DOI 10.1007/s10593-015-1659-8

*Chemistry of Heterocyclic Compounds* **2015**, *51*(1), 56-59

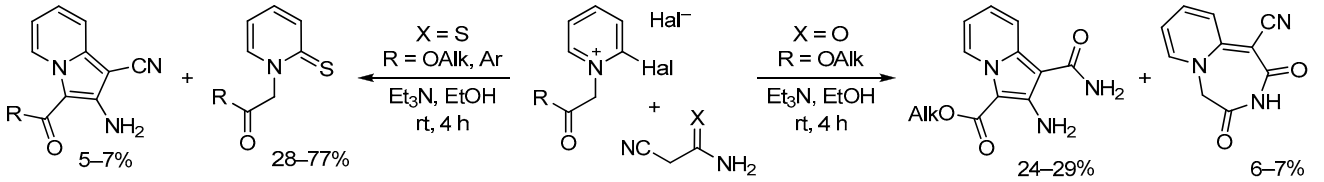
# Amide and thioamide of cyanoacetic acid in $Ad_NE$ type reactions with 2-halopyridinium salts

**Natalya M. Tverdokhleb[1], Gennadii E. Khoroshilov[1]***

[1] *Taras Shevchenko Lugansk National University, 1 Gogola Sq., Starobelsk 92700, Lugansk obl., Ukraine; e-mail: khoroshilov@inbox.ru*

Translated from Khimiya Geterotsiklicheskikh Soedinenii, 2015, *51*(1), 56–59

Submitted 25.11.2014
Accepted after revision 19.01.2015



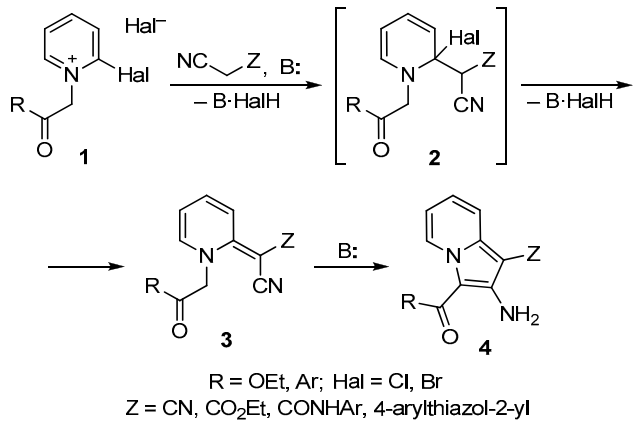

A mixture of pyridine-2-thiones and 2-amino-1-cyanoindolizines was obtained by condensation of *N*-[(alkoxycarbonyl)methyl]- or *N*-[(aroyl)-methyl]-2-chloro(bromo)pyridinium halides in the presence of 2 equivalents of triethylamine. Furthermore, reacting cyanoacetamide with *N*-[(alkoxycarbonyl)methyl]-2-chloro(bromo)pyridinium salts afforded a mixture of 2-amino-1-carbamoylindolizine-3-carboxylates and a novel heterocyclic system, 2,4-dioxo-2,3,4,5-tetrahydropyrido[1,2-*d*][1,4]diazepine-1-carbonitrile.

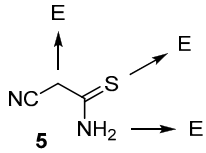
**Keywords**: 2-amino-1-carbamoylindolizines, 2-amino-1-cyanoindolizines, cyanoacetamide, 2-cyanothioacetamide, 2-halopyridinium salts, pyridine-2-thiones.

Kröhnke's salts [1–3] and their ester analogs **1**[4] in the presence of a base react with acetonitrile-derived CH acids by an $Ad_NE$ mechanism leading to the formation of nucleophilic substitution products **3** (Scheme 1). Compounds **3** may not always be isolated due to intramolecular Thorpe cyclization leading to the formation of an aromatic indolizine system **4**.[3,4]

Subjecting salts **1** to a reaction with CH acids possessing several nucleophilic centers is of interest from both theoretical and applied perspective. In this study, 2-cyanothioacetamide (**5**) having three nucleophilic centers[5] and its oxygen-containing analog cyanoacetamide (**8**) were used as model substrates.

**Scheme 1**

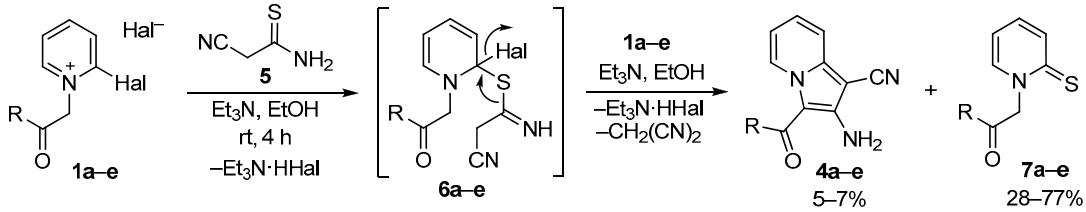


Salts **1a**–**e**[3,4] react with 2-cyanothioacetamide (**5**) in the presence of 2 equiv of triethylamine in ethanol solution at ambient temperature yielding mostly pyridine-2(1*H*)-thiones **7a**–**e** that contain indolizines **4a**–**e** as impurities (Scheme 2).

Presumptively, indolizines **4a**–**e** are form *via* intermediates **2** (Scheme 1, Z = CN) with successive elimination of a molecule of hydrogen halide followed by intramolecular Thorpe cyclization. The isolated yield of by-products **4**a–**e** after column chromatography does not exceed 5–7% which correlates well with the analysis of $^1$H NMR spectra of reaction mixtures. We propose compounds **6a**–**e** as intermediates in this conversion. Formation of pyridine-2(1*H*)-thiones **7a**–**e** proceeds with elimination of malononitrile, which participates in the competing reaction yielding by-products **4a**–**e**. Indolizines **4c**–**e** were identified by preparing them from salts **1c**–**e** and malononitrile,[6] as well as by comparative thin layer chromatography.

**Scheme 2**

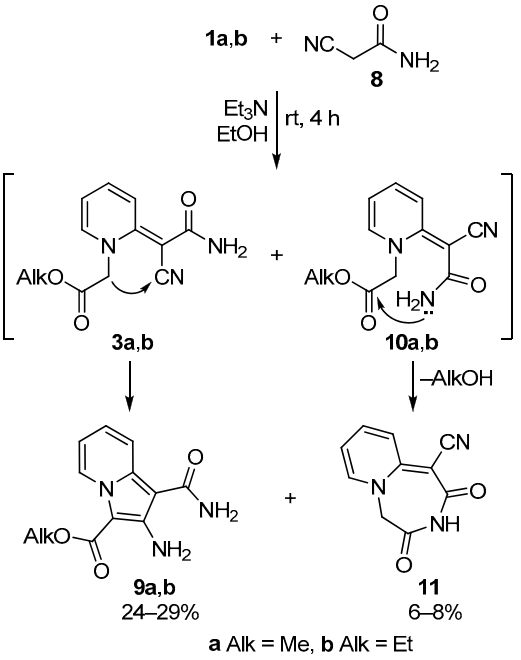



**a** R = OMe, **b** R = OEt, **c** R = Ph, **d** R = 4-MeOC$_6$H$_4$, **e** R = 4-ClC$_6$H$_4$; Hal = Cl, Br

Pyridine-2(1*H*)-thiones **7a**–**e** could conveniently be isolated in pure form by recrystallization, since by-products **4a**–**e** are present in only minor amounts. $^1$H NMR spectra of compounds **7a**–**e** are characterized by the methylene group proton singlets at 5.25–6.08 ppm. Protons of the pyridine ring appear as a pair of doublets (H-3,6), a triplet (H-5), and a multiplet (H-4). The signals in mass spectra correspond to corresponding molecular masses.

Cyanoacetamide (**8**) reacts with salts **1a**,**b** as a CH acid with the formation of a mixture of products **9a**,**b** and **11** (Scheme 3). The end products most likely form *via* intermediate π-isomers **3a**,**b** and **10**.

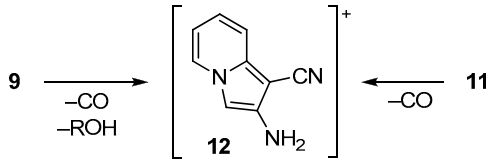
**Scheme 3**




**a** Alk = Me, **b** Alk = Et

The mixture of compounds **9a**,**b** and **11** was separated by column chromatography; compounds **9a**,**b** could also be purified by recrystallization from ethanol. The structures of 2-aminoindolizine-3-carboxylates **9a**,**b** and pyrido[1,2-*d*]-[1,4]diazepine-1-carbonitrile **11** are supported by physicochemical characterization. Thus, besides the characteristic pyridine ring proton signals, $^1$H NMR spectra of indolizines **9a**,**b** contain signals of $NH_2$ and $CONH_2$ protons. The latter appear as two broad singlets at 6.51–6.60 and 6.74–6.99 ppm. The spectrum of 1,4-diazepine **11** contains signals of methylene group protons at 4.89 ppm. The mass spectra of compounds **9a**,**b** and **11** exhibit molecular ion peaks. However, a fragment ion with a molecular mass of 158 is the base peak in all cases. Presumably, it is cation **12** which could form from both indolizines **9a**,**b** and pyrido[1,2-*d*][1,4]diazepine **11** (Scheme 4). Besides cation **12**, the formation of other fragment ions is conceivable, including structurally different ions with the same molecular mass.

**Sheme 4**




Thus, 2-cyanothioacetamide reacts with *N*-[(alkoxycarbonyl)methyl]- and *N*-[(aroyl)methyl]-2-halopyridinium salts as an S-nucleophile, while cyanoacetamide as a CH-acid, because in this case nucleophilicity of the oxygen atom of cyanoacetamide is considerably lower than that of its CH-acid site.

## Experimental

IR spectra were registered on a Perkin-Elmer Spectrum One spectrometer in KBr pellets. $^1$H and $^{13}$C NMR spectra were acquired on a Bruker Avance II‑400 (400 and 100 MHz, respectively) in DMSO-$d_6$, with TMS as internal standard. Mass spectra were recorded on MX-1321 (compounds **4**, **7a**, **9**, and **11**) and Varian 1200 L (compounds **7c**–**e**) mass spectrometers, EI ionization (70 eV) with direct sample injection. Elemental analysis was performed on a Eurovector EA-3000 elemental analyzer. Melting points were determined on a Kofler hot bench. Monitoring of the reaction progress and assessment of the purity of the synthesized compounds was done by TLC on Silufol UV-254 plates in acetone–hexane, 3:5, eluent system, visualization with UV or in an iodine chamber.

**Synthesis of salt 1a as a mixture of halides of 2-chloro-*N*-[(methoxycarbonyl)methyl]pyridinium (form A) and 2-bromo-*N*-[(methoxycarbonyl)methyl]-pyridinium (form B)**. A mixture of 2-chloropyridine (3.40 g, 30 mmol) and methyl bromoacetate (4.90 g, 32 mmol) were heated neat at 70°C for 6 h. Acetone (40 ml) was added to the mixture after cooling, and the resulting mixture kept for 24 h at room temperature. The formed precipitate was filtered off and washed with a minimum amount of acetone. Yield 2.39 g (30%), white crystals, mp 163–164°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz) (ratio of form **A** to form **B** 52:48): 3.83 (3H, s, $OCH_3$ (**A**+**B**)); 5.93 (2H, s, $NCH_2$ (**A**+**B**)); 8.29 (1H, t, *J* = 6.8, H-5 (**A**+**B**)); 8.51 (0.48H, d, *J* = 8.2, H-3 (**B**)); 8.60 (0.52H, d, *J* = 7.8,

H-3 (**A**)); 8.65 (0.52H, t, *J* =7.8, H-4 (**A**)); 8.82 (0.48H, t, *J* = 8.1, H-4 (**B**)); 9.45–9.49 (1H, m, H-6 (**A**+**B**)). $^{13}$C NMR spectrum, δ, ppm: 53.8; 59.9; 62.3; 96.0; 127.2; 127.4; 130.0; 130.5; 134.5; 147.4; 147.7; 148.4; 149.6; 149.7; 149.9; 165.7. Mass spectrum, *m/z* ($I_{rel}$, %): 232 [M(**B**,$^{81}$Br)]$^+$ (72), 230 [M(**B**,$^{79}$Br)]$^+$ (77), 188 [M(**A**,$^{37}$Cl)]$^+$ (32), 186 [M(**A**,$^{35}$Cl)]$^+$ (100).

Published procedures were followed in the synthesis of compounds **1b**[4] and **1c**–**e**[3]. Compounds **1b**–**e** are mixtures of 2-chloro- and 2-bromopyridinium halides.

**Synthesis of compounds 4a–e, 7a–e, 9a,b, 11** (General Method). $Et_3N$ (0.56 ml, 4.0 mmol) was added to a mixture of 2-chloro(bromo)pyridinium salt **1a**–**e** (2.0 mmol) and 2-cyanothioacetamide (**5**) (0.200 g, 2.0 mmol) (for compounds **4**, **7** **a**–**e**) or cyanoacetamide (0.168 g, 2.0 mmol) (**8**) (for compounds **9a**,**b**, **11**) and EtOH (10 ml). The reaction mixture was stirred at room temperature for 4 h, then kept at 0–2°C (fridge) for 24 h. The formed precipitate was filtered off, washed with MeOH (for compounds **4a**, **7a**) or EtOH. The precipitate contained compounds **4** and **7** (in reactions with 2-cyanothioacetamide (**5**)) or compounds **9** and **11** (in reactions with cyanoacetamide (**8**)) according to TLC. The dried precipitate was dissolved in acetone and subjected to column chromatography on silica gel. Compounds **7a**–**e** and **9a**,**b** could also be purified by recrystallization from MeOH (for compounds **7a**–**e**) or EtOH (for compounds **9a**,**b**).

**Methyl 2-amino-1-cyanoindolizine-3-carboxylate (4a)**. Yield 0.026 g (6%), beige powder, mp 148–150°C (EtOH), $R_f$ 0.47. IR spectrum, ν, cm$^{-1}$: 3448, 3341, 2202, 1673. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 3.83 (3H, s, $CO_2CH_3$); 6.35 (2H, s, $NH_2$); 6.92 (1H, t, *J* = 6.7, H-6); 7.31–7.35 (1H, m, H-7); 7.40 (1H, d, *J* = 8.6, H-8); 9.25 (1H, s, H-5). $^{13}$C NMR spectrum, δ, ppm: 51.2; 70.5; 99.4; 114.0; 114.9; 115.5; 128.0; 128.7; 139.8; 149.2; 161.4. Mass spectrum, *m/z* ($I_{rel}$, %): 216 [M+H]$^+$ (13), 215 [M]$^+$ (82), 183 (100). Found, %: C 61.42; H 4.25; N 19.49. $C_{11}H_9N_3O_2$. Calculated, %: C 61.39; H 4.22; N 19.52.

**Ethyl 2-amino-1-cyanoindolizine-3-carboxylate (4b)**. Yield 0.023 g (5%), beige powder, mp 151–152°C (EtOH) (mp 151°C)[4,7], $R_f$ 0.49.

**2-Amino-3-benzoylindolizine-1-carbonitrile (4c)**. Yield 0.036 g (7%), yellow powder, mp 161–162°C (mp 161–163°C)[6], $R_f$ 0.50.

**2-Amino-3-(4-methoxybenzoyl)indolizine-1-carbonitrile (4d)**. Yield 0.029 g (5%), yellow powder, mp 192–193°C (EtOH), $R_f$ 0.39. IR spectrum, ν, cm$^{-1}$: 3493, 3394, 2204, 1634. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 3.87 (3H, s, $OCH_3$); 5.66 (2H, s, $NH_2$); 6.90 (1H, t, *J* = 6.8, H-6); 7.03 (2H, d, *J* = 8.6, H Ar); 7.37–7.47 (2H, m, H-7,8); 7.55 (2H, d, *J* = 8.6, H Ar); 9.19 (1H, d, *J* = 6.8, H-5). $^{13}$C NMR spectrum, δ, ppm: 55.7; 110.3; 113.7; 114.6; 115.0; 115.1; 128.8; 129.2; 129.9; 131.0; 132.4; 140.3; 149.2; 162.2; 182.3. Mass spectrum, *m/z* ($I_{rel}$, %): 291 [M]$^+$ (60), 290 (93), 247 (26), 135 (100). Found, %: C 70.13; H 4.53; N 14.41. $C_{17}H_{13}N_3O_2$. Calculated, %: C 70.09; H4.50; N 14.42.

**2-Amino-3-(4-chlorobenzoyl)indolizine-1-carbonitrile (4e)**. Yield 0.041 g (7%), yellow powder, $R_f$ 0.4, mp 199–200°C (EtOH) (mp 199–201°C)[6].

Compounds **4c**–**e** were obtained in good yields by an counter synthesis from 2-chloro(bromo)pyridinium salts **1c**–**e** and malononitrile according to a known method.[6] In particular, a previously unknown compound **4d** was obtained according to method[6] from salt **1d** (0.69 g, 2.0 mmol) and malononitrile (0.13 g, 2.0 mmol) (yield 0.48 g, 82%). Characteristics of compounds **4c**–**e**, synthesized by 2-cyanothioacetamide synthesis (**5**), match those of compounds **4c**–**e** obtained employing the malononitrile route.

**Methyl 2-(2-thioxopyridin-1(2*H*)-yl)acetate (7a)**. Yield 0.102 g (28%), yellow needles, mp 70–71°C (MeOH), $R_f$ 0.30. IR spectrum, ν, cm$^{-1}$: 1742. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 3.67 (3H, s, $CO_2CH_3$); 5.26 (2H, s, $NCH_2$); 6.85 (1H, t, *J* = 6.6, H-5); 7.39–7.42 (1H, m, H-4); 7.47 (1H, d, *J* = 8.6, H-3); 8.12 (1H, d, *J* = 6.6, H-6). $^{13}$C NMR spectrum, δ, ppm: 52.7; 57.4; 113.7; 134.8; 136.0; 143.4; 167.7; 179.9. Mass spectrum, *m/z* ($I_{rel}$, %): 183 [M]$^+$ (15), 101 (18), 86 (100). Found, %: C 52.39; H 5.01; N 7.71; S 17.55. $C_8H_9NO_2S$. Calculated, %: C 52.44; H 4.95; N 7.64; S 17.50.

**Ethyl 2-(2-thioxopyridin-1(2*H*)-yl)acetate (7b)**. Yield 0.118 g (30%), yellow needles, mp 65–66°C (MeOH) (mp 71°C)[8], $R_f$ 0.34. IR spectrum, ν, cm$^{-1}$: 1743. $^1$H NMR, δ, ppm (*J*, Hz): 1.19 (3H, t, *J* = 7.1, $CO_2CH_2C\underline{H}_3$); 4.14 (2H, q, *J* = 7.1, $CO_2C\underline{H}_2CH_3$); 5.25 (2H, s, $NCH_2$); 6.84 (1H, t, *J* = 6.5, H-5); 7.38–7.42 (1H, m, H-4); 7.47 (1H, d, *J* = 8.5, H-3); 8.13 (1H, d, *J* = 6.6, H-6). $^{13}$C NMR spectrum, δ, ppm: 14.5; 57.5; 61.6; 113.7; 134.7; 136.0; 143.4; 167.2; 179.9. Mass spectrum, *m/z* ($I_{rel}$, %): 197 [M]$^+$ (100). Found, %: C 54.74; H 5.67; N 7.18; S 16.21. $C_9H_{11}NO_2S$. Calculated, %: C 54.80; H 5.62; N 7.10; S 16.25.

**2-(2-Thioxopyridin-1(2*H*)-yl)-1-phenylethanone (7c)**. Yield 0.339 g (74%), yellow powder, mp 184–185°C (MeOH) (mp 180°C[9], mp 187–190°C[10]), $R_f$ 0.31. IR spectrum, ν, cm$^{-1}$: 1668. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 6.08 (2H, s, $NCH_2$); 6.83 (1H, t, *J* = 6.6, H-5); 7.37–7.41 (1H, m, H-4); 7.49 (1H, d, *J* = 8.6, H-3); 7.58 (2H, t, *J* = 7.5, H Ph); 7.69 (1H, t, *J* = 7.3, H Ph); 8.07–8.09 (3H, m, H-6, H Ph). $^{13}$C NMR spectrum, δ, ppm: 61.9; 96.1; 113.2; 128.3; 129.1; 134.0; 134.6; 135.4; 143.4; 179.7; 191.6. Mass spectrum, *m/z* ($I_{rel}$, %): 229 [M]$^+$ (61), 212 (44), 105 (100). Found, %: C 68.12; H 4.86; N 6.09; S 13.99. $C_{13}H_{11}NOS$. Calculated, %: C 68.10; H 4.84; N 6.11; S 13.98.

**1-(4-Methoxyphenyl)-2-(2-thioxopyridin-1(2*H*)-yl)-ethanone (7d)**. Yield 0.394 g (76%), yellow powder, mp 150–151°C (MeOH), $R_f$ 0.27. IR spectrum, ν, cm$^{-1}$: 1670. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 3.88 (3H, s, $OCH_3$); 6.02 (2H, s, $NCH_2$); 6.80 (1H, t, *J* = 6.7, H-5); 7.05 (2H, d, *J* = 8.6, H Ar); 7.34–7.38 (1H, m, H-4); 7.48 (1H, d, *J* = 8.7, H-3); 8.03–8.04 (3H, m, H-6, H Ar). $^{13}$C NMR spectrum, δ, ppm: 56.0; 61.5; 113.2; 114.4; 128.2; 130.1; 134.6; 135.4; 143.5; 164.0; 179.7; 190.0. Mass spectrum, *m/z* ($I_{rel}$, %): 259 [M]$^+$ (49), 226 (35), 135 (100). Found, %: C 64.88; H 5.08; N 5.38; S 12.34. $C_{14}H_{13}NO_2S$. Calculated, %: C 64.84; H 5.05; N 5.40; S 12.36.

**1-(4-Chlorophenyl)2-(2-thioxopyridin-1(2*H*)-yl)-ethanone (7e)**. Yield 0.406 g (77%), yellow powder, mp 148–149°C (MeOH), $R_f$ 0.35. IR spectrum, ν, cm$^{-1}$: 1670. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 6.03 (2H, s, $NCH_2$);

6.82 (1H, t, *J* = 6.7, H-5); 7.36–7.40 (1H, m, H-4); 7.48 (1H, d, *J* = 8.6, H-3); 7.59 (2H, d, *J* = 8.5, H Ar); 8.07–8.09 (3H, m, H-6, H Ar). $^{13}$C NMR spectrum, δ, ppm: 61.8; 113.2; 129.3; 130.0; 134.0; 134.6; 135.3; 135.4; 143.4; 179.7; 190.7. Mass spectrum, *m/z* ($I_{rel}$, %): 263 $[M(^{35}Cl)]^+$ (47), 139 (91), 78 (100). Found, %: C 59.19; H 3.84; N 5.30; S 12.13. $C_{13}H_{10}ClNOS$. Calculated, %: C 59.20; H 3.82; N 5.31; S 12.16.

**Methyl 2-amino-1-carbamoylindolizine-3-carboxylate (9a)**. Yield 0.112 g (24%), white powder, mp 228–230°C (EtOH), $R_f$ 0.36. IR spectrum, ν, cm$^{-1}$: 3372, 3191, 1675. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 3.83 (3H, s, $CO_2CH_3$); 6.60 (2H, s, 2-$NH_2$); 6.90 (1H, t, *J* = 6.8, H-6); 6.99 (2H, br. s, $CONH_2$); 7.27–7.33 (1H, m, H-7); 7.79 (1H, d, *J* = 8.9, H-8); 9.29 (1H, d, *J* = 6.8, H-5). $^{13}$C NMR spectrum, δ, ppm: 51.0; 93.7; 99.3; 112.5; 116.5; 126.6; 128.0; 136.6; 149.0; 161.9; 167.8. Mass spectrum, *m/z* ($I_{rel}$, %): 233 $[M]^+$ (74), 216 (52), 185 (18), 158 (100). Found, %: C 56.63; H 4.80; N 18.00. $C_{11}H_{11}N_3O_3$. Calculated, %: C 56.65; H 4.75; N 18.02.

**Ethyl 2-amino-1-carbamoylindolizine-3-carboxylate (9b)**. Yield 0.144 g (29%), white powder, mp 203–205°C (EtOH), $R_f$ 0.46. IR spectrum, ν, cm$^{-1}$: 3370, 3191, 1673. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 1.40 (3H, t, *J* = 7.0, $CO_2CH_2C\underline{H}_3$); 4.35 (2H, q, *J* = 7.0, $CO_2C\underline{H}_2CH_3$); 6.51 (2H, s, 2-$NH_2$); 6.74–6.87 (3H, m, H-6, $CONH_2$); 7.21–7.25 (1H, m, H-7); 7.79 (1H, d, *J* = 9.0, H-8); 9.31 (1H, s, H-5). $^{13}$C NMR spectrum, δ, ppm: 15.0; 59.6; 93.8; 99.4; 112.5; 116.5; 126.5; 128.0; 136.6; 149.0; 161.6; 167.7. Mass spectrum, *m/z* ($I_{rel}$, %): 247 $[M]^+$ (50), 230 (21), 185 (11), 158 (100). Found, %: C 58.27; H 5.33; N 16.97. $C_{12}H_{13}N_3O_3$. Calculated, %: C 58.29; H 5.30; N 16.99.

**2,4-Dioxo-2,3,4,5-tetrahydropyrido[1,2-*d*][1,4]diazepine-1-carbonitrile (11)**. Yield 0.030 g (8%, from a mixture of compounds **9a** and **11**), 0.024 g (6%, from a mixture of compounds **9b** and **11**), yellow powder, mp >300 °C (decomp.), $R_f$ 0.10. IR spectrum, ν, cm$^{-1}$: 3502, 2188, 1673. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 4.89 (2H, s, 5-$CH_2$); 7.16 (1H, t, *J* = 6.8, H-8); 7.51 (1H, d, *J* = 8.7, H-10); 7.90–7.94 (1H, m, H-9); 8.36 (1H, d, *J* = 6.8, H-7); 10.61 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 60.8; 71.5; 117.5; 121.1; 122.9; 140.9; 141.4; 152.8; 163.9; 165.1. Mass spectrum, *m/z* ($I_{rel}$, %): 201 $[M]^+$ (4), 158 (100). Found, %: C 59.69; H 3.55; N 20.86. $C_{10}H_7N_3O_2$. Calculated, %: C 59.70; H 3.51; N 20.89.

## References


1. Kröhnke, F.; Heffe W. *Ber. Dtsch. Chem. Ges.* **1937**, *70*, 864.
2. Pauls, H.; Kröhnke, F. *Chem. Ber.* **1977**, *110*, 1294.
3. Khoroshilov, G. E.; Demchak, I. V. *Visn. Kharkiv. nats. un-tu, Khimiya.* **2007**, *770*, vip. 15(38), 210.
4. Khoroshilov, G. E.; Tverdokhleb, N. M.; Brovarets, V. S.; Babaev, E. V. *Tetrahedron* **2013**, *69*, 4353.
5. Jagodziński, T. S. *Chem. Rev.* **2003**, *103*, 197**.**
6. Khoroshilov, G. E. *Chem. Heterocycl. Compd.* **2001**, *37*, 1141. [*Khim. Geterotsikl. Soedin.* **2001**, 1245.]
7. Tverdokhleb, N. M.; Khoroshilov, G. E.; Zubatyuk, R. I.; Shishkin, O. V. *Chem. Heterocycl. Compd.* **2013**, *49*, 720. [*Khim. Geterotsikl. Soedin.* **2013**, 772.]
8. Babaev, E. V.; Smirnov, G. A.; Rybakov, V. B. *Chem. Heterocycl. Compd.* **2005**, *41*, 1071. [*Khim. Geterotsikl. Soedin.* **2005**, 1250.]
9. Pauls, H.; Kröhnke, F. *Chem. Ber.* **1976**, *109*, 3653.
10. Blank, B.; DiTullio, N. W.; Krog, A. J.; Saunders, H. J. *J. Chem.* **1978**, *21*, 489.