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SYNTHESIS, STRUCTURE, AND CHEMICAL PROPERTIES OF N-SUBSTITUTED 2(3)-IMINO-2,3-DIHYDROFURAN-3(2)-ONES. (REVIEW)

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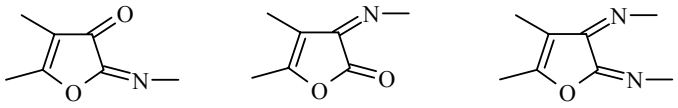
Published data on the synthesis, structure, and chemical properties of N-substituted 2(3)-imino-2,3-dihydrofuran-3(2)-ones to 2002 are reviewed.

Keywords: 2,3-diimino-2,3-dihydrofurans, N-substituted 2-imino-2H-furan-3-ones, 3-imino-3H-furan-2-ones, spectral characteristics, chemical transformations.

Data on the synthesis of a furan ring containing carbonyl and imine functions respectively at positions 2 and 3 of the heterocycle were first published a hundred years ago and concerned the synthesis of 2-hydroxyimino-2H-benzo[*b*]furan-3-one [1]. Limited but very varied material on the synthesis and chemical transformations of the imino derivatives of furan has now appeared.

This review is devoted to methods for the synthesis of N-substituted 2-imino-2H-furan-3-ones (**A**), 3-imino-3H-furan-2-ones (**B**), and the 2,3-diimino derivatives of 2,3-dihydrofuran (**C**).



A **B** **C**

It includes the imino derivatives of 2,3-dihydrofurandione itself and also the imino derivatives of its condensed benzo[*b*], phenanthro[9,10-*b*], and other analogs.

1. METHODS FOR THE SYNTHESIS OF N-SUBSTITUTED 2(3)-IMINO-2(3)H-FURAN-3(2)-ONES AND 2,3-DIIMINO-2,3-DIHYDROFURANS

Methods for the production of N-substituted imino derivatives of furan can be divided into two groups, i.e., methods based on the introduction of an imino function into an already existing furan ring and methods involving the construction of a furan ring with an R-imino group at position 2 or 3.

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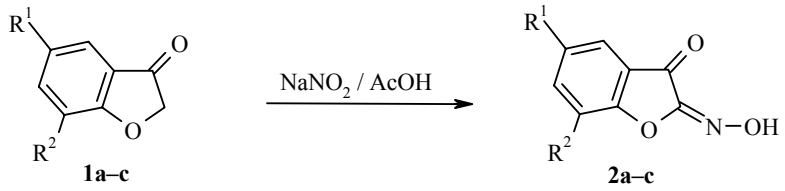
1.1. Syntheses Based on the Furan Heterocycle

Chronologically, the first were papers on the synthesis of the 2-oximes of 2H-benzo[*b*]furan-3-ones **2a-c** [1-4]. The 2-oximes were prepared by the reaction of coumaran-3-ones **1a-c**, containing an activated methylene group, with nitrous acid.

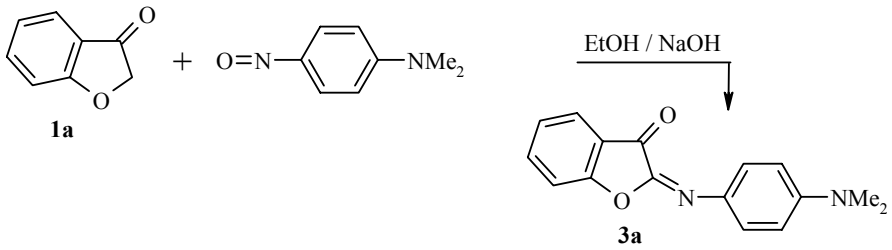


1a–c **2a–c**

1, 2 a R^1 = H, R^2 = H, **b** R^1 = Me, R^2 = H; **c** R^1 = R^2 = Br

2-Oximes unsubstituted in the aromatic ring (**2a**) [1], 5-methyl-substituted (**2b**) [2, 3], and 5,7-dibromine-substituted (**2c**) oximes [4] of 2H-benzo[*b*]furan-3-one derivatives were obtained in a similar way.

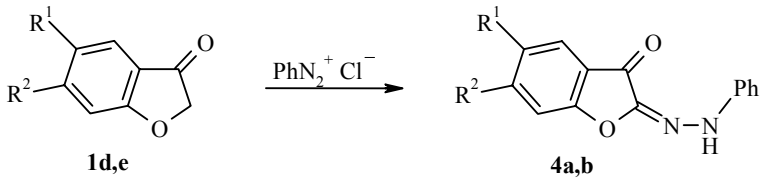
2-(4-Dimethylaminophenylimino)-2H-benzo[*b*]furan-3-one (**3a**) was obtained by the reaction of coumaran-3-one (**1a**) with 4-nitroso-N,N-dimethylaniline [5].



1a **3a**

In 1972 2-phenylimino-2H-benzo[*b*]furan-3-one (**3b**) was obtained with a yield of 36% by the analogous reaction of coumaran-3-one (**1a**) with nitrosobenzene [6].

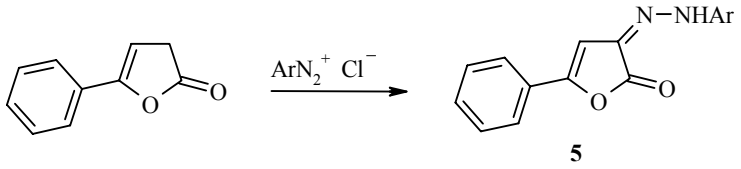
The activated methylene group of the coumaran-3-ones **1d**,**e** takes part in a coupling reaction with benzenediazonium chloride leading to the formation of 5-methyl-2-phenylhydrazono-2H-benzo[*b*]furan-3-one (**4a**) [7] and 6-methoxy-2-phenylhydrazono-5-chloro-2H-benzo[*b*]furan-3-one (**4b**) [8] respectively.



1d,e **4a,b**

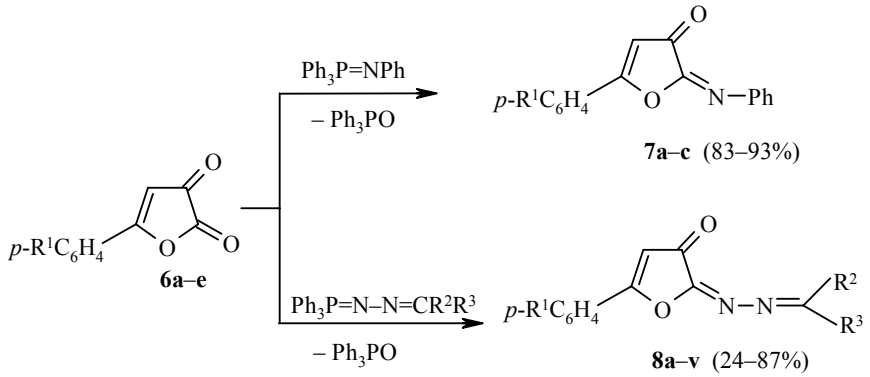
4 a R^1 = Me, R^2 = H; **b** R^1 = Cl, R^2 = MeO

More recently the reaction was used for the introduction of a hydrazone function at position 3 of the furan ring and the synthesis of 3-arylhydrazono-5-phenyl-3H-furan-2-ones **5** [9].



5

The 5-aryl-2,3-dihydrofuran-2,3-diones **6a-e** can be used as basic heterocycle for the synthesis of the 2-imino derivatives of furan-3-ones. Thus, reaction of the furandiones **6** with N-phenyltriphenylphosphine imine or the triphenylphosphoranylidenehydrazones of aldehydes and ketones (triphenylphosphazines) gave 5-aryl-2-phenylimino-2H-furan-3-ones **7a-e** [10, 11] and substituted 5-aryl-2-methylenehydrazono-2H-furan-3-ones **8a-v** [12-15] respectively.



6a–e

7a–c (83–93%)

8a–v (24–87%)

6 a R^1 = H, **b** R^1 = Me, **c** R^1 = MeO, **d** R^1 = Cl, **e** R^1 = Br; **7 a** R^1 = Me, **b** R^1 = Cl, **c** R^1 = Br;
8 a R^1 = Me, R^2 = R^3 = H; **b** R^1 = Cl, R^2 = R^3 = H; **c** R^1 = Br, R^2 = R^3 = H; **d** R^1 = Me, R^2 = R^3 = Ph;
e R^1 = Cl, R^2 = R^3 = Ph; **f** R^1 = Br, R^2 = R^3 = Ph; **g** R^1 = Me, R^2 = H, R^3 = PhCO; **h** R^1 = MeO, R^2 = H, R^3 = PhCO;
i R^1 = Cl, R^2 = H, R^3 = PhCO; **j** R^1 = Br, R^2 = H, R^3 = PhCO; **k** R^1 = Cl, R^2 = H, R^3 = $PhCH_2O$; **l** R^1 = Br, R^2 = H, R^3 = $PhCH_2O$;
m R^1 = Me, R^2 = H, R^3 = $PhCH_2O$; **n** R^1 = MeO, R^2 = H, R^3 = $PhCH_2O$; **o** R^1 = Br, R^2 = H, R^3 = $PhCH_2O$; **p** R^1 = Me,
R^2 = H, R^3 = 1-AdCO; **q** R^1 = Cl, R^2 = H, R^3 = 1-AdCO; **r** R^1 = H, R^2 = H, R^3 = EtOCO; **s** R^1 = Me, R^2 = H, R^3 = EtOCO; **t** R^1 = MeO,
R^2 = H, R^3 = EtOCO; **u** R^1 = Cl, R^2 = H, R^3 = EtOCO; **v** R^1 = Br, R^2 = H, R^3 = EtOCO

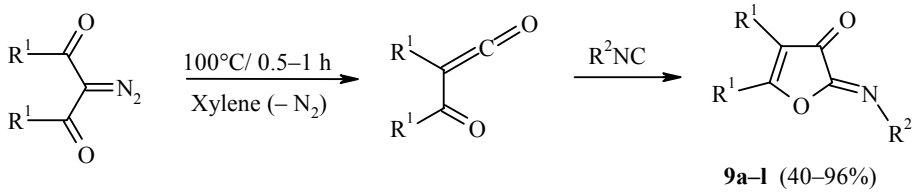
The formation of the 2-iminofuran-3-ones **7** and **8** by the Wittig and Staudinger types of reaction is distinguished by the fact that in the presence of a ketone carbonyl the reaction takes place at the lactone carbonyl group of the heterocycle. The authors explain such a direction of attack by the phosphine imine and triphenylphosphazines in terms of the electron density distribution in the 2,3-dioxo heterocycle. The direction of reaction of triphenylphosphazines with furandiones is the same if the hydrogen atom at position 4 of the heterocycle is replaced by a chlorine or bromine atom [16].

1.2. Construction of a Furan Ring with the R-Imino Function

Preparative methods have now been developed for the construction of all three types of structures under discussion: **A**, **B**, and **C**.

1.2.1 Synthesis of N-Substituted 2-Imino-2H-furan-3-ones A. Iminofurans of this type are synthesized by the reaction of acylketenes with isonitriles. The various methods differ in the processes used to generate the acylketenes. Thus, in [17] the acylketenes were generated during the thermolysis of 2-diazo-1,3-diketones, and they then formed the N-substituted 2-imino-4-R^1-5-R^1-2H-furan-3-ones **9a-l** with the isonitriles. It should be mentioned that only symmetrical diazodiketones were used. The yields of the iminofuranones **9**

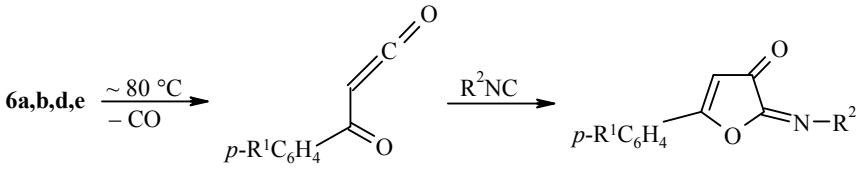
amounted to 40-96% and evidently depended both on the activity of the diene and dienophile in the [4+1] cycloaddition and on the rate of formation and the stability of the acylketenes during their formation under the conditions of a thermolytic Wolff rearrangement.



9a–l (40–96%)

9 a $R^1 = R^2 =$ Ph; **b** $R^1 = 4\text{-MeOC}_6H_4$, $R^2 =$ Ph; **c** $R^1 =$ Ph, $R^2 =$ 2,6-Xyl; **d** $R^1 = 4\text{-MeOC}_6H_4$, $R^2 =$ 2,6-Xyl; **e** $R^1 = 4\text{-ClC}_6H_4$, $R^2 =$ 2,6-Xyl; **f** $R^1 =$ Ph, $R^2 = \text{TosCH}_2$; **g** $R^1 = 4\text{-MeOC}_6H_4$, $R^2 =$ 2,6-Xyl; **h** $R^1 = 4\text{-MeOC}_6H_4$, $R^2 =$ *cyclo*-C_6H_{11}; **i** $R^1 = 4\text{-ClC}_6H_4$, $R^2 =$ *cyclo*-C_6H_{11}; **j** $R^1 =$ Ph, $R^2 =$ *cyclo*-C_6H_{11}; **k** $R^1+R^1 =$ biphenyl-2,2'-diyl, $R^2 =$ 2,6-Xyl; **l** $R^1 =$ *cyclo*-C_6H_{11}, $R^2 =$ 2,6-Xyl

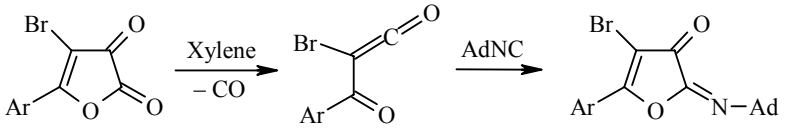
Under somewhat milder conditions, during the thermolysis of furandiones **6a**,**b**,**d**,**e** in solution (carbon tetrachloride, benzene, carbon tetrachloride–octane, etc.), aroylketenes are generated. They then react with phenyl-, *tert*-butyl-, tosylmethyl, and 1-adamantylisonitriles, forming N-phenyl (**7a**), N-*tert*-butyl (**10a-d**), N-tosylmethyl (**10e-h**), and N-(1-adamantyl) (**10i-l**) derivatives of 5-aryl-2-imino-2H-furan-3-ones [11, 18, 19].



7a (40%), **10a–l** (58–98%)

10 a $R^1 =$ H, $R^2 =$ *t*-Bu; **b** $R^1 =$ Me, $R^2 =$ *t*-Bu; **c** $R^1 =$ Cl, $R^2 =$ *t*-Bu; **d** $R^1 =$ Br, $R^2 =$ *t*-Bu; **e** $R^1 =$ H, $R^2 = \text{TosCH}_2$; **f** $R^1 =$ Me, $R^2 = \text{TosCH}_2$; **g** $R^1 =$ Cl, $R^2 = \text{TosCH}_2$; **h** $R^1 =$ Br, $R^2 = \text{TosCH}_2$; **i** $R^1 =$ H, $R^2 =$ Ad; **j** $R^1 =$ Me, $R^2 =$ Ad; **k** $R^1 =$ Cl, $R^2 =$ Ad; **l** $R^1 =$ Br, $R^2 =$ Ad

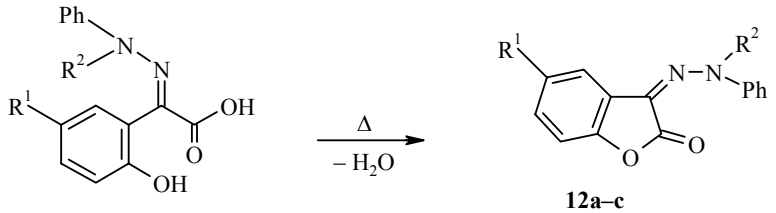
In [19] it was also shown that 2-(1-adamantylimino)-5-aryl-4-bromo-2H-furan-3-ones **10m**,**n** are formed during the thermolysis of 5-aryl-4-bromo-2,3-dihydrofuran-2,3-diones in the presence of 1-adamantyl isocyanide (1 h, xylene).



10m,**n** (50, 39%)

10 m Ar = Ph; **n** Ar = 4-ClC_6H_4

1.2.2. Synthesis of N-Substituted 3-Imino-3H-furan-2-ones B. This heterocycle is constructed by intramolecular cyclization of the 2-imino derivatives of *o*-hydroxyphenylglyoxalic acid [6, 7, 20-25] or the 2-imino derivatives of 4-R-2,4-dioxobutyric acids [26-29]. Thus, the synthesis of 2-phenylhydrazono-3H-benzo[*b*]furan-2-one (**12a**), 5-methyl-3-phenylhydrazono-3H-benzo[*b*]furan-2-one (**12b**) [7], and 3-benzoyl-phenylhydrazono-5-methyl 3H-benzo[*b*]furan-2-one (**12c**) [7] by intramolecular cyclization of the respective 2-imino derivatives of *o*-hydroxyphenylglyoxalic acid **11a-c** was described in [7, 21].



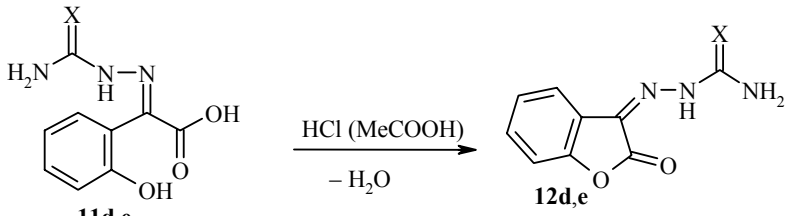
11a–c **12a–c**

12a (67%) [21]

11, **12 a** $R^1 = R^2 = H$; **b** $R^1 = Me$, $R^2 = H$; **c** $R^1 = Me$, $R^2 = PhCO$

There are a series of papers [6, 21-24] on the synthesis and chemical transformations of 3-semicarbazido- and 3-thiosemicarbazido-3H-benzo[*b*]furan-2-ones **12d** [21] and **12e** [21-24].

The imino derivatives of acids **11d**,**e** undergo cyclization when boiled in glacial acetic acid [21] and concentrated hydrochloric acid [22-24] respectively. An attempt at the synthesis of compound **12e** by the direct reaction of benzo[*b*]furan-2,3-dione with thiosemicarbazide in an aqueous medium led mainly to the formation of the acid **11e** [25].

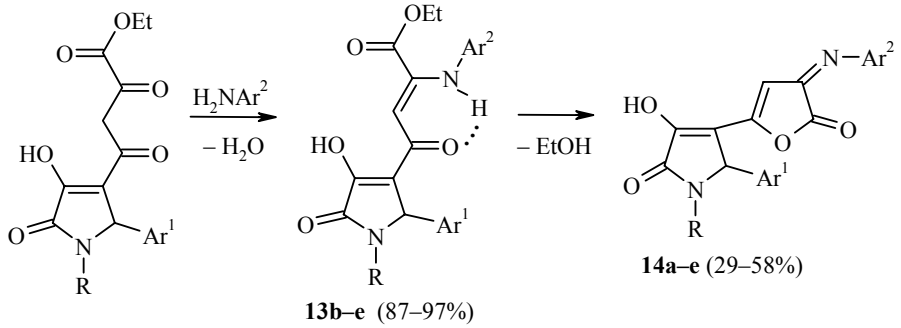


11d,e **12d**,**e**

12 d (40%); **e** (87%)

11, **12 d** X = O; **e** X = S

Intramolecular cyclization of the 2-imino derivatives of 4-R-2,4-dioxobutyric acids takes place spontaneously [26] on heating or under the influence of dehydrating agents [27-29]. Thus, when heated with arylamines (60°C) pyrrolyl pyruvates form the enamino ketones **13a-e**, which with stronger heating undergo cyclization to 3-arylimino-5-(1-R-aryl-3-hydroxy-2-oxo-2,5-dihydropyrrol-4-yl)-3H-furan-2-ones **14a-e** [26].

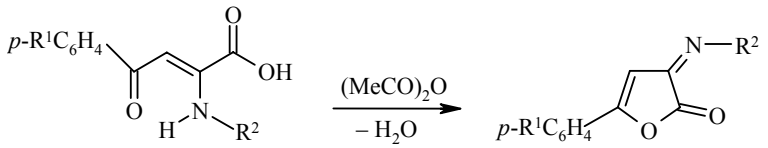


13b–e (87–97%) **14a–e** (29–58%)

13, **14 a** $Ar^1 = Ar^2 = Ph$, R = Me; **b** $Ar^1 = Ar^2 = R = Ph$; **c** $Ar^1 = 4\text{-}BrC_6H_4$, $Ar^2 = R = Ph$;
d $Ar^1 = 4\text{-}O_2NC_6H_4$, $Ar^2 = R = Ph$; **e** $Ar^1 = Ar^2 = R = 4\text{-}BrC_6H_4$

The authors were unable to isolate compound **13a** since it undergoes cyclization to the iminofuranone **14a** even at 20°C [26].

The 2-arylamino **15a-c**, 2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylamino) **15d-h**, and 2-diphenylmethylenehydrazino **15i-m** derivatives of 4-aryl-4-oxobut-2-enoic acids are more stable.

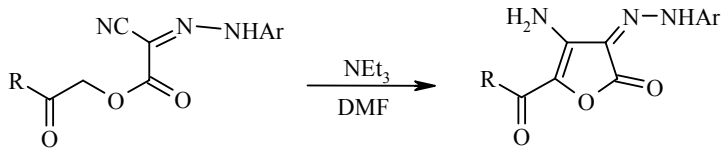


15a–m **16a–m** (45–90%)

15, **16 a** R^1 = Me, R^2 = Ph; **b** R^1 = Me, R^2 = 4-ClC_6H_4; **c** R^1 = H, R^2 = 1-naphthyl; **d** R^1 = H, R^2 = 4-Ant; **e** R^1 = Me, R^2 = 4-Ant; **f** R^1 = MeO, R^2 = 4-Ant; **g** R^1 = Cl, R^2 = 4-Ant; **h** R^1 = Br, R^2 = 4-Ant; **i** R^1 = H, R^2 = Ph_2C=N; **j** R^1 = Me, R^2 = Ph_2C=N; **k** R^1 = MeO, R^2 = Ph_2C=N; **l** R^1 = Cl, R^2 = Ph_2C=N, **m** R^1 = Br, R^2 = Ph_2C=N, Ant = 4-antipyryl

Compounds **15a-m** undergo cyclization smoothly to 5-aryl-3-R-imino-3H-furan-2-ones **16a-m** when heated in acetic anhydride [27-29].

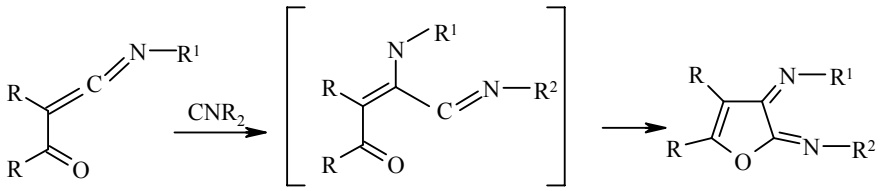
Under the influence of triethylamine the acylmethyl esters of 2-arylhydrazono-2-cyanoacetic acids undergo cyclization to 4-amino-3-arylhydrazono-5-acyl-3H-furan-2-ones **17a-c** [30].



17a–c (25–42%)

17 a R = Ph, Ar = *o*-Tol; **b** R = Ph, Ar = 2-naphthyl; **c** R = Me, Ar = *o*-Tol

1.2.3. Synthesis of 2,3-Diimino Derivatives of 2,3-Dihydrofurans C. The reaction of isonitriles with α-acylketene imines leads to the formation of the 2,3-diimino derivatives of 4,5-disubstituted 2,3-dihydrofurans **18a-k** [31].

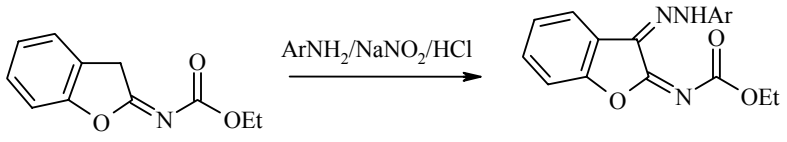


I_1 **18a–k** (36–95%)

18 a R^1 = 4-Tol, R^2 = 2,6-Xyl, R = Ph; **b** R^1 = 4-Tol, R^2 = 2,6-Xyl, R = 4-$MeOC_6H_4$; **c** R^1 = 4-Tol, R^2 = R = Ph; **d** R^1 = 4-Tol, R^2 = Ph, R = 4-$MeOC_6H_4$; **e** R^1 = 4-Tol, R^2 = *cyclo*-C_6H_{11}, R = Ph; **f** R^1 = 4-Tol, R^2 = 2,6-Xyl, R = 4-ClC_6H_4; **g** R^1 = 4-Tol, R^2 = 2,6-Xyl, R+R = biphenyl-2,2'-diyl; **h** R^1 = 4-Tol, R+R = biphenyl-2,2'-diyl, R^2 = *cyclo*-C_6H_{11}; **i** R^1 = 4-Tol, R+R = biphenyl-2,2'-diyl, R^2 = Ph; **j** R^1 = 4-Tol, R+R = biphenyl-2,2'-diyl, R^2 = 2-Py; **k** R+R = biphenyl-2,2'-diyl, R^1 = R^2 = 2,6-Xyl

4,5,$N_{(2)}$,$N_{(3)}$-tetraaryl-2,3-dihydro-2,3-furan diimines **18a-f** and $N_{(2)}$,$N_{(3)}$-diarylphenanthro[9,10-*b*]furan-2,3-diimines **18g-k** were prepared by this method with yields of 36-95% [31].

3-Arylhydrazono-2-ethoxycarbonylimino-2,3-dihydrobenzo[*b*]furans **19a-c** were synthesized by the diazotization of 2-ethoxycarbonyliminobenzo[*b*]furan [32].



19a–c (57–80%)

19 a Ar = 2-NCC_6H_4; **b** Ar = 3-MeC_6H_4; **c** Ar = 1-naphthyl

In addition, the synthesis of 3-thiosemicarbazido-2-phenylimino-2,3-dihydrobenzo[*b*]furan **19d** was described in [6] but was based on the reaction of iminofuranone **3b** itself with thiosemicarbazone.

2. THE SPECTRAL CHARACTERISTICS OF IMINOFURANONES

The IR spectra of the N-substituted 2-imino-2H-furan-3-ones **A** are characterized by the presence of an absorption band for the $C_{(3)}$=O group in the region of 1690-1738 cm^{-1}, the position of which in the spectrum depends on the character of the substituents at the imine nitrogen atom and at positions 4 and 5 of the heterocycle. Thus, the absorption band of the $C_{(3)}$=O carbonyl group is present in the IR spectra at 1732 cm^{-1} in iminofuranone **3b** [6], at 1710-1729 cm^{-1} in the iminofuranones **7a-c** [10, 11], at 1710-1728 cm^{-1} in compounds **8a-v** [14, 15], and at 1690-1705 cm^{-1} in compounds **10m**,**n** [19]. The authors of [19] consider that the strong absorption band in the region of 1690-1705 cm^{-1} is due to the superimposition of the stretching vibrations of the $C_{(3)}$=O and C=N bonds. In the IR spectra of compounds **9a-l** the authors record the presence of a split band in the region of 1700 cm^{-1} but do not give its assignment [17].

The ^1H NMR spectra of compounds of this type are individual in nature, and it is only possible to single out a large group of iminofuranones **7a-c**, **8a-v**, and **10a**,**n** not containing a substituent at position 4 of the heterocycle. The singlet of the methine proton in the ^1H NMR spectra is observed at 5.98-6.91 ppm (in carbon tetrachloride, deuterochloroform, DMSO-d_6) [10, 11, 14, 15, 19].

In the ^{13}C NMR spectrum of the iminofuranone **9b** (deuterochloroform) the singlet of the $C_{(3)}$=O carbon atom appears at 172.30 ppm [17].

The mass spectra of the iminofurans contain a molecular ion peak and peaks for the fragment ions $[M - RNC]^+$ and $[R - NCO]^+$ [11, 17].

The lactone carbonyl of N-substituted 3-imino-3H-furan-2-ones (**B**) gives a wide range of absorption in the IR spectra. Thus, the band for the stretching vibrations of the $C_{(2)}$=O group is observed in the IR spectra of the iminofurans at 1774 cm^{-1} (DMSO) for **12d** [21], at 1769 cm^{-1} for (**12l**) [21, 22], at 1775-1790 cm^{-1} for **14a-e** [26], at 1773-1820 cm^{-1} for **16a-m** [27-29], and at 1720-1740 cm^{-1} for **17a-c** [30].

Quantum-chemical calculations in the CNDO/2 approximation were carried out for the iminofuranone **10a**. According to the results, the most electron-deficient atoms in the molecule are the $C_{(5)}$, $C_{(3)}$, and $C_{(2)}$ carbon atoms, which provide targets for attack by nucleophilic reagents [33].

3. THE CHEMICAL PROPERTIES OF IMINOFURANONES

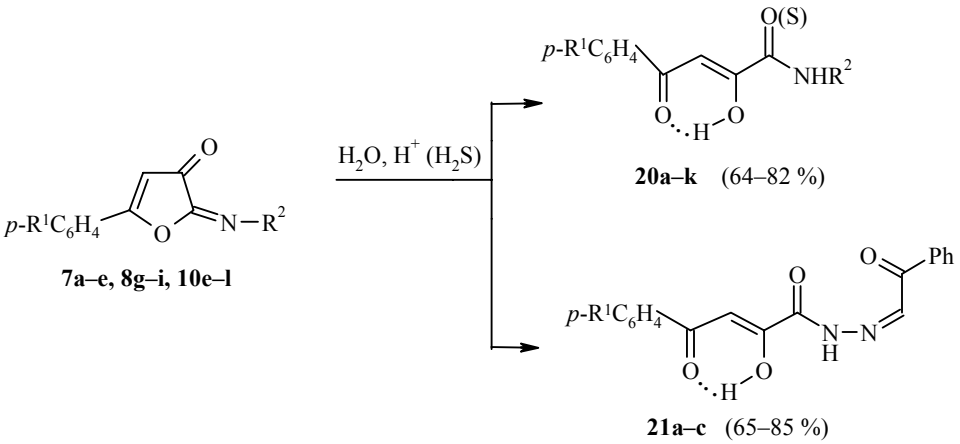
The presence of several carbon atoms similar in electronegativity in the structure of iminofuranones provides several directions for their reactions with nucleophilic reagents. Iminofuranones are characterized by ring opening, recyclization, and a series of reactions taking place with participation of the C=N bonds and also functional groups.

3.1. Ring Opening Reactions of Iminofuranones

Ring opening in iminofuranones takes place as a result of their hydrolysis and aminolysis.

3.1.1. Hydrolysis of Iminofuranones. Iminofuranones differ substantially in their stability in the hydrolysis process, depending on the type of structure **A**, **B**, and **C** and on the nature of the substituents. 2-Iminofuranones **A** are fairly inert toward water, but most of them are slowly hydrolyzed during storage. Thus, the iminofuranones **3a**,**b** form the anilide and 4-dimethylaminoanilide respectively of *o*-hydroxyphenylglyoxalic acid during storage [6, 20, 21].

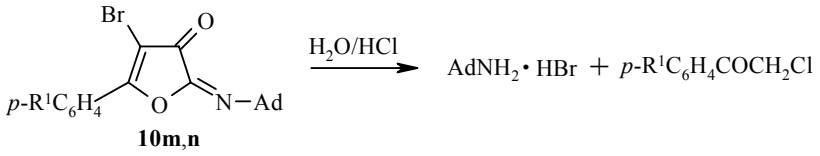
Acid hydrolysis (dioxane–water, catalytic amounts of HCl, 20-25°C) of the iminofuranones **7a-c**, **10e-l**, and **8g-i** gave the respective amides **20a-k** [11, 18, 19, 34] and substituted hydrazides **21a-c** [12-15] of 4-aryl-2-hydroxy-4-oxo-*Z*-but-2-enoic acids.



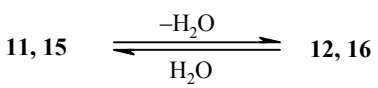
20 a R^1 = Me, R^2 = Ph; **b** R^1 = Cl, R^2 = Ph; **c** R^1 = Br, R^2 = Ph; **d** R^1 = H; R^2 = $TosCH_2$; **e** R^1 = Me, R^2 = $TosCH_2$; **f** R^1 = Cl, R^2 = $TosCH_2$; **g** R^1 = Br, R^2 = $TosCH_2$; **h** R^1 = H, R^2 = Ad; **i** R^1 = Me, R^2 = Ad; **j** R^1 = Cl, R^2 = Ad; **k** R^1 = Br, R^2 = Ad. **21 a** R^1 = Me; **b** R^1 = MeO; **c** R^1 = Cl

Under the influence of gaseous hydrogen sulfide the 2-iminofuranones **10i-l** form the N-(1-adamantyl)amides of 4-aryl-2-hydroxy-4-oxobut-3-enoic thioacids **20h-k** [35].

The iminofuranones **10m**,**n** behave differently under these conditions and undergo strong dissociation to chloro-*p*-R^1-acetophenones and 1-aminoadamantane hydrobromide [19].



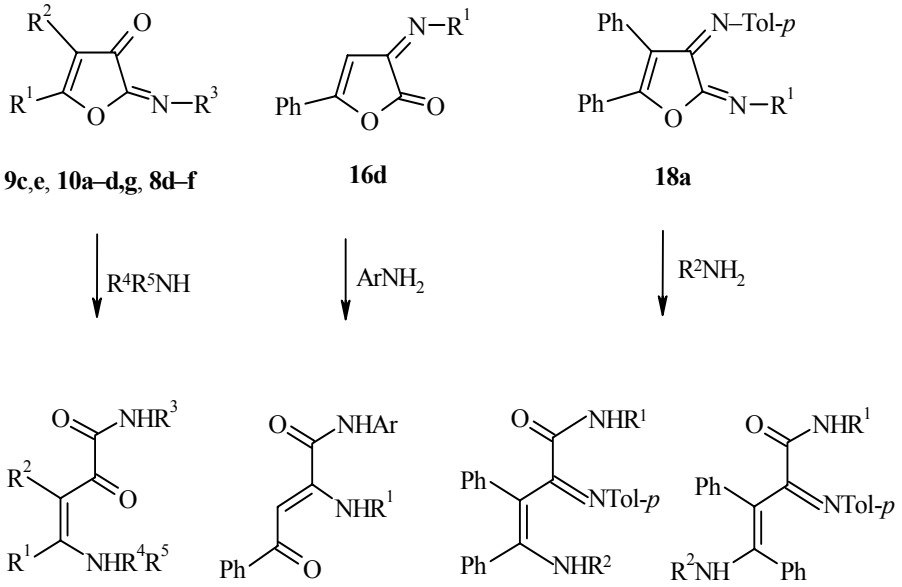
The dehydration of the acids **11a-c** and **15a-n**, leading to the formation of the 3-iminofuranones **12a-c** and **16a-m**, is reversible, and the products are easily hydrolyzed to the initial 2-imino derivatives of the acids [21-23, 27-29].



During acid hydrolysis of the 2-iminofuranones **9c**,**e**, having substituents at position 4 of the heterocycle, and 2,3-diiminofuranones **18b**,**f**,**g**,**i** only recyclization products are formed [17, 35] (see section 3.2).

3.1.2. Ring Opening of Iminofuranones under the Influence of NH- and SH-Nucleophiles. There are examples of ring opening under the influence of ammonia and primary and secondary amines for all types of iminofuranones [11, 17, 33, 35-39].

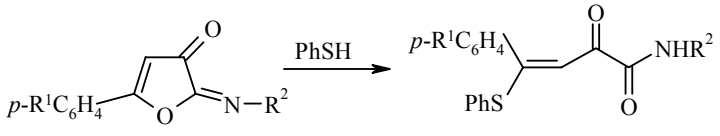
The 2-iminofuranones **9c**,**e** with ammonia and cyclohexylamine [17], the 2-iminofuranones **10a-d**,**g** with benzylamine and piperidine [11, 33, 37], and the iminofuranones **8d-f** with aniline and benzylamine [33, 38, 39] form the respective amides **22a-c** [17] and **22d-j** [11, 33, 37] and hydrazides **22k-m** [33, 38, 39] of N-substituted 4-amino-4-aryl-2-oxo-3-R^2-but-3-enoic acids. Under the influence of arylamines the 3-iminofuranones **16d** undergo decyclization with the formation of the arylamides of 2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylamino)-4-oxo-4-phenylbut-2-enoic acid **23a-d** [29]. The diiminofuran **18a** reacts with cyclohexylamine and *p*-toluidine with the formation of the 2,6-dimethylanilides of N-substituted 4-amino-3,4-diphenyl-2-(4-methylphenylamino)but-3-enoic acids **24a**,**b** [37].



Compound	R^1	R^2	R^3	R^4	R^5
22a	Ph	Ph	2,6-Xyl	H	H
22b	Ph	Ph	2,6-Xyl	H	*cyclo*-C_5H_9
22c	4-ClC_6H_4	4-ClC_6H_4	2,6-Xyl	H	*cyclo*-C_5H_9
22d	Ph	H	*t*-Bu	H	$PhCH_2$
22e	4-ClC_6H_4	H	*t*-Bu	H	$PhCH_2$
22f	4-ClC_6H_4	H	$TosCH_2$	H	$PhCH_2$
22g	Ph	H	*t*-Bu	$(CH_2)_5$	
22i	*o*-Tol	H	*t*-Bu	$(CH_2)_5$	
22j	4-BrC_6H_4	H	*t*-Bu	$(CH_2)_5$	
22k	*o*-Tol	H	$Ph_2C{=}N$	H	Ph
22l	4-ClC_6H_4	H	$Ph_2C{=}N$	H	Ph
22m	4-BrC_6H_4	H	$Ph_2C{=}N$	H	Ph

23a R^1 = 4-Ant, Ar = Ph; **b** R^1 = 4-Ant, Ar = 4-HOC_6H_4; **c** R^1 = 4-Ant, Ar = 4-$MeOC_6H_4$; **d** R^1 = 4-Ant, Ar = 4-ClC_6H_4; **24 a** R^1 = 2,6-Xyl, R^2 = *cyclo*-C_6H_{11}; **b** R^1 = 2,6-Xyl, R^2 = *o*-Tol

In the case of the iminofuranones **A** and **C** attack by the amine is directed at the $C_{(5)}$ carbon atom of the heterocycle, and this agrees fully with the quantum-chemical calculations [33].



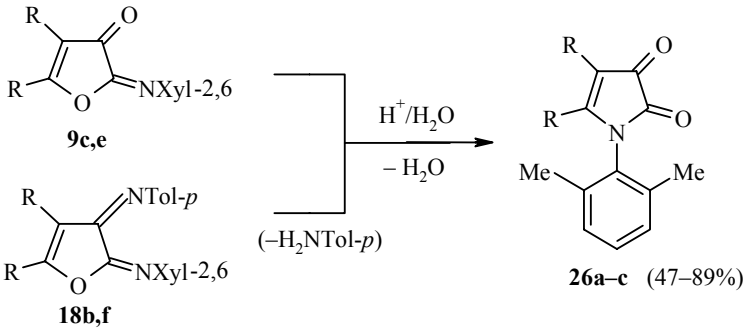
25

25 R^2 = Ad, $TosCH_2$

Like the amines, thiophenol attacks the $C_{(5)}$ atom of the iminofuranones **10e-l** with the formation of the N-substituted amides of 4-aryl-4-arylthio-2-oxo-3-butenoic acids **25** [33, 40].

3.2. The Recyclization of Iminofuranones

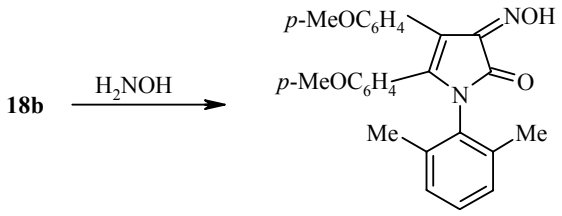
3.2.1. Recyclization as a Result of Hydrolysis and Aminolysis. Catalytic acid hydrolysis of the iminofuranones **9c**,**e** and diiminofuranones **18b**,**f** leads to the formation of 1,4,5-triaryl-2,3-dihydro-2,3-pyrrolediones **26a-c** [17, 36].



26 a R = Ph; **b** R = 4-ClC_6H_4; **c** R = 4-$MeOC_6H_4$

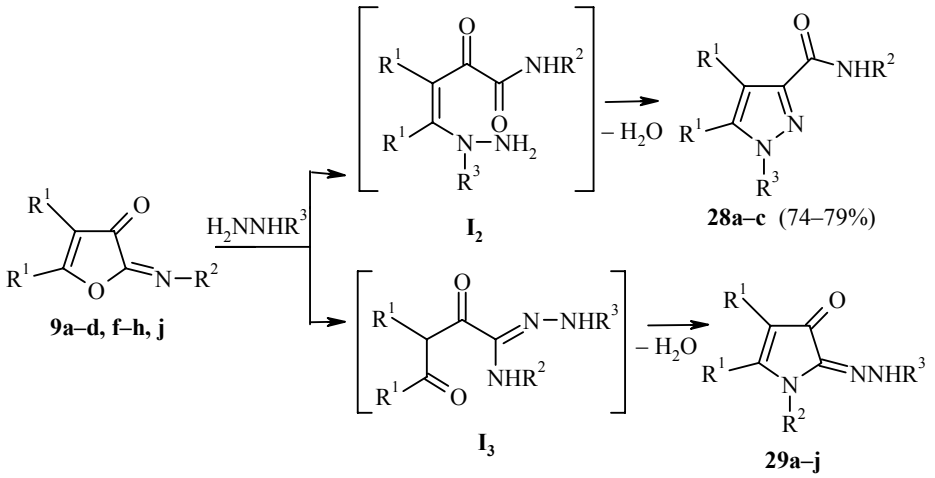
The pyrroledione **26b** is obtained with almost identical yields from the iminofuranone **9e** and the diiminofuranone **18f** respectively. The recyclization of compounds **9c**,**e** and **18b**,**f** probably includes opening of the ring to the corresponding amides of carboxylic acids, which under the reaction conditions undergo intramolecular cyclization to derivatives of pyrroledione.

Under the influence of hydroxylamine hydrochloride the diiminofuranone **18b** rearranges to the 3-oxime of 1-(2,6-dimethylphenyl)-4,5-bis(4-methoxyphenyl)-2,3-dihydropyrrole-2,3-dione **27** [36].



27 (49%)

3.2.2. Recyclization under the Influence of Hydrazines. The recyclization of iminofuranones under the influence of hydrazine and substituted hydrazines has been studied more comprehensively.

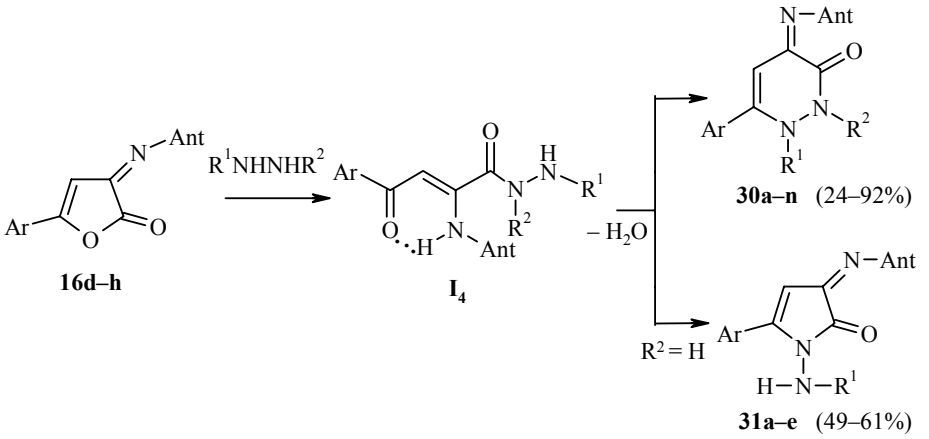


Compound	R^1	R^2	R^3
28a	Ph	2,6-Xyl	H
28b	4-$MeOC_6H_4$	2,6-Xyl	Me
28c	4-$MeOC_6H_4$	$TosCH_2$	Me
29a	Ph	*cyclo*-C_6H_{11}	Ph
29b	Ph	*cyclo*-C_6H_{11}	PhCO
29c	Ph	*cyclo*-C_6H_{11}	PhNHCO
29d	Ph	$TosCH_2$	PhCO
29e	Ph	Ph	Tos
29f	Ph	2,6-Xyl	2,4-$(O_2N)_2C_6H_3$
29g	Ph	*cyclo*-C_6H_{11}	PhCO
29h	Ph	Ph	Tos
29i	Ph	2,6-Xyl	PhCO
29j	Ph	*cyclo*-C_6H_{11}	Ph

Thus, the 2-iminofuranones **9c**,**d**,**g** undergo recyclization under the influence of hydrazine and methylhydrazine to the N-substituted amides of 3-pyrazolecarboxylic acids **28a-c**, while the 2-iminofuranones **9a-d**,**f**,**h**,**j** in reactions with aryl- and acylhydrazines form the 1,4,5-trisubstituted 2-hydrazono-2H-pyrrol-3-ones **29a-j** [17].

The authors consider that the formation of the pyrazole derivatives **28a-c** includes attack by the amino group of the hydrazine or by the secondary amino group of the methylhydrazine at the $C_{(5)}$ carbon atom of the heterocycle, opening of the iminofuranone ring, and intramolecular cyclization of the intermediately formed amide (intermediate $\mathbf{I}_2$) on account of the primary amino group and the α-carbonyl group $C_{(2)}$=O. The iminofuranones **10** react similarly with hydrazine [34]. On the other hand, the opening of the ring in the iminofuranones **9a-d**,**f**,**h**,**i** by the action of aryl- and acylhydrazines takes place as a result of attack by their primary amino group at the $C_{(2)}$ carbon atom of the heterocycle with the formation of the amidrazone $\mathbf{I}_3$ as intermediate, which then undergoes cyclization to the pyrrolone derivative **29** [17]. The reaction of **9j** with N-methyl-N-phenylhydrazine leads to 4,5-diphenyl-2-(N-methyl-N-phenylhydrazono)-1-cyclohexyl-2H-pyrrol-2-one **29j** with a yield of 5% [17]. According to data in [40], the intermediate amidrazones of the $\mathbf{I}_3$ type were isolated as a result of cleavage of the 2-(1-adamantylimino)-5-aryl-4-bromo-2H-furan-3-ones by the action of 2,4-dinitrophenylhydrazine and underwent cyclization to derivatives of 2-hydrazonopyrrol-3-ones **29** on heating.

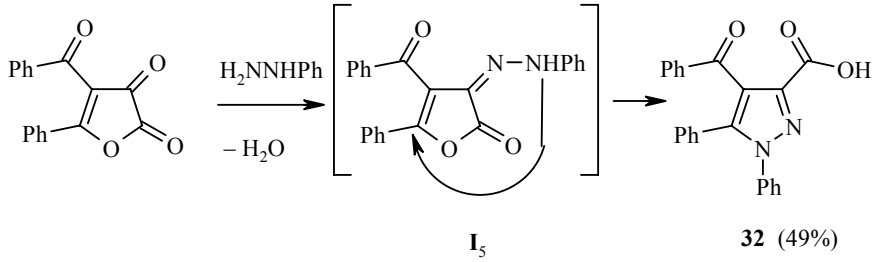
Recyclization by the action of substituted hydrazines is also characteristic of 3-iminofuran-2-ones. Thus, the iminofuranones **16d-h** react with alkyl- and arylhydrazines to form 6-aryl-4-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)-1,4-dihydro-2H-pyridazin-3-ones **30a-n** and 4-[5-aryl-1-(2,4-dinitrophenyl-amino)-2-oxo-1,2-dihydropyrrol-3-ylideneamino]-1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-ones **31a-e** [27, 41, 42].



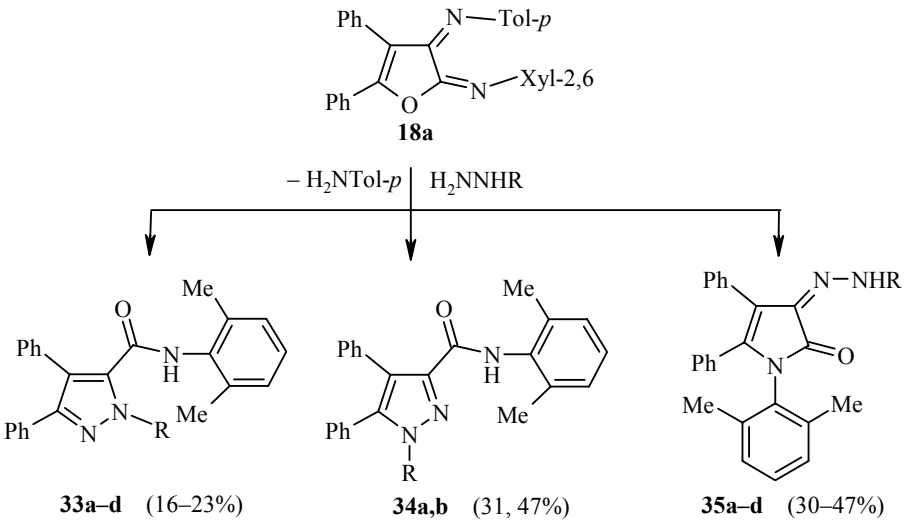
Compound	R^1	R^2	Ar
30a	Me	H	Ph
30b	Me	H	o-Tol
30c	Me	H	4-$MeOC_6H_4$
30d	Me	H	4-ClC_6H_4
30e	Me	H	4-BrC_6H_4
30f	Et	H	Ph
30g	Et	H	4-$MeOC_6H_4$
30i	Et	H	4-ClC_6H_4
30j	Et	H	4-BrC_6H_4
30k	Ph	H	Ph
30l	2,4-$(NO_2)_2C_6H_3$	H	4-MeC_6H_4
30m	2,4-$(NO_2)_2C_6H_3$	H	4-$MeOC_6H_4$
30n	Ph	Ph	Ph
31a	2,4-$(NO_2)_2C_6H_3$	H	Ph
31b	2,4-$(NO_2)_2C_6H_3$	H	o-Tol
31c	2,4-$(NO_2)_2C_6H_3$	H	4-$MeOC_6H_4$
31d	2,4-$(NO_2)_2C_6H_3$	H	4-ClC_6H_4
31e	2,4-$(NO_2)_2C_6H_3$	H	4-BrC_6H_4

Ring opening in the iminofuranones **16d-h** probably takes place as a result of attack by the amino group of the hydrazine at the $C_{(2)}$ carbon atom of the heterocycle with the formation of the intermediate hydrazide of but-2-enoic acid $\mathbf{I}_4$, which undergoes intramolecular cyclization to a derivative of pyridazine **30a-n** or pyrrolone **31a-e** [41, 42].

In [43] the formation of 4-benzoyl-1,5-diphenylpyrazole-3-carboxylic acid **32** was described. In the opinion of the authors the reaction takes place through the intermediate 4-benzoyl-5-phenyl-3-phenylhydrazono-3H-furan-2-one $\mathbf{I}_5$, formed after attack by the phenylhydrazine at the $C_{(3)}$=O carbonyl group of 4-benzoyl-5-phenyl-2,3-dihydrofuran-2,3-dione [43].



2,6-Dimethylphenylamides of 1,3,4-triphenylpyrazole-5-carboxylic (**33a**) and 1,4,5-triphenylpyrazole-3-carboxylic acids (**34a**) are formed with yields of 16 and 31% respectively as a result of the recyclization of diiminofuran **18a** by the action of phenylhydrazine [36].



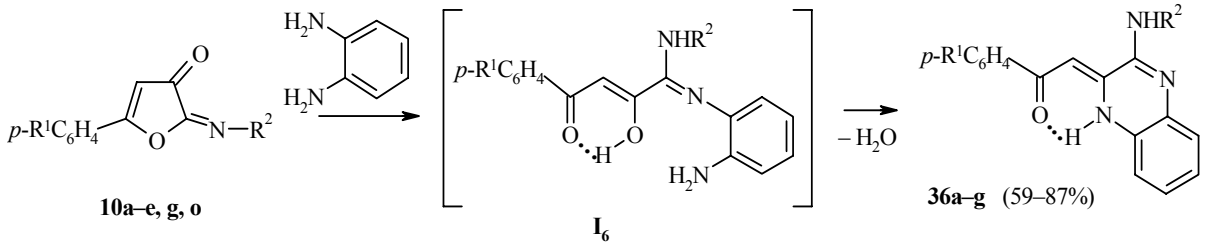
33a–d (16–23%) **34a,b** (31, 47%) **35a–d** (30–47%)

33 a R = Ph, **b** R = Tos, **c** R = PhCO, **d** R = EtOCO; **34 a** R = Ph, **b** R = Me;
35 a R = 4-$O_2NC_6H_4$, **b** R = Tos, **c** R = PhCO, **d** R = EtOCO

The formation of the two pyrazole derivatives may result from attack of the primary (compound **33**) and secondary (compound **34**) amino group of the substituted hydrazine at the $C_{(5)}$ carbon atom of the heterocycle.

In the reactions of compound **18a** with methylhydrazine attack by the secondary amino group mostly takes place at the $C_{(5)}$ carbon atom of the heterocycle (with the formation of compound **34b**), while the reaction with tosyl- or acylhydrazines leads to the formation of the pyrazoles **33b-d** but with yields of 17-23%, since yet another direction of recyclization with the formation of 3-hydrazono-1,4,5-triaryl-3H-pyrrol-2-ones **35b-d** is realized in this reaction [36]. The reaction of compound **18a** with N'-methyl-N'-phenylhydrazine leads to 1-(2,6-dimethylphenyl)-4,5-diphenyl-3-(N'-methyl-N'-phenylhydrazono)-3H-pyrrol-2-one **35e** with a yield of 72% [36].

3.2.3. Recyclization of Iminofuranones under the Influence of Vicinal Diamines. 2-Iminofuran-3-ones **10a-e**,**g**,**o** react with *o*-phenylenediamine to form N-substituted 2-amino-3-phenacylidene-3,4-dihydroquinoxalines **36a-g** [18, 34, 44].

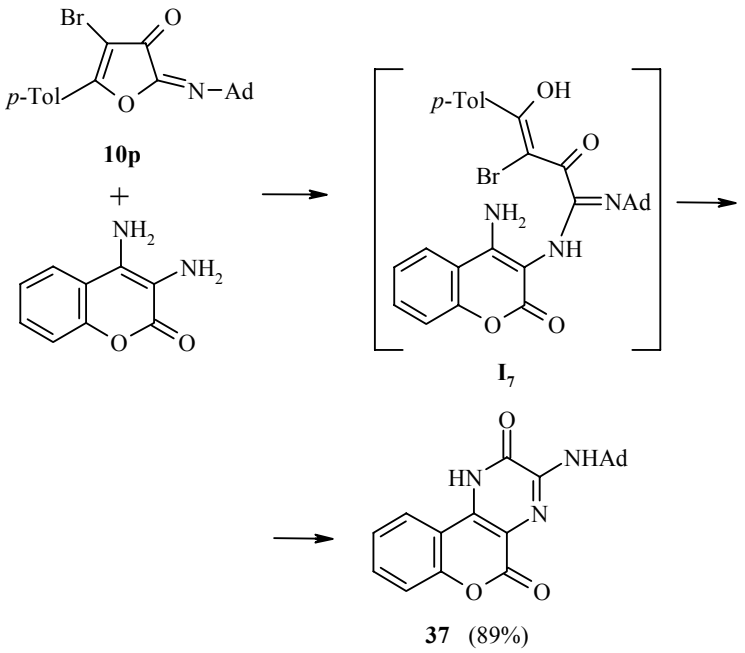


10a–e, g, o **I**$_6$ **36a–g** (59–87%)

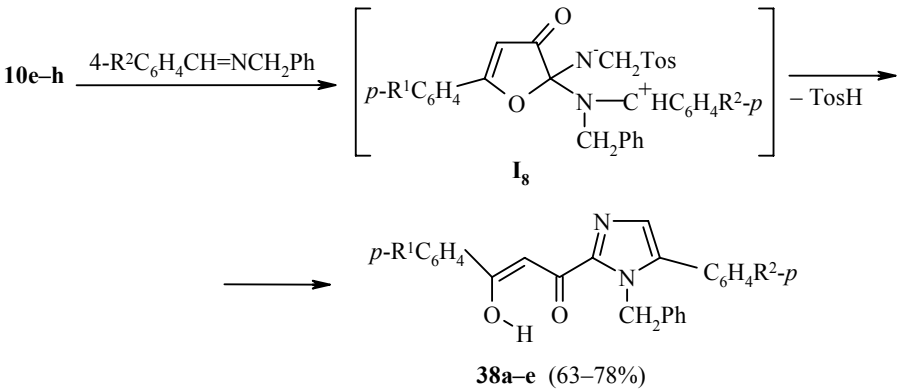
36 a R^1 = H, R^2 = *t*-Bu; **b** R^1 = Me, R^2 = *t*-Bu; **c** R^1 = Cl, R^2 = *t*-Bu; **d** R^1 = Br, R^2 = *t*-Bu;
e R^1 = H, R^2 = $TosCH_2$; **f** R^1 = Cl, R^2 = $TosCH_2$; **g** R^1 = H, R^2 = 2,5-Xyl

The authors consider that the amino group of the *o*-phenylenediamine initially attacks at position 2 of the heterocycle nucleophilically. This leads to opening of the ring with the formation of substituted amidines **I**$_6$, and they undergo cyclization to the quinoxaline derivatives **36** [44].

Analogous attack occurs during the reaction of the iminofuranone **10p** with 3,4-diaminocoumarin, but cyclization of the intermediate amidine $\mathbf{I}_7$ to 3-(1-adamantylamino)-1,2-dihydro-5H-chromeno[4,3-*b*]pyrazine-2,5-dione **37** is accompanied by cleavage of the bromo-*p*-methylacetophenone [45].



3.2.4. Recyclization under the Influence of Azomethines. The only example of such reactions was described in [46, 47]. The reaction of the iminofuranones **10e-h** with substituted N-(benzylidene)benzylamines leads to the formation of 5-aryl-2-aroylacetyl-1-benzylimidazoles **38a-e** [46, 47].

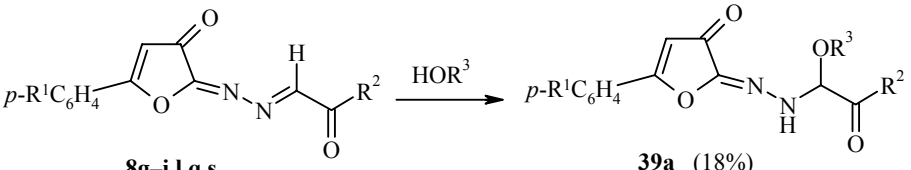


38 a R^1 = H, R^2 = Me_2N; **b** R^1 = Me, R^2 = Me_2N; **c** R^1 = H, R^2 = MeO; **d** R^1 = Cl, R^2 = MeO; **e** R^1 = Br, R^2 = MeO

The authors consider that the formation of compounds **38** begins with attack at position 2 of the heterocycle by the trigonal nitrogen atom of the azomethine with the formation of a zwitterionic adduct $\mathbf{I}_8$. A series of consecutive transformations of the adduct $\mathbf{I}_8$ (three stages of transformations) results in the elimination of toluenesulfinic acid and the formation of an imidazole system. The reaction mechanism is hypothetical, but the structure of compounds **38** was confirmed by X-ray crystallographic analysis of compound **38d** [47].

3.3. Reactions Taking Place with Participation of the Azomethine Bond of Iminofurans

3.3.1. Addition of OH and NH Nucleophiles at the C=N Bond. 5-Aryl-2-methylenehydrazono-2H-furan-3-ones **8**, in which the C=N bond is activated by acyl substituents, add water, alcohols, and amines at this bond [12, 14, 15, 36, 38, 48]. Thus, the iminofuranone **8i** is capable of forming the product from the addition of water 2-benzoyloxymethylhydrazono-5-(4-chlorophenyl)-2H-furan-3-one (**39a**) even during crystallization from solvents containing water [14, 15, 48]

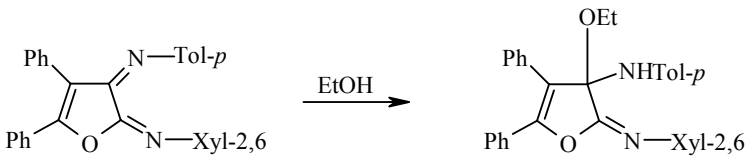


8g–i,l,q,s

39a (18%)
39b–l (65–90%)

Compound	R^1	R^2	R^3
39a	Cl	Ph	H
39b	H	Ph	Me
39c	Me	Ph	Me
39d	MeO	Ph	Me
39e	Cl	Ph	Me
39f	Cl	4-BrC_6H_4	Me
39g	Cl	Ph	Et
39h	Br	$PhCH_2$	Me
39i	Br	$PhCH_2$	Et
39j	Cl	Ad	Me
39k	Me	EtO	Me
39l	Me	EtO	D_3C

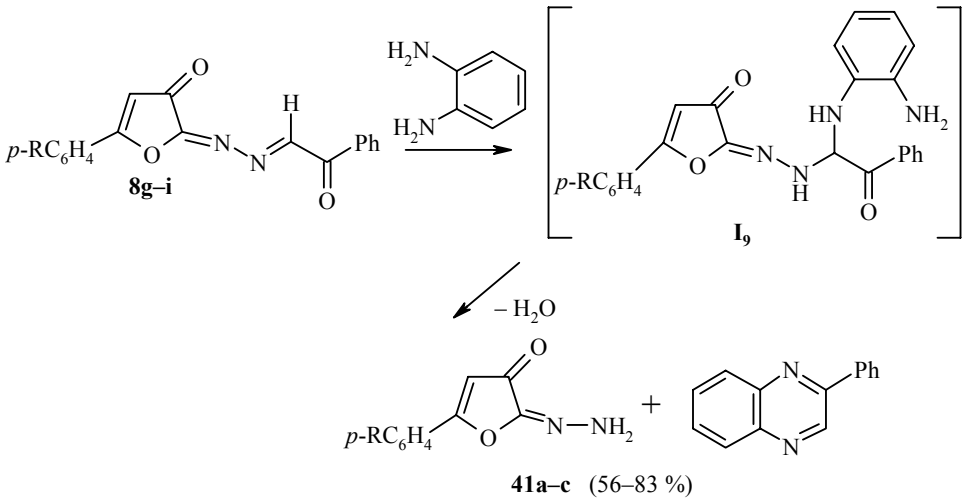
Aliphatic alcohols add vigorously at the activated C=N bond of compounds **8g-i**,**l**,**q**,**s** with the formation of compounds **39b-e** [12, 14, 15]. In [36] the addition of ethanol at the $C_{(3)}$=N bond of the diiminofuran **18a**, leading to the formation of 2-(2,6-dimethylphenylimino)-3-(4-methylanilino)-4,5-diphenyl-3-ethoxy-2,3-dihydrofuran **40**, was described.



18a

40 (87%)

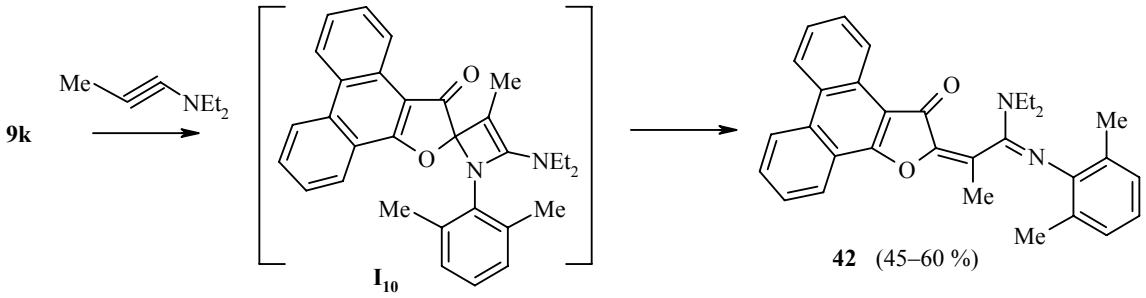
In contrast to the reactions for compounds **10** described in section 3.2.3, *o*-phenylenediamine reacts with compounds **8g-i** by attacking with the amino group not the $C_{(2)}$ atom of the heterocycle but the carbon atom of the activated C=N bond. As a result the 5-aryl-2-hydrazono-2H-furan-3-ones **41a-c** and 2-phenylquinoxaline are formed [12, 15, 38, 48].



8g–i **I$_9$** **41a–c** (56–83 %)

41 a R=Me, **b** R=MeO, **c** R= Cl

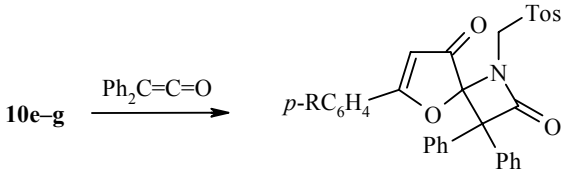
The reaction probably takes place through the formation of the intermediate N,N-aminal **I**$_9$, which is stabilized with the formation of the hydrazones **41** and 2-phenylquinoxaline [48]. The iminofuranone **9k** reacts with an ynamine through the C=N double bond [17].



9k **I$_{10}$** **42** (45–60 %)

The initially formed [2+2]-cycloadduct **I**$_{10}$ is transformed as a result of cleavage at the $C_{(2)}$–N bond into 2-(2,3-dihydro-3-oxophenanthro[9,10-*b*]furan-2-ylidene)-N'-(2,6-dimethylphenyl)-N,N-diethylpropionamidine **42** [17].

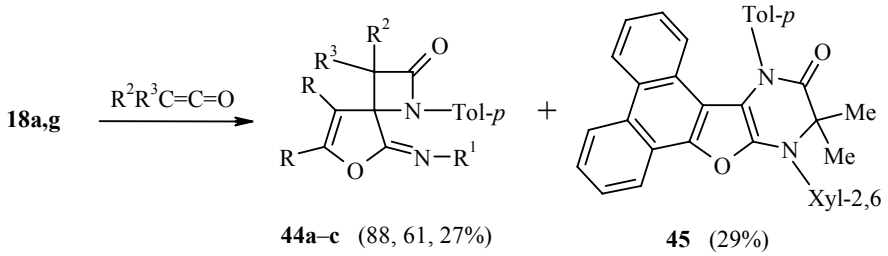
3.3.2. Cycloaddition at the C=N Bond of Iminofurans. The cycloaddition of ketenes and acylketenes at the C=N bond of iminofurans of types **A** and **C** was studied. Thus, the iminofuranones **10e-g** react with diphenylketene according to a [2+2]-cycloaddition scheme with the formation of 5'-aryl-3,3-diphenylspiro-1-tosylmethyl[azetidine-2,2'-3'H-furan]-3',4-diones **43a-c** [49].



10e–g **43a–c** (33–37%)

43 a R = H, **b** R = Me, **c** R = Cl

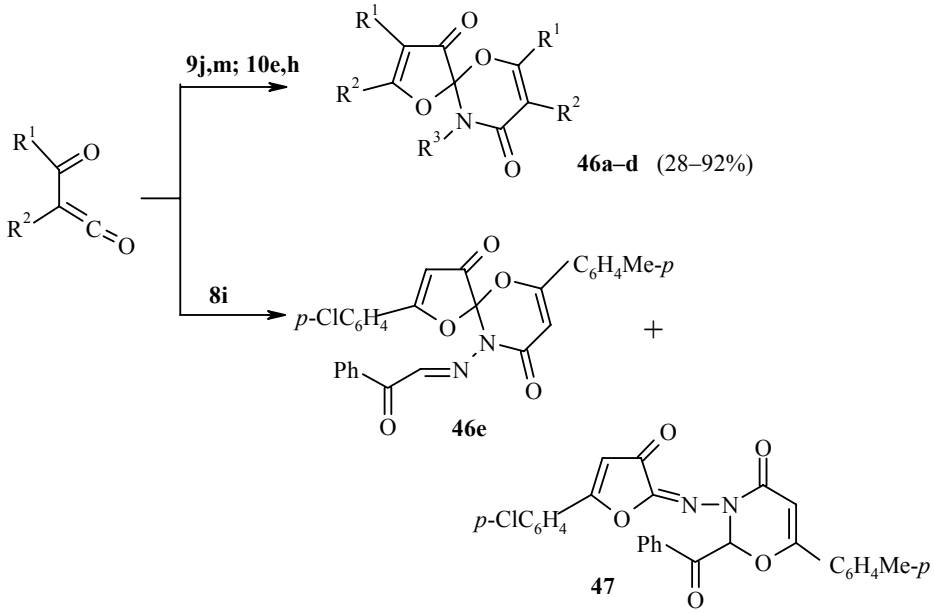
Derivatives of spiro[azetidine-2,3'-furan]-4-ones **44a-c** are also formed during reaction of the diiminofurans **18a**,**g** with diphenylketene, phenylbenzoylketene, and dimethylketene. In the last case, however, 10,11-dihydro-11,11-dimethyl-10-(2,6-dimethylphenyl)-13-(4-methylphenyl)phenanthro[9',12':2,3]furo[4,5-*b*]-pyrazin-13H-12-one **45** is formed in addition to compound **44c** with a comparable yield [36].



44a–c (88, 61, 27%) **45** (29%)

44 a R^1 = 2,6-Xyl, R = R^2 = R^3 = Ph; **b** R^1 = 2,6-Xyl, R = R^2 = Ph, R^3 = PhCO;
c R^1 = Ph, R+R = biphenyl-2,2'-diyl, R^2 = R^3 = Me

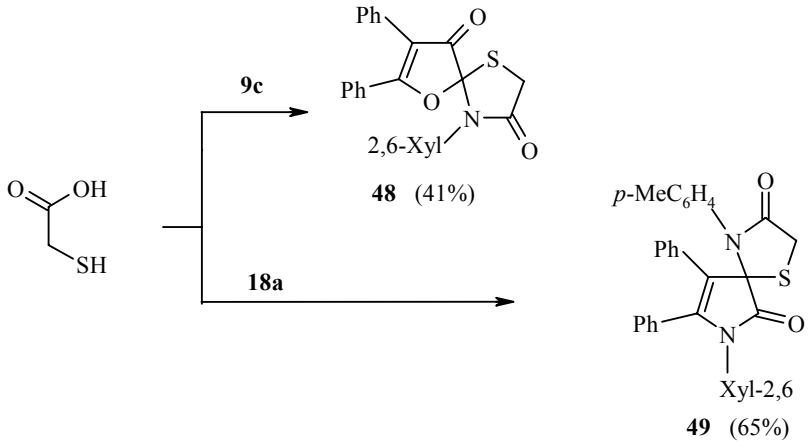
The products from the alternative cyclization path through the $C_{(2)}$=N bond were not isolated in these transformations. The iminofuranones **8i**, **9j**,**m**, **10e**,**h** react with acylketene as dienophiles through their C=N bond according to a [4+2] cycloaddition scheme with the formation of derivatives of spiro[furan-2(3H),2'-[2H][1,3]-oxazines] **46a-e** [17, 50-52]. In the case of compound **8i**, however, attack by the diene on the activated C=N bond of the azine system also occurs and leads to the formation of 2-benzoyl-3-[5-(4-chlorophenyl)-3-oxo-2,3-dihydro-2-furanylideneamino]-6-(4-methylphenyl)- 3,4-dihydro-2H-1,3-oxazin-4-one (**47**) [52].



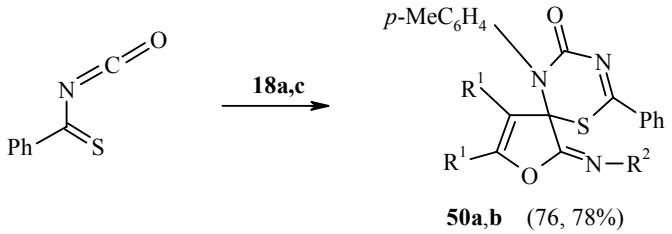
46a–d (28–92%)

46 a R^1 = R^2 = Ph, R^3 = *cyclo*-C_6H_{11}; **b** R^3 = 2,6-MeC_6H_4, R^1+R^2 = dimethylpropane-1,3-diyl;
c R^2 = H, R^3 = $TsCH_2$, R^1 = Ph; **d** R^2 = H, R^3 = $TsCH_2$, R^1 = 4-BrC_6H_4

Mercaptoacetic acid adds at the C=N bond of iminofuranone **9c** with the formation of 3'-(2,6-dimethylphenyl)-4,5-diphenylspiro[furan-2(3H),2'-[1,3]thiazolidine]-3,4'-dione (**48**) and at the $C_{(3)}$=N bond of compound **18a** also with the formation of a spiro product **49**, but the diiminofuran rearranges to pyrrolone during the reaction [36].



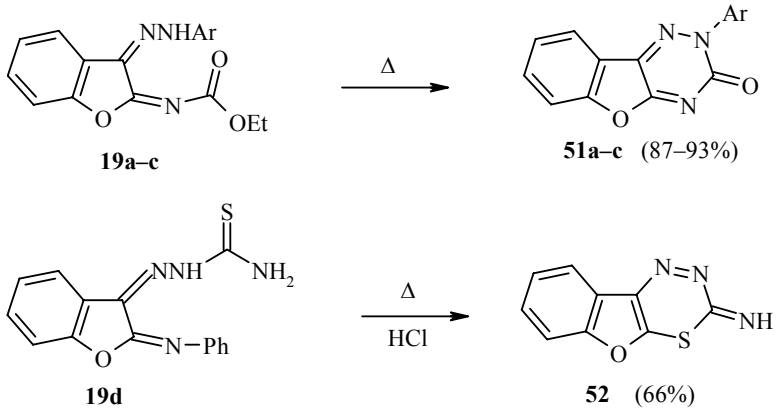
Thiobenzoyl isocyanate enters into [4+2]-cycloaddition at the $C_{(3)}$=N bond of the iminofurans **18a**,**c** with the formation of derivatives of spiro[furan-3(2H),2'-[2H-1,3,5]thiadiazines] **50a**,**b** [31].



50 a R^1 = Ph, R^2 = 2,6-Xyl; **b** R^1 = 4-$MeOC_6H_4$, R^2 = Ph

3.4. Reactions Taking Place at the Functional Groups of Iminofurans

The thermal intramolecular cyclization of diiminobenzofurans **19a-c** to 2-arylbenzofuro[2,3-*e*]-[1,2,4]triazin-3(2H)-ones **51a-c** [32] and diiminobenzofuran **19d** to 1,3,4-thiadiazino[6,5-*b*]benzofuran 2-imine **52** [6] can be included among such transformations.



51 a Ar = 2-NCC_6H_4; **b** Ar = 3-Tol; **c** R = 1-naphthyl

In addition, reactions of carbonyl compounds with 2-hydrazonofuran-3-ones **40a-c**, which take place exclusively at the amino group of the latter, were described in [15, 38, 48].

CONCLUSION

Analysis of the published data shows that iminofuranones and diiminofurans represent an interesting class of furan derivatives. Alternative methods of synthesis have been worked out for the iminofuranones **A** and **B**, and this gives the researcher the opportunity to choose between one or other method according to task in hand.

The structure of iminofuranones gives rise to abundant synthetic potential. The presence of several electron-deficient centers in their molecules makes it possible to control the direction of attack by the nucleophilic reagent and the structure of the final reaction products by varying the substituents in the heterocycle and at the imino functions. A number of OH, SH, and NH nucleophiles have already been tested in reactions with iminofuranones. Broad synthetic possibilities are presented by the recyclization of iminofuranones and cyclization at the C=N bonds of iminofurans.

The practical application of iminofuranones remains untouched, but there is reason to suppose that iminofuranones could prove no less promising in pharmacological respects than derivatives of furan itself.

Thus, iminofuranones are accessible and convenient subjects for the creation of various acyclic and heterocyclic structures and are promising for further investigations in heterocyclic chemistry.

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