into N-alkylpiperidines (XXXII) [75]. The reaction is conducted at Cu/Al_2O_3, Cu/MgO, and Cu/ZnO catalysts at 220-240°C under hydrogen at 1.5 MPa:



A prospective method for the stereoselective synthesis of the hydroxyalkyl derivatives of pyrrolidine (XX) ($R^2 = R^3$ = H), cyclopenta[b]pyrrolidine (XXV) (R^2 = H, n = 1), and octahydroindole (XXV) (R^2 = H, n = 2) involves hydroamination of compounds (XXVII) ($R^1 = CH_3$) and (XXXIII) in the presence of nickel–ruthenium catalyst in an acidic aqueous alcohol medium at 60-80°C in hydrogen at 6-7 MPa [76-78]. The selected conditions made it possible to combine amination and cleavage of the furan ring in the initial α,β-enols:



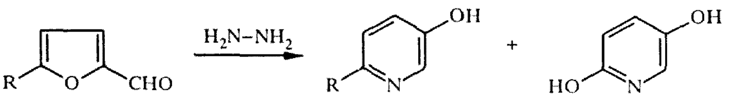
If methylamine hydrochloride is used as nitrogen-containing reagent, the yields of the desired products amount to 60-80%. In the case of the weaker nucleophile ammonia (in the form of ammonium chloride or acetate) hydrogenation of the initial substances occurs. The reactivity of α,β-enols (XXVII) is higher than that of α,β-enols (XXXIII). For the latter it is highest when n = 1, and this is due to the rigidity of their structure [79].

3. TRANSFORMATIONS OF FURANS INTO NITROGEN-, SULFUR-, OR SELENIUM-CONTAINING HETEROCYCLES CATALYZED BY ACIDS OR BASES IN A HOMOGENEOUS MEDIUM

3.1. Synthesis of Nitrogen-Containing Heterocycles

The transformations discussed in this section are based on cleavage of the furan ring as a result of ammonolysis or hydrolysis followed by azacyclization.

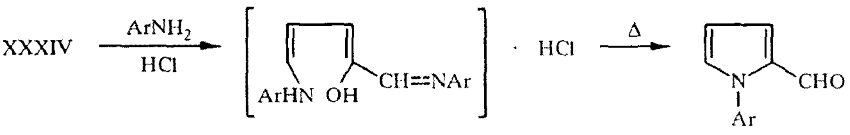
The transformation of furans containing a carbonyl group attached to the ring into pyridine and pyrrole compounds under the conditions of alkaline or acid catalysis is well known. Thus, furfural (XXXIV) (R = H) forms a mixture of 3-hydroxypyridine (XXXV) (R = H) and 2,5-dihydroxypyridine when treated with hydrazine sulfate under pressure at 150°C. Under similar conditions 5-methylfurfural (XXXIV) (R = Me) is converted into 6-methyl-3-hydroxypyridine (XXXV) (R = Me) [80]:



XXXIV XXXV

R = H, Me

A considerable number of investigations have been devoted to the reaction of furfural with aromatic amines and their salts, which takes place when the reagents are heated together in methanol or ethanol under the conditions of acid hydrolysis and leads to the formation of 2-pyrrolecarbaldehydes (XXXVII) [81-87]:

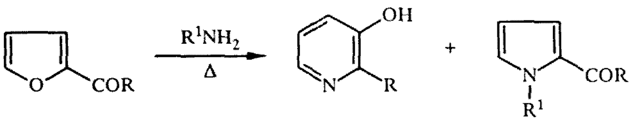


XXXVI

Ar = 4-NO_2-C_6H_4, 4-$NH_2SO_2C_6H_4$, 4-nitronaphthyl-1,4-phthalimidyl 2-OH-5-NO_2-C_6H_3, 2-OH-4-NO_2-C_6H_3, 2-OH-3-Cl-5-NO_2-C_6H_2, 2-OH-4-NO_2-6-Cl-C_6H_2

The pH of the medium and the temperature are of great significance for the reaction. Under optimum conditions the yield of the aldehydes (XXXVI) amounts to 80% [86, 87].

After prolonged boiling with ammonia, primary aromatic amines, their salts, and hydroxylamine the 2-acylfurans form 2-substituted 3-hydroxypyridines (XXXVII) and small amounts of the corresponding 2-acylpyrroles (XXXVIII):

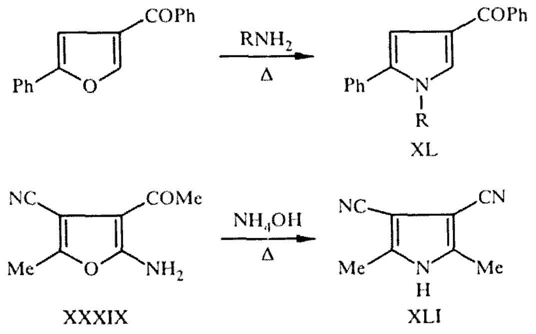


XXXVII XXXVIII

R = Me, Et, CH_2Ph, $(CH_2)_2Ph$; R^1 = H, Ar

The reaction has been studied well, and numerous examples are described in the reviews [4, 8, 9].

If there is a carbonyl group at the β position of the furan ring the products from transformation of the furans are the pyrroles (XL, XLI) respectively [88, 89]:

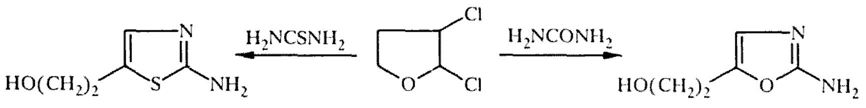


XL

XXXIX

XLI

2,5-Dichloro- and 2-chlorotetrahydrofurans behave similarly to the acylfurans in reactions with amines. Their aromatization with the formation of N-substituted pyrroles takes place as a result of the loss of HCl [9]. 2-Amino-5-(2-hydroxyethyl)oxazole (XLIII) is formed in the reaction of 2,3-dichlorotetrahydrofuran (XLII) with urea, and the corresponding 2-aminothiazole (XLIV) is formed with thiourea [90]:



XLIV

XLII

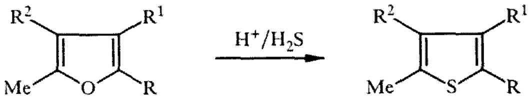
XLIII

After prolonged heating with ammonia, ammonium acetate, primary aliphatic or aromatic amines or their salts, and hydrazine or its derivatives the condensed derivatives of tetrahydrofuran were converted into azaindolines, isoindoles, tetrahydroindoles, octahydrocarbazoles, pyrazoles, pyrazolines, imidazolines, and oxadiazoles, and this is described in the reviews [4, 9].

3.2. Recyclization of Furans to Thiophenes and Selenophenes under the Conditions of Acid Catalysis

The recyclization of furans to thiophenes was discovered in 1976 by Kharchenko, Gubina, and coworkers [91, 92]. More recently, the reaction was used for the synthesis of selenophenes [93].

It was also established that the furan compounds (XLVa-j) are converted by the action of hydrogen sulfide in alcohol solution under the conditions of acid catalysis at room temperature into the corresponding thiophene analogs [94-98]:



XLV.a-j

XLVI a-j

a R = H, b R = Alk(C_1—C_4), c R = R^1 = R^2 = Alk(C_1—C_3), d R = C_6H_4X (X = H, CH_3, OCH_3, Cl, Br), e R = CHR^3OH, $(CH_2)_3OH$, $(CH_2)_2CHOHR^4$ (R^3 = Alk, Ar), f R = $CHR^5CH_2COR^6$ (R^5 = Alk, R^6 = Ar), g $(CH_2)_nOCH_2CH_2OH$, n = 2, 3, h $(CH_2)_2COOC_2H_5$, $(CH_2)_2OCOCH_3$, and (2-oxocyclopentyl)methyl, (2-oxocyclohexyl)methyl, (2-oxocyclopentyl)methyl, (2-oxocyclohexyl)methyl, R^1 not specified, R^2 = H

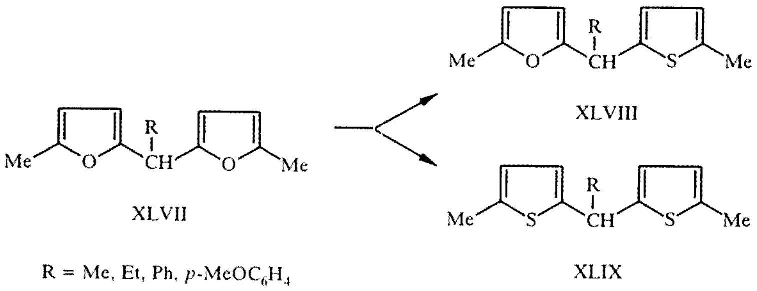
It was shown that successful recyclization requires an excess both of the nucleophilic reagent (the reaction takes place in a stream of hydrogen sulfide or hydrogen selenide) and of the acid [optimum concentration 2.4-3.5 M (perchloric, trifluoroacetic, or hydrochloric acid, hydrogen chloride gas).

2,5-Dialkylfurans are converted into thiophenes most easily. Increase in the length of the α,α'-alkyl substituents does not affect the transformation rate. The recyclization of tri- and tetraalkylfurans was realized, although the reaction in this case was significantly slower [96].

2-Alkyl-5-arylfurans (XLVd) react with hydrogen sulfide under considerably more rigorous conditions than 2,5-dialkylfurans (XLVb) (hydrogen chloride concentration 3.5 M, reaction temperature 50-60°C, reaction time 50 h). The reaction rate depends on the nature of the substituent in the aryl fragment [97].

The furan alcohols (XLVe,i), the hydroxy ethers (XLVg), the ketones (XLVf,j), and the esters (XLVh), containing functional groups at the γ-carbon atom of the side chain, enter into reaction with hydrogen sulfide under conditions similar to those used in the case of 2,5-dimethylfuran [98]. The introduction of carbonyl and carboxyl groups at the α position of the side chain prevents recyclization of these furan derivatives. Irrespective of the position of the functional group, aldehydes of the furan series react with hydrogen sulfide with the formation of trithiacyclohexanes.

The transformation of di(2-furyl)alkyl- and di(2-furyl)arylmethanes (XLVII) into the thiophene analogs was studied [99]:



XLVII

XLVIII

XLIX

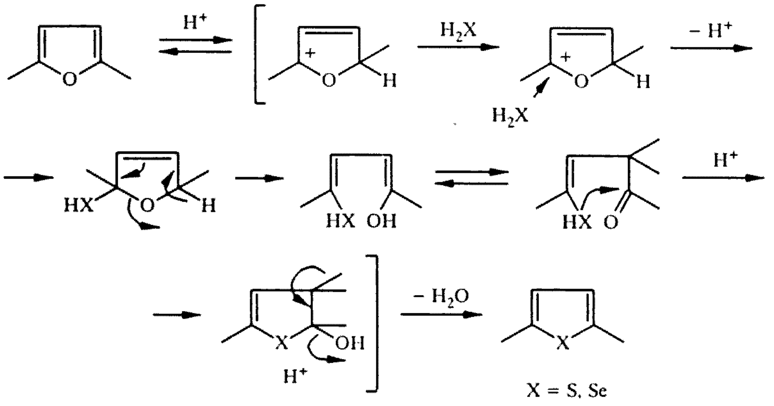
R = Me, Et, Ph, p-$MeOC_6H_4$

If the reaction is conducted in ethanol saturated with hydrogen chloride to a concentration of 2.5-3.5 M, the recyclization of one furan ring occurs. With propyl alcohol it is possible to obtain both the monothienyl (XLVIII) and the dithienyl (XLIX) derivatives, and this also depends on the nature of the substituent.

Conditions were developed for the recyclization of 2-methyl-, 2-ethyl-, and 2-arylfurans. The reaction takes place under the action of hydrogen sulfide in absolute ethanol saturated with hydrogen chloride in the presence of small amounts of zinc chloride at 60°C with a low concentration of the initial compound in the solution [100].

The recyclization of furans to selenophenes was also realized for many of the above-mentioned 2,5-disubstituted furans under identical conditions. For its successful realization it is essential to conduct the reaction in an inert gas atmosphere [97, 98, 101].

In order to determine the mechanism of the acid-catalyzed recyclization of furans to thiophenes and selenophenes kinetic investigations were carried out into the reaction of 2,5-dialkylfurans (XLVb) in the presence of hydrochloric acid and in an anhydrous medium. The experiments in the presence of hydrochloric acid showed that the transformation of the furans (XLVb) into the corresponding thiophenes and selenophenes can take place in two independent directions, i.e., through the intermediate formation of dicarbonyl compounds followed by reaction of the intermediates with the nucleophiles (A) and by direct recyclization (B) according to the following scheme [102]:



X = S, Se

Comparison of the rate constants of recyclization and hydrolysis shows that realization of the process by path B, presented in the scheme, is preferred to path A.

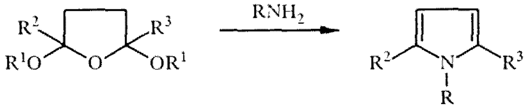
Study of the kinetics in the absolute media showed that recyclization takes place by a mechanism of acid catalysis and depends to significant degree on the concentration of hydrogen chloride. It was established that the reaction had zero order with reference to the nucleophile and second order with reference to the acid component. The latter made it possible to suppose that the opening of the furan ring may be due to the formation of a doubly protonated form of the substrate [103]. Quantum-chemical calculations confirmed the possibility of double protonation with the addition of the second proton to the oxygen of the ring [96].

3.3. Synthesis of Nitrogen- and Sulfur-Containing Heterocycles from 2,5-Dialkoxydihydro- and 2,5-Dialkoxytetrahydrofurans

Since the transformation of furans into N- and S-containing heterocycles under the conditions of acid catalysis is based on hydrolytic cleavage of the furan ring, 2,5-dialkoxydihydro- and 2,5-dialkoxytetrahydrofurans, which became available with the discovery of the electrolytic alkoxylation method by Clauson-Kaas [104], are often used as the starting compounds in these transformations.

The transformation of alkoxyfurans into N-containing heterocycles has been studied most fully. Syntheses of pyrrole, substituted pyridazines, tropinones, and hydroxy- and dihydroxypyridines from the dimethoxydihydro and dimethoxytetrahydro derivatives of furan, furfurylamine, and acylfurans respectively were described in [105-107]. These processes involve cleavage of the furan ring by the action of acids or bases followed by inter- or intramolecular condensation with the nucleophilic reagent, leading to cyclization at the new heteroatom. The method for the synthesis of pyridine systems proposed by Clauson-Kaas forms the basis of an industrial process for the production of pyridoxine (vitamin B_6) [108, 109].

The reaction of 2,5-dialkoxytetrahydrofuran (L) with ammonia and primary aliphatic of aromatic amines, which takes place when the reagents are heated together and often under the conditions of acid catalysis (by acetic acid or toluenesulfonic acid), forms the basis of the synthesis of pyrrole and its N-R-derivatives (LI) [105, 110-120]:



L LI

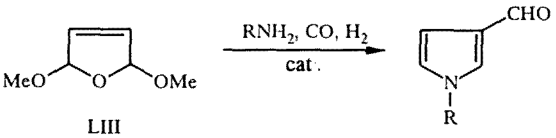
R^1 = Me, Et, R^2 = R^3 = H, Alk, Ar, oxo, hydroxy, thio, cyano, and nitro derivatives of the latter

Primary amines containing the fragments of benzothiophenes [121], flavones [122], pyrazines, pyridines [123], thiazolines [123, 124], and triazoles [125] have also been used as amine component.

N-Substituted condensed pyrroles containing carbazole, phenothiazine, dibenzophenazine, and pyrazine heterocycles were obtained from compound (L) [126, 127].

An industrial method for the production of pyrrole and its N-R-homologs (R = H, Alk, Ar) by the vapor-phase reaction (350-400°C) of compound (L) with ammonia and amines on the surface of oxide or zeolite catalysts has been described. With 100% conversion of the initial furan compound the yield of the desired products amounted to 85% [128].

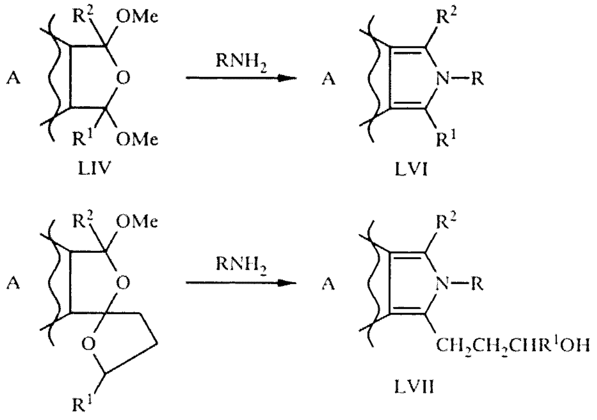
A method was developed for the synthesis of 3-pyrrolecarbaldehyde (LII) by the hydroformylation of 2,5-dimethoxy-2,5-dihydrofuran (LIII) at the $HRh(CO)(PPh_3)$ catalyst in the presence of primary amines [129]. The reaction is carried out at 100°C at an initial pressure of 10 MPa with a 1:1 mixture of CO and H_2:



LIII LII

R = Me, Bu, Ph

A modification of the transformations above is the method for the synthesis of the condensed pyrroles — dihydro- and tetrahydroisoindoles (and the methanoisoindoles). When heated with primary amines under the conditions of acid catalysis the Diels–Alder adducts obtained from 2,5-dimethoxydihydrofurans and 2-methoxyspirononenes are transformed into compounds of the isoindole series (LVI, LVII) [130-132].

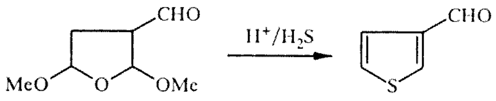


LIV LVI

LV LVII

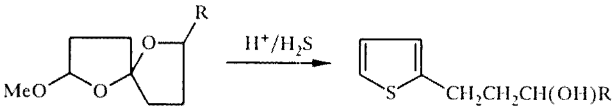
A = 1,4-but(en)ylene with substituents, 1,3-cyclopentan(en)ylene; R = Alk, Ar;
R^1, R^2 = H, Alk, Ar

A few examples of the transformation of 2,5-dialkoxytetrahydrofurans into thiophene derivatives are known. Thus, the action of hydrogen sulfide under the conditions of acid catalysis leads to the recyclization of 2,5-dimethoxytetrahydrofuran into thiophene and of compound (LVIII) into 3-thiophenecarbaldehyde (LIX) [133, 134]:



LVIII LIX

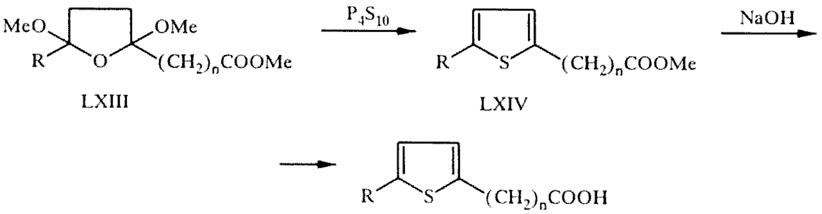
The synthesis of thiophene is conducted at room temperature under the influence of hydrochloric acid, while compound (LIX) is obtained at 60-300°C in the presence of mineral or organic acids. The transformation of the methoxydioxaspirononanes (LX) into the alcohols (LXI) was realized under conditions similar to the synthesis of thiophene:



LX LXI

R = H, Me

The 2-thienylalkanecarboxylic acids (LXII) were obtained by boiling the 2,5-dimethoxytetrahydrofuranalkanoic esters (LXIII) with phosphorus polysulfide in toluene followed by alkaline hydrolysis of the reaction products (LXIV) [135].



LXIII LXIV

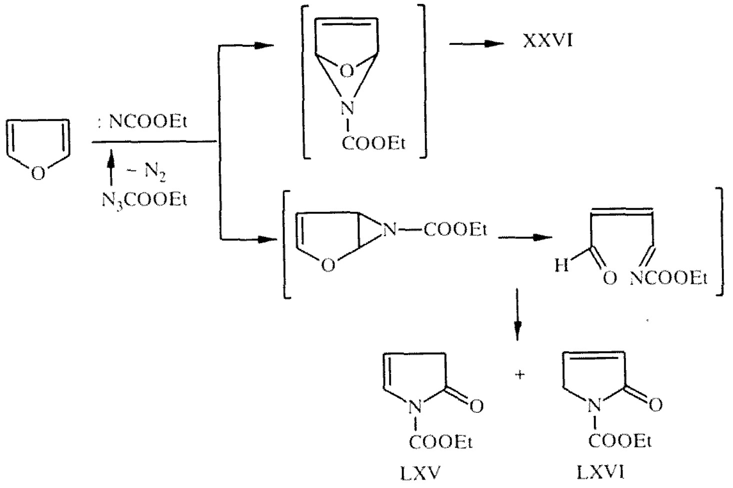
R = H, Me; n = 1...3

LXII

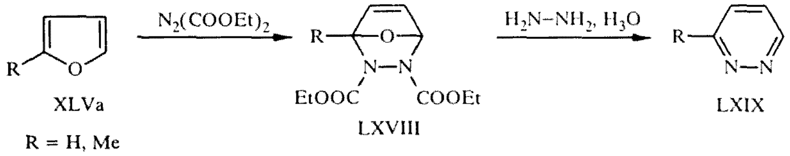
4. SYNTHESIS OF HETEROCYCLES FROM THE PRODUCTS FROM CYCLOADDITION OF COMPOUNDS OF THE FURAN SERIES

Great possibilities for the production of O- and N-containing heterocycles are opened up by their synthesis through the Diels–Alder adducts of furans with heterodienophiles or cycloaddition with carbenes. The products of the heterodiene syntheses of furan and its homologs are bridged systems, which are easily cleaved by the action of acid or hν radiation [136-138].

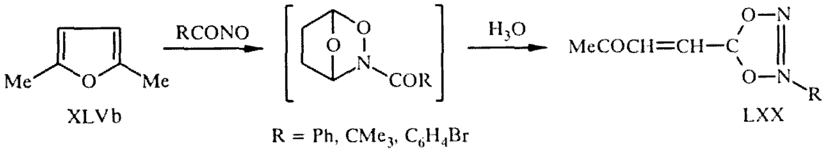
The N-substituted 2-pyrrolidinones (LXV, LXVI) are produced by the hydrolytic cleavage of the products from the cycloaddition of ethoxycarbonylnitrene to furan. There are two possible schemes for the mechanism of this transformation: a) the furan acts as a 2π-component; 2) the furan acts as a 4π-component [139]:



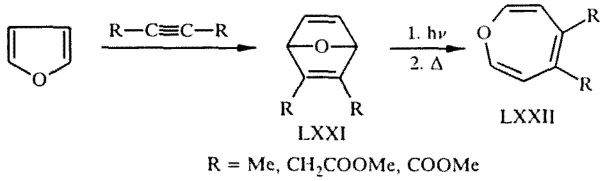
The reaction of the furans (XLVk) with azadicarboxylic ester gives the adducts (LXVIII), which are converted into the pyridazines (LXIX) when treated with hydrazine in an acidic medium [140-142]:



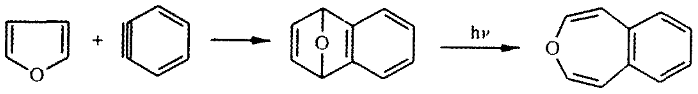
The reaction of the furan (XLVb) with nitrosocarbonyl compounds leads to the formation of substituted 1,4,2-dioxazoles (LXX) [143]:



Oxanorbornadienes (LXXI) are formed when furan is boiled with acetylenic dienophiles. Photoirradiation of the products followed by heating leads to the formation of the oxepins (LXXII) [144]:

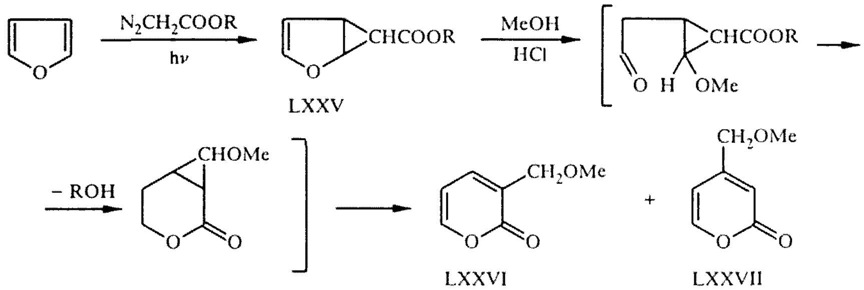


3-Benzoxepin (LXXIV) was synthesized by photolysis of the adduct (LXXIII) [145]:



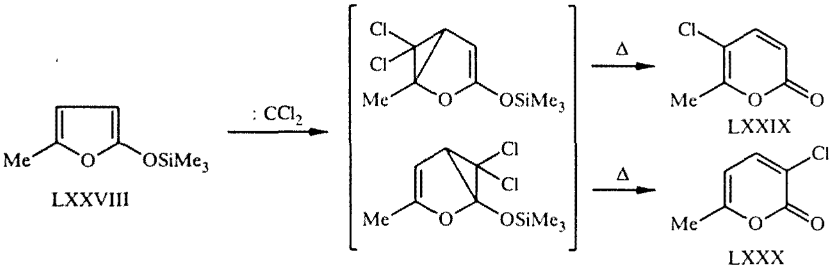
LXXIII LXXIV

The photochemical reaction of furan with diazoacetic ester gives the adduct (LXXV), the acid hydrolysis of which leads to the formation of the 2-pyrones (LXXVI, LXXVII) [146]:



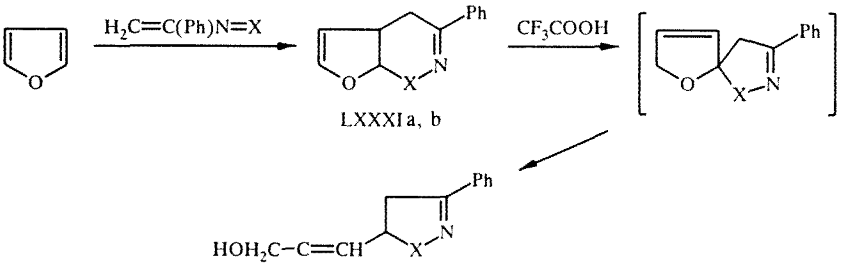
LXXV LXXVI LXXVII

The adducts obtained in the reaction of compound (LXXVIII) with dichlorocarbene, generated by the Reimer–Tiemann reaction, were converted by heating into the chlorine-substituted 2-pyrones (LXXIX, LXXX) [147]:



LXXVIII LXXIX LXXX

In heterodiene syntheses with nitroso- and azaolefins furan exhibits the characteristics of a dienophile. The diene condensation products are the furoxazines (LXXXIa) (X = O) and furopyridazines (LXXXIb) (X = NPh), which are converted by the action of trifluoroacetic acid into the corresponding derivatives of isoxazole and pyrazole (LXXXIIa,b) [148, 149]:



LXXXIa, b

LXXXIIa, b X = O, N–Ph

The paths for the transformation of furans into other heterocycles examined above do not cover all the transformation methods. However, they clearly illustrate the possibilities for the further development and application of the presented methods in organic synthesis.

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