Reactions of Quinolizine- and Pyridino[1,2–*a*]pyrimidine-3-diazonium Tetrafluoroborates with Aliphatic Amines*

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Dedicated to Professor Willi Kantlehner on the occasion of his 60th birthday

Reactions of 1-cyano-4-oxo-4*H*-quinolizine-3-diazonium tetrafluoroborate (**1a**) and 4-oxo-4*H*-pyridino[1,2–*a*]pyrimidine-3-diazonium tetrafluoroborate (**1b**) with aliphatic amines **2a – g** were studied. Treatment of heteroaryldiazonium salts **1** with secondary amines **2a – d** afforded the corresponding *N*-alkyl-*N*'-heteroaryltriazenes **3a – h** in high yields. On the other hand, reactions of **1a** with aliphatic primary amines **2e – g** resulted in an unexpected rearrangements into the corresponding picolinic acid *N*-alkylcarboxamides **4a – c**.

Key words: Diazonium Salts, Triazenes, Rearrangement, Pyridines, Pyrimidines

Introduction

For more than a century, diazo compounds and diazonium salts have been the topic of extensive studies. The interest in this kind of compounds is not surprising, since they are important reagents and substrates in a variety of fundamental organic transformations, such as Sandmeyer reaction, Schiemann reaction, Gomberg-Bachmann reaction, Meerwein reaction, Wolff rearrangement, and other transformations [1]. Two typical examples of industrial application and utilization of diazo compounds are production of azo-dyes [1] and the use of α-diazonaphthoquinone derivatives in the microlithography processes for the production of computer chips [2]. Recently, aryldiazonium tetrafluoroborates found use in functionalisation of carbon nanotubes [3].

Another typical reaction of diazonium salts is coupling with primary and secondary amines leading to the corresponding triazenes, which are also important and useful types of organic compounds [1]. Due to their relative stability, triazenes can be used as protectig groups for primary and secondary amines [4] and as linkers in solid-phase synthesis [5]. On the other hand, many triazenes exhibit biological activity – for example, 5-(3,3-dimethyltriaz-1-enyl)imidazole-4-carboxamide (Decarbazine®) is used for treatment of cancer [6].

Alkyl 2-substituted 3-(dimethylamino)propenoates and their cyclic analogs are easily available and versatile reagents for the preparation of a variety of heterocyclic systems, functionalised heterocycles, and natural product analogs [7]. In this connection, stable quinolizine-3-diazonium tetrafluoroborates [8] and azino[1,2-*x*]pyrimidine-3-diazonium tetrafluoroborates [9, 10] were prepared in three steps and good yields from methyl (*Z*)-2-benzyloxycarbonylamino-3-(dimethylamino)propenoate. These stable heteroaryldiazonium salts turned out to be useful reagents in heterocyclic synthesis. They were employed in 'ring switching' transformations into 1-heteroaryl-1*H*-1,2,3-triazole-4-carboxylates [9, 10], in aza-Wolff rearrangements into alkyl indolizine-3-carboxylates [8], and in coupling with 1,3-dicarbonyl compounds followed by cyclisation into alkyl 1-heteroaryl-4-hydroxy-1*H*-pyrazole-3-carboxylates [11] (Fig. 1).

In continuation of our work in this field, we report the transformations of 1-cyano-4-oxo-4*H*-quinolizine-3-diazonium tetrafluoroborate (**1a**) and 4-oxo-4*H*-pyridino[1,2–*a*]pyrimidine-3-diazonium tetrafluorobo-

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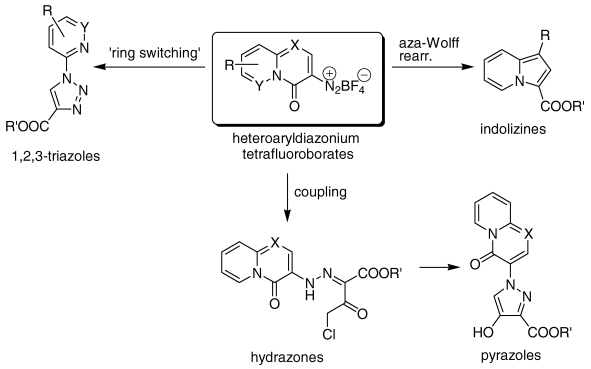


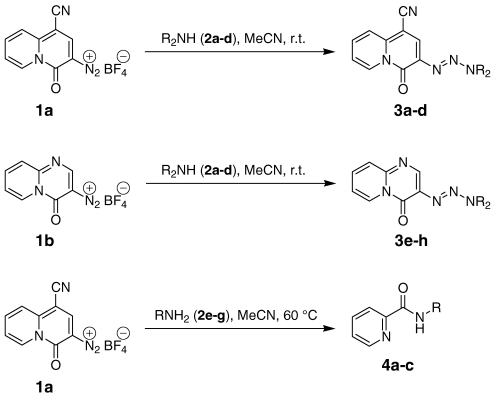
Fig. 1. Previous synthetic applications of quinolizine- and azino[1,2-*x*]pyrimidine-3-diazonium tetrafluoroborates.

rate (**1b**) with secondary amines **2a – d** into heteroaryltriazenes **3a – h** and unusual rearrangements of **1a** into *N*-alkylpyridine-2-carboxamides **4a – c**, which took place upon treatment with primary amines **2e – g**.

Results and Discussion

1-Cyano-4-oxo-4*H*-quinolizine-3-diazonium tetrafluoroborate (**1a**) [8] and 4-oxo-4*H*-pyridino[1,2-*a*]pyrimidine-3-diazonium tetrafluoroborate (**1b**) [9] were prepared according to the procedures described previously in the literature. For reactions with amines, the following secondary and primary amines were chosen: diethylamine (**2a**), pyrrolidine (**2b**), piperidine (**2c**), dicyclohexylamine (**2d**), *n*-propylamine (**2e**), *n*-butylamine (**2f**), and *n*-pentylamine (**2g**). Treatment of **1a,b** with 2 equivalents of secondary amines **2a – d** in acetonitrile at room temperature afforded the corresponding 3,3-dialkyl-1-heteroaryltriaz-1-enes **3a – h** as yellow solids in 81 – 98% yields. On the other hand, when **1a** was treated with excess primary amines **2e – g** in acetonitrile at 60 °C, *N*-alkylpyridine-2-carboxamides **4a – c** were obtained in moderate yields (Scheme 1).

So far, we do not have a firm explanation for rearrangement of diazonium salt **1a** into pyridine-2-carboxamides **4**. To the best of our knowledge, no closely related rearrangements have been described in the literature yet. Two hypothetical explanations for formation of **4a – c** are given in Scheme 2. Presumably, formation of the corresponding triazenes **5** should take place first. From this point on, the triazene **5** could rearrange, *via* the spiro compound **6**, into intermediate **7**. Reaction of **7** with alkylamine **2f – g** would give *N*-alkylpyridinecarboxamide **4** *via* elimination of the conjugated triazene intermediate



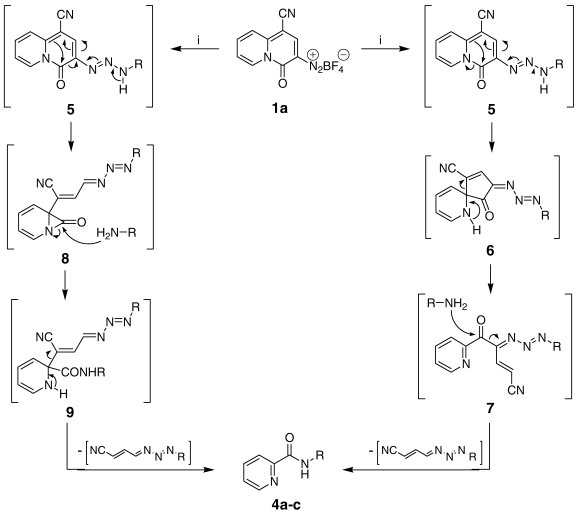
Reaction	R_2N	RNH	Yield [%]
1a + 2a → 3a	Et_2N	-	98
1a + 2b → 3b	pyrrolidin-1-yl	-	92
1a + 2c → 3c	piperidin-1-yl	-	83
1a + 2d → 3d	dicyclohexylamino	-	84
1b + 2a → 3e	Et_2N	-	92
1b + 2b → 3f	pyrrolidin-1-yl	-	86
1b + 2c → 3g	piperidin-1-yl	-	81
1b + 2d → 3h	dicyclohexylamino	-	88
1a + 2e → 4a	-	*n*-propylamino	54
1a + 2f → 4b	-	*n*-butylamino	43
1a + 2g → 4c	-	*n*-pentylamino	43

Scheme 1.

10 (Path A). Alternatively, the triazene **5** could isomerise into the dihydroaziridino[1,2–*a*]pyridine intermediate **8**. Ring opening of **8** with primary amine **2** followed by elimination of **10** would give the product **4** (Path B). Both hypothetical explanations are based on cleavage of the O=$C-N$(Py) and O=$C-C$=N single bonds and formation of the (Py)$C-C$=O single bond (Scheme 2).

Structure Determination

Structures of novel compounds were confirmed by spectroscopic methods and by analyses for C, H, and N. Since *N*-alkylpyridine-2-carboxamides **4a – c** were obtained as oily liquids, their structure could not be unambigously determined by X–ray analysis or, in the case of literature-known **4c** [12], by melting point comparison. Therefore, we carried out the independent synthesis of *N*-pentylpyridine-2-carboxamide (**4c**) from ethyl pyridine-2-carboxylate



Reagents and conditions: (i) R–NH_2 (**2e–g**, excess), acetonitrile, 60 °C.

Scheme 2.

and *n*-pentylamine following the literature procedure [12]. Spectral data of **4c** obtained from ethyl pyridine-2-carboxylate and *n*-pentylamine (**2g**) by the literature procedure were identical to the data of **4c** obtained upon heating of 1-cyano-4-oxo-4*H*-quinolizine-3-diazonium tetrafluoroborate (**1a**) with excess *n*-pentylamine.

Conclusion

1-Cyano-4-oxo-4*H*-quinolizine-3-diazonium tetrafluoroborate (**1a**) and 4-oxo-4*H*-pyridino[1,2-*a*]pyrimidine-3-diazonium tetrafluoroborate (**1b**) exhibit typical reactivity towards secondary amines **2a – d** by formation of the corresponding *N*,*N*-dialkyl-*N*'-heteroaryl triazenes **3a – h** in high yields. On the other hand, unusual rearrangement into *N*-alkylpyridine-2-carboxamides **4a – c** took place when diazonium salt **1a** was heated with excess primary aliphatic amines **2e – g**.

Experimental Section

Melting points were determined on a Kofler micro hot stage. The ^{1}H NMR, ^{13}C NMR, HMBC, and NOESY spectra were obtained on a Bruker Avance DPX 300 at 300 MHz for ^{1}H and at 75.5 MHz for ^{13}C nucleus with [D_6]-DMSO as solvent and TMS as the internal standard. Mass spectra were recorded on an AutoSpecQ spectrometer and IR spectra on a Perkin-Elmer Spectrum BX FTIR spectrophotometer. Microanalyses were performed on a Perkin-Elmer CHN Analyser 2400. Column chromatography (CC) was performed on silica gel (Fluka, silica gel 60, 0.035 – 0.070 mm).

All starting materials were commercially available (in most cases from Fluka) and purified following standard techniques. The following compounds were prepared according to the literature procedures: 1-cyano-4-oxo-4*H*-quinolizine-3-diazonium tetrafluoroborate (**1a**) [8] and 4-oxo-4*H*-pyridino[1,2–*a*]pyrimidine-3-diazonium tetrafluoroborate (**1b**) [9].

*Synthesis of N-alkyl-N′-heteroaryltriazenes (***3a** – **h***)*

General procedure

A mixture of **1a** (0.100 g, 0.352 mmol) or **1b** (0.100 g, 0.385 mmol), acetonitrile (2 ml), and aliphatic amine **2** (2 equiv.) was stirred at r. t. for 12 – 48 h. Volatile components were evaporated *in vacuo*, and the residue was purified by column chromatography (EtOAc). Fractions containing the product were combined and evaporated *in vacuo* to give **3**.

The following compounds were prepared in this manner:

*1-Cyano-3-(3,3-diethyltriaz-1-enyl)-4H-quinolizin-4-one (***3a***)*

Prepared from compound **1a** and diethylamine (**2a**, 0.052 g, 0.70 mmol), 48 h, 93 mg (98%) of yellow solid. – M.p. 119 – 121 °C. – IR (KBr): $\nu = 2982, 2934, 2210$ (CN), 1680 (C=O), 1625, 1482, 1226, 761 cm^{-1}. – ^{1}H NMR ([D_6]-DMSO): $\delta = 1.23$ (6H, br s, $2 \times CH_2CH_3$), 3.79 (4H, q, $J = 7.2$ Hz, $2 \times CH_2CH_3$), 7.40 (1H, ddd, $J = 1.5, 6.8, 7.3$ Hz, 7–H), 7.79 – 7.91 (2H, m, 8–H, 9–H), 7.92 (1H, s, 2–H), 9.15 (1H, dd, $J = 1.1, 7.3$ Hz, 6–H). – ^{13}C NMR ($CDCl_3$): $\delta = 12.6, 18.7, 41.8, 44.9, 85.3, 116.6, 117.9, 123.7, 125.4, 128.9, 132.1, 133.7, 142.9, 155.5$. – MS (EI): $m/z = 269$ (M^+); MS (FAB): $m/z = 270$ (MH^+). – $C_{14}H_{15}N_5O \times 1/2$ H_2O (269.3): calcd. C 60.42, H 5.79, N 25.16; found C 60.74, H 5.54, N 24.76. – HRMS ($C_{14}H_{15}N_5O$): calcd. 269.127660; found 269.128350.

*1-Cyano-3-(pyrrolidin-1-yldiazenyl)-4H-quinolizin-4-one (***3b***)*

Prepared from compound **1a** and pyrrolidine (**2b**, 0.050 g, 0.70 mmol), 22 h, 87 mg (92%) of yellow solid. – M.p. 194 – 195 °C. – IR (KBr): $\nu = 2971, 2874, 2207$ (CN), 1680 (C=O), 1482, 1283, 761 cm^{-1}. – ^{1}H NMR ([D_6]-DMSO): $\delta = 1.99$ (4H, br s, $4 \times CH_2$), 3.60 (2H, br s, CH_2), 3.91 (2H, br s, CH_2), 7.40 (1H, ddd, $J = 1.5, 6.5, 7.1$ Hz, 7–H), 7.79 – 7.89 (2H, m, 8–H, 9–H), 7.90 (1H, s, 2–H), 9.15 (1H, dd, $J = 1.4, 7.1$ Hz, 6–H). – ^{13}C NMR ($CDCl_3$): $\delta = 24.1, 47.5, 52.0, 85.3, 116.7, 117.8, 123.7, 125.4, 129.0, 132.2, 133.7, 142.9, 155.4$. – MS (EI): $m/z = 267$ (M^+); MS (FAB): $m/z = 268$ (MH^+). – $C_{14}H_{13}N_5O \times 1/3$ H_2O (267.3): calcd. C 61.53, H 5.04, N 25.63; found C 61.53,

H 4.95, N 25.43. – HRMS ($C_{14}H_{13}N_5O$): calcd. 267.112010; found 267.112800.

*1-Cyano-3-(piperidin-1-yldiazenyl)-4H-quinolizin-4-one (**3c**)*

Prepared from compound **1** and piperidine (**2c**, 0.060 g, 0.70 mmol), 20 h, 82 mg (83%) of yellow solid. – M.p. 167 – 169 °C. – IR (KBr): $\nu = 2943$, 2853, 2210 (CN), 1680 (C=O), 1482, 1107, 761 cm^{-1}. – ^1H NMR ([D$_6$]-DMSO): $\delta = 1.67$ (6H, br s, $3 \times CH_2$), 3.81 (4H, br s, $2 \times CH_2$), 7.42 (1H, ddd, $J = 1.5$, 6.6, 7.1 Hz, 7–H), 7.81 – 7.92 (2H, m, 8–H, 9–H), 7.96 (1H, s, 2–H), 9.17 (1H, dd, $J = 1.3$, 7.1 Hz, 6–H). – ^{13}C NMR ($CDCl_3$): $\delta = 24.6$, 25.7, 31.4, 85.4, 116.8, 117.8, 123.7, 125.4, 129.0, 132.3, 133.2, 143.1, 155.5. – MS (EI): $m/z = 281$ (M^+). – $C_{15}H_{15}N_5O$ (281.3): calcd. C 64.04, H 5.37, N 24.90; found C 63.80, H 5.30, N 25.15. – HRMS ($C_{15}H_{15}N_5O$): calcd. 281.127660; found 281.128850.

*1-Cyano-3-(3,3-dicyclohexyltriaz-1-enyl)-4H-quinolizin-4-one (**3d**)*

Prepared from compound **1a** and dicyclohexylamine (**2d**, 0.127 g, 0.70 mmol), 12 h, 112 mg (84%) of yellow solid. – M.p. 202 – 203 °C. – IR (KBr): $\nu = 2926$, 2859, 2216 (CN), 1687 (C=O), 1418, 1196, 757 cm^{-1}. – ^1H NMR ([D$_6$]-DMSO): $\delta = 1.18 - 1.82$ (20H, m, $10 \times CH_2$), 3.68 (1H, br s, C*H*), 4.94 (1H, br s, C*H*), 7.39 (1H, ddd, $J = 1.5$, 6.8, 7.1 Hz, 7–H), 7.77 – 7.90 (2H, m, 8–H, 9–H), 7.88 (1H, s, 2–H), 9.14 (1H, dd, $J = 1.1$, 7.1 Hz, 6–H). – ^{13}C NMR ($CDCl_3$): $\delta = 25.7$, 25.9, 26.5, 30.1, 31.3, 35.0, 55.3, 58.6, 85.4, 116.6, 118.2, 123.6, 124.7, 128.7, 131.7, 134.4, 142.5, 155.5. – MS (EI): $m/z = 377$ (M^+); MS (FAB): $m/z = 378$ (MH^+). – $C_{22}H_{27}N_5O$ (377.5): calcd. C 70.00, H 7.21, N 18.55; found C 69.97, H 7.32, N 18.78. – HRMS ($C_{22}H_{27}N_5O$): calcd. 377.221561; found 377.222750.

*3-(3,3-Diethyltriaz-1-enyl)-4H-pyridino[1,2–a]pyrimidin-4-one (**3e**)*

Prepared from compound **1b** and diethylamine (**2a**, 0.056 g, 0.77 mmol), 48 h, 87 mg (92%) of yellow solid. – M.p. 90 – 92 °C. – IR (KBr): $\nu = 2973$, 1681 (C=O), 1632, 1482, 1241, 779 cm^{-1}. – ^1H NMR ([D$_6$]-DMSO): $\delta = 1.22$ (6H, t, $J = 7.1$ Hz, $2 \times CH_2CH_3$), 3.76 (4H, q, $J = 7.1$ Hz, $2 \times CH_2CH_3$), 7.33 (1H, ddd, $J = 1.5$, 6.4, 7.1 Hz, 7–H), 7.66 (1H, dd, $J = 1.5$, 9.1 Hz, 9–H), 7.83 (1H, ddd, $J = 1.5$, 6.4, 9.1 Hz, 8–H), 8.28 (1H, s, 2–H), 9.00 (1H, dd, $J = 1.5$, 7.1 Hz, 6–H). – ^{13}C NMR ($CDCl_3$): $\delta = 12.9$, 41.6, 48.8, 115.6, 126.9, 127.7, 130.5, 134.0, 142.3, 148.7, 155.1. – MS (EI): $m/z = 245$ (M^+); MS (FAB): $m/z = 246$ (MH^+). – $C_{12}H_{15}N_5O$ (245.3): calcd. C 58.76, H 6.16, N 28.55; found C 59.10, H 6.25, N 26.68. – HRMS ($C_{12}H_{15}N_5O$): calcd. 245.127660; found 245.128250.

*3-(Pyrrolidin-1-yldiazenyl)-4H-pyridino[1,2–a]pyrimidin-4-one (**3f**)*

Prepared from compound **1b** and pyrrolidine (**2b**, 0.055 g, 0.77 mmol), 24 h, 86 mg (86%) of yellow solid. – M.p. 141 – 143 °C. – IR (KBr): $\nu = 2868$, 1675 (C=O), 1628, 1398, 1329, 1237 cm^{-1}. – ^1H NMR ([D$_6$]-DMSO): $\delta = 1.98$ (4H, t, $J = 6.8$ Hz, $2 \times CH_2$), 3.64 – 3.85 (4H, m, $2 \times CH_2$), 7.32 (1H, ddd, $J = 1.5$, 6.4, 7.1 Hz, 7–H), 7.66 (1H, dd, $J = 1.5$, 9.1 Hz, 9–H), 7.83 (1H, ddd, $J = 1.5$, 6.4, 9.1 Hz, 8–H), 8.29 (1H, s, 2–H), 9.00 (1H, dd, $J = 1.5$, 7.1 Hz, 6–H). – ^{13}C NMR ($CDCl_3$): $\delta = 24.1$, 47.3, 51.5, 115.7, 126.8, 127.8, 130.5, 134.1, 142.5, 148.7, 155.1. – MS (EI): $m/z = 243$ (M^+); MS (FAB): $m/z = 244$ (MH^+). – $C_{12}H_{13}N_5O \times 1.5H_2O$ (243.3): calcd. C 53.32, H 5.97, N 25.91; found C 53.41, H 5.63, N 25.48. – HRMS ($C_{12}H_{13}N_5O$): calcd. 243.112010; found 243.112850.

*3-(Piperidin-1-yldiazenyl)-4H-pyridino[1,2–a]pyrimidin-4-one (**3g**)*

Prepared from compound **1b** and piperidine (**2c**, 0.066 g, 0.77 mmol), 22 h, 80 mg (81%) of yellow solid. – M.p. 166 – 168 °C. – IR (KBr): $\nu = 2938$, 2858, 1691 (C=O), 1476, 1182, 777 cm^{-1}. – ^1H NMR ([D$_6$]-DMSO): $\delta = 1.66$ (6H, br s, $3 \times CH_2$), 3.77 (4H, br s, $2 \times CH_2$), 7.34 (1H, ddd, $J = 1.5$, 6.8, 7.1 Hz, 7–H), 7.68 (1H, dd, $J = 1.5$, 8.9 Hz, 9–H), 7.85 (1H, ddd, $J = 1.5$, 6.8, 8.9 Hz, 8–H), 8.32 (1H, s, 2–H), 9.02 (1H, dd, $J = 1.5$, 7.1 Hz, 6–H). – ^{13}C NMR ($CDCl_3$): $\delta = 24.6$, 25.6, 31.3, 115.8, 126.9, 127.8, 130.0, 134.3, 142.3, 148.9, 155.1. – MS (EI): $m/z = 257$ (M^+); MS (FAB): $m/z = 258$ (MH^+). – $C_{13}H_{15}N_5O$ (257.3): calcd. C 60.69, H 5.88, N 27.22; found C 60.93, H 5.86, N 27.52. – HRMS ($C_{13}H_{15}N_5O$): calcd. 257.127660; found 257.128300.

*3-(3,3-Dicyclohexyltriaz-1-enyl)-4H-pyridino[1,2–a]pyrimidin-4-one (**3d**)*

Prepared from compound **1b** and dicyclohexylamine (**2d**, 0.140 g, 0.77 mmol), 17 h, 120 mg (88%) of yellow solid. – M.p. 120 – 124 °C. – IR (KBr): $\nu = 2926$, 2857, 1700 (C=O), 1683, 1407, 1194, 771 cm^{-1}. – ^1H NMR ([D$_6$]-DMSO): $\delta = 1.20 - 1.81$ (20H, m, $10 \times CH_2$), 3.65 (2H, br s, C*H*), 4.94 (1H, br s, C*H*), 7.32 (1H, ddd, $J = 1.5$, 6.8, 7.1 Hz, 7–H), 7.66 (1H, dd, $J = 1.5$, 9.0 Hz, 9–H), 7.82 (1H, ddd, $J = 1.5$, 6.8, 9.0 Hz, 8–H), 8.24 (1H, s, 2–H), 8.99 (1H, dd, $J = 1.5$, 7.1 Hz, 6–H). – ^{13}C NMR ($CDCl_3$): $\delta = 24.9$, 25.1, 26.0, 26.4, 30.1, 34.9, 54.7, 58.2, 115.8, 126.8, 127.6, 131.2, 133.8, 141.9, 148.4, 155.3. – MS (EI): $m/z = 353$ (M^+); MS (FAB): $m/z = 354$ (MH^+). – $C_{20}H_{27}N_5O$ (353.5): calcd. C 63.13, H 7.95, N 18.41; found C 63.36, H 7.80, N 17.47. – HRMS ($C_{20}H_{27}N_5O$): calcd. 353.221561; found 353.222456.

*Synthesis of picolinic acid N-alkylcarboxamides (***4a** – **c***)*

General procedure

A mixture of **1a** (0.100 g, 0.352 mmol), acetonitrile (3 ml), and aliphatic amine **2e – g** (3 ml, excess) was heated at 60 °C for 25 – 30 h. Volatile components were evaporated *in vacuo*, and the residue was purified by column chromatography (*n*-hexane–EtOAc, 1:1). Fractions containing the product were combined and evaporated *in vacuo* to give **4**.

The following compounds were prepared in this manner:

*N-Propyl pyridine-2-carboxamide (***4a***)*

Prepared from compound **1a** and *n*-propylamine (**2e**), 25 h, 31 mg (54%) of yellow oil. – IR (KBr): $\nu = 3389$, 2964, 2932, 2875, 1670 (C=O) cm^{-1}. – ^{1}H NMR ($CDCl_3$): $\delta =$ 0.98 (3H, t, $J = 7.5$ Hz, $CH_2CH_2CH_3$), 1.61 – 1.69 (2H, m, $CH_2CH_2CH_3$), 3.43 (2H, td, $J = 6.8$, 7.5 Hz, $CH_2CH_2CH_3$), 7.39 (1H, ddd, $J = 1.4$, 4.9, 7.5 Hz, 5–H), 7.82 (1H, ddd, $J = 1.5$, 7.5, 8.7 Hz, 4–H), 8.07 (1H, br s, N*H*), 8.19 (1H, ddd, $J = 0.8$, 1.4, 8.7 Hz, 3–H), 8.52 (1H, ddd, $J = 0.8$, 1.5, 4.9 Hz, 6–H). – ^{13}C NMR ($CDCl_3$): $\delta = 11.9$, 23.3, 41.5, 122.6, 126.4, 137.7, 148.4, 150.5, 164.7. – MS (EI): $m/z =$ 164 (M^+); MS (FAB): $m/z = 165$ (MH^+). – $C_9H_{12}N_2O \times 1/5$ H_2O (164.2): calcd. C 64.42, H 7.45, N 16.69; found C 64.58, H 7.69, N 16.28. – HRMS ($C_9H_{12}N_2O$): calcd. 164.094963; found 164.095650.

*N-Butyl pyridine-2-carboxamide (***4b***)*

Prepared from compound **1a** and *n*-butylamine (**2f**), 28 h, 27 mg (43%) of yellow oil. – IR (KBr): $\nu = 3390$, 2959, 2932, 2868, 1670 (C=O), 1528 cm^{-1}. – ^{1}H NMR ($CDCl_3$): $\delta = 0.95$ (3H, t, $J = 7.2$ Hz, $CH_2CH_2CH_2CH_3$), 1.39 – 1.49 (2H, m, $CH_2CH_2CH_2CH_3$), 1.57 – 1.67 (2H, m, $CH_2CH_2CH_2CH_3$), 3.47 (2H, td, $J = 6.8$, 7.2 Hz, $CH_2CH_2CH_2CH_3$), 7.40 (1H, ddd, $J = 1.2$, 4.9, 7.5 Hz, 5–H), 7.83 (1H, ddd, $J = 1.5$, 7.5, 8.7 Hz, 4–H), 8.04 (1H, br s, N*H*), 8.19 (1H, ddd, $J = 0.8$, 1.2, 8.7 Hz, 3–H), 8.53 (1H, ddd, $J = 0.8$, 1.5, 4.9 Hz, 6–H). – ^{13}C NMR ($CDCl_3$): $\delta = 14.2$, 20.6, 32.1, 39.5, 122.6, 126.4, 137.7, 148.4, 150.5, 164.6. – MS (EI): $m/z = 178$ (M^+); MS (FAB): $m/z = 179$ (MH^+). – $C_{10}H_{14}N_2O \times 1/6$ H_2O (178.2): calcd. C 66.27, H 7.97, N 15.46; found C 66.41, H 8.30, N 15.37. – HRMS ($C_{10}H_{14}N_2O$): calcd. 178.110613; found 178.111250.

*N-Pentyl pyridine-2-carboxamide (***4c***)*

Prepared from compound **1a** and *n*-pentylamine (**2g**), 30 h, 30 mg (43%) of yellow oil. – IR (KBr): $\nu = 3389$, 2957, 2930, 2860, 1670 (C=O), 1529 cm^{-1}. – ^{1}H NMR ($CDCl_3$): $\delta = 0.90$ (3H, t, $J = 7.2$ Hz, $CH_2CH_2CH_2CH_2CH_3$), 1.33 – 1.39 (4H, m, $CH_2CH_2CH_2CH_2CH_3$), 1.56 – 1.67 (2H, m, $CH_2CH_2CH_2CH_2CH_3$), 3.45 (2H, td, $J = 6.7$, 7.2 Hz, $CH_2CH_2CH_2CH_2CH_3$), 7.39 (1H, ddd, $J = 1.4$, 4.9, 7.5 Hz, 5–H), 7.82 (1H, ddd, $J = 1.5$, 7.5, 8.9 Hz, 4–H), 8.04 (1H, br s, N*H*), 8.18 (1H, ddd, $J = 0.8$, 1.4, 8.9 Hz, 3–H), 8.52 (1H, ddd, $J = 0.8$, 1.5, 4.9 Hz, 6–H). – ^{13}C NMR ($CDCl_3$): $\delta = 14.4$, 22.8, 29.5, 29.7, 39.8, 122.6, 126.4, 137.7, 148.4, 150.5, 164.6. – MS (EI): $m/z = 192$ (M^+); MS (FAB): $m/z = 193$ (MH^+). – $C_{11}H_{16}N_2O \times 1/6$ H_2O (192.3): calcd. C 67.66, H 8.43, N 14.35; found C 68.02, H 8.55, N 14.19. – HRMS ($C_{11}H_{16}N_2O$): calcd. 192.126263; found 192.127050.

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