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NITROGEN-CONTAINING HETEROCYCLIC *O*-, AND *S*-NUCLEOPHILES IN REACTIONS WITH 4-NITROPHTHALONITRILE AND 4-BROMO-5-NITROPHTHALONITRILE

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Authors developed a new method for the synthesis of mono- and disubstituted ortho-dicarbonitriles containing 5- and 6-membered heterocyclic moieties based on the S_NAr-reaction between 4-nitrophthalonitrile, 4-bromo-5-nitrophthalonitrile and phenols (thiols) containing various heterocyclic systems.

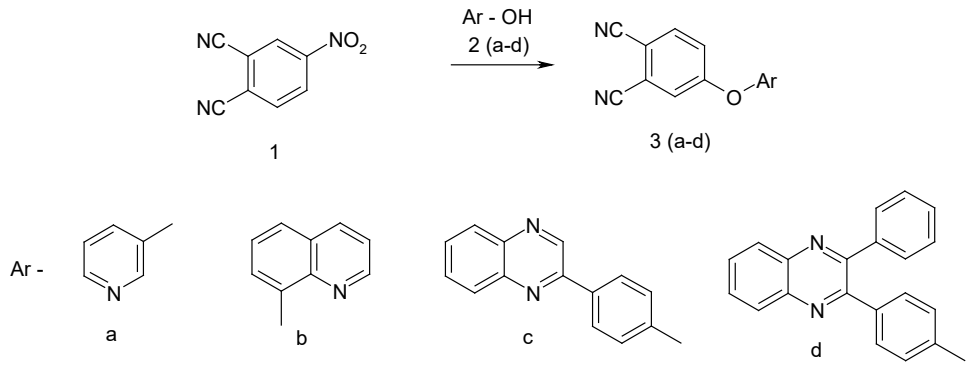
The activated aromatic nucleophilic substitution reaction (S_NAr reaction) is one of the most widespread and well studied by chemists [1]. Many examples of halogen atom and/or nitro group substitution reactions in electron acceptor group-activated aromatic systems under the action of mono- and bifunctional *O*-, *S*-, *N*-nucleophiles have been described in the scientific literature [2-6].

The substituted *ortho*-dicarbonitriles are precursors for phthalocyanines [7-9], hexazocyclanes [10] and some other compounds containing anhydride, imide, isoindoline and tetrazole fragments, which are widely used in production of dyes, polyetherimides, pharmaceuticals and biologically active compounds [11-17].

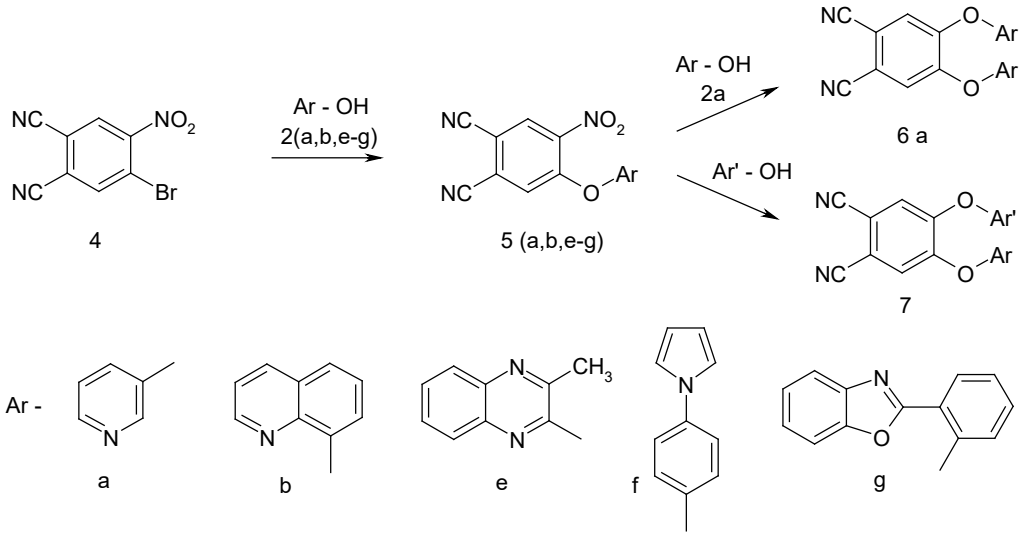
This work shows the new possibilities of this reaction, exemplified by the interaction of 4-nitrophthalonitrile and 4-bromo-5-nitrophthalonitrile with a number of nitrogen-bearing heterocyclic *O*-, and *S*-nucleophiles. The resulting compounds are new and have never been referenced before. Both of these substrates contain a large number of electron acceptor groups. According to many papers [1], such configuration of substituents in the benzene ring reduces the electron density in the considered aromatic substrate systems and facilitates the nucleophilic attack by proton-donor nucleophiles on the carbon atoms connected with nucleofugal groups and results to the formation of relatively stable intermediates.

We have used two approaches to carry out the reactions of 4-nitrophthalonitrile **1** with *O*- and *S*-nucleophiles. We obtained the best results by the reaction in anhydrous DMF for strongly acidic phenols **2a** containing electron acceptor substituents. For weak acidic reagents **2 (b-d)** it is better to use the binary solvent DMF-H_2O. In both cases, K_2CO_3 was used as the deprotonating agent in the presence of which the reactive nucleophilic complex was generated

in situ, as it is available and provides a comparatively high speed of the process. The reaction of 4-nitrophthalonitrile with thiophenols is proceeding easier [18].



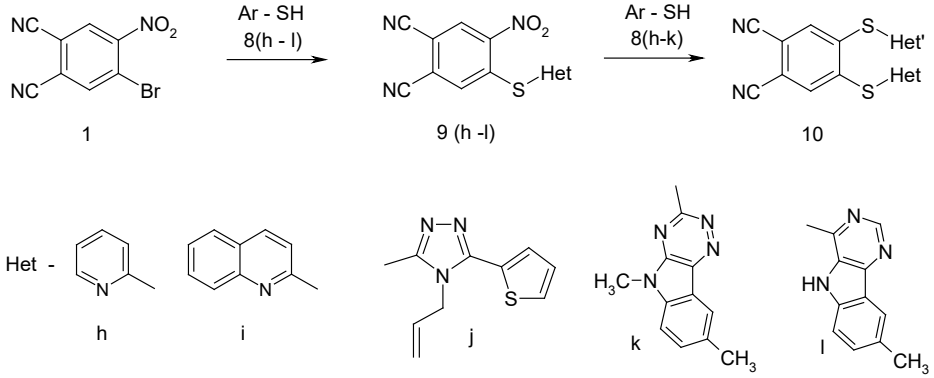
4-bromo-5-nitrophthalonitrile is more reactive than 4-nitrophthalonitrile **1** in the S_NAr reaction due to the high mobility of the bromine atom. It was confirmed by the reaction with pyridine-3-ol **2a**, quinoline-8-ol **2b**and other **2(e-g)**. The bromine substitution reaction with heterocyclic *O*-nucleophiles **2(a, b, e-g)** proceeded successfully in anhydrous DMF at room temperature and gave good yield of monosubstitution products **5(a, b, e-g)**.



The synthesized 4-heteryloxy-5-nitrophthalonitriles **5(a, b, e-g)** contain the activated nitro group, which at higher temperature can also enter into nucleophilic substitution reactions to form the corresponding symmetrical dihydyldioxyphthalonitriles, e.g. **6a** or any other asymmetrical combination of substituents in product **7**. In order to achieve this, it is sufficient to add equimolar quantities of the respective phenol and potassium carbonate to the reaction mixture at the end of the reaction and continue stirring at a higher temperature.

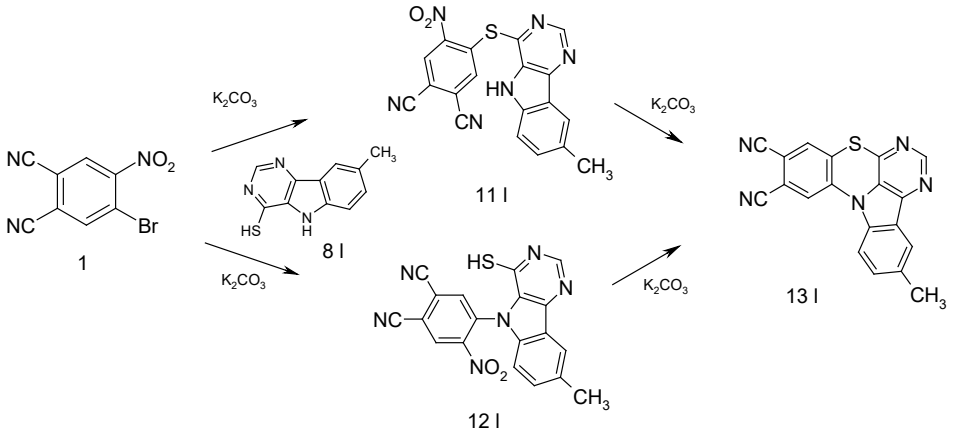
We use various substituted heterocyclic compounds containing the mercapto group **8(h-l)** as a reagent generating *in situ S*-nucleophile for the bromine atom substitution reaction in **4**-bromo-5-nitrophthalonitrile. During S_NAr-reactions in the **4-bromo-5-nitrophthalonitrile** the bromine atom is substituted first to form the corresponding 4-heteryl-5-nitrothiophthalonitriles **9(h-k).** This reaction proceeded within a few minute in the binary solvent DMF-H_2O at room temperature. The yield of the target products was 79–93%.

We could not obtain a pure monosubstitution product **9l** using as a reagent 8-methyl-5*H*-pyrimido[5,4-*b*] indole-4-thiol **8l**, containing two reactive *S*- and *N*-nucleophilic centres. It depends on the molecule of compound **8l** after deprotonation both reaction centres (thiol and imine) under selected reaction conditions are able to react with 4-bromo-5-nitrophthalonitrile **1** by S_NAr and substitute the bromine atom. According to ^1H NMR spectroscopy, the product isolated after the reaction contained a mixture of two compounds **11l** and **12l** in the ratio 1 : 3 clearly confirms the different activity of the *S*- and *N*-nucleophilic centres.



The disadvantage of this reaction can be successfully overcome if the final product of the synthesis is to obtain the product of the disassembly - 3-methyl-8-thia-5,7-12b-triazabenzo[a]aceantrilene-10,11-dicarbonitrile **13l**.

When the reaction was carried out at a higher temperature and with twice the potassium carbonate redundancy, the deprotonation of the thiol and imine groups **8l** took place at the very beginning to form the corresponding *S*- and *N*-nucleophilic centres *in situ*. At the first stage of synthesis these reagents acting with different rates into heterophase intermolecular nucleophilic substitution reaction of bromine atom in **4**-bromo-5-nitrophthalonitrile formed monosubstitution products **11l** and **12l** respectively. These newly obtained compounds contained a sufficiently mobile nitro group, which was intramolecularly attacked by the reaction centre remaining in the reagent (second stage), leading to the closure of the cycle and the formation of the thiazine system. Under the chosen conditions, the transformation of compound **11l** to **13l** could proceed via an intramolecular anionotropic Smiles' rearrangement similar to described in [19]. The advantage of this synthesis is the target compound **13l** has the same structure no matter of direction of the reaction. The product **13l** formed during the reaction was slightly soluble in DMF and precipitated out of the reaction mixture, which did not require additional purification.



Thus, using 4-nitrophthalonitrile, 4-bromo-5-nitrophthalonitrile, 4-bromo-5-nitrophthalonitrile and various monofunctional *O*-, *S*-heterocyclic nucleophiles it becomes possible to synthesise a wide range of *ortho*-dicarbonitriles containing versatile 5- and 6-membered heterocyclic systems, not referenced before.

Experimental part

IR spectra were recorded on a Perkin Elmer RX-1 FT-IR spectrometer at 700–4000 cm^{-1} (suspended in Vaseline oil).

^1H NMR spectra were recorded on Bruker DRX-500 for 5% solutions of samples in DMSO-d^6 at 30 °C. The signals of residual solvent protons in proton spectra ($\delta\delta_H$ 2.50 ppm) or DMSO-d^6 signal in carbon spectra ($\delta\delta_C$ 39.5 ppm) were used as references for chemical shifts.

Elemental analyses were carried out on a Hewlett-Packard HP-85B C, H, N-analyser.

We prepare **4-nitrophthalonitrile 1** and **4-bromo-5-nitrophthalonitrile** according to this procedure [2].

Heterocyclic phenols, thiols as well as other reagents and solvents are commercially available.

4-(Pyridine-3-yloxy)phthalonitrile 3a. A flask equipped with stirrer, reflux condenser and thermometer was filled with 1.73 g (0.01 mol) of 4-nitrophthalonitrile **1**, (0.01 mol) pyridine-3-ol **2a**, 1.56 g (0.01 mol) K_2CO_3 and 30 cm^3 DMF. The reaction mixture was stirred at 80-95 °C for 1.5 h, then cooled to 5-10 °C and poured into 100 cm^3 of cold water. The resulting precipitate was filtered off, washed with water (3×50 cm^3) and dried at 70 °C. The yield of target product was 76% of the theory.

4-Hetheryloxyphthalonitriles 3(b-d), 4-heteryloxy-5-nitrophthalonitriles 5(a-g), 4-heterylthio-5-nitrophthalonitriles 9(h-k) (general methodology). We put 0.01 mole of 4-nitrophthalonitrile **1** (bromo-5-nitrophthalonitrile **4**), 0.01 mole of phenol (thiol) **2(a-g)**, **8(h-k)** and 30 $cm^3$of DMF into a flask equipped with stirrer, reflux condenser and thermometer. After dissolving the reagents under vigorous stirring of reaction mixture, we add a solution of 1.56 g (0.01 mol) K_2CO_3 in 10 cm^3 of water. In presence of 4-nitrophthalonitrile we stir the mixture at 60–90 °C for 0.5-1.5 h. Using of bromo-5-nitrophthalonitrile allows the reaction proceeding without heating. The reaction mixture was only stirred at room temperature for 0.5 h. At the end of the reaction the both contents of the flask were cooled down to 5–10 °C. The precipitate was filtered off, washed with 2-propanol (50 cm^3), water (3×50 cm^3) and dried at 70 °C. The yield of the target products was 78–93%.

4,5-bis-(pyridine-3-yloxy)phthalonitrile 6a. A flask equipped with stirrer, reflux condenser and thermometer was filled with 2.52 g (0.01 mol) of bromo-5-nitrophthalonitrile **4**, 1.9 g (0.02 mol) pyridine-3-ol **2a**, 3.12 g (0.01 mol) K_2CO_3 and 30 cm^3 DMF. The reaction mixture was stirred at 90–95 °C for 1.5 h, then cooled to 5–10 °C and poured into 100 cm^3 of cold water. The resulting precipitate was filtered off, washed with water (3×50 cm^3) and dried at 70 °C. The yield of the target products was 78-80%.

The symmetrical compounds **6(b-g)** and **10** can be prepared by a similar procedure using the corresponding phenols and thiols. In order to obtain the asymmetric products of reactions **7** etc., the same procedure can be used. But instead of bromo-5-nitrophthalonitrile equimolar

amounts of compounds **5(a-g)** or **9(h-k)** and the corresponding phenols **2(a-g)** or thiols **8(h-k)** should be taken.

3a: Yield 76%, *melting temperature (Tm)* = 182–185 °C. IR (υ_{max}, oil): 1250 (C-O-C), 2238 (CN). Found, %: C 70.52; H 3.20; N 18.93. $C_{15}H_8N_6O_2$. Calculated, %: C 70.58; H 3.19; N 19.00. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.53 (m, 2H), 7.7 (d, 1H), 7.91 (d, 1H), 8.14 (d, 1H), 8.53 (m, 2H).

3b: Yield 89.5 %, *Tm* = 194–196 °C. IR (υ_{max}, oil): 1251 (C-O-C), 2237 (CN). Found, %: C 75.37; H 3.32; N 15.51. $C_{17}H_9N_3O$. Calculated, %: C 75.27; H 3.34; N 15.49. ^{1}H NMR (500 MHz, DMSO-d6, δ, ppm): 7.20 (d, 1H), 7.60 (m, 3H), 7.9 (m, 3H), 8.45 (d, 1H), 8.75 (d, 1H).

3c: Yield 93 %, *Tm* = 190–193 °C. IR (υ_{max}, oil): 1249 (C-O-C), 2236 (CN). Found, %: C 75.81; H 3.46; N 16.18. $C_{22}H_{12}N_4O$. Calculated, %: C 75.85; H 3.47; N 16.08. ^{1}H NMR (500 MHz, DMSO-d6, δ, ppm): 7.3 (d, 1H), 7.49 (d, 1H), 7.75 (m, 3H), 8.1 (m, 5H), 8.3 (d, 1H), 9.55 (s, 1H).

3d: Yield 90%, *Tm* = 202–205 °C. IR (υ_{max}, oil): 1250 (C-O-C), 2238 (CN). Found, %: C 70.52; H 3.20; N 18.93. $C_{28}H_{16}N_4O$. Calculated, %: C 70.58; H 3.19; N 19.00. ^{1}H NMR (500 MHz, DMSO-d6, δ, ppm): 7.12 (d, 2H), 7.5 (m, 9H), 7.85 (d, 2H), 8.1 (m, 3H).

6a: Yield 74%, *Tm* = 188–190 °C. IR (υ_{max}, oil): 1253 (C-O-C), 2236 (CN). Found, %: C 68.77; H 3.20; N 17.77. $C_{18}H_{10}N_4O_2$. Calculated, %: C, 68.79; H, 3.21; N, 17.83. ^{1}H NMR (500 MHz, DMSO-d6, δ, ppm): 7.48 (t, 2H), 7.56 (d, 2H), 7.94 (s, 2H), 8.39 (s, 2H), 8.47 (d, 2H)

5b: Yield 92%, *Tm* = 190–192 °C. IR (υ_{max}, oil): 2236 (CN), 1350, 1540 (NO_2); 1020, 1250 (C-O-C). Found, %: C 64.49; H 2.55; N 17.75. $C_{17}H_9N_5O_3$. Calculated, %: C 64.56; H 2.55; N 17.71. ^{1}H NMR (500 MHz, DMSO-d6, δ, ppm): 7.41–7.58 (m, 6H, J=22), 7.95 (s, 1H), 8.84 (s, 1H).

5e: Yield 72%, *Tm* = 232–234 °C. IR (υ_{max}, oil): 2235 (CN), 1350, 1540 (NO_2); 1020, 1250 (C-O-C). Found, %: C 70.52; H 3.20; N 18.93. $C_{17}H_9N_5O_3$. Calculated, %: C 61.63; H 2.74; N 21.14. ^{1}H NMR (500 MHz, DMSO-d6, δ, ppm): 2.78 (s, 3H), 7.65 (d, 1H), 7.75 (m, 2H), 8.05 (d, 1H), 8.67 (s, 1H), 9.05 (s, 1H).

5f: Yield 76%, *Tm* = 223–224 °C. IR (υ_{max}, oil): 2238 (CN), 1350, 1540 (NO_2); 1020, 1250 (C-O-C). Found, %: C 65.43; H 3.02; N 16.99. $C_{18}H_{10}N_4O_3$. Calculated, %: C, 65.45; H, 3.05; N, 16.96. ^{1}H NMR (500 MHz, DMSO-d6, δ, ppm): 6.28 (d, 2H), 7.35 (d, 2H), 7.4 (t, 2H), 7.72 (d, 2H), 7.98 (s, 1H), 8.95 (s, 1H).

5g: Yield 80%, *Tm* = 217–219 °C. IR (υ_{max}, oil): 2238 (CN), 1350, 1540 (NO_2); 1020, 1250 (C-O-C). Found, %: C 65.94; H 2.62; N 14.69. $C_{21}H_{10}N_4O_4$. Calculated, %: C, 65.97; H, 2.64; N, 14.65. ^{1}H NMR (500 MHz, DMSO-d6, δ, ppm):7.4 (m, 2H), 7.65 (m, 3H), 7.79 (s, 1H), 7.82 (t, 2H), 8.38 (d, 1H), 8.98 (s, 1H).

9h: Yield 77%, *Tm* = 206–208 °C. ИК (υ_{max}, oil): 2235 (CN), 1350, 1550 (NO_2). Found, %: C 55.29; H 2.13; N 19.89; S, 11.32. $C_{13}H_6N_4O_2S$. Calculated, %: C, 55.32; H, 2.14; N, 19.85; S, 11.36. ^{1}H NMR (500 MHz, DMSO-d6, δ, ppm):7.5 (t, 1H), 7.73 (d, 1H), 7.95 (t, 1H), 8.18 (s, 1H), 8.6 (d, 1H), 8.98 (s, 1H).

9i: Yield 81%, *Tm* = 228–230 °C. IR (υ_{max}, oil): 2238 (CN), 1350, 1540 (NO_2). Found, %: C 61.40; H 2.40; N 16.87; S, 9.63. $C_{17}H_8N_4O_2S$. Calculated, %: C, 61.44; H, 2.43; N, 16.86; S, 9.65.

^{1}H NMR (500 MHz, DMSO-d6, δ, ppm): 7.68 (t, 1H), 7.71 (d, 1H), 7.81 (t, 1H), 7.87 (d, 1H), 8.04 (d, 1H), 8.45 (d, 1H), 8.55 (s, 1H), 9.02 (s, 1H).

9j: Yield 73%, *Tm* = 184-187 °C. IR (υ_{max}, oil): 2230 (CN), 1350, 1540 (NO_2). Found, %: C 51.75; H 2.55; N 21.35; S, 16.30. $C_{17}H_{10}N_6O_2S_2$. Calculated, %: C, 51.77; H, 2.56; N, 21.31; S, 16.26. ^{1}H NMR (500 MHz, DMSO-d6, δ, ppm): 4.65 (d, 1H), 4.80 (d, 2H), 5.15 (d, 1H), 6.00 (m, 1H), 7.25 (t, 1H), 7.60 (d, 1H), 7.85 (d, 1H), 7.90 (s, 2H)

9k: Yield 93%, *Tm* = >300 °C. IR (υ_{max}, oil): 2230 (CN), 1350, 1540 (NO_2). Found, %: C 55.79; H 2.34; N 25.36; S, 8.26. $C_{18}H_9N_7O_2S$. Calculated, %: C, 55.81; H, 2.34; N, 25.31; S, 8.28. ^{1}H NMR (500 MHz, DMSO-d6, δ, ppm): 3.80 (s, 3H), 7.57 (m, 2H), 7.85 (d, 1H), 8.45 (d, 1H), 8.75 (s, 1H), 9.05 (s, 1H)

13l: Yield 86%, *Tm* = >300 °C. IR (υ_{max}, oil): 2230 (CN). Found, %: C 67.09; H 2.68; N 20.58; S 9.47. $C_{19}H_9N_5S$. Calculated, %: C 67.24; H, 2.67; N 20.64; S, 9.45. ^{1}H NMR (500 MHz, DMSO-d6, δ, ppm): 2.45 (s, 3H), 7.60 (d, 1H, J=8.1), 8.00 (s, 1H), 8.10 (s, 1H), 8.40 (d, 2H, J=8,3), 8.60 (s, 1H).

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