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Synthesis of nitro pyrido- and dipyrido[1,4]oxazines

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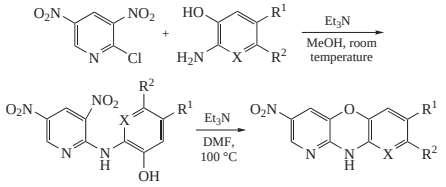
3-Nitro-10*H*-pyrido[3,2-*b*][1,4]benzoxazines and first representative of a new heterocyclic system, 10*H*-dipyrido[2,3-*e*:3′,2′-*b*][1,4]oxazine, were obtained by reaction of 2-chloro-3,5-dinitropyridine with various *o*-aminophenols followed by intramolecular substitution of the nitro group.

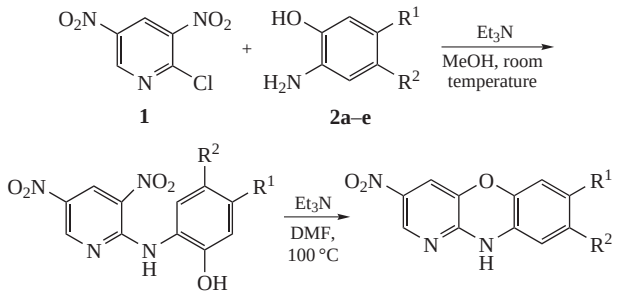


Nitro(het)arenes represent a unique class of aromatic compounds possessing dual reactivity towards reactions with nucleophiles. They undergo nucleophilic aromatic substitution (S_NAr) when the nitro group acts as one of the best nucleofugal groups as well as activating groups for the substitution of other types of nucleofugs, *e.g.* halogens.[1] At the same time, nitro(het)arenes also tend to additions to the aromatic ring (for example, S_N^HAr).[2]

This work is a part of our ongoing research on application of available (het)aromatic nitro compounds as precursors of various fused heterosystems.[3] Here we report on reactions of 2-chloro-3,5-dinitropyridine with different *o*-aminophenols. Such interactions may lead to nitro azaphenoxazines. Phenoxazines are tricyclic heterocycles which have found use as therapeutic agents and scaffolds in medicinal chemistry.[4] For example, phenoxazine moiety is a part of Dactinomycin, a naturally occurring antibiotic.[5] Due to their photophysical properties,[6] phenoxazines have been applied as dyes in dye-sensitized solar cells[7] and chemosensors.[8] Some azaphenoxazines (including nitro derivatives) were used in therapy and diagnostics of neurodegenerative disorders, such as Parkinson's and Alzheimer's diseases,[9,10] however, the synthesis of these compounds has not been reported.

We have found that reaction of 2-chloro-3,5-dinitropyridine **1** with *o*-aminophenols **2a–e** in methanol in the presence of Et_3N afforded compounds **3a–e**, the products of replacement of chlorine atoms with amino group of *o*-aminophenol (Scheme 1).†

Heating of **3a–e** in DMF in the presence of base causes the intramolecular nucleophilic substitution of *ortho*-positioned nitro group leading to tricycles **4a–e** (Scheme 1).



1 **2a–e**

3a–e, 86–93% **4a–e**, 83–95%

a $R^1 = R^2 = H$ **d** $R^1 = H$, $R^2 = Cl$
b $R^1 = Me$, $R^2 = H$ **e** $R^1 = H$, $R^2 = Br$
c $R^1 = H$, $R^2 = Me$

Scheme 1

† All chemicals were of commercial grade and used directly without purification. Melting points were measured on a Stuart SMP20 apparatus. The ^1H and ^{13}C NMR spectra were recorded from solutions in DMSO-d_6 with a Bruker Avance 300 FT-spectrometer (300 and 75 MHz respectively). Chemical shifts are reported in ppm downfield from TMS. All reactions were monitored by TLC analysis using ALUGRAM SIL G/UV254 plates, which were visualized by UV light.

General procedure for the synthesis of **3a–e**, **7**. Triethylamine (0.42 ml, 3 mmol) was added to a solution of **1** (0.6 g, 1 mmol) and corresponding *o*-aminophenol (3 mmol) in MeOH (30 ml). The reaction mixture was stirred at room temperature for 1–2 h (TLC monitoring). Then the mixture was poured into water (150 ml) and acidified with HCl to pH 5–6. The precipitate was filtered off, washed with water and dried in air.

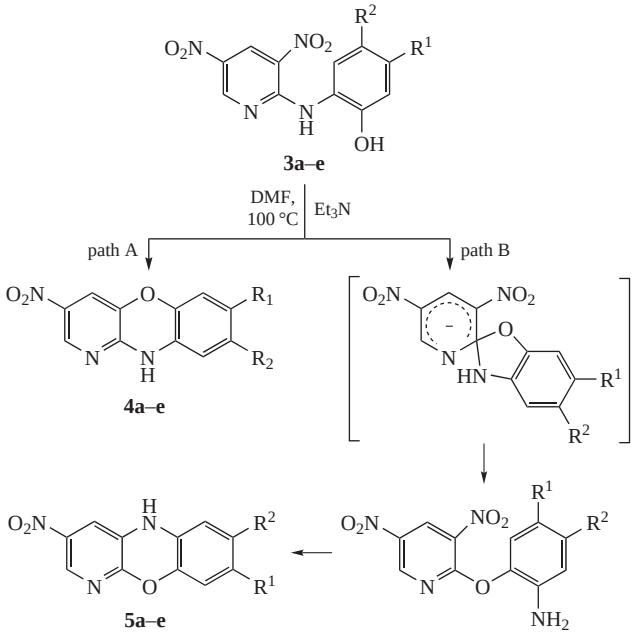
2-[(3,5-Dinitropyridin-2-yl)amino]phenol **3a**. Yield 93%, mp 240–241 °C (lit.,[13] 240–241 °C). ^1H NMR, δ: 6.84–7.11 (m, 3H), 8.25 (d, 2H, *J* 7.7 Hz), 9.05 (s, 1H), 9.32 (s, 1H), 10.43 (s, 1H), 10.92 (s, 1H). ^{13}C NMR, δ: 150.70, 150.52, 148.45, 134.50, 131.02, 127.23, 126.00, 125.34, 122.40, 119.18, 115.05. Found (%): C, 47.94; H, 2.68; N, 20.72. Calc. for $C_{11}H_8N_4O_5$ (%): C, 47.83; H, 2.92; N, 20.28.

2-[(3,5-Dinitropyridin-2-yl)amino]-5-methylphenol **3b**. Yield 86%, mp 232–233 °C. ^1H NMR, δ: 2.27 (s, 3H), 6.68 (d, 1H, *J* 8.2 Hz), 6.78 (s, 1H), 8.10 (d, 1H, *J* 8.2 Hz), 9.05 (d, 1H, *J* 2.0 Hz), 9.27 (d, 1H, *J* 2.3 Hz), 10.17 (s, 1H), 10.82 (s, 1H). ^{13}C NMR, δ: 150.49, 148.27, 135.53, 134.23, 130.90, 127.01, 122.81, 122.19, 121.98, 119.72, 115.56, 20.74. Found (%): C, 49.70; H, 3.30; N, 19.19. Calc. for $C_{12}H_{10}N_4O_5$ (%): C, 49.66; H, 3.47; N, 19.30.

2-[(3,5-Ddinitropyridin-2-yl)amino]-4-methylphenol **3c**. Yield 90%, mp 234–235 °C. ^1H NMR, δ: 2.27 (s, 3H), 6.88 (s, 2H), 8.08 (s, 1H), 9.07 (s, 1H), 9.34 (s, 1H), 10.18 (s, 1H), 10.89 (s, 1H). ^{13}C NMR, δ: 150.54, 146.14, 134.39, 130.96, 127.87, 127.12, 126.34, 125.05, 122.64, 114.79, 20.58. Found (%): C, 49.52; H, 3.65; N, 19.12. Calc. for $C_{12}H_{10}N_4O_5$ (%): C, 49.66; H, 3.47; N, 19.30.

4-Chloro-2-[(3,5-dinitropyridin-2-yl)amino]phenol **3d**. Yield 87%, mp 250–251 °C. ^1H NMR, δ: 6.95 (d, 1H, *J* 8.5 Hz), 7.10 (d, 1H, *J* 8.3 Hz), 8.38 (s, 1H), 9.07 (s, 1H), 9.38 (s, 1H), 10.79 (s, 1H), 10.90 (s, 1H). ^{13}C NMR, δ: 150.43, 146.98, 134.95, 130.93, 127.54, 126.57, 125.04, 122.53, 121.06, 115.93. Found (%): C, 42.68; H, 2.12; Cl, 11.84; N, 17.99. Calc. for $C_{11}H_7ClN_4O_5$ (%): C, 42.53; H, 2.27; Cl, 11.41; N, 18.04.

It is known[11] that such reactions can in principle give two isomeric products **4** or **5** (Scheme 2). In the case of path A the substitution of *ortho*-NO_2 occurs under the action of phenolate anion and tricycles **4** are formed. Product **5** can be formed as a result of Smiles rearrangement (path B). Such transformations have been reported for the synthesis of phenoxazines on the basis of nitroarenes.[12]



Scheme 2

4-Bromo-2-[(3,5-dinitropyridin-2-yl)amino]phenol **3e**. Yield 91%, mp 247–248 °C. ^{1}H NMR, δ: 6.92 (d, 1H, *J* 8.6 Hz), 7.20 (dd, 1H, *J* 8.4 and 2.2 Hz), 8.49 (d, 1H, *J* 2.0 Hz), 9.07 (d, 1H, *J* 2.4 Hz), 9.39 (d, 1H, *J* 2.4 Hz), 10.85 (s, 1H), 10.91 (s, 1H). ^{13}C NMR, δ: 150.44, 147.44, 134.94, 130.94, 128.04, 127.55, 126.95, 123.96, 116.53, 109.97. Found (%): C, 37.55; H, 1.90; Br, 22.43; N, 15.69. Calc. for $C_{11}H_7BrN_4O_5$ (%): C, 37.21; H, 1.99; Br, 22.50; N, 15.78.

2-[(3,5-Dinitropyridin-2-yl)amino]pyridin-3-ol **7**. Yield 55%, mp 245–246 °C. ^{1}H NMR, δ: 6.87–7.09 (m, 3H), 8.27 (d, 2H, *J* 7.6 Hz), 9.07 (s, 1H), 9.33 (s, 1H), 10.44 (s, 1H), 10.93 (s, 1H). ^{13}C NMR, δ: 150.67, 150.50, 148.42, 134.49, 131.00, 127.21, 125.97, 125.33, 122.35, 119.17, 115.03. Found (%): C, 43.43; H, 2.37; N, 25.10. Calc. for $C_{10}H_7N_5O_5$ (%): C, 43.33; H, 2.55; N, 25.27.

General procedure for the synthesis of **4a–e**, **8**. Triethylamine (0.14 ml, 1 mmol) was added to a solution of compound **3a–e** or **7** in DMF (15 ml). The reaction mixture was kept at 100 °C for 4–8 h (TLC monitoring). Then the mixture was poured into water (150 ml) and acidified with HCl to pH 1–2. The precipitate that formed was filtered off, washed with water and dried in air.

*3-Nitro-10*H*-pyrido[3,2-*b*][1,4]benzoxazine* **4a**. Yield 83%, mp 267–268 °C (lit.,[13] 275–276 °C). ^{1}H NMR, δ: 6.65–6.87 (m, 4H), 7.44 (d, 1H, *J* 2.1 Hz), 8.45 (d, 1H, *J* 2.2 Hz), 10.35 (s, 1H). ^{13}C NMR, δ: 150.55, 141.98, 140.62, 138.56, 137.93, 128.62, 124.70, 123.57, 115.28, 115.22, 113.92. Found (%): C, 57.50; H, 3.01; N, 18.52. Calc. for $C_{11}H_7N_3O_3$ (%): C, 57.65; H, 3.08; N, 18.33.

*7-Methyl-3-nitro-10*H*-pyrido[3,2-*b*][1,4]benzoxazine* **4b**. Yield 89%, mp 257–258 °C. ^{1}H NMR, δ: 2.14 (s, 3H), 6.56–6.73 (m, 3H), 7.44 (s, 1H), 8.46 (s, 1H), 10.30 (br. s, 1H). ^{13}C NMR, δ: 150.52, 141.69, 140.67, 138.38, 137.60, 133.14, 125.84, 124.74, 115.78, 114.95, 113.73, 20.13. Found (%): C, 59.50; H, 3.51; N, 17.52. Calc. for $C_{12}H_9N_3O_3$ (%): C, 59.26; H, 3.73; N, 17.28.

*8-Methyl-3-nitro-10*H*-pyrido[3,2-*b*][1,4]benzoxazine* **4c**. Yield 88%, mp 277–278 °C. ^{1}H NMR, δ: 2.15 (s, 3H), 6.51–6.64 (m, 3H), 7.42 (s, 1H), 8.45 (s, 1H),10.20 (br. s, 1H). ^{13}C NMR, δ: 150.49, 140.41, 139.79, 138.58, 137.84, 133.79, 128.15, 123.62, 115.57, 114.94, 113.72, 20.14. Found (%): C, 59.63; H, 3.25; N, 17.58. Calc. for $C_{12}H_9N_3O_3$ (%): C, 59.26; H, 3.73; N, 17.28.

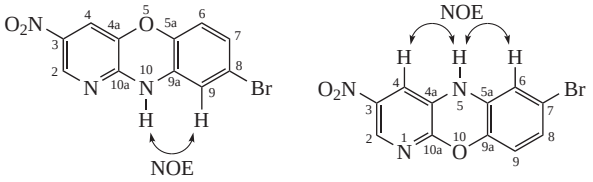


Figure 1 Cross-peak interaction of protons in isomeric **4e** and **5e**.

To the best of our knowledge the only azaphenoxazine **4a** has been described so far.[13] It was synthesized in a manner similar to indicated in Scheme 1, however its structure was assigned based on elemental analysis and ^{1}H NMR spectrum.† At the same time, these data are insufficient to distinguish **4a** from its isomer **5a**. We carried out a detailed study of the structures of compounds **4** using various NMR experiments. For example, ^{1}H-^{1}H NOESY spectrum of **4e** contains characteristic cross-peak corresponding to the interaction of spatially close H^9 and NH protons (Figure 1).

In case of Smiles rearrangement (formation of compound **5e**) two cross-peaks are expected to appear in NOESY spectrum, corresponding to the interaction of NH proton with H^4 and H^6. These data allowed us to unambiguously confirm the structure of compounds **4**.

In addition, the structures of **3a** and **4a** were proved by single-crystal X-ray diffraction studies.‡ The structure of **3a** (Figure 2)

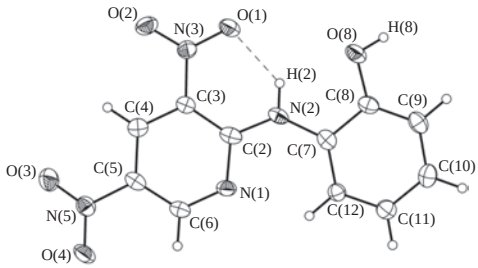


Figure 2 General view of one of three independent molecules in crystal of **3a** in thermal ellipsoid representation at 50% probability level. Selected bond lengths (Å): O(1)–N(3) 1.250(4), O(2)–N(3) 1.224(4), O(3)–N(5) 1.213(4), O(4)–N(5) 1.232(4), O(8)–C(8) 1.369(5), N(1)–C(6) 1.326(5), N(1)–C(2) 1.364(5), N(2)–C(2) 1.342(5), N(2)–C(7) 1.405(5), N(3)–C(3) 1.446(5), N(5)–C(5) 1.452(5), C(2)–C(3) 1.424(5), C(3)–C(4) 1.379(5), C(4)–C(5) 1.384(5), C(5)–C(6) 1.376(6), C(7)–C(12) 1.395(5), C(7)–C(8) 1.408(5), C(8)–C(9) 1.369(6), C(9)–C(10) 1.392(6), C(10)–C(11) 1.392(6), C(11)–C(12) 1.366(5). Corresponding bond lengths in two other independent molecules are very close to given values.

*8-Chloro-3-nitro-10*H*-pyrido[3,2-*b*][1,4]benzoxazine* **4d**. Yield 95%, mp 223–224 °C. ^{1}H NMR, δ: 6.61–6.71 (m, 3H), 7.41 (s, 1H), 8.41 (s, 1H), 10.25 (br. s, 1H). ^{13}C NMR, δ: 149.79, 140.89, 140.38, 138.39, 138.29, 130.29, 128.04, 122.55, 116.54, 114.44, 114.24.

*8-Bromo-3-nitro-10*H*-pyrido[3,2-*b*][1,4]benzoxazine* **4e**. Yield 79%, mp 253–254 °C. ^{1}H NMR, δ: 6.69–6.91 (m, 3H), 7.49 (s, 1H, H-4), 8.48 (s, 1H, H-2), 10.41 (br. s, 1H, NH). ^{13}C NMR, δ: 150.40 (C-3), 141.95 (C-9a), 141.02 (C-2), 138.96 (C-10a), 138.82 (C-4a), 131.17 (C-5a), 126.11 (C-7), 117.70 (C-9), 117.57 (C-6), 116.29 (C-8), 114.87 (C-4). Found (%): C, 42.99; H, 2.01; Br, 25.81; N, 13.52. Calc. for $C_{11}H_6BrN_3O_3$ (%): C, 42.88; H, 1.96; Br, 25.94; N, 13.64.

*3-Nitro-10*H*-dipyrido[2,3-*e*:3′,2′-*b*][1,4]oxazine* **8**. Yield 80%, mp 264–265 °C. ^{1}H NMR, δ: 6.76 (s, 1H), 7.04 (d, 1H, *J* 2.1 Hz), 7.52 (s, 1H), 7.67 (s, 1H), 8.48 (s, 1H), 10.80 (s, 1H). ^{13}C NMR, δ: 150.71, 143.24, 142.49, 140.25, 138.79, 138.61, 121.64, 119.31, 114.50. Found (%): C, 52.50; H, 2.22; N, 24.52. Calc. for $C_{10}H_6N_4O_3$ (%): C, 52.18; H, 2.63; N, 24.34.

‡ *Crystallographic data.*

For **3a**: crystals are monoclinic, space group $P2_1/c$, a = 6.96480(10), b = 11.2318(2) and c = 43.2214(7) Å, β = 92.7800(10)°, V = 3377.11(9) Å^3, Z = 12 (Z' = 3), d_{calc} = 1.630 g cm^{-3}, R_1 = 0.0751 [for 5841 reflections with $I > 2\sigma(I)$], wR_2 = 0.1785, GOF = 1.059.

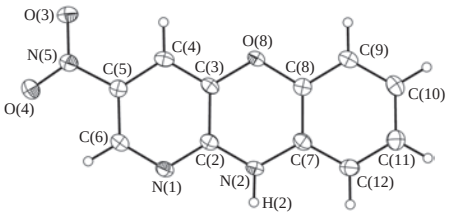
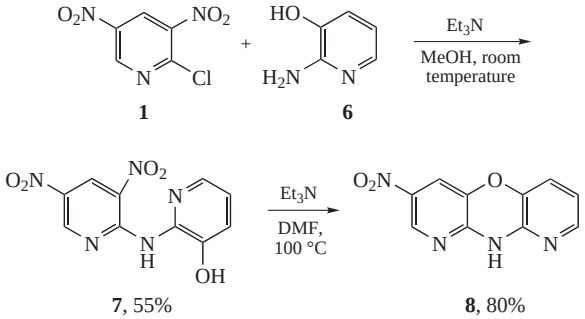


Figure 3 General view of **4a** in crystal in thermal ellipsoid representation at 50% probability level. Selected bond lengths (Å): O(3)–N(5) 1.2337(14), O(4)–N(5) 1.2278(14), O(8)–C(3) 1.3755(15), O(8)–C(8) 1.3961(16), N(1)–C(2) 1.3403(16), N(1)–C(6) 1.3430(17), N(2)–C(2) 1.3488(17), N(2)–C(7) 1.4019(16), N(5)–C(5) 1.4458(17), C(2)–C(3) 1.4253(17), C(3)–C(4) 1.3609(19), C(4)–C(5) 1.4055(17), C(5)–C(6) 1.3751(18), C(7)–C(12) 1.3864(19), C(7)–C(8) 1.3951(18), C(8)–C(9) 1.3773(18), C(9)–C(10) 1.390(2), C(10)–C(11) 1.3862(19), C(11)–C(12) 1.3879(18).

contains three independent molecules in the unit cell. These molecules are almost planar, except for out-of-plane rotation of nitro groups. Relative orientation of pyridine and phenyl rings is fixed by intramolecular N(2)–H(2)···O(1) hydrogen bond [N···O 2.633(4), 2.653(4) and 2.637(4) Å]. Intramolecular N(2)–H(2)···O(8) hydrogen bond with oxygen atom of hydroxyl group [N···O 2.577(4), 2.582(4) and 2.579(4) Å] can also be considered, but the corresponding five-membered H-bonded ring is not energetically favorable. Hydrogen atoms of hydroxyl groups in **3a** participate in relatively weak intermolecular H-bonds with oxygen atoms of nitro groups. The heterocyclic fragment in **4a** (Figure 3) is virtually planar. As in case of **4a**, the bond N(2)–C(2) is shorter than N(2)–C(7) by *ca*. 0.05 Å that implies more effective conjugation of the lone pair of the nitrogen atom with π-system of the pyridine ring than with one of the phenyl ring. Small changes in the bond length distribution are expected in **4a** comparing to **3a**, as the central ring in the former in not aromatic. The difference in bond lengths is also observed for O(8)–C(3) and O(8)–C(8) bonds in **4a**, the latter being *ca*. 0.02 Å shorter. Hydrogen atom of amino group in **4a** participates in intermolecular N–H···N hydrogen bond with nitrogen atom of pyridine ring [N···N 2.9969(15) Å], connecting molecules into centrosymmetric dimers.

Pyridine analogue of *o*-aminophenols, 2-aminopyridin-3-ol **6**, reacts with chloride **1** in the similar manner. In this case the formation of new hetrerocyclic system, 3-nitro-10*H*-dipyrido-[2,3-*e*:3′,2′-*b*][1,4]oxazine **8** occurs (Scheme 3).

In conclusion, we accessed a series of new 3-nitro-10*H*-pyrido-[3,2-*b*][1,4]benzoxazines **4a**–**e** as well as representative of new heterocyclic system, 10*H*-dipyrido[2,3-*e*:3′,2′-*b*][1,4]oxazine **8**. Such compounds are analogues of anti-neurodegenerative drugs. Moreover, the products obtained possess a broad potential for further functionalizations such as cycloaddition reactions, reductions, oxidative and vicarious nucleophilic substitution of hydrogen, *etc*.[1,15]



Scheme 3

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For **4a**: crystals are monoclinic, space group $P2_1/n$, a = 5.62730(10), b = 8.1437(2) and c = 20.7305(5) Å, β = 96.5350(10)°, V = 943.84(4) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.613 g cm^{-3}, R_1 = 0.0348 [for 1530 reflections with $I > 2\sigma(I)$], wR_2 = 0.0991, GOF = 1.028.

Both experiments were performed on a Bruker Apex DUO diffractometer at 120 K using CuKα radiation (λ = 1.54178 Å). The structures were solved by direct methods and refined by full-matrix least-squares technique against F^2_{hkl} in anisotropic approximation. Hydrogen atoms bonded to carbon atoms were placed into calculated positions and refined in riding model with U_{iso}(H) = 1.2U_{eq}(C), hydrogen atoms bonded to nitrogen and oxygen atoms were found from difference Fourier synthesis and refined in isotropic approximation. All calculations were performed using SHELX software package.[14]

CCDC 1455656 and 1455657 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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