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SYNTHESIS OF SUBSTITUTED 4-ARYLOXYPTHALIC ACIDS BASED ON 4-NITRO-*N*-METHYLPHTHALIMIDE

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Abstract. *Based on an activated aromatic nucleophilic substitution reaction between 4-nitro-N-methylphthalimide and phenols containing different substituents we obtained both identified and unidentified 4-aryloxy-N-methylphthalimides. Their alkaline hydrolysis gave 4-aryloxyphthalic acids.*

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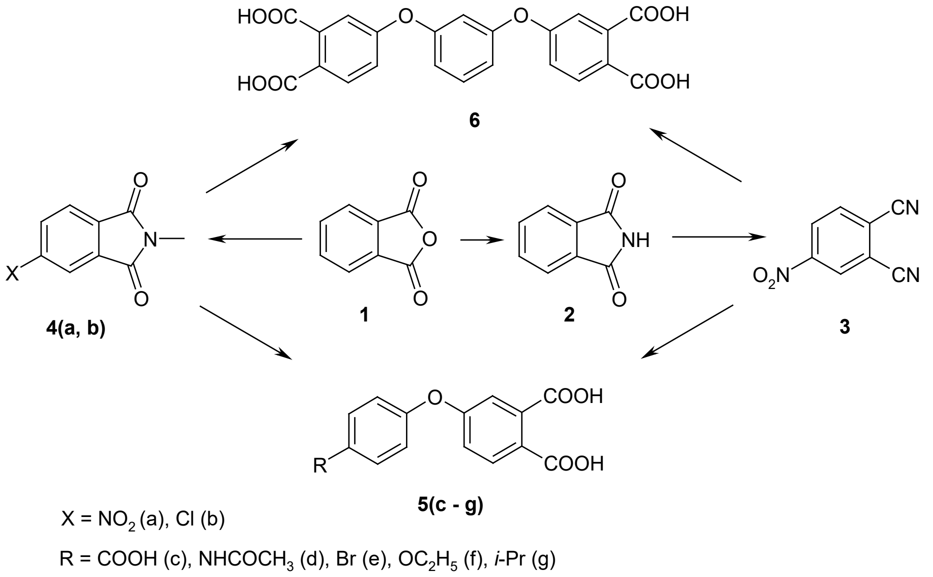
Introduction

Phthalic anhydride **1** and phthalimide **2** based on it are convenient starting reagents for the production of 4-nitrophthalonitrile (4-NPN) **3** and 4-chloro- / 4-nitro-*N*-methylphthalimide **4 (a, b)**, respectively [1]. As a result of these substrates interaction with various mono- and bifunctional *O*-nucleophilic reagents and their subsequent functionalization, 4-(aryloxy) valuable for practical use are formedphthalic **5(c-g)** and 4,4'-(arylenedioxy)diphthalic **6** acids (if other bisphenols are used instead of resorcinol) (Fig. 1), and dianhydrides based on them [2].

Indeed, based on 4-nitrophthalonitriles there were obtained a lot of diaryl esters - substituted phthalonitriles for producing phthalocyanines, polyethyrimides, and other materials promising for use in various branches of science and technology [**3-9**]. In addition, the features of this reaction course S_NAr with various *S*- and *N*-nucleophiles leading to the production of desired phthalonitriles with good yields are described in details in [10-13].

Reactions involving 4-nitro-*N*-methylphthalimide **4a** and 4-chloro-*N*-methylphthalimide **4b** are much less common in the literature [14, 15]. According to the authors of these works, both substrates are good raw materials for preparing intermediates for dianhydride P, under the condition of azeotropic water distillation formed during the reaction. On the evidence papers, high process parameters (good yield, high conversion, ability to run reaction by-products in the recycle to generate the initial phthalimide, etc.) are given as proof.

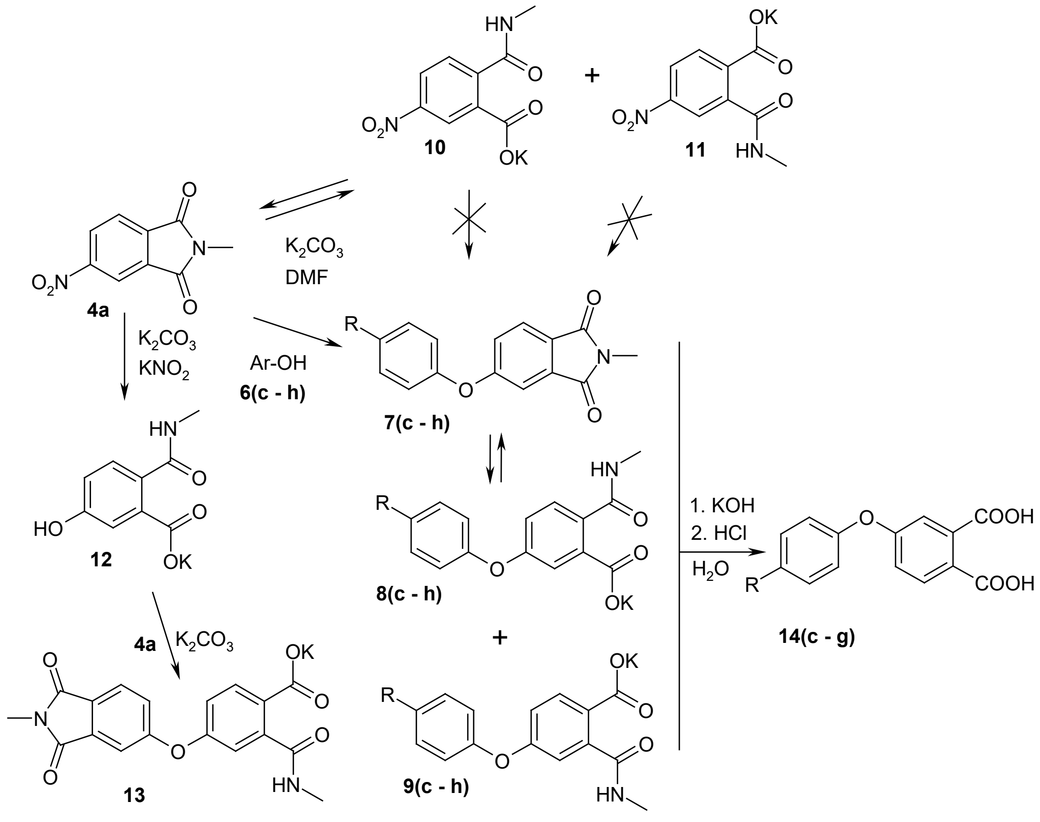


X = NO_2 (a), Cl (b)

R = COOH (c), $NHCOCH_3$ (d), Br (e), OC_2H_5 (f), *i*-Pr (g)

Fig. 1. The scheme of obtaining 4-(aryloxy)phthalic **5(c-g)** and 4,4'-(arylenedioxy)diphthalic acids **6**

In this paper, the possibility of an alternative method for obtaining various phenoxy-pthalic acids based on the reaction of interaction of 4-nitro-*N*-methylphthalimide **4a** and substituted phenols **6(c-h)** is discussed (Fig. 2).



R = COOH (c), $NHCOCH_3$ (d), Br (e), OC_2H_5 (f), i-Pr (g), CH_3 (h)

Fig. 2. Reactions involving 4-nitro-*N*-methylphthalimide **4a**

When conducting this heterophase reaction at 120-140 °C in a DMFA in the presence of K_2CO_3 without azeotropic distillation of water formed during deprotonization of phenols and hydrolysis of the initial **4a** and desired phthalimides **7(c-h),** a very low yield of desired reaction products **7(c-h)** was observed for all used reagents **6(c-h)**. The reaction path was controlled by TLC (eluent: heptane/ethyl acetate = 2.5/1). Detailed analysis of the reaction mass showed a number of by-products (see Fig. 2), imides **4a, 7(c-h)**, and various amide acids **8(c-h)** and **9(c-h)**, It correlates with the results of work [15], which shows more significant utilizing of 4-nitro-*N*-methylphthalimide **4a** in the presence of K_2CO_3, DMPA and *para*-cresol **6h** than the phenol 6h used. Additionally, the desired product of monosubstituting the nitro group **7h**, the corresponding isomeric 4-nitroamide acids 10 were isolated from the reaction mass**, 11**, formed from the initial unreacted 4-nitro-*N*-methylphthalimide 4a.

It can be explained by the simultaneous influence of several factors on the reaction: the reaction takes place under heterophase conditions, low speed and, as a result, only partial deprotonation of phenols, the presence of equilibrium between phthalimide **4a**, and the corresponding salts of 4-nitroamide acids **10** and **11** (see Fig. 2) [16]. Characteristically, the yield of the reaction products increases as the reaction time increases to 7-9 hours. It can be explained as follows: Firstly, 4-nitro-*N*-methylphthalimide **4a** is reformed from 4-nitroamide acids **10** and **11**. Their salts are inactive in the S_NAr substitution reaction of the nitro group. Secondly, formed during the deprotonation of phenols **6 (c-h)** and directly during the S_NAr reaction of $KHCO_3$ at a temperature of 120-140 °C decomposes to form K_2CO_3, which again participates in the deprotonation of phenol, leading to the formation of an *O*-nucleophile [17-18] (Fig. 3). However, among the products of side reactions, there may be insignificant amounts of 4-hydroxyamide acids **12** and diphenyl oxides **13** formed as a result of the nitrite ion reaction with the initial substrate **4a** [19].

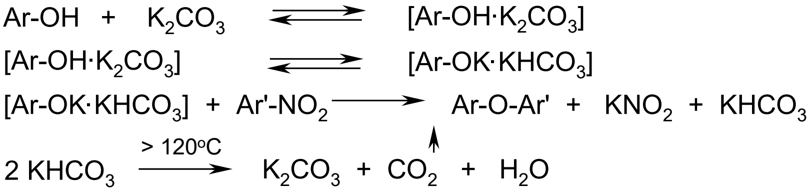


Fig. 3. Reactions involving potassium carbonate and potassium bicarbonate [18]

The feature and advantage of the proposed method for the synthesis of 4-aryloxyphthalic acids **14(c-g)** represents the possibility to perform hydrolysis of all the isolated products of the S_NAr reaction without the additional purification. All three formed compounds – 4-aryloxypthalimides **7(c-g)**, and 4-aryloxyamide acids **8(c-g), 9(c-g)** – are quantitatively hydrolyzed to the corresponding dikali salts of 4-aryloxypthalic acids when boiled in an aqueous KOH solution, after acidification of which HCl is released only one desired 4-aryloxypthalic acid **14(c-g)**. The insignificant impurities of compounds **4a, 10-13** are also hydrolyzed to the corresponding phthalic acids. But they have greater solubility, therefore remain in the filtrate.

The developed method of synthesis of 4-aryloxypthalic acids is not suitable for obtaining 4,4'-(arylenedioxy)tetraphthalic acids (for example, **6**) – intermediates in the synthesis of 4,4'-(arylenedioxy)diphthalic anhydrides. It is due to the large number of monosubstituting intermediates in bisphenol. Indeed, it is almost impossible to separate the monosubstituting intermediates at the subsequent stages of hydrolysis and monomer production. Therefore, the most effective way to obtain various 4,4'-(arylenedioxy)diphthalic acids is the method using 4-nitrophthalonitrile [6].

Experimental Part

IR spectra were recorded on a PerkinElmer RX-1 IR Fourier spectrometer with a wavelength of 700-4000 cm^{-1} (KBr).

^1H NMR spectra were recorded on the Bruker DRX-500 for five percent solutions of samples in DMSO-d_6 at 30 °C. The signals of residual solvent protons in proton spectra (δ_H 2.50 ppm) or the DMSO-d_6 signal in carbon spectra (δ_C 39.5 ppm) were used as a reference for counting chemical shifts.

Elemental analyses were performed on the C, H, N analyzer "Hewlett-Packard HP-85B".

4-Nitro-*N*-methylphthalimide **1,** phenols **6(c-g)**, as well as other reagents and solvents are commercially available ones.

4-Aryloxy-*N*-methylphthalimides 7 (c-g). Method A (general technique). 0.01 mol of 4-nitro-*N*-methylphthalimide **4a**, 0.01 mol of phenol **6(c-g)**, and 15 cm^3 DMFA were loaded into a flask equipped with a stirrer, a reverse refrigerator, and a thermometer. After dissolving the reagents under intensive stirring, (0.012 mol) K_2CO_3 was added to the reaction mixture (in the case of obtaining **6c** – 0.022 mol). The reaction was conducted at a temperature of 120-140 °C for 7-9 hours. The reaction path was controlled by TLC. At the end of the reaction, the content of the flask was cooled to room temperature and poured into 100 cm^3 of cold water. The precipitate (**7c-g**) was filtered, washed with water (3×50 cm^3) and dried at 70 °C. The isolated product was recrystallized from a mixture of isopropanol / DMFA (1:1). The desired reaction products (**7c-g**) were obtained with a yield of 14-29% of the theoretical one.

Method B (general technique). The synthesis was conducted similarly to method A. At the end of the reaction the content of the flask was cooled down to room temperature and poured into acidified HCl water (pH1). The precipitate was filtered, washed with water (3 ×50 cm^3) and dried at 70 °C. A mixture of products (**7c-g, 8c-g, 9c-g**) was obtained with a yield of 78-91% of the theory, counting on imide, and without purification subjected to the hydrolysis.

4-(Aryloxy)phthalic acids 14(c-g) (general procedure). 30 cm^3 of water, a senary molar excess of KOH was loaded into a flask equipped with a stirrer, a reverse refrigerator and a thermometer, and **7 (c-g)** or a mixture (**7-9 c-g**) was sprinkled with stirring. After 2 hours of boiling, the reaction mass is homogenized. Boiling is continued until no methylamine is released. After the reaction was finished, the content of the flask was cooled down to room temperature, filtered off and the filtrate was acidified with HCl to pH 1. The precipitate (**14c-g**) was filtered, washed with water (3 ×50 cm^3) and dried at 70 °C. The desired reaction products (**14c-g**) were obtained with a yield of 62-70% of the theoretical one.

7c: White powder. Yield - 14%, m.p. = 216.5-217.2 °C. IR (υ_{max}, KBr): 2672-2552 (val. COOH), 1697-1682 (C=O), 1279 (C-O-C), 935 (def. COOH). Found, %: C 64.68; H 3.78; N 4.74. $C_{16}H_{11}NO_5$. Calculated, %: C 64.65; H 3.73; N 4.71. NMR^1 H (400 MHz, DMSO-d_6, δ, ppm): 2.71 (s, 3H, N-CH$_3$), 7.12 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.1 Hz, 1H), 7.52 (s, 1H), 7.99 (d, J = 8.7 Hz, 2H), 8.27 (d, J=7.5 Hz, 1H).

7d: White powder. Yield - 23%, m.p. = 207.6-209.0 °C. IR (υ_{max}, KBr): 3371 (NH), 1699 (C=O), 1224 (C-O-C). Found, %: C 65.84; H 4.57; N 9.06. $C_{17}H_{14}N_2O_4$. Calculated, %: C 65.80; H 4.55; N 9.03. NMR^1 H (400 MHz, DMSO-d$_6$, δ, ppm): 2.09 (s, 3H, CH$_3$), 2.88 (s, 3H, N-CH$_3$) 7.22 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 1H), 7.50 (s, 1H), 7.92 (d, J = 8.7 Hz, 2H), 8.35 (d, J = 7.1 Hz, 1H), 10.29 (s, 1H, NH).

7d: White powder. Yield - 25%, m.p. = 133.5-134.3 °C. IR (υ_{max}, KBr): 1704 (C=O), 1235 (C-O-C), 1067 (C-Br). Found, %: C 54.26; H 3.05; N 4.21. $C_{15}H_{10}BrNO_3$. Calculated, %: C 54.24; H 3.03; N 4.22. NMR^1 H (400 MHz, DMSO-d$_6$, δ, ppm): 2.71 (s, 3H, N-CH$_3$), 7.12 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.1 Hz, 1H), 7.52 (s, 1H), 7.99 (d, J = 8.7 Hz, 2H), 8.27 (d, J=7.5 Hz, 1H).

7f: White powder. Yield - 29 %, m.p. = 134.3-135.5 °C. IR (υ_{max}, KBr): 1700 (C=O), 1239 (C-O-C). Found, %: C 68.73; H 5.13; N 4.80. $C_{17}H_{15}NO_4$. Calculated, %: C 68.68; H 5.09; N 4.71. NMR^1 H (400 MHz, DMSO-d$_6$, δ, ppm): 1.91 (t, 3H, CH$_3$), 2.89 (s, 3H, N-CH$_3$), 3.70 (m, 2H, CH$_2$), 7.12 (d, J = 8.2 Hz, 2H), 7.20 (s, 1H), 7.31 (d, J = 8.5 Hz, 1H), 7.35 (d, J = 8.3 Hz, 2H), 7.85 (d, J = 8.13 Hz, 1H).

7g: White crystalline powder. Yield - 28%, m.p. = 90-91 °C. IR (υ_{max}, KBr): 1698 (C=O), 1229 (C-O-C). Found, %: C 73.22; H 5.84; N 4.77. $C_{18}H_{17}NO_3$. Calculated, %: C 73.20; H 5.80; N 4.74. NMR^1 H (400 MHz, DMSO-d$_6$, δ, ppm): 2.5 (d, 6H, 2CH$_3$), 2.95 (m, 1H, CH), 3.00 (s, 3H, N-CH$_3$), 7.08 (D, J = 8.0 Hz, 2H), 7.21 (s, 1H), 7.27 (d, J = 8.5 Hz, 1H), 7.35 (d, J = 8.3 Hz, 2H), 7.83 (d, J = 7.59 Hz, 1H).

14c: Beige powder. Yield - 66%, m.p. = >300 °C. IR (υ_{max}, KBr): 2481 (val. COOH), 1713 (C=O), 1254 (C-O-C), 942 (def. COOH). Found, %: C 60.00; H 3.39. $C_{15}H_{10}O_7$. Calculated, %. C 59.61; H 3.33. NMR^1 H (400 MHz, DMSO-d$_6$, δ, ppm): 7.12 (d, J = 8.7 Hz, 2H), 7.21 (d, J = 8.7 Hz, 1H), 7.72 (s, 1H), 7.95 (d, J = 8.7 Hz, 2H), 8.22 (d, J = 8.7 Hz, 1H).

14d: White powder. Yield - 66%, m.p. = >300 °C. IR (υ_{max}, KBr): 1690 (C=O), 1554 (COO$^-$), 1263(C-O-C),). Found, %: C 61.59; H 4.11. $C_{14}H_{11}NO_5$. Calculated, %. C 61.54; H 4.06. NMR^1 H (400 MHz, DMSO-d$_6$, δ, ppm): 6.72 (d, J = 8.1 Hz, 2H), 6.99 (d, J = 8.2 Hz, 1H), 7.30 (s, 1H), 7.62 (d, J = 8.3 Hz, 2H), 7.98 (d, J = 7.2 Hz, 1H).

14e: White powder. Yield - 65%, m.p. = 188-190 °C. IR (υ_{max}, KBr): 2474 (val. COOH), 1710 (C=O), 1250 (C-O-C), 1060 (C-Br), 940 (def. COOH). Found, %: C 49.92; H 2.72. $C_{14}H_9BrO_5$. Calculated, %: C 49.88; H 2.69. NMR^1 H (400 MHz, DMSO-d$_6$, δ, ppm): 7.14 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.15 Hz, 1H), 7.57 (s, 1H), 7.93 (d, J = 8.9 Hz, 2H), 8.33 (d, J=7.1 Hz, 1H).

14f: Light beige powder. Yield - 67%, m.p. = >300 °C. IR (υ_{max}, KBr): 2479 (val. COOH), 1713 (C=O), 1253 (C-O-C). Found, %: C 63.90; H 4.69. $C_{16}H_{14}O_6$. Calculated, %. C 63.57; H 4.67. NMR^1 H (400 MHz, DMSO-d$_6$, δ, ppm): 1.94 (t, 3H, CH$_3$), 3.65 (m, 2H, CH$_2$), 6.98 (d, J = 8.60 Hz, 2H), 7.10 (s, 1H), 7.25 (d, J = 8.51 Hz, 1H), 7.31 (d, J = 8.30 Hz, 2H), 7.75 (d, J = 8.12 Hz, 1H).

14g: Light beige powder. Yield - 66%, m.p. = >300 °C. IR (υ_{max}, KBr): 2470 (val. COOH), 1711 (C=O), 1261 (C-O-C), 941 (def. COOH). Found, %: C 68.09; H 5.42. $C_{17}H_{16}O_5$. Calculated, %: C 67.99; H 5.37; O 26.64. NMR^1 H (400 MHz, DMSO-d$_6$, δ, ppm): 2.44 (d, 6H, 2CH$_3$), 2.90 (m, 1H, CH), 7.10 (d, J = 7.44 Hz, 2H), 7.22 (s, 1H), 7.31 (d, J = 8.54 Hz, 1H), 7.44 (d, J = 8.27 Hz, 2H), 7.89 (d, J = 8.10 Hz, 1H).

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