

## 2-Acyl(aryl)-1,1,3,3-tetracyanopropenides: V.\* Reaction with Hydrazine Hydrate

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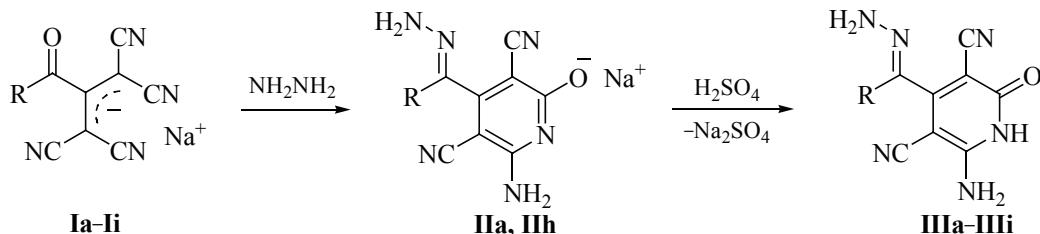
**Abstract**—Reactions of 2-acyl(aryl)-1,1,3,3-tetracyanopropenides with hydrazine hydrate followed by neutralization led to the formation of 2-amino-4-[hydrazono(aryl)methyl]-2-oxo-1,2-dihydropyridine-3,5-dicarbonitriles.

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2-Acyl(aryl)-1,1,3,3-tetracyanopropenides **I** [2] demonstrated their opportunities as promising blocks for designing highly functionalized heterocyclic compounds. They underlie the domino processes affording 2-halodihydrofurans [2], 2-alkylsulfinyldihydrofurans [3], 2-halopyridines [4], and furo[3,4-*c*]pyridines [1]. Besides propenides **I** are intermediates in the reactions of tetracyanocyclopropyl ketones with some nucleophiles. For instance, the reaction of tetracyanocyclopropyl ketones with hydroxide ion and primary amines proceeds through the intermediate formation of propenides **I** which transform subsequently into the derivatives of pyrrolo[3,4-*c*]pyridine [5] and pyrrolo[2,3-*b*]pyrrole [6]. The reaction of tetracyanocyclopropyl ketones with hydrazine hydrate occurred with the retention of the three-membered ring except for the pivaloyltetracyanocyclopropane that gave in this reaction substituted pyrrolo[2,3-*c*]pyridazine [7]. It was presumed that the intermediate in this reaction

was 2-pivaloyl-1,1,3,3-tetracyanopropenide (**II**). To test this assumption and to extend this reaction to the other 2-acyl(aryl)-1,1,3,3-tetracyanopropenides we examined the reactions of propenides **Ia–Ii** with hydrazine hydrate.

Propenides **Ia–Ii** react with hydrazine hydrate in equimolar amounts in inert solvents at the room temperature with a notable self-heating. At the excess of hydrazine hydrate the reaction is accompanied with tarring hampering the isolation of the reaction products and decreasing their yields. In the reaction of propenides **Ia**, **Ih** in anhydrous dioxane we obtained the corresponding sodium 6-amino-4-[hydrazono(aryl)methyl]-3,5-dicyanopyridin-2-olates **IIa**, **IIh**. Pyridones **IIIa**, **IIIh** were obtained by neutralization of the water solutions of salts **IIa**, **IIh** with sulfuric acid. 2-Amino-4-[hydrazono(aryl)methyl]-2-oxo-1,2-dihydropyridine-3,5-dicarbonitriles **IIIb–IIIg**, **IIIi** were isolated after the neutralization of the reaction mixture with sulfuric acid.



R = Ph (**a**), 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**b**), 4-MeOC<sub>6</sub>H<sub>4</sub> (**c**), 4-BrC<sub>6</sub>H<sub>4</sub> (**d**), 3-ClC<sub>6</sub>H<sub>4</sub> (**e**), 3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub> (**f**), C<sub>4</sub>H<sub>3</sub>S (**g**), 2,5-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**h**), *t*-Bu (**i**).

\* For communication IV, see [1].

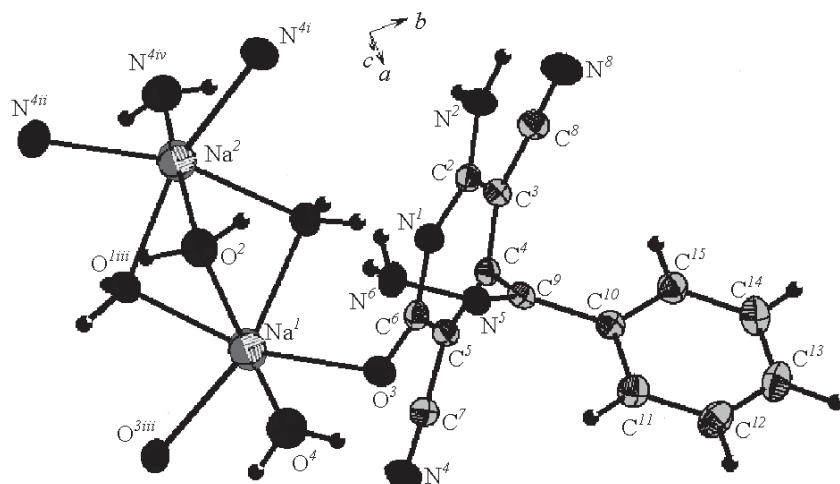
The composition and structure of compounds **IIa**, **IIIh** and **IIIa–IIIi** were derived from the data of  $^1\text{H}$ ,  $^{13}\text{C}$ , NMR, IR, and mass spectra.  $^1\text{H}$  NMR spectra of compounds **IIIa–IIIi** contain singlets of the protons of the NH group of the pyridine ring (pyridone) in the region 11.41–11.49 ppm, of the aromatic amino group (7.59–8.30 ppm), and of the amino group of the hydrazone fragment (6.25–7.48 ppm). The signals of the aromatic substituents appear with the characteristic multiplicity in the usual region. The probable alternative structure of pyrido[3,4-*d*]-pyridazines is rejected based on the  $^{13}\text{C}$  NMR spectra of compounds **IIIh**, **IIIi**, for the spectra contained the carbon atom signals from two cyano groups. Mass spectra are similar, they contain molecular ion peaks of relatively high intensity, and also ions  $[M - 28]^+$  and  $[\text{ArC}=\text{N}]^+$ . The IR spectra of compounds **IIIa–IIIi** contain absorption bands of the hydrazone fragment ( $1650$ – $1682\text{ cm}^{-1}$ ), of the conjugated cyano groups ( $2200$ – $2235\text{ cm}^{-1}$ ), and also of amino groups ( $3150$ – $3200$  and  $3300$ – $3350\text{ cm}^{-1}$ ). In the  $^1\text{H}$  NMR spectra of salts **IIa**, **IIIh** the signals from the pyridine unit NH are absent and besides the signals of the  $\text{NH}_2$  groups are shifted upfield.

The structure of salt **IIa** was established by XRD analysis of a single crystal (see the figure). Two independent sodium atoms are located in the crystallographic plane *m* and are linked by bridging atoms of water  $\text{O}^1$  (in a general position) and  $\text{O}^2$  (located in the *m* plane). The octahedral surrounding of the atom  $\text{Na}^1$  is completed by the water atom  $\text{O}^4$  and by the atom  $\text{O}^3$ , and of the atom  $\text{Na}^2$ , also by

the water atom  $\text{O}^{4iv}$  and the atom  $\text{N}^{4i}$  of the nitrile group. In the polymer chain  $\text{Na}^1-\text{O}^2-\text{Na}^2-\text{O}^4-\text{Na}^1-\text{O}^2$  etc. the interatomic distance  $\text{Na}^1\dots\text{Na}^2$  is  $3.204(2)\text{ \AA}$ .

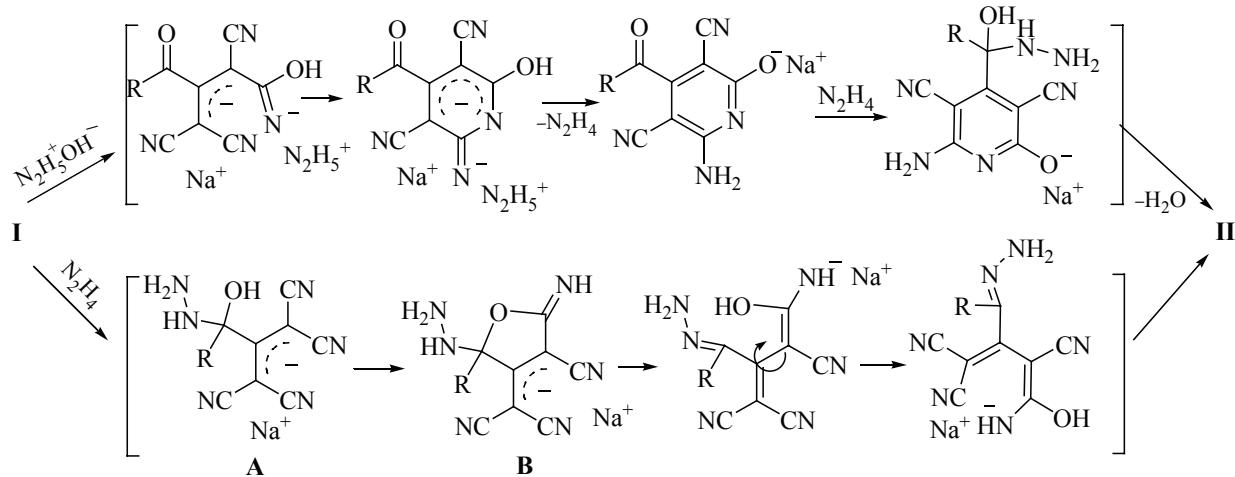
At least two ways are presumable of the formation of compounds **II** from propenides **I**.

The first route assumes an independent occurrence of heterocyclization due to the addition of a hydroxide ion to a cyano group and of the nucleophilic substitution at the carbonyl group under the action of hydrazine. However it was shown in [5] no direct addition of the hydroxide ion to cyano groups of propenides **I** was observed even at the action of alkali metal hydroxides. Therefore the alternative path is more probable where the formation of the hydrazone fragment and of the pyridine ring are the stages in the single process. The reaction starts with the nucleophilic addition of hydrazine to the carbonyl group affording a tetrahedral intermediate, hydrazinehydrin **A**. Then a closure occurs of a furan ring resulting from the hydroxy group addition to the cyano group with the formation of intermediate **B**. As has been stated formerly [8], iminofurans are unstable when containing a labile hydrogen atom bound to a heteroatom in the  $\beta$ -position with respect to an oxygen. They cannot be isolated since they undergo a spontaneous iminolactone-lactame rearrangement. In our case due to the opening of the furan ring the hydrazone fragment and the carboxamide function are formed, and for the latter the addition to the cyano group to give a pyridine system is preferable.



$$i = 0.5 + x, y, 0.5 - z; ii = -0.5 + x, 0.5 - y, 0.5 - z; iii = x, 0.5 - y, z; iv = -0.5 + x, 0.5 - y, 0.5 - z.$$

A fragment of the crystal structure of **IIa** molecule showing the spatial arrangement of atoms in the molecule and the way of coordination of sodium cations ( $\text{Na}^1$ ,  $\text{Na}^2$ ). Thermal ellipsoids are shown with the 50% probability.



## EXPERIMENTAL

The monitoring of the reaction progress and checking the purity of obtained compounds was performed by TLC on Silufol UV-254 plates (development under UV irradiation, in iodine vapor, and also by thermal decomposition). IR spectra were recorded on a Fourier spectrophotometer FSM-1202 from mulls in mineral oil.  $^1H$  and  $^{13}C$  NMR spectra were registered on a spectrometer Bruker DRX-500 (500.13 and 125.76 MHz respectively) in  $DMSO-d_6$ , internal reference TMS. Mass spectra were taken on an instrument Simadzu GCMS-QP2010S DI (electron impact, 70 eV).

XRD study on a crystal of compound **IIa** obtained by slow evaporation from the water solution was performed on a diffractometer StadiVari Pilatus 100K STOE,  $CuK_{\alpha}$  radiation from the generator GeniX<sup>3D</sup> Cu HF equipped with a microfocus X-ray tube and multilayer thin-film ellipsoidal monochromator FOX3D HF Xenocs (France). Data array, establishing and refining of the unit cell parameters, the diffraction data processing was performed with the use of the program package STOE X-Area. The main crystallographic parameters are as follows:  $C_{14}H_9N_6NaO \cdot 2H_2O$ ,  $M$  336.29;  $a$  9.8673(2),  $b$  34.8250(9),  $c$  8.8329(2) Å;  $V$  3035.24(12) Å<sup>3</sup>;  $d_{\text{calc}}$  1.472 g/cm<sup>3</sup>; space group  $Pnma$ ,  $Z$  8. The structure was solved by the direct method applying software SHELXS-97 [9]. The refinement of the positions and thermal parameters of nonhydrogen atoms was carried out in full-matrix anisotropic approximation. Hydrogen atoms were localized from the difference Fourier synthesis and freely refined in an isotropic approximation. The final  $R$ -factor for 1619 reflections with  $I > 2\sigma(I)$  is 0.035. Molecular graphics

was done using program DIAMOND [10].

The crystallographic data are deposited to the Cambridge Crystallographic Data Center and can be freely obtained at the address CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>), CCDC 889154.

**Sodium 6-amino-4-[hydrazone(phenyl)methyl]-3,5-dicyanopyridin-2-olate hydrate (IIa).** To a solution of 0.27 g (1 mmol) of propenide **Ia** in 2 ml of dioxane was added 0.05 g (1 mmol) of hydrazine hydrate, the mixture was stirred for 10 min, left overnight, the separated precipitate was filtered off and washed with dioxane. Yield 0.165 g (55%), decomp.  $>150^{\circ}\text{C}$ . IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3224 (NH<sub>2</sub>), 2210 (C≡N), 1630 (C=O).  $^1H$  NMR spectrum,  $\delta$ , ppm: 6.14 s (2H, NH<sub>2</sub>), 6.53 br.s (2H, NH<sub>2</sub>), 7.24 t (1H<sub>arom</sub>,  $J$  7.3 Hz), 7.32 t (2H<sub>arom</sub>,  $^3J$  7.4 Hz), 7.39 d (2H<sub>arom</sub>,  $^3J$  7.9 Hz). Found, %: C 50.24; H 3.87; N 24.67.  $C_{14}H_9N_6NaO \cdot 2H_2O$ . Calculated, %: C 50.00; H 3.90; N 24.99.

**Sodium 6-amino-4-[hydrazone(2,5-dimethoxyphenyl)methyl]-3,5-dicyanopyridine-2-olate hydrate (IIIh)** was obtained similarly. Yield 78%. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3237 (NH<sub>2</sub>), 2209 (C≡N), 1642 (C=O).  $^1H$  NMR spectrum,  $\delta$ , ppm: 3.51 s (3H, OCH<sub>3</sub>), 3.70 s (3H, OCH<sub>3</sub>), 5.97 s (2H, NH<sub>2</sub>), 6.50 br.s (2H, NH<sub>2</sub>), 6.82 d.d (1H<sub>arom</sub>,  $^3J$  8.9,  $^4J$  3.1 Hz), 6.88 d (1H<sub>arom</sub>,  $^3J$  8.9 Hz), 7.04 d (1H<sub>arom</sub>,  $^4J$  3.1 Hz). Found, %: C 48.52; H 4.25; N 21.09.  $C_{16}H_{13}N_6NaO_3 \cdot 2H_2O$ . Calculated, %: C 48.49; H 4.32; N 21.20.

**6-Amino-4-[hydrazone(phenyl)methyl]-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (IIIa).** *a.* To a solution of 1.34 g (5 mmol) of propenide **Ia** in 8 ml of acetonitrile was added a solution of 0.25 g (5 mmol)

of hydrazine hydrate in 2 ml of acetonitrile, the mixture was stirred for 1 min and left overnight, then it was neutralized with 5% H<sub>2</sub>SO<sub>4</sub>, the separated precipitate was filtered off, washed with water, and recrystallized from the mixture acetonitrile–dioxane, 1:1. Yield 1.13 g (81%), mp 143–146°C (decomp.). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3387, 3326 (NH<sub>2</sub>), 2223 (C≡N), 1670 (C=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.14 s (2H, NH<sub>2</sub>), 7.26 t (1H<sub>arom</sub>,  $^3J$  7.4 Hz), 7.34 t (2H<sub>arom</sub>,  $^3J$  7.4 Hz), 7.43 d (2H<sub>arom</sub>,  $^3J$  7.8 Hz), 7.78 br.s (2H, NH<sub>2</sub>), 11.82 (1H, NH). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 278 (100) [M]<sup>+</sup>, 250 (70) [M – 28]<sup>+</sup>, 103 (32) [PhC=N]<sup>+</sup>. Found, %: C 46.91; H 2.48; N 23.44. C<sub>14</sub>H<sub>9</sub>BrN<sub>6</sub>O. Calculated, %: C 47.08; H 2.54; N 23.53.  $M$  356.00.

b. To a solution of 0.3 g (1 mmol) of salt **IIa** in 3 ml of water was added 5% H<sub>2</sub>SO<sub>4</sub> till neutral pH, the separated precipitate was filtered off and worked up as in procedure *a*. Yield 0.26 g (93%).

Compounds **IIIb**–**IIIi** were synthesized by procedure *a*.

**2-Amino-4-[(hydrazono)(3,4-dimethoxyphenyl)methyl]-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (IIIb).** Yield 65%, mp 139–140°C (decomp.). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3320, 3214 (NH<sub>2</sub>), 2230 (C≡N), 1659 (C=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 3.76 s (3H, OCH<sub>3</sub>), 3.77 s (3H, OCH<sub>3</sub>), 6.67 d.d (1H<sub>arom</sub>,  $^3J$  8.3,  $^4J$  1.9 Hz), 6.87 d (1H<sub>arom</sub>,  $^3J$  8.5 Hz), 6.89 s (2H, NH<sub>2</sub>), 7.28 d (1H<sub>arom</sub>,  $^4J$  1.9 Hz), 7.90 br.s (2H, NH<sub>2</sub>), 12.50–11.50 br.s (1H, NH). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 338 (4), 307 (1). Found, %: C 56.31; H 4.33; N 24.21. C<sub>16</sub>H<sub>14</sub>N<sub>6</sub>O<sub>3</sub>. Calculated, %: C 56.80; H 4.17; N 24.84.  $M$  338.11.

**2-Amino-4-[hydrazono(4-methoxyphenyl)methyl]-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (IIIc).** Yield 73%, t.decomp. 130–140°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3340, 3320 (NH<sub>2</sub>), 2219 (C≡N), 1674 (C=O), 1654 (C=N). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 3.76 s (3H, OCH<sub>3</sub>), 6.84 s (2H, NH<sub>2</sub>), 6.89–6.93 m (2H<sub>arom</sub>, AArBBr system,  $^3J$  8.9 Hz), 7.35–7.39 m (2H<sub>arom</sub>, AArBBr system,  $^3J$  8.9 Hz), 7.94 br.s (2H, NH<sub>2</sub>), 10.80–12.60 br.s (1H, NH). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 308 (9). Found, %: C 58.33; H 3.71; N 26.93. C<sub>15</sub>H<sub>12</sub>N<sub>6</sub>O<sub>2</sub>. Calculated, %: 58.44; H 3.92; N 27.26.  $M$  308.10.

**2-Amino-4-[(4-bromophenyl)(hydrazono)methyl]-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (IIId).** Yield 64%, t.decomp. >185°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3387, 3222 (NH<sub>2</sub>), 2224 (C≡N), 1665 (C=O). <sup>1</sup>H NMR

spectrum,  $\delta$ , ppm: 7.22 s (2H, NH<sub>2</sub>), 7.35–7.39 m (2H<sub>arom</sub>, AArBBr system,  $^3J$  8.6 Hz), 7.52–7.54 m (2H<sub>arom</sub>, AA'BB' system,  $^3J$  8.6 Hz), 7.70–8.30 s (2H, NH<sub>2</sub>), 11.7 s (1H, NH). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 358 (34), 356 (30), 184 (18), 182 (20). Found, %: C 46.91; H 2.48; N 23.44. C<sub>14</sub>H<sub>9</sub>BrN<sub>6</sub>O. Calculated, %: C 47.08; H 2.54; N 23.53.  $M$  356.00.

**2-Amino-4-[(hydrazono)(3-chlorophenyl)methyl]-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (IIIe).** Yield 84%, t.decomp. 190–200°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3403, 3338, 3216 (NH<sub>2</sub>), 2225 (C≡N), 1675 (C=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.30–7.38 m (3H<sub>arom</sub>), 7.40 s (2H, NH<sub>2</sub>), 7.47 s (1H<sub>arom</sub>), 7.81 s (2H, NH<sub>2</sub>), 11.82 s (1H, NH). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 314 (9), 312 (28) [M]<sup>+</sup>, 286 (13), 284 (37) [M – 28]<sup>+</sup>, 140 (22), 139 (75), 138 (30), 137 (61), 109 (100). Found, %: C 53.73; H 2.98; N 26.84. C<sub>14</sub>H<sub>9</sub>ClN<sub>6</sub>O. Calculated, %: C 53.77; H 2.90; N 26.87.  $M$  312.05.

**2-Amino-4-[hydrazono(3-nitrophenyl)methyl]-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (IIIf).** Yield 62%, mp 231–232°C (decomp.). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3398, 3211 (NH<sub>2</sub>), 2223 (C≡N), 1664 (C=O), 1537, 1375 (NO<sub>2</sub>). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.48 s (2H, NH<sub>2</sub>), 7.64 t (1H, C<sub>6</sub>H<sub>4</sub>,  $^3J$  8.0 Hz), 7.75 d (1H, C<sub>6</sub>H<sub>4</sub>,  $^3J$  8.0 Hz), 8.09 d.d (1H, C<sub>6</sub>H<sub>4</sub>,  $^3J$  8.0,  $^4J$  1.9 Hz), 8.10 br.s (2H, NH<sub>2</sub>), 8.27 t (1H, C<sub>6</sub>H<sub>4</sub>,  $^4J$  1.9 Hz), 11.8 (1H, NH). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 323 (2), 297 (5.5). Found, %: C 52.18; H 2.86; N 30.09. C<sub>14</sub>H<sub>9</sub>N<sub>7</sub>O<sub>3</sub>. Calculated, %: C 52.02; H 2.81; N 30.33.  $M$  323.08.

**2-Amino-4-[hydrazono(2-thienyl)methyl]-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (IIIg).** Yield 64%, t.decomp. >170°C (decomp.). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3400, 3230 (NH<sub>2</sub>), 2225 (C≡N), 1676 (C=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 6.78 d.d (1H, C<sub>4</sub>H<sub>3</sub>S,  $^3J$  3.6,  $^4J$  1.0 Hz), 6.97 d.d (1H, C<sub>4</sub>H<sub>3</sub>S,  $^3J$  5.1,  $^3J$  3.6 Hz), 7.08 s (2H, NH<sub>2</sub>), 7.39 d.d (1H, C<sub>4</sub>H<sub>3</sub>S,  $^3J$  5.1,  $^4J$  1.0 Hz), 7.80 br.s (2H, NH<sub>2</sub>), 11.70 br.s (1H, NH). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 284 (8). Found, %: C 50.57; H 2.71; N 29.39. C<sub>12</sub>H<sub>8</sub>N<sub>6</sub>OS. Calculated, %: C 50.70; H 2.84; N 29.56.  $M$  284.05.

**2-Amino-4-[(hydrazono)(2,5-dimethoxyphenyl)methyl]-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (IIIh)** was obtained by procedure *b*. Yield 97%, t.decomp. 220–230°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3410, 3214 (NH<sub>2</sub>), 2230 (C≡N), 1670 (C=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 3.54 s (3H, OCH<sub>3</sub>), 3.71 s (3H, OCH<sub>3</sub>), 6.85 d.d (1H<sub>arom</sub>,  $^3J$  8.9,  $^4J$  3.1 Hz), 6.92 d (1H<sub>arom</sub>,  $^3J$  8.9 Hz), 7.12 d (1H<sub>arom</sub>,  $^4J$  3.1 Hz), 7.16 s (2H, NH<sub>2</sub>), 7.59 br.s (2H, NH<sub>2</sub>), 11.62 br.s (1H, NH). <sup>13</sup>C NMR spectrum,  $\delta$ ,

ppm: 55.19 ( $\text{CH}_3$ ), 56.55 ( $\text{CH}_3$ ), 73.47 ( $\text{C}^3$ ), 87.69 ( $\text{C}^5$ ), 112.67 ( $\text{C}^6$ ), 114.25 ( $\text{C}^3'$ ), 114.42 ( $\text{C}^4'$ ), 114.76 ( $\text{CN}$ ), 115.46 ( $\text{CN}$ ), 126.30 ( $\text{C}^1$ ), 133.11 ( $\text{C}^4$ ), 148.75 ( $\text{C}=\text{NNH}_2$ ), 153.21 ( $\text{C}^2$ ), 155.13 ( $\text{C}^5$ ), 159.50 ( $\text{C}^6$ ), 160.25 ( $\text{C}^2$ ). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 338 (27) [ $M]^+$ , 310 (30) [ $M-28$ ] $^+$ , 124 (93), 109 (100). Found, %: C 56.75; H 4.19; N 24.81.  $\text{C}_{16}\text{H}_{14}\text{N}_6\text{O}_3$ . Calculated, %: C 56.80; H 4.17; N 24.84.  $M$  338.11.

**2-Amino-4-(1-hydrazono-2,2-dimethylpropyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (IIIi).** Yield 78%, mp 217–218°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3395, 3192 ( $\text{NH}_2$ ), 2231 ( $\text{C}\equiv\text{N}$ ), 1672 ( $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.17 s [9H,  $\text{C}(\text{CH}_3)_3$ ], 6.25 s (2H,  $\text{NH}_2$ ), 7.69 s (2H,  $\text{NH}_2$ ), 11.72 br.s (1H, NH).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 29.40, 29.51, 29.55 [ $\text{C}(\text{CH}_3)_3$ ], 33.47 [ $\text{C}(\text{CH}_3)_3$ ], 73.42 ( $\text{C}^3$ ), 88.12 ( $\text{C}^5$ ), 115.56 ( $\text{CN}$ ), 116.39 ( $\text{CN}$ ), 145.09 ( $\text{C}^4$ ), 157.26 ( $\text{C}^6$ ), 159.03 ( $\text{C}=\text{NNH}_2$ ), 160.12 ( $\text{C}^2$ ). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 258 (1), 88 (19), 58 (41), 57 (45). Found, %: C 55.84; H 5.48; N 32.37.  $\text{C}_{12}\text{H}_{14}\text{N}_6\text{O}$ . Calculated, %: C 55.80; H 5.46; N 32.54.  $M$  258.12.

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