A NOVEL SYNTHESIS OF 1,6-DIAMINO-2-PYRIDONES AND [1,2,4]TRIAZOLO[1,5-*a*]PYRIDINE DERIVATIVES

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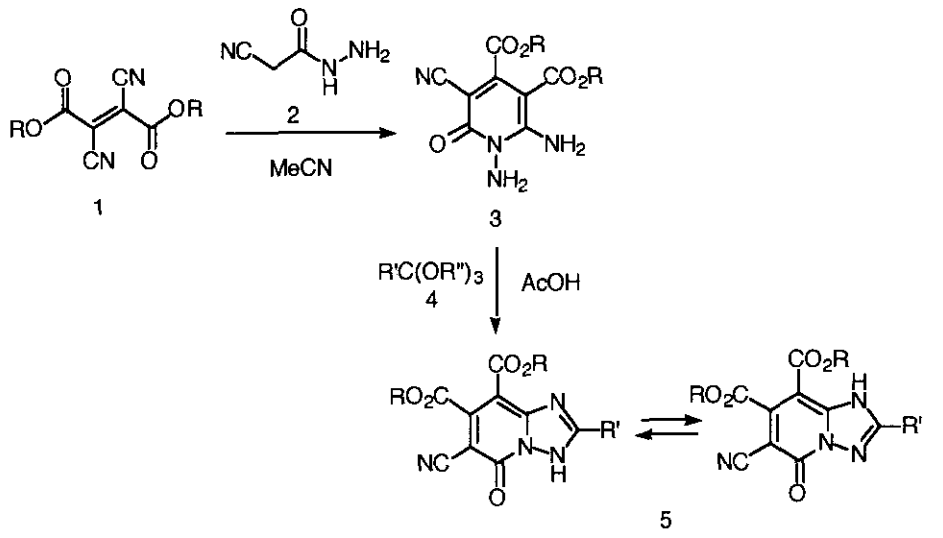
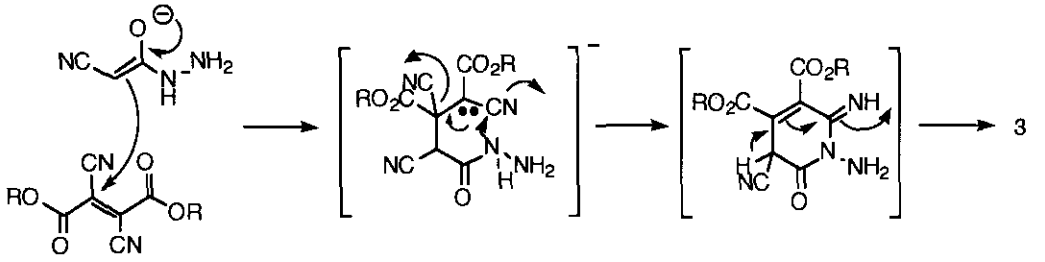
Abstract — 3-Cyano-1,6-diamino-2-pyridone derivatives (**3**) possessing various alkoxycarbonyl groups are prepared directly from the reaction of dialkyl (*E*)-2,3-dicyanobutendioates (**1**) with cyanoacetohydrazide (**2**). The resulting diamine (**3**) (R = Et) is readily cyclized to 2-substituted [1,2,4]triazolo[1,5-*a*]pyridine derivatives (**5**) in high yields by treatment with orthocarboxylic esters (**4**) such as trimethyl orthoformate or triethyl orthoacetate etc. Furthermore, 3-cyano-6-amino-2-pyridones (**6**) are although obtained in excellent yields by the reductive deamination of **3**. The structural study of **6** was carried out by spectroscopic methods in some details.

A number of methods are known for the synthesis of amino pyridones[1-5] and [1,2,4]triazolo[1,5-*a*]pyridones,[6-9] however, their synthesis is usually difficult. In a previous paper[10] we described a new method leading to excellent yields of **1** as the starting material for a series of our research.[11] The resulting alkyl derivatives of **1**, except methyl (R = Me) and ethyl (R = Et)[12,13] are hitherto unknown compounds. Although the dimethyl and diethyl esters **1** have a long history,[10] preparation of heterocyclic compounds starting from these esters has not yet been reported. Thus, we have designed a simple synthesis for 1,6-diamino-2-pyridone derivatives (**3**) by the reaction of cyanoacetohydrazide (**2**) with **1** bearing alkyl groups such as ethyl, propyl, and butyl etc. We now wish to report a convenient method for one-step synthesis of the novel 3-cyano-1,6-diamino-2-pyridone-4,5-dicarboxylates (**3**) from **1** and **2**, and 2-substituted [1,2,4]triazolo[1,5-*a*]pyridine derivatives (**5**) from **3a** and orthocarboxylic esters (**4**) such as trimethyl orthoformate, triethyl orthoacetate, or orthopropionate (Scheme 1). This method consists of the reaction of **1** with **2** in a 1 : 1 molar ratio, carried out in MeCN under reflux, affords **3**. A possible reaction process is illustrated in Scheme 2. Presumably, a Michael addition by active methylene to the ethylenic double bond leads to open-chain adduct, which cyclizes by intramolecular nucleophilic attack at the cyano group to form pyridone ring.



1, 3	R	4	R'	R"	5	R	R'
a	Et	**a**	H	Me	**a**	Et	H
b	Pr	**b**	Me	Et	**b**	Et	Me
c	*i*-Pr	**c**	Et	Et	**c**	Et	Et
d	Bu						
e	*i*-Bu						

Scheme 1



Scheme 2

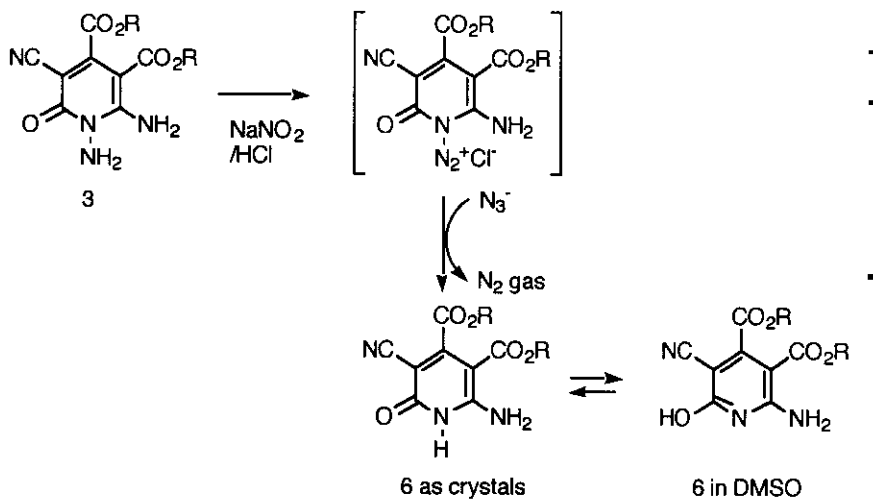
The IR spectra of **3** showed absorption bands due to the NH_2 groups of the 1,6-positions in the 3379-3199 cm^{-1} region (three to four bands), an α,β-unsaturated C≡N at 2222-2226 cm^{-1}, and two ester and an amide C=O groups at 1740-1695 (two bands) and 1676-1665 cm^{-1}, respectively. On the other hand, ^1H NMR spectra revealed signals at δ 8.90-8.95 and 8.59-8.63 each corresponding to one proton and at δ 5.62-5.63 corresponding to two protons. These were assigned to the 6- and 1-NH_2 protons, respectively. Appearance of the IR absorption band at 1695 cm^{-1} and ^1H NMR signal at δ 8.59 would indicate the formation of an intramolecular hydrogen-bond between the 5-ester and 6-NH_2 groups.

These assignments are further supported by the fact that the two singlet signals (δ 8.90 and δ 8.59) for 6-NH_2 protons are merged into one singlet, δ *ca.* 8.6, at over 60 ℃ in DMSO.

1,6-Diaminopyridones are of interest because of this system bearing suitable substituents as an intermediate for the synthesis of fused heterocycles.[14] Actually, we now observed that diethyl 3-cyano-1,6-diamino-2-pyridone-4,5-dicarboxylate (**3a**) easily undergoes cyclization, on treatment with **4** in acetic acid under reflux, to form diethyl 2-alkyl-6-cyano-1(3),5-dihydro-5-oxo[1,2,4]triazolo[1,5-*a*]pyridine-7,8-dicarboxylates (**5**) in good yields, for which some tautomeric forms are possible (Scheme 1). The IR absorption of **5a** showed bands at 3166 and 3133 cm^{-1}. This observation seems to indicate that the structure of such system, in general, exists in tautomeric forms, since the two bands can be attributed to the NH group in the 1,3-positions. On the other hand, ethoxy and amido carbonyl bands appeared in the region nearly the same with those observed for the compounds (**3**). Moreover, any signals for NH proton of **5** were not observed on ^1H NMR spectra due to this tautomerization.

Trimethyl orthobutyrate is not suitable as a cyclization reagent of **3**, because of the cyclized product (**5**) simultaneously undergoes 1(3)-N- and 5-O-methylations.

Finally, **3** lead directly to 6-amino-3-cyano-2-pyridones (**6**) in excellent yields by the reaction with sodium nitrite in diluted hydrochloric acid followed by treatment with sodium azide. It seems that, azide anion act as a reducing agent in this reaction (Scheme 3).



6	R
a	Et
b	Pr
c	*i*-Pr
d	Bu

Scheme 3

The IR spectra of **6** recorded in KBr have stretching bands at 3220-3238 (NH) and 1649-1675 cm^{-1} (N-C=O). These bands are characteristics of a 2-pyridone system. On the other hand, the IR spectra of **6** in DMSO show stretching bands at 3400 cm^{-1}, assigned to iminolic

hydroxyl group, and no absorption band for amido carbonyl vibration. The iminol form of **6** in DMSO is further supported by ^{1}H NMR spectra. Namely, the singlet for unsaturated OH protons at δ 11.72-11.76 and two singlets at δ 7.43-7.46 and δ 8.48-8.50 each for one proton (hydrogen bonded 6-NH_2) appeared, respectively.
The structure of the obtained compounds (**3**, **5**, and **6**), is also confirmed by the elemental analysis and MS spectral data.

The principal advantages of the method described here are that the time of reaction is short, the work up is convenient, and the reaction is easily carried out and proceeds under mild conditions to give, in general, high yields of pyridone and fused pyridine rings.

Table 1 NMR Data of Compounds (**3, 5,** and **6**)

Pro-duct	^{1}H-NMR(DMSO-d_6/TMS) δ (ppm), J (Hz)	^{13}C-NMR (DMSO-d_6/TMS) δ (ppm)
3a	1.22 (t, 3H, J=7.1, CH_3), 1.31 (t, 3H, J=7.1, CH_3), 4.22 (q, 2H, J=7.1, CH_2), 4.34 (q, 2H, J=7.1, CH_2), 5.63 (br s, 2H, 1-NH_2), 8.61, 8.91 (each br s, 1H, 6-NH_2)	13.6, 13.7 (CH_3), 61.2, 62.1 (OCH_2), 83.5 (C5), 86.8 (C3), 115.1 (CN), 150.9 (C6), 156.6 (C4), 158.6 (N-C=O), 163.7, 164.7 (COO)
3b	0.89 (t, 3H, J=7.3, CH_3), 0.95 (t, 3H, J=7.3, CH_3), 1.61 (sext, 2H, J=7.2, CH_2), 1.71 (sext, 2H, J=7.2, CH_2), 4.13 (t, 2H, J=6.6, OCH_2), 4.23 (t, 2H, J=6.6, OCH2), 5.63 (br s, 2H, 1-NH_2), 8.62, 8.92 (each br s, 1H, 6-NH_2)	10.1, 10.2 (CH_3), 21.1, 21.3 (CH_2), 66.8, 67.6 (OCH_2), 83.6 (C5), 86.9 (C3), 115.2 (CN), 151.0 (C6), 156.7 (C4), 158.7 (N-C=O), 163.9, 164.9 (COO)
3c	1.23 (d, 6H, J=6.4, $2CH_3$), 1.34 (d, 6H, J=6.4, $2CH_3$), 5.08 (sept, 1H, J=6.4, OCH), 5.12 (sept, 1H, J=6.4, OCH), 5.63 (br s, 2H, 1-NH_2), 8.59, 8.95 (each br s, 1H, 6-NH_2)	21.1, 21.2 (CH_3), 69.2, 70.2 (OCH), 83.5 (C5), 86.8 (C3), 115.0 (CN), 150.7 (C6), 156.7 (C4), 158.6 (N-C=O), 163.4, 164.1 (COO)
3d	0.89 (t, 3H, J=7.3, CH_3), 0.91 (t, 3H, J=7.3, CH_3), 1.32 (sext, 2H, J=7.3, CH_2), 1.40 (sext, 2H, J=7.3, CH_2), 1.57 (quint, 2H, J=6.8, CH_2), 1.68 (quint, 2H, J=6.8, CH_2), 4.17 (t, 2H, J=6.4, OCH_2), 4.26 (t, 2H, J=6.4, OCH_2), 5.62 (br s, 2H, 1-NH_2), 8.61, 8.91 (each br s, 1H, 6-NH_2)	13.35, 13.39 (CH_3), 18.4, 18.5 (CH_2), 29.7, 29.9 (CH_2), 65.0, 65.8 (OCH_2), 83.5 (C5), 86.8 (C3), 115.1 (CN), 150.8 (C6), 156.6 (C4), 158.6 (N-C=O), 163.8, 164.8 (COO)
3e	0.89 (d, 6H, J=6.8, $2CH_3$), 0.95 (d, 6H, J=6.8, $2CH_3$), 1.90 (nonet, 1H, J=6.8, CH), 1.99 (nonet, 1H, J=6.8, CH), 3.98 (d, 2H, J=6.8, OCH_2), 4.04 (d, 2H, J=6.8, OCH_2), 5.62 (br s, 2H, 1-NH_2), 8.63, 8.90 (each br s, 1H, 6-NH_2)	18.7, 18.8 (CH_3), 27.0, 27.2 (CH), 71.2, 72.0 (OCH_2), 83.6 (C5), 86.8 (C3), 115.1 (CN), 150.8 (C6), 156.7 (C4), 158.6 (N-C=O), 163.8, 164.8 (COO)

Table 1 (Continued)

Product	^{1}H-NMR(DMSO-d_6/TMS) δ (ppm), J (Hz)	^{13}C-NMR (DMSO-d_6/TMS) δ (ppm)
5a	1.28 (t, 3H, *J*=7.1, CH_3), 1.33 (t, 3H, *J*=7.1, CH_3), 4.33 (q, 2H, *J*=7.1, OCH_2), 4.39 (q, 2H, *J*=7.1, OCH_2), 9.10 (s, 1H, 2-H)	13.6, 14.1 (CH_3), 61.2, 62.3 (OCH_2), 85.0 C8), 89.9 (C6), 115.2 (CN), 144.4 (CH), 146.0 (C8a), 148.4 (C7), 154.1 (N-C=O), 161.2, 164.6 (COO)
5b	1.27 (t, 3H, *J*=7.1, CH_3), 1.34 (t, 3H, *J*=7.1, CH_3), 2.56 (s, 3H, 2-CH_3), 4.33 (q, 2H, *J*=7.1, OCH_2), 4.39 (q, 2H, *J*=7.1, OCH_2)	11.4 (2-CH_3), 13.6, 14.0(CH_3), 61.3, 62.3 (OCH_2), 85.2 (C8), 89.3 (C6), 115.2 (CN), 146.6 (C8a), 148.1 (C7), 153.8 (N-C=O), 161.3, 164.6 (COO)
5c	1.28 (t, 3H, *J*=7.1, CH_3), 1.33 (t, 3H, *J*=7.8, 2-$CH_2\underline{C}H_3$), 1.34 (t, 3H, *J*=7.1, CH_3), 2.93 (q, 2H, *J*=7.8, 2-$C\underline{H}_2CH_3$), 4.33 (q, 2H, *J*=7.1, OCH_2), 4.39 (q, 2H, *J*=7.1, OCH_2)	10.9 (2-$CH_2\underline{C}H_3$), 13.6, 14.0 (CH_3), 19.1 (2-$\underline{C}H_2CH_3$), 61.3, 62.3 (OCH_2), 85.2 (C8), 89.4 (C6), 115.2 (CN), 146.7 (C8a), 148.1 (C7), 153.9 (N-C=O), 161.4, 164.6 (COO)
6a	1.21 (t, 3H, *J*=7.1, CH_3), 1.31 (t, 3H, *J*=7.1, CH_3), 4.19 (q, 2H, *J*=7.1, OCH_2), 4.32 (q, 2H, *J*=7.1, OCH_2), 7.45, 8.48 (each br s, 1H, 6-NH_2), 11.74 (br s, 1H, N=C-OH)	13.6, 13.7 (CH_3), 60.9, 62.0 (OCH_2), 85.8 (C5), 87.1 (C3), 114.9 (CN), 153.9 (C6), 156.3 (C4), 158.9 (N=C-OH), 163.3, 164.7 (COO)
6b	0.88 (t, 3H, *J*=7.3, CH_3), 0.94 (t, 3H, *J*=7.3, CH_3), 1.60 (sext, 2H, *J*=7.1, CH_2), 1.71 (sext, 2H, *J*=7.1, CH_2), 4.10 (t, 2H, *J*=6.6, OCH_2), 4.21 (t, 2H, *J*=6.6, OCH_2), 7.45, 8.49 (each br s, 1H, 6-NH_2), 11.76 (br s, 1H, N=C-OH)	10.1, 10.2 (CH_3), 21.1, 21.3 66.5, 67.5 (OCH_2), 85.9 (C5), 87.1 (C3), 114.9 (CN), 153.9 (C6), 156.3 (C4), 158.9 (N=C-OH), 163.4, 164.8 (COO)
6c	1.22 (d, 6H, *J*=6.4, $2CH_3$), 1.33 (d, 6H, *J*=6.4, $2CH_3$), 5.05 (sept, 1H, *J*=6.4, OCH), 5.11 (sept, 1H, *J*=6.4, OCH), 7.43, 8.50 (each br s, 1H, 6-NH_2), 11.72 (br s, 1H, N=C-OH)	13.6, 13.7 (CH_3), 60.9, 92.0 (OCH), 85.8 (C5), 87.1 (C3), 114.9 (CN), 153.9 (C6), 156.3 (C4), 158.9 (N=C-OH), 163.3, 164.7 (COO)
6d	0.89 (t, 3H, *J*=7.3, CH_3), 0.91 (t, 3H, *J*=7.3, CH_3), 1.32 (sext, 2H, *J*=7.1, CH_2), 1.41 (sext, 2H, *J*=7.1, CH_2), 1.56 (quint, 2H, *J*=6.8, CH_2), 1.67 (quint, 2H, *J*=6.8, CH_2), 4.14 (t, 2H, *J*=6.6, OCH_2), 4.25 (t, 2H, *J*=6.6, OCH_2), 7.46, 8.49 (each br s, 1H, 6-NH_2), 11.76 (br s, 1H, N=C-OH)	10.1, 10.2 (CH_3), 21.1, 21.3 66.5, 67.5 (OCH_2), 85.9 (C5), 87.1 (C3), 114.9 (CN), 153.9 (C6), 156.3 (C4), 158.9 (N=C-OH), 163.4, 164.8 (COO)

EXPERIMENTAL

Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 1000 PC spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL EX-400 (400 MHz) instrument. ^{13}C NMR spectra were taken on a JEOL EX-400 (100 MHz) instrument. MS spectra were obtained with a JEOL AX-500 spectrometer (EI: 70 eV).

Dialkyl 3-Cyano-1,6-diamino-2-pyridone-4,5-dicarboxylates (3)

General Procedure: A mixture of dialkyl (*E*)-2,3-dicyanobutendioate (**1**) (2.0 mmol) and cyanoacetohydrazide (**2**) (2.0 mmol) in acetonitrile (10 mL) was heated at 80 ℃ for 3 h. The mixture was concentrated to dryness under reduced pressure, and then ethanol (10 mL) was added to the resulting viscous oil and the suspension thus obtained was set aside either at rt or in a refrigerator. The deposited solid was isolated by filtration, and recrystallized from 2-propanol to give **3** as almost colorless plates.

Diethyl 3-Cyano-1,6-diamino-2-pyridone-4,5-dicarboxylates (3a)

3a: Yield 64%; mp 181.5-182.5 ℃; IR (KBr): 3370, 3282, 3199 (NH), 2223 (CN), 1736, 1699 (COO), 1668 (N-C=O); MS *m/z* (int. %): 294 (M^+, 91), 248 (28), 220 (100); *Anal.* Calcd for $C_{12}H_{14}N_4O_5$: C, 48.98; H, 4.80; N, 19.04. Found: C, 48.98; H, 4.75; N, 18.99.

Dipropyl 3-Cyano-1,6-diamino-2-pyridone-4,5-dicarboxylates (3b)

3b: Yield 60%; mp 174.0-174.5 ℃; IR (KBr): 3373, 3282, 3206 (NH), 2224 (CN), 1739, 1695 (COO), 1668 (N-C=O); MS *m/z* (int. %): 322 (M^+, 48), 280 (8), 238 (9), 220 (100); *Anal.* Calcd for $C_{14}H_{18}N_4O_5$: C, 52.17; H, 5.63; N, 17.38. Found: C, 52.26; H, 5.62; N, 17.34.

Di*i*-propyl 3-Cyano-1,6-diamino-2-pyridone-4,5-dicarboxylates (3c)

3c: Yield 51%; mp 205.5-207.0 ℃; IR (KBr): 3371, 3296, 3275, 3210 (NH), 2226 (CN), 1731, 1693 (COO), 1666 (N-C=O); MS *m/z* (int. %): 322 (M^+, 37), 280 (37), 238 (100), 220 (76); *Anal.* Calcd for $C_{14}H_{18}N_4O_5$: C, 52.17; H, 5.63; N, 17.38. Found: C, 52.19; H, 5.63; N, 17.34.

Dibutyl 3-Cyano-1,6-diamino-2-pyridone-4,5-dicarboxylates (3d)

3d: Yield 70%; mp 142.0-143.0 ℃; IR (KBr): 3372, 3281, 3209 (NH), 2224 (CN), 1737, 1694 (COO), 1668 (N-C=O); MS *m/z* (int. %): 350 (M^+, 50), 294 (18), 238 (23), 220 (100); *Anal.* Calcd for $C_{16}H_{22}N_4O_5$: C, 54.85; H, 6.33; N, 15.99. Found: C, 54.82; H, 6.33; N, 15.94.

Di*i*-butyl 3-Cyano-1,6-diamino-2-pyridone-4,5-dicarboxylates (3e)

3e: Yield 86%; mp 133.5-134.0 ℃; IR (KBr): 3379, 3303, 3279, 3211 (NH), 2226 (CN), 1740, 1695 (COO), 1665 (N-C=O); MS *m/z* (int. %): 350 (M^+, 81), 294 (30), 238 (96), 220 (100); *Anal.* Calcd for $C_{16}H_{22}N_4O_5$: C, 54.85; H, 6.33; N, 15.99. Found: C, 54.87; H, 6.32; N, 15.93.

Diethyl 2-Substituted 6-Cyano-1(3),5-dihydro-5-oxo[1,2,4]triazolo[1,5-*a*]pyridine-7,8-dicarboxylates (5)

General Procedure: To a solution of diethyl 3-cyano-1,6-diamino-2-pyridone-4,5-dicarboxylate (**3a**) (2.0 mmol) in acetic acid (2 mL), trialkyl orthocarboxylate (4) (2 mL, excess) was added and refluxed for variable time (10 min - 0.5 h). After the solution was cooled at rt, deposited crystals were collected by filtration and recrystallized from EtOH-DMF (2:1) to give **5** as colorless needles.

Diethyl 6-Cyano-1(3),5-dihydro-5-oxo[1,2,4]triazolo[1,5-*a*]pyridine-7,8-dicarboxylate (5a)

5a was obtained in 83 % yield by the reaction with trimethyl orthoformate under reflux for 10 min. **5a**: mp 289.5-290.0 ℃ (decomp); IR (KBr): 3166, 3133 (NH), 2222 (CN), 1744, 1720 (COO), 1667 (N-C=O); MS *m/z* (int. %): 304 (M^+, 54), 258 (14), 230 (100); *Anal.* Calcd for $C_{13}H_{12}N_4O_5$: C, 51.32; H, 3.98; N, 18.41. Found: C, 51.16; H, 3.90; N, 18.36.

Diethyl 6-Cyano-1(3),5-dihydro-2-methyl-5-oxo[1,2,4]triazolo[1,5-*a*]pyridine-7,8-dicarboxylate (5b)

5b was obtained in 77 % yield by the reaction with triethyl orthoacetate under reflux for 0.5 h. **5b**: mp 194.0-194.5 ℃ (decomp); IR (KBr): 3157 (br.) (NH), 2229 (CN), 1740, 1700 (COO), 1685 (N-C=O); MS *m/z* (int. %): 318 (M^+, 56), 244 (100), 172 (96).

Diethyl 6-Cyano-1(3),5-dihydro-2-ethyl-5-oxo[1,2,4]triazolo[1,5-*a*]pyridine-7,8-dicarboxylate (5c)

5c was obtained in 85 % yield by the reaction with triethyl orthopropionate under reflux for 0.5 h. **5c**: mp 254.0-255.0 ℃ (decomp); IR (KBr): 3254, 3196 (NH), 2226 (CN), 1744, 1705 (COO), 1672 (N-C=O); MS *m/z* (int. %): 332 (M^+, 60), 258 (100), 186 (58).

Dialkyl 6-Amino-3-cyano-2-pyridone-4,5-dicarboxylates (6)

General Procedure: Sodium nitrite (0.10 g, 1.5 mmol) in water (0.5 mL) was added to a solution of the appropriate 1,6-diaminopyridone (**3**) (1.0 mmol) in acetone (10 mL) and 4N-HCl (5 mL) at 0 ℃. After the mixture was stirred for 15 min, a solution of sodium azide (0.14 g, 2.2 mmol) and $AcONa \cdot 3H_2O$ (3.0 g, 22 mmol) dissolved in water (5 mL) was added dropwise to the reaction mixture at 0-5 ℃ with good stirring. The stirring was continued for 10 min, water (100 mL) was added to the mixture and the extraction was carried out with ethyl acetate. Then the solvent was removed under reduced pressure, leaving a crystalline solid. Recrystallization from 2-propanol gave **6** as colorless plates.

Diethyl 6-Amino-3-cyano-2-pyridone-4,5-dicarboxylate (6a)

6a: Yield 93 %; mp 227.0-227.5 ℃; IR (KBr): 3392, 3276, 3237 (NH), 2224 (CN), 1749, 1701 (COO), 1649 (N-C=O); IR (DMSO): 3401 (OH), 3287, 3219 (NH), 2218 (CN), 1738, 1681

(COO); MS *m/z* (int. %): 279 (M^+, 100), 206 (81), 161 (34), 134 (40); *Anal.* Calcd for $C_{12}H_{13}N_3O_5$: C, 51.61; H, 4.69; N, 15.05. Found: C, 51.56; H, 4.66; N, 14.98.

Dipropyl 6-Amino-3-cyano-2-pyridone-4,5-dicarboxylate (6b)

6b: Yield 72 %; mp 160.5-161.5 ℃; IR (KBr): 3400, 3282, 3238 (NH), 2226 (CN), 1744, 1696 (COO), 1653 (N-C=O); IR (DMSO): 3418 (OH), 3288, 3215 (NH), 2218 (CN), 1735, 1690 (COO); MS *m/z* (int. %): 307 (M^+, 79), 223 (45), 206 (100), 161 (25), 134 (43).

Di*i*-propyl 6-Amino-3-cyano-2-pyridone-4,5-dicarboxylate (6c)

6c: Yield 88 %; mp 230.5-231.5 ℃; IR (KBr): 3392, 3284, 3220 (NH), 2220 (CN), 1743, 1695 (COO), 1675 (N-C=O); MS *m/z* (int. %): 307 (M^+, 57), 223 (100), 206 (62), 161 (34), 134 (32).

Dibutyl 6-Amino-3-cyano-2-pyridone-4,5-dicarboxylate (6d)

6d: Yield 96 %; mp 140.0-142.0 ℃; IR (KBr): 3391, 3277, 3233 (NH), 2224 (CN), 1750, 1694 (COO), 1656 (N-C=O); MS *m/z* (int. %): 335 (M^+, 50), 279 (36), 223 (58), 206 (100).

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