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SYNTHESIS OF 5-NITRO-1,2,3,4-TETRAHYDRO-1,4-PHTHALAZINEDIONE AND 1,8-DINITRO-5,7,12,14-TETRAHYDROPHTHALAZINO-[2,3-*b*]PHTHALAZINE-5,7,12,14-TETRAONE

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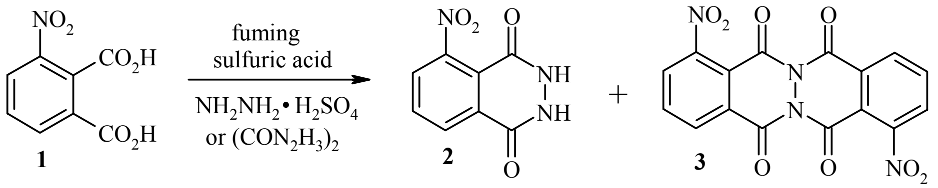
We have observed that when 3-nitrophthalic acid (**1**) is reacted with hydrazine sulfate or oxalic acid dihydrazide in fuming sulfuric acid at a temperature of 85-90°C, a mixture of 5-nitro-1,2,3,4-tetrahydro-1,4-phthalazinedione (**2**) and 1,8-dinitro-5,7,12,14-tetrahydrophthalazino[2,3-*b*]phthalazine-5,7,12,14-tetraone (**3**) is formed with percentage ratio 80:20 (HPLC data), and at a temperature of 75-80°C the ratio is 30:70.



These aspects were not covered in the papers [1-3], which were devoted to synthesis of phthalazine derivatives. Obviously the initial step of the reaction is formation of compound **3**, which then is converted to phthalazine **2** under the influence of the reaction conditions. This hypothesis is confirmed by the fact that when compound **3** is held in fuming sulfuric acid at a temperature of 90°C, it is converted to compound **2**.

The ^{1}H NMR spectra were recorded on a Bruker AC-300 SF (300 MHz) spectrometer in DMSO-d$_6$, internal standard HMDS (δ 0.05 ppm). The IR spectra were recorded on a Specord M-80 (East Germany) in nujol. The elemental composition was determined on a CHN-1 elemental analyzer (Czech SSR). The mass spectra were obtained on an MX-1310. High performance liquid chromatography was run on a Hitachi chromatograph, model L-7100 pump, model L-7400 UV 190-600 detector (254 nm), column ($l \times d$) 250 × 4 mm, support NUCLEOSIL - 100-5 C18, mobile phase 80:20 acetonitrile–water (rate, 1 ml/min), P = 115 bar, solvent for the sample was acetonitrile. As the internal standard, we used 1-chloro-4-nitrobenzene.

Synthesis of Compounds 2 and 3. 3-Nitrophthalic acid (4.7 mmol) was added at room temperature to a mixture of fuming sulfuric acid (20 ml) and hydrazine sulfate (or oxalic acid dihydrazide) (4.7 mmol). The reaction mixture was stirred for 8 h at 85-90°C (80°C when oxalic acid dihydrazide was used), cooled down to

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room temperature, and poured over ice. The precipitate was filtered out and treated with boiling 2-propanol. The insoluble part was separated by hot filtration and dried. When hydrazine sulfate was used, 0.17 g (19%) of bright orange compound **3** was obtained. The precipitate formed after cooling the filtrate was dried in air. 0.73 g (75%) of bright yellow phthalazine **2** was obtained.

5-Nitro-1,2,3,4-tetrahydro-1,4-phthalazine (2). Mp 297-300°C. IR spectrum, ν, cm^{-1}: 3334 (N–H), 1655 (C=O), 1510, 1350 (NO$_2$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.18 (1H, d, *J* = 10, H-8); 8.08 (1H, d, *J* = 9, H-6); 8.06 (1H, t, $J_{7,8}$ = 10, $J_{7,6}$ = 9, H-7); 11.95 (2H, br. s, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 207 [M]$^+$ (73), 178 (38), 161 [M$^+$-NO$_2$] (10), 148 (77), 104 (74), 75 (100). Found, %: C 46.09; H 2.23; N 20.18. $C_8H_5N_3O_4$. Calculated, %: C 46.39; H 2.43; N 20.28.

1,8-Dinitro-5,7,12,14-tetrahydrophthalazino[2,3-*b*]phthalazine-5,7,12,14-tetraone (3). Mp >300°C. IR spectrum, ν, cm^{-1}: 1648 (C=O), 1510, 1350 (NO$_2$). ^{1}H NMR spectrum, ppm (*J*, Hz): 8.52 (2H, d, *J* = 10, H-4,11); 8.42 (2H, d, *J* = 9, H-2,9); 8.24 (2H, t, $J_{3,4}$ = 10, $J_{3,2}$ = 9, H-3,10). Mass spectrum, *m*/*z* (I_{rel}, %): 382 [M]$^+$ (9), 352 (5), 294 (6), 177 (10), 161 (12), 103 (55), 75 (100). Found, %: C 50.37; H 1.48; N 14.84. $C_{16}H_6N_4O_8$. Calculated, %: C 50.27; H 1.58; N 14.66.

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REFERENCES

1. M. C. Cardia, S. Distino, E. Maccioni, L. Bonsignore, and A. DeLogu, *J. Heterocycl. Chem.*, **40**, 1011 (2003).
2. T. J. Kealy, *J. Am. Chem. Soc.*, **84**, 966 (1962).
3. E. H. Huntress, L. N. Stainly, and A. S. Parker, *J. Am. Chem. Soc.*, **56**, 241 (1934).