# Reactions of cyanofurazans with β-dicarbonyl compounds

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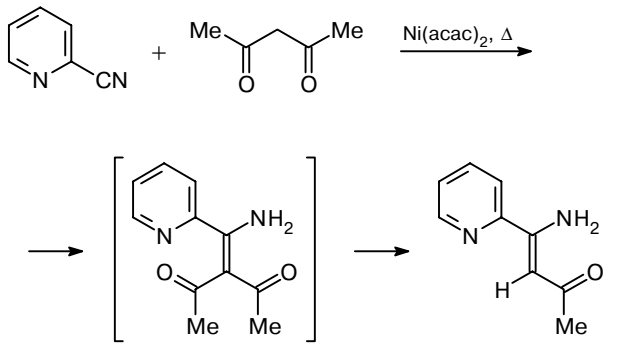
In the presence of nickel acetylacetonate, β-dicarbonyl compounds readily add at the nitrile group of 4-R-3-cyanofurazans to form enaminofurazans. The adducts obtained from 4-amino-3-cyanofurazan underwent intramolecular cyclization on heating with AcOH in EtOH to give furazano[3,4-*b*]pyridine derivatives in high yields.

**Key words:** furazans, cyanofurazans, β-diketones, β-oxo esters, enamines, furazano[3,4-*b*]pyridines.

It is known that transition metal acetylacetonates catalyze the addition of β-dicarbonyl compounds, which contain the active methylene group, at the C≡N bond of some activated nitriles, *e.g.*, of trihalogenoacetonitriles,[1—4] benzoylacetonitrile,[5] and malononitrile.[6,7] This methodology also proved to be efficient in the synthesis of polyfunctional compounds based on cyanoheterocycles. Thus acetylacetone adds to 2-cyanopyridine in the presence of $Ni(acac)_2$ at 110—120 °C to give adduct **1** (Scheme 1). Under the reaction conditions, the latter decomposes to form 4-amino-4-(2-pyridyl)but-3-en-2-one (**2**).[8]

**Scheme 1**




**1** **2**

It was reasonable to expect that the use of more reactive heterocyclic nitriles will allow one to perform the reactions with compounds containing the reactive methylene group under milder conditions, thus preventing decomposition of the primary adduct.

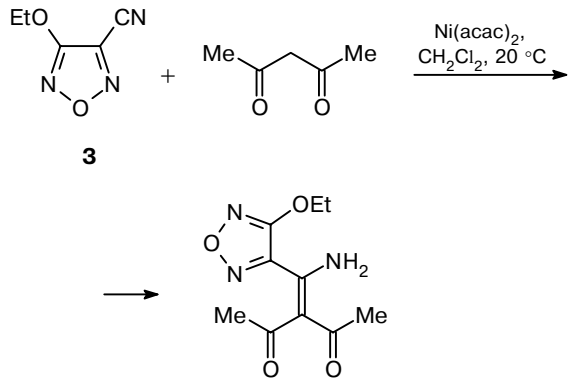
Based on the results of studies on the reactions of a number of cyanoheterocycles with enols, the heterocycles were arranged in the activity series according to their ability to activate the C≡N bond.[9] It was demonstrated that furazan (1,2,5-oxadiazole) is among the most active compounds in this series due to its pronounced electron-withdrawing properties.

In the present work, we report the results of studies on the reactions of cyanofurazans with β-dicarbonyl compounds (for the preliminary communication, see Ref. 10).

## Results and Discussion

We found that acetylacetone in the presence of a catalytic amount of $Ni(acac)_2$ added to 3-cyano-4-ethoxyfurazan (**3**) even at room temperature to give enaminodione **4** in 77% yield (Scheme 2).

**Scheme 2**




**3**

**4**

The $^1H$ NMR spectrum (in DMSO-$d_6$) of enaminodione **4** has a broadened signal for two Ac groups (δ 2.24) and two broad signals of the amino group at δ 8.8 (free NH) and δ 10.4 (NH bound to the O atom of the acetyl group through an intramolecular hydrogen

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**Table 1.** Yields, melting points, the parameters of the IR and mass spectra, and the data from elemental analysis for enaminodiones **4** and **6** and furazano[3,4-*b*]pyridines **8**, **10**, and **12**

| Compound | Yield (%) | M.p./°C (solvent for crystallization) | Found / Calculated (%) | | | Molecular formula (mol. weight) | IR, ν/cm$^{-1}$ | Mass spectrum, *m/z* |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | | | |
| **4** | 77 | 104—105 ($C_6H_6$—heptane, 1 : 1) | 50.25<br>50.21 | 5.45<br>5.48 | 17.38<br>17.56 | $C_{10}H_{13}N_3O_4$<br>(239.23) | — | 239 $[M]^+$ |
| **6a** | 86 | ~150 | 45.43<br>45.71 | 4.81<br>4.80 | 26.08<br>26.66 | $C_8H_{10}N_4O_3$<br>(210.19) | 3395, 3295, 3200 ($NH_2$); 1650 (CO) | 210 $[M]^+$ |
| **6b** | 83 | 208—210 (MeOH) | 57.12<br>57.35 | 4.51<br>4.44 | 20.53<br>20.58 | $C_{13}H_{12}N_4O_3$<br>(272.26) | 3405, 3320 ($NH_2$); 3250, 3205 (CH); 1650 (CO); 1595 (C=N); 1510, 1410, 1265, 1030, 880, 750 | 254 $[M^+ - H_2O]$ |
| **6c** | 87 | 206—208 (MeOH) | 64.48<br>64.67 | 4.25<br>4.22 | 16.89<br>16.76 | $C_{18}H_{14}N_4O_3$<br>(334.33) | 3435, 3320, 3240, 3170 (NH, CH); 1640 (CO); 1600, 1570 (C=N); 1470, 1320, 1280, 1000, 970, 900 | — |
| **8a** | 90 | 197—198 | 49.95<br>50.00 | 4.23<br>4.20 | 29.32<br>29.15 | $C_8H_8N_4O_2$<br>(192.18) | 3450, 3350, 3300, 3240 (NH); 2230 (C≡N); 1680, 1650, 1620, 1580 (C=N); 1475, 1420, 1140, 1100, 875, 850 | 192 $[M]^+$, 162 $[M^+ - NO]$ |
| **8b** | 82 | 257—258 (MeOH) | 61.23<br>61.41 | 3.65<br>3.96 | 22.34<br>22.04 | $C_{13}H_{10}N_4O_2$<br>(254.25) | 3395, 3310, 3225, 3060 (NH, CH); 1665 (CO); 1645 (C=N); 1595, 1540, 1505, 1495, 1380, 1335, 1260, 1030, 960, 890 | 254 $[M]^+$, 224 $[M^+ - NO]$ |
| **8c** | 88 | 176—178 | 68.41<br>68.35 | 3.95<br>3.82 | 17.59<br>17.71 | $C_{18}H_{12}N_4O_2$<br>(316.32) | 3405, 3330, 3245, 3165 (NH, CH); 1640 (CO); 1595 (C=N); 1450, 1275, 920, 690 | 316 $[M]^+$, 286 $[M^+ - NO]$ |
| **10a** | 90 | 179—180 ($C_6H_6$) | 48.94<br>48.65 | 4.70<br>4.54 | 25.12<br>25.21 | $C_9H_{10}N_4O_3$<br>(222.20) | — | — |
| **10b** | 83 | 168—170 (MeOH) | 58.96<br>59.15 | 4.13<br>4.25 | 19.61<br>19.71 | $C_{14}H_{12}N_4O_3$<br>(284.27) | 3410, 3350, 3260 ($NH_2$); 3000 (CH); 1700 (CO); 1640 (C=N); 1600, 1550, 1290 | 284 $[M]^+$ |
| **12** | 67 | 238—239 (MeOH) | 58.06<br>57.98 | 5.14<br>5.21 | 24.46<br>24.14 | $C_{11}H_{12}N_4O_2$<br>(232.24) | 3415, 3210, 3010, 2960 (NH, CH); 2600—2300, 1790, 1670, 1640, 1450, 1395 | 232 $[M]^+$ |

bond) along with signals of the EtO group (δ 1.35 and 4.35). The integral intensity of the signals is in complete agreement with the structure of **4**. The mass spectrum of compound **4** has a molecular ion peak at $m/z$ = 239 (Table 1).

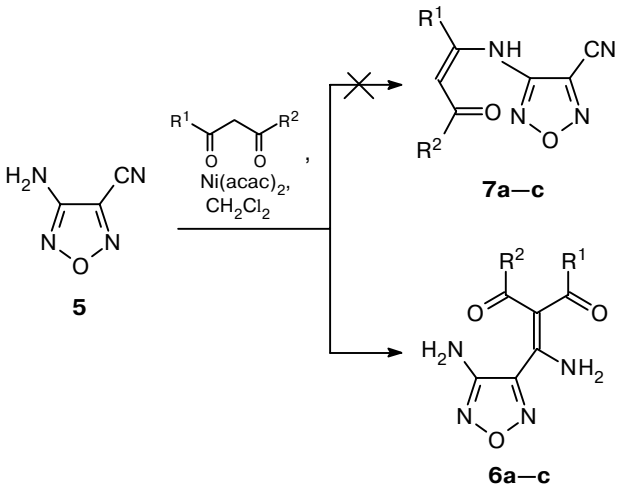
4-Amino-3-cyanofurazan (**5**) is a more promising furazan derivative for the use in the analogous reaction because its structure is favorable for annelation with the furazan ring of the second heterocycle.

Actually, as in the case of nitrile **3**, the addition of acetylacetone, benzoylacetone, or dibenzoylmethane to cyanofurazan **5** proceeded under mild conditions ($CH_2Cl_2$, 20 °C, catalytic amount of $Ni(acac)_2$) to form the expected enaminodiones **6a—c** in 83—87% yields (Scheme 3). As compounds **6a—c** were formed, they precipitated, and hence no additional purification was required.

The reaction is characterized by high regioselectivity. Thus an alternative condensation involving the amino group to give enamines **7a—c** (analogous to that generally observed in the reactions of aminofurazans with various carbonyl compounds[11]) did nor occur under these conditions.

Although the time of conversion of the starting compounds in the reaction performed in boiling $CH_2Cl_2$ is shorter, the resulting enaminodiones **6a—c** underwent partial cyclization to the corresponding furazano[3,4-*b*]pyridines (**8a—c**). It should be noted that the reactions of nitrile **5** with β-diketones can also be promoted by sodium acetate in aqueous methanol. How-

**Scheme 3**



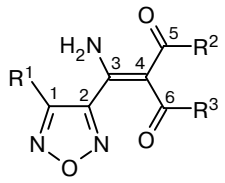

$R^1 = R^2 = Me$ (**a**), $R^1 = Me$, $R^2 = Ph$ (**b**); $R^1 = R^2 = Ph$ (**c**)

ever, prolonged heating at 50—60 °C was required for complete conversion of the reactants. The reaction was accompanied by the formation of a number of by-products, which substantially hampered isolation and purification of enaminodiones **6a—c**.

Compounds **6a—c** were obtained as white powders readily soluble in DMSO, less soluble in acetone and alcohol, and insoluble in hexane. Their structures were confirmed by spectral methods (see Tables 1 and 2). Thus the mass spectra have molecular ion peaks. The $^1$H NMR spectra are in complete agreement with the proposed structures. For example, the spectrum of compound **6a** has a broad signal of two MeCO groups at δ 2.12, the signal of the amino group bound to the furazan ring at δ 6.3, and two low-field broad signals at δ 7.4 (free NH group) and 10.42 (H-bound NH group). It thus follows that the amino group of the enaminodione fragment is involved in intramolecular hydrogen bonding.

In the $^{13}$C NMR spectra (see Table 2), three most common and characteristic signals can be noted. Thus

**Table 2.** Chemical shifts (δ) in the $^1$H and $^{13}$C NMR spectra of enaminodiones **4**, **6a—c**, and **9a** (DMSO-$d_6$)




| Compound | $R^1$ | $R^2$ | $R^3$ | δ | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $^1$H | $^{13}$C | | | | | |
| | | | | | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) |
| **4** | OEt | Me | Me | 1.35 (t, 3 H, $MeCH_2$); 2.24 (s, 6 H, 2 As); 4.35 (q, 2 H, $OCH_2$); 8.80 (br.s, 1 H, NH); 10.42 (br.s, 1 H, NH) | — | — | — | — | — | — |
| **6a*** | $NH_2$ | Me | Me | 2.12 (br.s, 6 H, 2 As); 6.30 (s, 2 H, $NH_2$): 8.74 (br.s, 1 H, NH); 10.40 (br.s, 1 H, NH) | 156.8 | 146.1 | 150.1 | 115.7 | 197.5 | 197.5 |
| **6b**** | $NH_2$ | Me | Ph | 2.16 (s, 3 H, Me); 6.39 (s, 2 H, $NH_2$); 7.30—7.60 (m, 5 H, Ph); 8.79 (br.s, 1 H, NH); 10.75 (br.s, 1 H, NH) | 155.2 | 144.5 | 151.7 | 112.9 | 196.3 | 195.6 |
| **6s** | $NH_2$ | Ph | Ph | 6.25 (s, 2 H, $NH_2$); 7.10—7.55 (m, 10 H, Ph); 9.2 (br.s, 1 H, NH); 10.2 (br.s, 1 H, NH) | 155.4 | 144.9 | 152.7 | 111.2 | 194.5 | 194.5 |
| **9a** | $NH_2$ | Me | OEt | 0.95 (t, 3 H, $MeCH_2$); 2.30 (s, 3 H, Me); 3.87 (q, 2 H, $OCH_2$); 6.19 (s, 2 H, $NH_2$); 8.95 (br.s, 1 H, NH); 10.76 (br.s, 1 H, NH) | — | — | — | — | — | — |

* The signal of the substituent $R^2$ in the $^{13}$C NMR spectrum is observed at δ 31.2.
** The signal of the substituent $R^2$ in the $^{13}$C NMR spectrum is observed at δ 29.9.

**Table 3.** Nuclear Overhauser effect (NOE) for compound **6b**

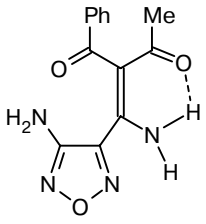
| Irradiated signal, δ | NOE on protons (%) | | | | |
|---|---|---|---|---|---|
| | Me, δ 2.16 | *m*-Ph, δ 7.80 | $NH_2$, δ 6.39 | $NH_2$, δ 8.79 | $NH_2$, δ 10.75 |
| $CH_3$, 2.16 | — | +1.1 | — | — | — |
| $NH_2$, 6.39 | — | +1.5 | — | −23 | −23 |
| $NH_2$, 8.79 | — | — | −21 | — | — |
| $NH_2$, 10.75 | — | — | −21 | — | — |

the chemical shift of the C atom of the furazan ring bound to the amino group is observed at δ 154.9—155.4. The signals for another C atom of the ring bound to the enamino group are observed at higher field (at δ 141.8—144.9). The C atom of the enamine fragment bound to the amino group gives a signal at δ 151.7—152.7.

The IR spectrum (in KBr) of compound **6a** has a band of the carbonyl group (1650 $cm^{-1}$) along with three bands at 3395, 3295, and 3200 $cm^{-1}$, which should be assigned to vibrations of NH (the free group and the group involved in intramolecular hydrogen bonding). No absorption at 2100—2200 $cm^{-1}$ characteristic of the nitrile group was observed.

Compound **6b** contains nonequivalent substituents at the double bond (Ac and Bz). The configuration of this enaminodione was established by measuring the nuclear Overhauser effect (NOE) in the $^1H$ NMR spectra (Table 3).

It can be seen from Table 3 that NOE on the protons of the benzene ring (1.5%), but not on the protons of the methyl group, was observed upon preirradiation of the protons of the amino group directly bound to the furazan ring (δ 6.39), which corresponds to the *E* configuration of compound **6b**.



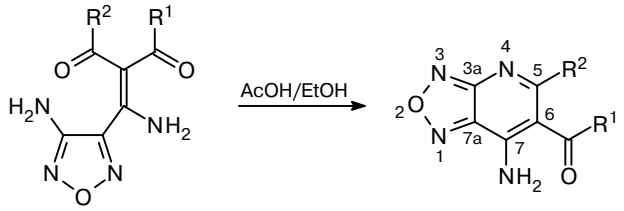

*E*-**6b**

The observed small values of NOE for the protons of the benzoyl group may be due to relaxation at the benzene ring. The large negative values of NOE between two amino groups are indicative of intense intra- and intermolecular exchange of the NH protons. The presence of the hydrogen bond between one of the NH protons of the enamine fragment and the acetyl group leads to the nonequivalence of the protons of this amino group.

We found that heating of the resulting enaminodiones in ethanol in the presence of acetic acid afforded the corresponding furazano[3.4-*b*]pyridines (**8a—c**) in high yields (Scheme 4). It should be noted that the isolation of enaminodiones **6a—c** in individual form is not necessary for the synthesis of annelated derivatives **8a—c**. Condensation of nitrile **5** with β-dicarbonyl compounds followed by heating of the reaction mixtures with acetic acid in ethanol gave rise directly to the cyclization products. In this case, the final furazano[3,4-*b*]pyridines were obtained in substantially higher yields than in the two-stage procedure.

Enaminodiones **6a** and **6c** prepared from symmetrical β-diketones can produce the only condensation products, *viz.*, **8a** and **8c**, respectively.

**Scheme 4**

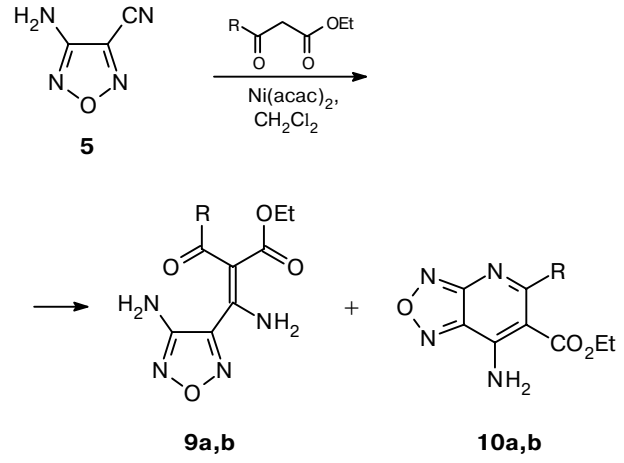



**6a—c** **8a—c**

Enaminodione **6b** also gave the only product **8b** due apparently to the *E* configuration of the starting enaminodione **6b**. In the $^{13}C$ NMR spectrum of furazano[3,4-*b*]pyridine **8b** measured without suppression of the H—C coupling, the signal for the C atom of the carbonyl group is observed as a quartet at δ 201, which is indicative of the presence of the MeCO group.

Nickel acetylacetonate also efficiently catalyzed the reactions of nitrile **5** with β-oxo esters. Thus the reaction with ethyl acetoacetate in the presence of $Ni(acac)_2$ proceeded rapidly in $CH_2Cl_2$ (Scheme 5).

**Scheme 5**




**5**

**9a,b** **10a,b**

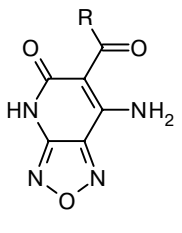
R = Me (**a**), Ph (**b**)

In this case, a substantial portion of the resulting enaminodione **9a** underwent intramolecular cyclocondensation even at room temperature to give ethyl furazano[3,4-*b*]pyridine-3-carboxylate **10a**. After 10 h (the time required for complete consumption of the

starting nitrile **5**), the reaction mixture contained products **9a** and **10a** in approximately equal amounts. Pure enamino ester **9a** was isolated by column chromatography on silica gel.

Analogously, the reaction of nitrile **5** with ethyl benzoylacetate afforded a mixture of enamino ester **9b** and bicyclic compound **10b**.

Intramolecular cyclization of enamino esters **9a** and **9b** also proceeded regioselectively. Heating of these compounds (generally, of the reaction mixture containing compounds **9** and **10**) in the presence of acetic acid resulted in condensation of the acyl carbonyl group with the amino group in the furazan ring to form esters **10a** and **10b**, respectively. No products, which might be formed in the reaction involving the ethoxycarbonyl group, (such as **11**) were detected.



**11**

Catalysis of the addition of acyclic β-dicarbonyl compounds to reagents containing the C≡N bond is based on the intermediate formation of chelate complexes of the ketoenol type. Hence, cyclic β-diketones which cannot form such chelates do not react with activated nitriles in the presence of catalytic amounts of $Ni(acac)_2$. However, it was shown[12] that, for example, the addition of cyclohexane-1,3-dione or dimedone to cyanamides can be performed in the presence of an equimolar amount of nickel acetate $Ni(OAc)_2$. In this case, the corresponding nickel enolate was apparently formed as the reaction intermediate. In the study of the reaction of cyanofurazan **5** with dimedone, we used an analogous approach. Actually, nitrile **5** rapidly disappeared (according to the TLC data) upon refluxing with dimedone and $Ni(OAc)_2$ (taken in a ratio of 2 : 2 : 1) in DMF. After treatment with dilute HCl, tricylcic compound **12** was isolated in 67% yield (Scheme 6).

As we mentioned in the preliminary communication,[10] furazano[3,4-*b*]pyridines have been previously unknown. Only *N*-oxides of this heterocyclic system have been described. The synthesis of unsubstituted furazano[3,4-*b*]pyridine has been reported only recently.[13] The results of investigations on derivatives of this heterocyclic system were surveyed in the review.[14]

Furazano[3,4-*b*]pyridines synthesized in the present study were characterized by the data from mass spectrometry, IR spectroscopy, and elemental analysis (see Table 1) and by $^1H$ and $^{13}C$ NMR spectroscopy (Table 4). Single crystals of compound **8a** were studied by X-ray diffraction analysis.[10]

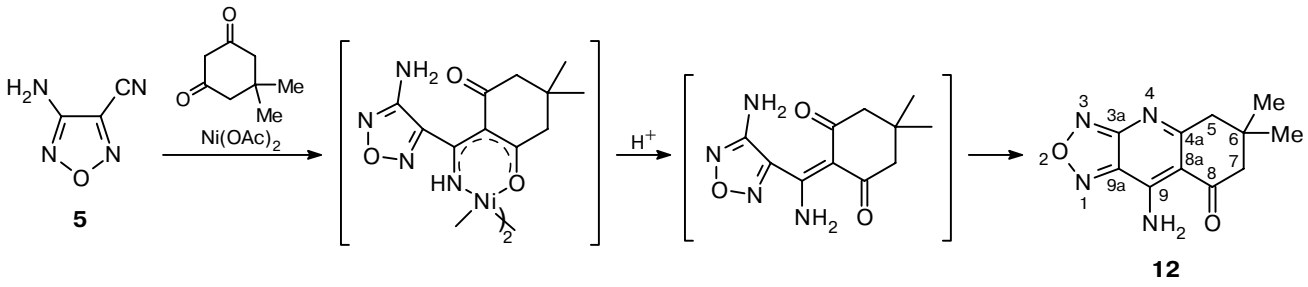
All signals in the $^{13}C$ NMR spectra of furazano[3,4-*b*]pyridines (see Table 4) were unambiguously assigned. Thus the C atoms of the furazan rings (C(3a)) bound to the N atom of the pyridine ring give signals at δ 157.9—159.8, which are no different from that observed in the spectrum of unsubstituted furazano[3,4-*b*]pyridine (*cf.* lit.[13]: δ 158.4). The signals for the other C atoms of the furazan rings (C(7a)) are observed at higher field and are also located in a narrow range (δ 139.5—140.0). The presence of substituents in the pyridine moiety of the molecule leads to a substantial change in the corresponding chemical shifts (by 10—20 ppm) compared to those observed in the spectrum of the parent compound of this class of bicycles.

In conclusion, it should be noted that the results of our study demonstrated the efficiency of the catalytic addition of β-dicarbonyl compounds to cyanofurazans in the synthesis of polyfunctional furazan derivatives. This method provided the basis for the development of a convenient procedure for the preparation of furazano[3,4-*b*]pyridine derivatives. Enaminodiones under study are convenient starting compounds for their conversions into various non-cyclic and annelated furazan derivatives. Synthetic possibilities of the resulting enaminodiones and furazano[3,4-*b*]pyridines will be described in more detail elsewhere.

## Experimental

The IR spectra were measured on a Perkin—Elmer 577 spectrophotometer in KBr pellets. The mass spectra (EI) were obtained on a Varian MAT-311A instrument (70 eV). The $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AM-300 instrument (300 and 75 MHz, respectively) in DMSO-$d_6$. The assignment of the signals in the $^{13}C$ NMR spectra were made based on the double heteronuclear resonance. The nuclear Overhauser effect was measured using the NOEDIF program included in the software of the spectrometer. The purities of the compounds were monitored by TLC on Silufol UV-254 plates.

**Scheme 6**




**5** **12**

**Table 4.** Chemical shifts (δ) in the $^1H$ and $^{13}C$ NMR spectra of furazano[3,4-*b*]pyridines **8a—c** and **10a,b** (DMSO-$d_6$)

| Compound | δ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $^1H$ | $^{13}C$ | | | | | | |
| | | C(3a) | C(7a) | C(7) | C(6) | C(5) | C=O | Other C atoms |
| **8a** | 2.51 (s, 3 H, Me); 2.58 (s, 3 H, Me); 8.23 (br.s, 2 H, $NH_2$) | 158.0 | 139.7 | 142.2 | 113.7 | 167.6 | 202.2 | 26.2 (Me); 31.6 (CO<u>Me</u>) |
| **8b** | 3.34 (s, 3 H, Me); 7.50—7.60 (m, 5 H, Ph); 8.79 (br.s, 2 H, $NH_2$) | 157.9 | 139.5 | 144.3 | 111.9 | 169.1 | 200.2 | 31.6 (Me); 140.8 (*i*), 130.2 (*p*), 128.62, 128.56 (*m*, *o*) (Ph) |
| **8s** | 7.18—7.56 (m, 10 H, 2 Ph); 8.30 (br.s, 2 H, $NH_2$) | 159.8 | 140.0 | 144.6 | 110.3 | 168.5 | 195.7 | 138.5 (*i*), 132.8 (*p*), 128.0, 128.2 (*m*, *o*), (CO<u>Ph</u>); 140.2 (*i*), 129.5 (*p*), 128.8, 129.0 (*m*, *o*) (Ph) |
| **10a** | 1.42 (t, 3 H, <u>Me</u>$CH_2$); 2.65 (s, 3 H, Me); 4.40 (q, 2 H, $OCH_2$); 8.60 (br.s, 2 H, $NH_2$) | 157.9 | 139.7 | 145.9 | 102.1 | 169.7 | 166.7 | 13.9 ($CH_2$<u>Me</u>); 27.8 (Me); 61.0 ($CH_2$) |
| **10b** | 0.74 (t, 3 H, <u>Me</u>$CH_2$); 3.92 (q, 2H, $OCH_2$); 7.40—7.50 (m, 5 H, Ph); 8.62 (br.s, 2 H, $NH_2$) | 158.4 | 139.6 | 145.8 | 102.6 | 169.2 | 166.8 | 13.1 (Me); 60.9 ($CH_2$); 141.5 (*i*), 129.1 (*p*), 127.96, 127.67 (*m*, *o*) (Ph) |

3-Cyano-4-ethoxyfurazan[15] and 4-amino-3-cyanofurazan[16] were prepared according to procedures reported previously.

The yields, the melting points, the data from elemental analysis, and the spectral characteristics of the compounds synthesized are given in Tables 1, 2, and 4.

**3-Acetyl-4-amino-4-(4-ethoxyfurazan-3-yl)but-3-en-2-one (4).** A mixture of cyanofurazan **3** (0.59 g, 4.2 mmol), acetylacetone (2 mL), and $Ni(acac)_2$ (0.11 g, 0.42 mmol) in dry $CH_2Cl_2$ (7 mL) was stirred for 5 h. The solvent was distilled off *in vacuo* and the residue was purified by column chromatography on $SiO_2$ (benzene—hexane as the eluent). Product **4** was obtained in a yield of 0.78 g.

**3-Acetyl-4-amino-4-(4-aminofurazan-3-yl)but-3-en-2-one (6a).** A mixture of cyanofurazan **5** (1.1 g, 10 mmol), acetylacetone (1.2 g, 1.25 mL, 12 mmol), and $Ni(acac)_2$ (0.026 g, 0.1 mmol) in dry $CH_2Cl_2$ (40 mL) was stirred at ~20 °C for 6 h, kept for 12 h, and then refluxed for 3 h. The precipitate that formed was filtered off and washed with $CH_2Cl_2$ to obtain a product in a yield of 1.82 g. The product melted at ~150 °C and immediately crystallized to form a yellow compound with a higher melting point.

**4-Amino-4-(4-aminofurazan-3-yl)-3-benzoylbut-3(*E*)-en-2-one (6b)** was prepared analogously starting from benzoylacetone. The reaction was performed at ~20 °C for 36 h.

**3-Amino-3-(4-aminofurazan-3-yl)-2-benzoyl-1-phenylprop-2-en-1-one (6c)** was prepared analogously starting from dibenzoylmethane. The reaction at ~20 °C was completed in 50 h.

**6-Acetyl-7-amino-5-methylfurazano[3,4-*b*]pyridine (8a).** A solution of enaminodione **6a** (0.5 g, 2.4 mmol) in EtOH (5 mL) with five drops of AcOH was refluxed for 2 h. The precipitate that formed was filtered and product **8a** was obtained in a yield of 0.41 g.

**6-Acetyl-7-amino-5-phenylfurazano[3,4-*b*]pyridine (8b)** was prepared analogously from enaminodione **6b** upon refluxing for 5 h.

**7-Amino-6-benzoyl-5-phenylfurazano[3,4-*b*]pyridine (8c)** was prepared analogously from enaminodione **6c** upon refluxing for 10 h.

**4-Amino-4-(4-aminofurazan-3-yl)-3-ethoxycarbonylbut-3-en-2-one (9a).** A mixture of ethyl acetoacetate (0.13 g, 1 mmol), cyanofurazan **5** (0.11 g, 1 mmol), and $Ni(acac)_2$ (0.012 g, 0.046 mmol) in dry $CH_2Cl_2$ (3 mL) was stirred at ~20 °C for 10 h. The solvent was evaporated *in vacuo* and the residue was chromatographed on a column with $SiO_2$ ($CHCl_3$ as the eluent). Product **9a** was obtained in a yield of 0.07 g.

**7-Amino-6-ethoxycarbonyl-5-methylfurazano[3,4-*b*]pyridine (10a).** A mixture of cyanofurazan **5** (0.11 g, 1 mmol), ethyl acetoacetate (0.2 g, 1.5 mmol), and $Ni(acac)_2$ (0.012 g, 0.046 mmol) in dry $CH_2Cl_2$ (10 mL) was refluxed for 3 h. Then three drops of acetic acid were added. The mixture was refluxed for 1 h and concentrated *in vacuo* to dryness. The residue was recrystallized from a 20 : 1 $C_6H_6$—MeOH mixture and product **10a** was obtained in a yield of 0.18 g.

**7-Amino-6-ethoxycarbonyl-5-phenylfurazano[3,4-*b*]pyridine (10b)** was prepared analogously from ethyl benzoylacetate.

**9-Amino-6,6-dimethyl-5,6,7,8-tetrahydrofurazano[3.4-*b*]quinolin-8-one (12).** A mixture of cyanofurazan **5** (0.44 g, 4 mmol), dimedone (0.56 g, 4 mmol), and nickel acetate (0.36 g, 2 mmol) in DMF (10 mL) was refluxed for 2 h. The solvent was distilled off *in vacuo*. A solution of 8.6 *M* HCl in ethanol (0.46 mL) and MeOH (4 mL) were added to the residue. The reaction mixture was stirred for 10 min and then water (5 mL) was added. The precipitate that formed was filtered off and dried in a desiccator over $P_2O_5$. The resulting dark powder (0.61 g) was purified on a column with $SiO_2$ ($CHCl_3$ as the eluent). The product was obtained as a pale-gray powder in a yield of 0.46 g. $^1H$ NMR ($CDCl_3$), δ: 1.12 (s, 6 H, 2 Me); 2.58 and 2.99 (both s, 2 H each, $CH_2$); 6.75 and 10.25 (both br.s, 1 H each, NH). $^{13}C$ NMR (DMSO-$d_6$), δ: 27.6 and 31.1 (both Me); 48.1 (C(5)); 51.9 (C(7)); 95.5 (C(6)); 104.5 (C(8a)); 140.1 (C(9a)); 147.2 (C(9)); 158.2 (C(3a)); 172.5 (C(4a)); 199.2 (C(8)).

## References

1. K. Uehara, Y. Ohashi, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1447.

2. A. S. Veronese, C. Talmelli, V. Gandolfi, B. Corain, and M. Basato, *J. Mol. Catalysis*, 1986, **34**, 195.
3. V. A. Dorokhov, A. V. Komkov, L. S. Vasil′ev, O. G. Azarevich, and M. F. Gordeev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2639 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 2311 (Engl. Transl.)].
4. V. A. Dorokhov, L. S. Vasil′ev, F. E. Surzhikov, and V. S. Bogdanov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1329 [*Russ. Chem. Bull.*, 1995, **44**, 1283 (Engl. Transl.)].
5. V. A. Dorokhov, S. V. Baranin, A. Yu. Yagodkin, V. S. Bogdanov, and Z. K. Dem′yanets, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2295 [*Russ. Chem. Bull.*, 1995, **44**, 2201 (Engl. Transl.)].
6. A. S. Veronese, V. Gandolfi, B. Corain, and M. Basato, *J. Mol. Catal.*, 1986, **36**, 339.
7. V. A. Dorokhov, O. G. Azarevich, V. S. Bogdanov, B. I. Ugrak, and L. S. Vasil′ev, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1432 [*Russ. Chem. Bull.*, 1994, **43**, 1356 (Engl. Transl.)].
8. L. S. Vasil′ev, V. S. Bogdanov, E. M. Shashkova, N. K. Khoa, K. L. Cherkasova, and V. A. Dorokhov, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1323 [*Russ. Chem. Bull.*, 1993, **42**, 1266 (Engl. Transl.)]; V. A. Dorokhov, V. S. Bogdanov, L. S. Vasil′ev, and N. K. Khoa, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 710 [*Russ. Chem. Bull.*, 1996, **45**, 671 (Engl. Transl.)].
9. Y. Terui, M. Yamakawa, T. Honma, Y. Tada, and K. Tori, *Heterocycles*, 1982, **19**, 221.
10. L. S. Vasil′ev, A. B. Sheremetev, V. A. Dorokhov, N. K. Khoa, M. O. Dekaprilevich, Yu. T. Struchkov, and L. I. Khmelnitskii, *Mendeleev Commun.*, 1994, 57.
11. A. B. Sheremetev, N. N. Makhova, and W. Friedrichsen, *Adv. Heterocycl. Chem.*, 2001, **78**, 64.
12. V. A. Dorokhov and M. F. Gordeev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1211 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 1104 (Engl. Transl.)].
13. L. W. Deady and N. H. Quazi, *Spectrosc. Lett.*, 1995, **28**, 1033.
14. A. B. Sheremetev, *Usp. Khim.*, 1999, **68**, 154 [*Russ. Chem. Rev.*, 1999, **68** (Engl. Transl.)].
15. A. B. Sheremetev, Yu. A. Strelenko, T. S. Novikova, and L. I. Khmelnitskii, *Tetrahedron*, 1993, **49**, 5905.
16. V. G. Andrianov and A. V. Eremeev, *Khim. Geterotsikl. Soedin.*, 1994, 693 [*Chem. Heterocycl. Compd.,* 1994 (Engl. Transl.)].

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