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2-Acyl(aroyl)-1,1,3,3-tetracyanopropenides: III.* Heterocyclization by the Action of Hydrogen Halides

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Abstract—2-Acyl(aroyl)-1,1,3,3-tetracyanopropenides reacted with hydrogen halides along two concurrent pathways with formation of furan or pyridine derivatives. The reaction in butan-2-ol afforded 2-amino-4-acyl-(aroyl)-6-halopyridine-3,5-dicarbonitriles, whereas the major products in the reactions with HCl and HBr in aqueous solution were the corresponding 2-(5-amino-2-aryl-2-chloro(bromo)-4-cyano-2,3-dihydrofuran-3-ylidene)malononitriles. The reaction with aqueous hydrogen iodide was accompanied by reductive deiodination and produced 2-(5-amino-2-aryl-4-cyano-2,3-dihydrofuran-3-ylidene)malononitriles.

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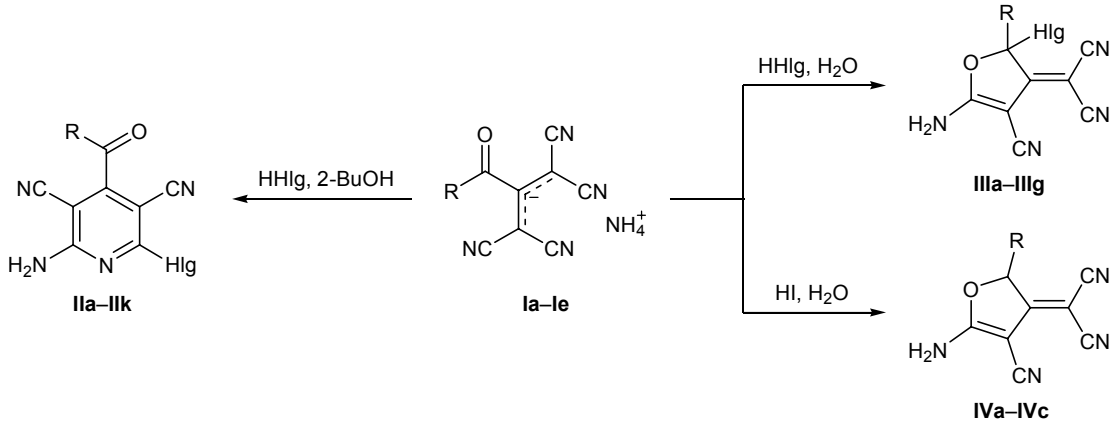
2-Acyl(aroyl)-1,1,3,3-tetracyanopropenides **I** [2] are promising starting compounds for the synthesis of various heterocycles. The presence of two electrophilic centers, carbonyl and cyano groups, in the anions of salts **I**, gives rise to two possible heterocyclization pathways by the action of nucleophilic reagents; the nature of counterion (alkali metal or ammonium cation) almost does not affect the reactivity of compounds **I**. We previously described the transformation of salts **I** into dihydrofuran derivatives via reactions with concentrated hydrochloric acid [3] and with thiols in aqueous medium under acidic conditions [1]. On the other hand, it is known that polycyanopropenides are typically converted into compounds of the pyridine series [4–8]. In this case, heterocyclization is also performed by the action of hydrogen halides which simultaneously act as reagent and catalyst. For example, the reaction of 2-alkyl(aryl)-1,1,3,3-tetracyanopropenides with hydrogen chloride leads to the corresponding 4-alkyl(aryl)-2-amino-6-chloropyridine-3,5-dicarbonitriles [7], whereas 2-amino-6-chloropyridine-3,4,5-tricarbonitrile was obtained from pentacyanopropenide [8]. Taking the above stated into account, we examined the possibility of using propenides **I** for the synthesis of pyridine derivatives. For this purpose, reactions of compounds **I** with hydrogen halides were carried out in different solvents by mixing the reactants in different modes.

We found that organic solvents favor formation of pyridine derivatives. The best results were obtained using butan-2-ol as solvent; in this case, the products were exclusively the corresponding 2-amino-4-acyl-(aroyl)-6-halopyridine-3,5-dicarbonitriles **IIa**–**IIk** (Scheme 1). The reactions in other common organic solvents, such as dioxane, acetonitrile, and acetone, also led to formation of pyridines **II**, but as mixtures with the corresponding 2-(5-amino-2-aryl-4-cyano-2-halo-2,3-dihydrofuran-3-ylidene)malononitriles **IIIa**–**IIIg**. The latter were obtained as the major products by reaction of propenides **I** with HCl and HBr in aqueous medium. The reaction of salts **I** with HI in water followed a different pathway to produce iodine-free 2-(5-amino-2-aryl-4-cyano-2,3-dihydrofuran-3-ylidene)malononitriles **IVa**–**IVc** (Scheme 1).

The structure of compounds **IIa**–**IIk**, **IIIa**–**IIIg**, and **IVa**–**IVc** was determined on the basis of their ^{1}H and ^{13}C NMR, IR, and mass spectra. Signals from protons in aryl substituents appeared in the ^{1}H NMR spectra of **IIa**–**IIc**, **IIe**–**IIj**, **IIIa**–**IIIc**, **IIIe**–**IIIg**, and **IVa**–**IVc** in the region δ 7.15–8.06 ppm. The *tert*-butyl group in compounds **IId**, **IIk**, and **IIId** gave rise to a singlet at δ 1.05–1.28 ppm. Unlike pyridines **IIa**–**IIk**, furans **IIIa**–**IIIg** and **IVa**–**IVc** characteristically dis-

* For communication II, see [1].

Scheme 1.



I, R = Ph (**a**), 4-ClC_6H_4 (**b**), 4-MeC_6H_4 (**c**), *t*-Bu (**d**), 4-$MeOC_6H_4$ (**e**); **II**, Hlg = Cl, R = Ph (**a**), 4-ClC_6H_4 (**b**), 4-MeC_6H_4 (**c**), *t*-Bu (**d**); Hlg = Br, R = Ph (**e**), 4-ClC_6H_4 (**f**), 4-MeC_6H_4 (**g**); Hlg = I, R = Ph (**h**), 4-ClC_6H_4 (**i**), 4-MeC_6H_4 (**j**), *t*-Bu (**k**); **III**, Hlg = Br, R = Ph (**a**), 4-ClC_6H_4 (**b**), 4-MeC_6H_4 (**c**), *t*-Bu (**d**); Hlg = Cl, R = Ph (**e**), 4-BrC_6H_4 (**f**), 4-$MeOC_6H_4$ (**g**); **IV**, R = Ph (**a**), 4-ClC_6H_4 (**b**), 4-MeC_6H_4 (**c**).

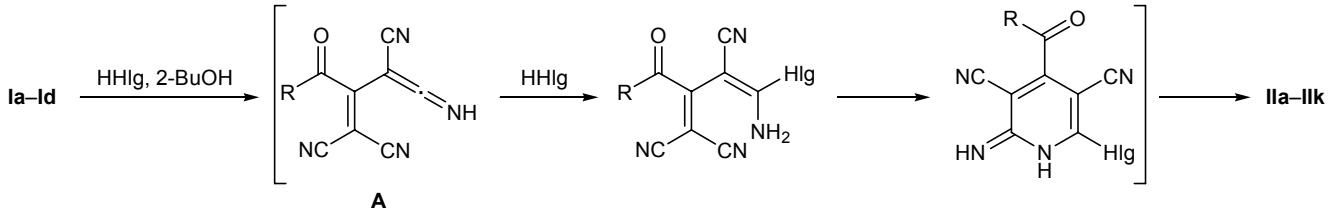
played in the ^{1}H NMR spectra two singlets at δ 8.2–9.0 ppm (Δδ = 0.5 ppm) from the NH_2 protons instead of a broadened singlet at δ 10.43–10.54 ppm in the spectra of **IIa**–**IIk**. Radically different structures of compounds **IIa**–**IIe** and **IIIa**–**IIIg** were reflected in their ^{13}C NMR spectra. Pyridine **IIe** showed signals from the carbonyl carbon atom at δ_C 190.2 ppm and two cyano groups at δ_C 113.03 and 114.76 ppm, whereas three C≡N signals were present in the spectrum of **IIIe** (δ_C 110.47, 112.44, 113.13 ppm) together with the signal at δ_C 70 ppm from the $=\mathbf{C}(CN)_2$ carbon atom and low-intensity signal at δ_C 105.34 ppm from C^2 in the furan ring [3]. Furans **IVa**–**IVc** were characterized by the presence in their ^{1}H NMR spectra of a singlet at δ 6.81–6.87 ppm due to proton in position *2* of the furan ring.

The IR spectra of all isolated compounds were consistent with the assumed structures. The IR spectra of **IIa**–**IIe** contained absorption bands at 1650–1682 cm^{-1} due to stretching vibrations of the carbonyl group; absorption bands at 2200–2235 cm^{-1} were assigned to conjugated cyano groups, and bands at 3150–3200 and 3300– 3350 cm^{-1} were typical of NH stretching vibrations. In the IR spectra of **IIIa**–**IIIg** and **IVa**–**IVc** we observed absorption bands assignable to C=C bond (1590–1670 cm^{-1}), conjugated cyano groups (2200–2235 cm^{-1}), and amino group (3100–3150, 3300–3350 cm^{-1}).

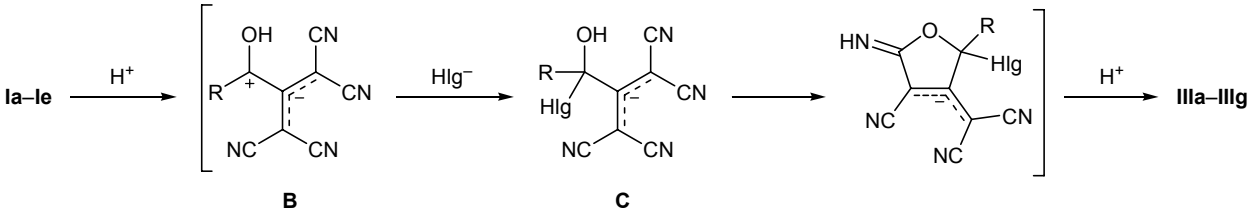
Presumably, the direction of transformation of propenides **I** in reactions with hydrogen halides is determined by the site of primary proton addition. Here, solvation effect is crucial. Protonation in organic solvents is likely to occur at the nitrogen atom of one cyano group. Ketene imine **A** thus formed takes up hydrogen halide molecule, and subsequent heterocyclization gives six-membered pyridine ring (Scheme 2). When the reaction is carried out in aqueous medium, initial protonation of **I** involves the carbonyl oxygen atom (intermediate **B**), and the subsequent nucleophilic attack is directed at the carbonyl carbon with formation of structure **C** which undergoes heterocyclization with formation of furan ring, finally leading to compounds **IIIa**–**IIIg** (Scheme 3).

Apart from the solvent nature, the yield and selectivity also depend on the mode of addition of hydrogen halides. The best yields of both furan and pyridine derivatives were obtained when gaseous hydrogen halide was slowly passed through a solution of salt **I** in

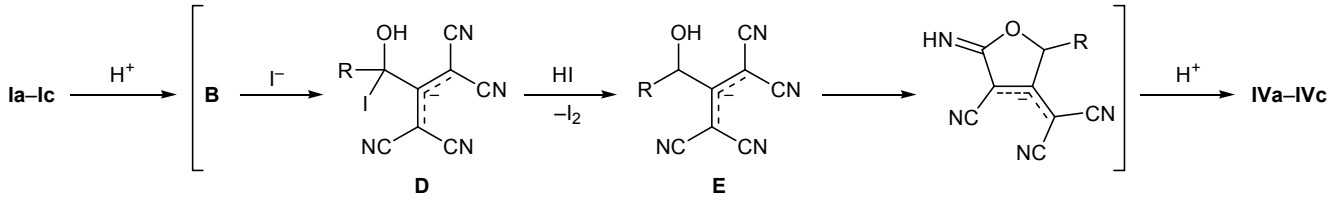
Scheme 2.



Scheme 3.



Scheme 4.



the corresponding solvent at 60–65°C. Dropwise addition of hydrohalic acids also ensured formation of pyridines **II** in butan-2-ol, but the yields were lower. Reaction of **I** with excess concentrated hydrohalic acid led to the formation of mixtures of compounds **II** and **III**. Thus slow addition of hydrogen halide favors selective protonation of the substrate and its subsequent transformations due to solvation effect. In the reaction with excess hydrogen halide protonation occurs at both nitrogen and oxygen atoms, and a mixture of products is formed.

The formation of dihydrofurans **IV** in the reaction of hydrogen iodide with salts **I** in aqueous solution may be rationalized taking into account reducing power of HI and oxidative ability of intermediate iodohydrin **D** (Scheme 4). In this case, the reaction also begins with protonation of the carbonyl oxygen atom with formation of zwitterion **B** which takes up iodide ion to give iodohydrin **D**. The latter is reduced to intermediate alcohol **E** by the action of excess HI, and the subsequent heterocyclization of **E** yields dihydrofurans **IVa**–**IVc**.

The yield and purity of compounds **IVa**–**IVc** also depended on the reaction conditions. The use of gaseous hydrogen iodide ensured the results. Slow addition of concentrated hydroiodic acid to aqueous solutions of salts **I** afforded dihydrofurans **IVa**–**IVc** in moderate yield.

EXPERIMENTAL

The progress of reactions and the purity of the isolated compounds were monitored by TLC on Silufol UV-254 plates; spots were detected under UV light, by treatment with iodine vapor, or by thermal decomposition). The IR spectra were recorded on an FSM-1202 spectrometer with Fourier transform from samples dispersed in mineral oil. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRX-500 spectrometer at 500.13 and 125.76 MHz, respectively, using DMSO-d_6 as solvent and tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Shimadzu GCMS-QP2010S DI instrument.

2-Amino-4-benzoyl-6-chloropyridine-3,5-dicarbonitrile (IIa). *a*. A solution of 2.63 g (0.01 mol) of ammonium 2-benzoyl-1,1,3,3-tetracyanopropenide in 5 ml of butan-2-ol was heated to 70–75°C, and gaseous hydrogen chloride was passed through the solution at a flow rate of 0.5–1.0 ml/s over a period of 10 min. The mixture was cooled, and the precipitate was filtered off, washed with 20 ml of water, and recrystallized from 1,4-dioxane. Yield 2.2 g (78%), mp 219–220°C. IR spectrum, ν, cm^{-1}: 3177 (NH_2), 2233 (C≡N), 1660 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.66 t (2H, H_{arom}, ^3J = 7.8 Hz), 7.86 t (1H, H_{arom}, ^3J = 7.4 Hz), 8.03 d (2H, H_{arom}, ^3J = 7.4 Hz), 8.56 br.s and 9.01 br.s (1H each, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 284 (11), 282 (34). Found, %: C 59.12; H 2.55; N 19.79. $C_{14}H_7ClN_4O$. Calculated, %: C 59.48; H 2.50; N 19.82. *M* 282.68.

b. A solution of 2.63 g (0.01 mol) of ammonium 2-benzoyl-1,1,3,3-tetracyanopropenide in 5 ml of butan-2-ol was heated to 60°C, 2 ml of concentrated hydrochloric acid was added dropwise over a period of 15 min, and the mixture was stirred for 30 min at 55–65°C and poured into 100 ml of hot (90°C) water. The precipitate was filtered off and washed with diethyl ether. Yield 1.58 g (56%), decomposition point 219–220°C (from 1,4-dioxane).

Compounds **IIb**–**IIg** were synthesized as described above in *a*.

2-Amino-6-chloro-4-(4-chlorobenzoyl)pyridine-3,5-dicarbonitrile (IIb). Yield 67%, mp 238–240°C. IR spectrum, ν, cm^{-1}: 3204 (NH_2), 2210 (C≡N), 1650 (C=O). ^1H NMR spectrum, δ, ppm: 7.73 d (2H, H_{arom}, ^3J = 6.1 Hz), 8.05 d (2H, H_{arom}, ^3J = 5.9 Hz), 8.49 br.s and 9.00 br.s (1H each, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 320 (3), 319 (3), 318 (15), 317 (14), 316 (28). Found, %: C 53.31; H 1.93; N 17.01. $C_{14}H_6Cl_2N_4O$. Calculated, %: C 53.02; H 1.91; N 16.98. *M* 317.13.

2-Amino-6-chloro-4-(4-methylbenzoyl)pyridine-3,5-dicarbonitrile (IIc). Yield 73%, mp 246–247°C (decomp.). IR spectrum, ν, cm^{-1}: 3201 (NH_2), 2253 (C≡N), 1682 (C=O). ^1H NMR spectrum, δ, ppm: 2.45 s (3H, CH_3), 7.46 d (2H, H_{arom}, ^3J = 8.1 Hz), 7.91 d (2H, H_{arom}, ^3J = 8.2 Hz), 8.45 br.s and 8.95 br.s (1H each, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 298 (9), 297 (4), 296 (28). Found, %: C 60.73; H 3.11; N 18.83. $C_{15}H_9ClN_4O$. Calculated, %: 60.72; H 3.06; N 18.88. *M* 296.71.

2-Amino-6-chloro-4-pivaloylpyridine-3,5-dicarbonitrile (IId). Yield 84%, sublimes at 243–246°C, mp 254–255°C (in a sealed capillary). IR spectrum, ν, cm^{-1}: 3222 (NH_2), 2204 (C≡N), 1665 (C=O). ^1H NMR spectrum, δ, ppm: 1.05 s (9H, *t*-Bu), 8.41 br.s and 8.92 br.s (1H each, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 264 (10), 263 (3), 262 (34). Found, %: C 54.81; H 4.28; N 21.64. $C_{12}H_{11}ClN_4O$. Calculated, %: C 54.87; H 4.22; N 21.33. *M* 262.69.

2-Amino-4-benzoyl-6-bromopyridine-3,5-dicarbonitrile (IIe). Yield 2.6 g (71%), mp 231–232°C (decomp.). IR spectrum, ν, cm^{-1}: 3211 (NH_2), 2221 (C≡N), 1664 (C=O). ^1H NMR spectrum, δ, ppm: 7.66 t (2H, H_{arom}, ^3J = 7.7 Hz), 7.85 t (1H, H_{arom}, ^3J = 7.6 Hz), 8.02 d (2H, H_{arom}, ^3J = 8.2 Hz), 8.46 br.s and 9.00 br.s (1H each, NH_2). ^{13}C NMR spectrum, δ_C, ppm: 86.41 (C^3), 95.53 (C^5), 113.03, 114.76 (5-CN, 3-CN), 129.69 (2C, C^m), 130.15 (2C, C^o), 132.75 and 136.14 (C^i, C^p), 147.85 (C^6), 157.55 (C^4), 159.61 (C^2), 190.21 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 328 (20), 326 (21). Found, %: C 51.48; H 2.19; N 17.07. $C_{14}H_7BrN_4O$. Calculated, %: C 51.40; H 2.16; N 17.13. *M* 327.14.

2-Amino-6-bromo-4-(4-chlorobenzoyl)pyridine-3,5-dicarbonitrile (IIf). Yield 74%, mp 257–258°C (decomp.). IR spectrum, ν, cm^{-1}: 3230 (NH_2), 2205 (C≡N), 1666 (C=O). ^1H NMR spectrum, δ, ppm: 7.73 d (2H, H_{arom}, ^3J = 8.5 Hz), 8.06 d (2H, H_{arom}, ^3J = 8.6 Hz), 8.47 br.s and 9.02 br.s (1H each, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 364 (4), 363 (3), 362 (19), 360 (15). Found, %: C 46.87; H 1.71; N 15.39. $C_{14}H_6BrClN_4O$. Calculated, %: C 46.50; H 1.67; N 15.49. *M* 361.58.

2-Amino-6-bromo-4-(4-methylbenzoyl)pyridine-3,5-dicarbonitrile (IIg). Yield 78%, mp 217–218°C. IR spectrum, ν, cm^{-1}: 3192 (NH_2), 2240 (C≡N), 1660 (C=O). ^1H NMR spectrum, δ, ppm: 2.35 s (3H, CH_3), 7.15 m (2H, H_{arom}, ^3J = 8.3 Hz), 7.35 m (2H, H_{arom}, ^3J = 8.2 Hz), 8.44 br.s and 8.97 br.s (1H each, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 342 (19), 340 (21). Found, %: C 52.84; H 2.68; N 16.37. $C_{15}H_9BrN_4O$. Calculated, %: C 52.81; H 2.66; N 16.42. *M* 341.16.

2-Amino-4-benzoyl-6-iodopyridine-3,5-dicarbonitrile (IIh). *a*. A solution of 2.63 g (0.01 mol) of ammonium 2-benzoyl-1,1,3,3-tetracyanopropenide in 5 ml of butan-2-ol was heated to 60°C, 2 ml of concentrated hydroiodic acid was added dropwise under stirring over a period of 15 min, and the mixture was stirred for 30 min at 70–75°C and poured into 100 ml of boiling water. The precipitate was filtered off, washed with diethyl ether, and recrystallized from methanol. Yield 2.1 g (56%), decomposition point 173–175°C. IR spectrum, ν, cm^{-1}: 3153 (NH_2), 2201 (C≡N), 1664 (C=O). ^1H NMR spectrum, δ, ppm: 7.65 t (2H, H_{arom}, ^3J = 7.8 Hz), 7.84 t (1H, H_{arom}, ^3J = 7.4 Hz), 7.99 d (2H, H_{arom}, ^3J = 7.3 Hz), 8.30 br.s and 9.89 br.s (1H each, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 375 (1), 374 (11). Found, %: C 44.98; H 1.92; N 14.83. $C_{14}H_7IN_4O$. Calculated, %: C 44.94; H 1.89; N 14.97. *M* 374.14.

b. A solution of 2.63 g (0.01 mol) of ammonium 2-benzoyl-1,1,3,3-tetracyanopropenide in 5 ml of butan-2-ol was heated to 70–75°C, and gaseous hydrogen iodide was passed through the solution at a flow rate of 0.5–1.0 ml/s over a period of 20 min. After cooling, the precipitate was filtered off, washed with 20 ml of water, and recrystallized from dioxane.

Compounds **IIi**–**IIk** were synthesized as described above for **IIh** according to method *a*.

2-Amino-4-(4-chlorobenzoyl)-6-iodopyridine-3,5-dicarbonitrile (IIi). Yield 54%, mp 185–187°C (decomp.). IR spectrum, ν, cm^{-1}: 3203 (NH_2), 2215 (C≡N), 1662 (C=O). ^1H NMR spectrum, δ, ppm: 7.74 d (2H, H_{arom}, ^3J = 5.9 Hz), 8.06 d (2H, H_{arom}, ^3J = 5.9 Hz), 8.39 br.s and 8.89 br.s (1H each, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 410 (3), 408 (10). Found, %: C 41.19; H 1.52; N 13.65. $C_{14}H_6ClIN_4O$. Calculated, %: C 41.15; H 1.48; N 13.71. *M* 408.58.

2-Amino-6-iodo-4-(4-methylbenzoyl)pyridine-3,5-dicarbonitrile (IIj). Yield 61%, mp 166–167°C (decomp.). IR spectrum, ν, cm^{-1}: 3213 (NH_2), 2224 (C≡N), 1660 (C=O). ^1H NMR spectrum, δ, ppm: 2.34 s (3H, CH_3), 7.18 d (2H, H_{arom}, ^3J = 7.8 Hz), 7.36 d (2H, H_{arom}, ^3J = 7.9 Hz), 8.45 br.s and 9.01 br.s (1H each, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 389 (2), 388 (13). Found, %: C 46.45; H 2.37; N 14.38. $C_{15}H_9IN_4O$. Calculated, %: C 46.41; H 2.34; N 14.43. *M* 388.16.

2-Amino-6-iodo-4-pivaloylpyridine-3,5-dicarbonitrile (IIk). Yield 74%, mp 182–183°C (decomp.). IR spectrum, ν, cm^{-1}: 3210 (NH_2), 2198 (C≡N), 1671 (C=O). ^1H NMR spectrum, δ, ppm: 1.28 s (9H, *t*-Bu), 8.31 br.s and 8.82 br.s (1H each, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 355 (2), 354 (18). Found, %: C 40.78; H 3.17; N 15.78. $C_{12}H_{11}IN_4O$. Calculated, %: C 40.70; H 3.13; N 15.82. *M* 354.15.

2-(5-Amino-2-bromo-4-cyano-2-phenyl-2,3-dihydrofuran-3-ylidene)malononitrile (IIIa). Gaseous hydrobromic acid was slowly passed over a period 20 min (flow rate 0.5–1.0 ml/s) through a solution of 2.63 g (0.01 mol) of ammonium 2-benzoyl-1,1,3,3-tetracyanopropenide in 10 ml of water, heated to 65–70°C. The precipitate was filtered off, washed with water, and recrystallized from methanol. Yield 2.22 g (68%), decomposition point 239–241°C. IR spectrum, ν, cm^{-1}: 3290 (NH_2), 2225 (C≡N), 1668 (C=C). ^1H NMR spectrum, δ, ppm: 7.35–7.56 m (5H, H_{arom}), 10.51 s (2H, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 328 (16), 326 (17). Found, %: C 51.45; H 2.19; N 17.04. $C_{14}H_7BrN_4O$. Calculated, %: C 51.40; H 2.16; N 17.13. *M* 327.14.

Compounds **IIIb**–**IIId** were synthesized in a similar way.

2-[5-Amino-2-bromo-2-(4-chlorophenyl)-4-cyano-2,3-dihydrofuran-3-ylidene]malononitrile (IIIb). Yield 76%, decomposition point 246–248°C. IR spectrum, ν, cm^{-1}: 3290, 3124 (NH_2); 2201 (C≡N); 1666 (C=C). ^1H NMR spectrum, δ, ppm: 7.65 d (2H, H_{arom}, ^3J = 6.01 Hz), 7.74 d (2H, H_{arom}, ^3J = 6.0 Hz), 10.48 br.s (2H, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 362 (26), 361 (15), 364 (5), 363 (3). Found, %: C 46.52; H 1.71; N 15.43. $C_{14}H_6BrClN_4O$. Calculated, %: C 46.50; H 1.67; N 15.49. *M* 361.58.

2-[5-Amino-2-bromo-4-cyano-2-(4-methylphenyl)-2,3-dihydrofuran-3-ylidene]malononitrile (IIIc). Yield 59%, decomposition point 243–245°C. IR spectrum, ν, cm^{-1}: 3260, 3128 (NH_2); 2215 (C≡N); 1665 (C=C). ^1H NMR spectrum, δ, ppm: 2.41 s (3H, CH_3), 7.31 d (2H, H_{arom}, ^3J = 8.0 Hz), 7.74 d (2H, H_{arom}, ^3J = 8.02 Hz), 10.46 br.s (2H, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 343 (2), 342 (16), 341 (3), 340 (17). Found, %: C 52.91; H 2.72; N 16.31. $C_{15}H_9BrN_4O$. Calculated, %: C 52.81; H 2.66; N 16.42. *M* 341.16.

2-(5-Amino-2-bromo-2-*tert*-butyl-4-cyano-2,3-dihydrofuran-3-ylidene)malononitrile (IIId). Yield 65%, decomposition point 245–246°C. IR spectrum, ν, cm^{-1}: 3318, 3115 (NH_2); 2253 (C≡N); 1663 (C=C). ^1H NMR spectrum, δ, ppm: 1.23 s (9H, *t*-Bu), 10.49 s and 10.53 s (1H each, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 309 (3), 308 (20), 307 (3), 306 (21). Found, %: C 47.08; H 3.69; N 18.07. $C_{12}H_{11}BrN_4O$. Calculated, %: C 46.93; H 3.61; N 18.24. *M* 307.15

Compounds **IIIe**–**IIIg** were synthesized in a similar way by passing gaseous hydrogen chloride.

2-(5-Amino-2-chloro-4-cyano-2-phenyl-2,3-dihydrofuran-3-ylidene)malononitrile (IIIe). Yield (74%), mp 150–151°C (decomp.) [2].

2-[5-Amino-2-(4-bromophenyl)-2-chloro-4-cyano-2,3-dihydrofuran-3-ylidene]malononitrile (IIIf). Yield 67%, mp 133–136°C (decomp.); published data [2]: mp 135–136°C (decomp.).

2-[5-Amino-2-chloro-4-cyano-2-(4-methoxyphenyl)-2,3-dihydrofuran-3-ylidene]malononitrile (IIIg). Yield 81%, mp 140–142°C (decomp.); published data [2]: 141–142°C (decomp.).

2-(5-Amino-4-cyano-2-phenyl-2,3-dihydrofuran-3-ylidene)malononitrile (IVa). *a*. A solution of 2.63 g (0.01 mol) of ammonium 2-benzoyl-1,1,3,3-tetracyanopropenide in 10 ml of water was heated to 65–70°C, and 2.7 ml of 56% hydroiodic acid was added dropwise under stirring over a period of 20 min. The precipitate was filtered off, washed with 3 ml of 1% aqueous potassium iodide and with water, and recrystallized from 1,4-dioxane. Yield 1.41 g (57%), mp 263–264°C (decomp.). IR spectrum, ν, cm^{-1}: 3318, 3115 (NH_2); 2223 (C≡N); 1663 (C=C). ^1H NMR spectrum, δ, ppm: 6.81 s (1H, CH), 7.41–7.52 m (5H, Ph), 10.07 s (2H, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 249 (7), 248 (43). Found, %: C 67.89; H 3.31; N 22.43. $C_{14}H_8N_4O$. Calculated, %: C 67.74; H 3.25; N 22.57. *M* 248.24.

b. A solution of 2.63 g (0.01 mol) of ammonium 2-benzoyl-1,1,3,3-tetracyanopropenide in 5 ml of water was heated to 70–75°C, and gaseous hydrogen iodide was passed through the solution over a period of 20 min at a flow rate of 1.5–2.0 ml/s. The mixture was cooled, and the precipitate was filtered off, washed

with 20 ml of water, and recrystallized from 1,4-dioxane. Yield 1.74 g (70%), mp 263–264°C (decomp.).

Compounds **IVb** and **IVc** were synthesized as described for **IVa** according to method *a*.

2-[5-Amino-2-(4-chlorophenyl)-4-cyano-2,3-dihydrofuran-3-ylidene]malononitrile (IVb). Yield 61%, mp 266–268°C (decomp.). IR spectrum, ν, cm^{-1}: 3321, 3113 (NH_2); 2230 (C≡N); 1660 (C=C). ^1H NMR spectrum, δ, ppm: 6.85 s (1H, CH), 7.47–7.50 m (2H, H_{arom}, ^3J = 8.5 Hz), 7.53–7.56 m (2H, H_{arom}, ^3J = 8.5 Hz), 10.10 s (2H, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 284 (13), 283 (4), 282 (39). Found, %: C 60.06; H 2.61; N 19.73. $C_{14}H_7ClN_4O$. Calculated, %: C 59.48; H 2.50; N 19.82. *M* 282.68.

2-[5-Amino-4-cyano-2-(4-methylphenyl)-2,3-dihydrofuran-3-ylidene]malononitrile (IVc). Yield 64%, mp 249–251°C (decomp.). IR spectrum, ν, cm^{-1}: 3327, 3115 (NH_2); 2221 (C≡N); 1664 (C=C). ^1H NMR spectrum, δ, ppm: 2.45 s (3H, CH_3), 6.79 s (1H, CH), 7.43 d (2H, H_{arom}, ^3J = 7.9 Hz), 7.47 d (2H, H_{arom}, ^3J = 8.0 Hz), 10.09 s (2H, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 263 (7), 262 (40). Found, %: C 68.71; H 3.91; N 21.31 $C_{15}H_{10}N_4O$. Calculated, %: C 68.69; H 3.84; N 21.36. *M* 262.27.

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REFERENCES

1. Karpov, S.V., Kayukov, Ya.S., Bardasov, I.N., Ershov, O.V., Nasakin, O.E., and Kayukova, O.V., *Russ. J. Org. Chem*., 2011, vol. 47, p. 1161.
2. Bardasov, I.N., Kayukova, O.V., Kayukov, Ya.S., Ershov, O.V., Nasakin, O.E., and Tafeenko, V.A., *Russ. J. Org. Chem*., 2009, vol. 45, 1325.
3. Karpov, S.V., Kayukov, Ya.S., Bardasov, I.N., Kayukova, O.V., Ershov, O.V., and Nasakin, O.E., *Russ. J. Org. Chem*., 2011, vol. 47, p. 405.
4. Duindam, A., Lishinsky, V.L., and Sikkama, D.J., *Synth. Commun*., 1993, vol. 23, p. 2605.
5. Mittelbach, M. and Junek, H., *J. Heterocycl. Chem*., 1982, vol. 19, p. 1021.
6. Granik, V.G., Grizik, S.I., Solov'eva, N.P., Anisimova, O.S., and Sheinker, Yu.N., *Zh. Org. Khim*., 1984, vol. 20, p. 673.
7. Vieth, S., Gruendemann, E., Jaehnisch, K., Winter, G., and Reck, G., *Monatsh. Chem*., 1991, vol. 122, p. 1035.
8. Kantehner, W. and Greiner, U., *Justus Liebigs Ann. Chem*., 1990, p. 965.