ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 5, pp. 731–735. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © V.A. Kuznetsov, K.M. Shubin, A.A. Shchipalkin, F.S. Teplyakov, M.L. Petrov, 2008, published in Zhurnal Organicheskoi Khimii, 2008, Vol. 44, No. 5, pp. 739–743.

Benzo[4,5]imidazo[2,1-*a*]phthalazines: I. Substituted *o*-Nitrophenylhydrazines in the Synthesis of Phthalazin-1(2*H*)-ones

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Received May 18, 2007

Abstract—Efficient cyclization procedure was developed for 2-nitro-, 2,4-dinitro-, 2-nitro-5-chloro-, and 4,5-dichloro-2-nitrophenylhydrazines with 2-acylbenzoic acids by heating the reagents in a mixture of of concentrated sulfuric acid and ethanol. A series of new phthalazin-1-ones was obtained with a substituted 2-nitrophenyl group in the position *2* and various substituents in the position *4*.

DOI: 10.1134/S1070428008050175

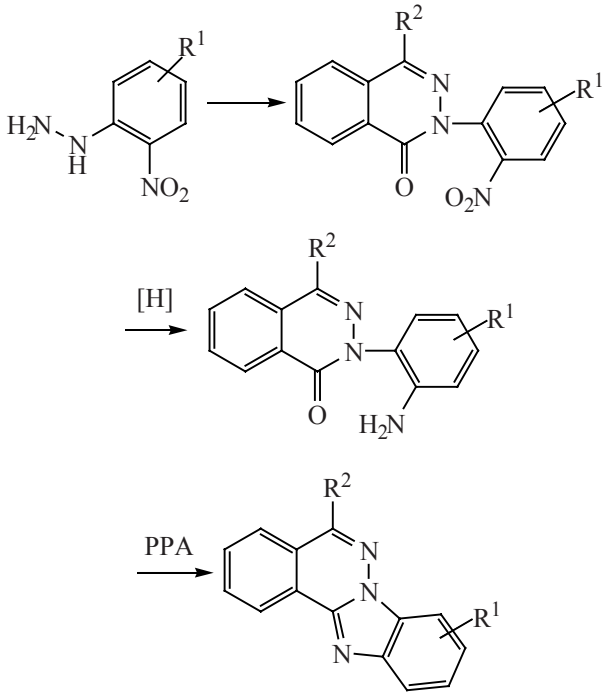
Benzo[4,5]imidazo[2,1-*a*]phthalazine has been known as a heterocyclic system since 1937 [1]. However up till now only three studies were reported on the synthesis and characteristics of these compounds. 12-Methyl-9-trifluoromethyl-12*H*-benzo-[4,5]imidazo-[2,1-*a*]-phthalazin-5-one described in [2] possesses a betaine structure and therefore its properties are fundamentally unlike those of the other known members of this series.

Only several members of this class compounds were synthesized in [1], and their preparation was a complex multistage process that was not of a general character. An interesting route to 5-arylbenzo[4,5]imidazo-[2,1-*a*]phthalazines was tested using *o*-aminophenol [3]. This procedure is far better than that used in the early publication, although some limitations arise with respect to the choice of the introduced substituents. Despite the found biological activity of the target compounds no further research was performed.

We developed a new method of synthesis for benzo[4,5]-imidazo[2,1-*a*]phthalazines. As already mentioned in the preliminary communication [4] the procedure made it possible to prepare a series of new substituted compounds of this class and led to a simplification of the synthesis. We plan to treat in detail the synthetic route developed by us in a series of publications (Scheme 1).

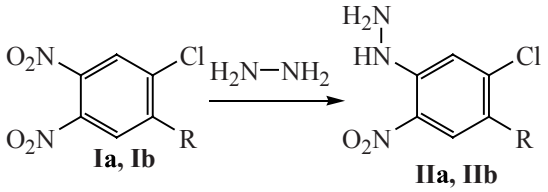
In this paper we consider the first stage of this scheme: The synthesis of phthalazin-1-ones by a reaction of *o*-nitrophenylhydrazines with *o*-acylbenzoic acids. 2-Nitrophenylhydrazines **IIa** and **IIb** were synthesized from the corresponding *o*-dinitrobenzenes and hydrazine hydrate (Scheme 2).

Scheme 1.



R^1 = H, 4-NO_2, 5-Cl, 4,5-Cl_2; R^2 = H, Me, Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-EtC_6H_4, 3,4-$Me_2C_6H_3$, 3,5-$Me_2C_6H_3$, 2,5-$Me_2C_6H_3$.

Scheme 2.



Ia, Ib **IIa, IIb**

R = H (**a**), Cl (**b**).

Compounds **IIa** and **IIb** can be obtained by a direct nucleophilic substitution of the nitro group in compounds **Ia** and **Ib** with hydrazine hydrate [5, 6]. Under the conditions we chose the reaction proceeded exclusively selectively and with a good yield. We also used in the cyclization commercial nitrophenylhydrazines: 2-nitro- (**IIc**) and 2,4-dinitrophenylhydrazine (**IId**).

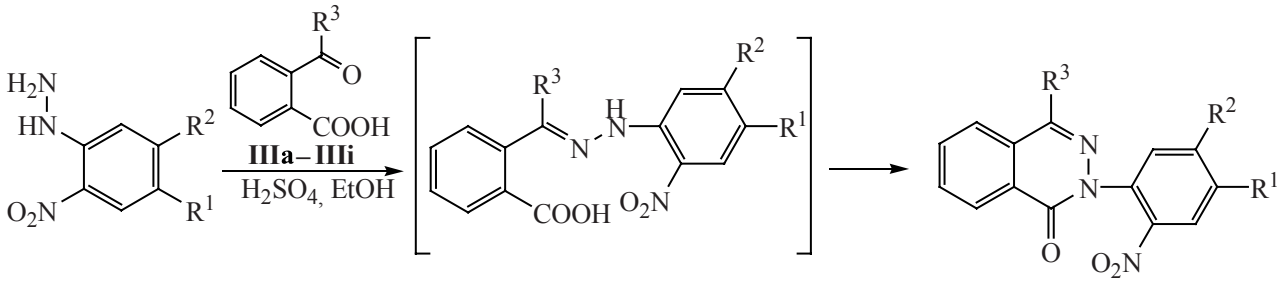
The synthesis of phthalazin-1-ones from *o*-nitrophenylhydrazines and *o*-acylbenzoic acids was only perfunctory investigated [7–10]. The main difficulty consists in the high stability against cyclization of the intermediately formed hydrazone iriginating from the accumulation of electron-withdrawing substituents in the aromatic ring of the hydrazine [7]. Although several ways of performing this reaction were previously described the behavior of 2-nitro-5-chlorophenylhydrazine (**IIa**) in the process was not studied.

It turned out that the reported procedures did not give plausible results with this compound. In particular, on boiling the mixture of *o*-acylbenzoic acid and hydrazine **IIa** in ethanol (or in ethanol containing anhydrous HCl) the phthalazin-1-one formed very slowly. Therewith the reaction mixture contained a considerable amount of the intermediately formed hydrazone. In contrast, the heating of the same reagents mixture in 98% H_2SO_4 resulted in a very fast reaction. However under these conditions also formed an impurity, and the increased temperature and prolonged process resulted in its fast accumulation and in reduction in the yield of the target product. The impurity is likely of acid character, it is insoluble in water at neutral and acid pH values, but it dissolves at alkaline pH giving a solution of saturated violet color. To ensure a more stable and reproducible process we used a mixture of sulfuric acid with ethanol. Therewith the boiling point of the mixture can be easily adjusted by the components ratio within the range 90–160°C. The optimum temperature range proved to be 100–120°C corresponding to the boiling point of the mixture 98% sulfuric acid–ethanol, 1:2. The reaction carried out in this mixture resulted in cyclization of 2-nitro-5-chlorophenylhydrazine (**IIa**) with *o*-acylbenzoic acids in good yields.

The efficiency of the developed procedure was tested on a number of 2-nitrophenylhydrazines. Introducing into the reaction hydrazines **IIb–IId** led to the formation in good yields of the corresponding phthalazin-1(2*H*)-ones **V**.

The composition and structure of newly synthesized compounds was confirmed by elemental analysis, IR and ^{1}H NMR spectra. For instance, the IR spectrum of compound **IVa** in the region 1670 cm^{-1} contained stretching vibrations bands of the carbinyl group in the position *1* of the phthalazine ring. In the region 1604 cm^{-1} the band of stretching vibrations of the endocyclic C=N bond was observed. The symmetric and antisymmetric stretching vibrations of NO_2 group gave rise to bands at 1526 and 1350 cm^{-1}.

Scheme 3.



IIa–IId **IVa–IVd, Va–Vd**

II, R^1 = H, R^2 = Cl (**a**), R^1 = R^2 = Cl (**b**), R^1 = R^2 = H (**c**), R^1 = NO_2, R^2 = H (**d**); **III**, R^3 = Me (**a**), R^3 = H (**b**), R^3= Ph (**c**), R^3 = 4-Me–C_6H_4 (**d**), R^3 = 4-Cl–C_6H_4 (**e**), R^3 = 4-Et–C_6H_4 (**f**), R^3 = 3,4-Me_2–C_6H_3 (**g**), R^3 = 3,5-Me_2–C_6H_3 (**h**), R^3 = 2,5-Me_2–C_6H_3 (**i**); **IV**, R^1 = H, R^2 = Cl, R^3= Me (**a**), R^1 = H, R^2 = Cl, R^3 = H (**b**), R^1 = H, R^2 = Cl, R^3= Ph (**c**), R^1 = H, R^2 = Cl, R^3 = 4-Me–C_6H_4 (**e**), R^1 = H, R^2 = Cl, R^3= 4-Cl–C_6H_4; (**f**), R^1 = H, R^2 = Cl, R^3= 4-Et–C_6H_4 (**g**), R^1 = H, R^2 = Cl, R^3 = 3,4-Me_2–C_6H_3 (**d**), R^1 = H, R^2 = Cl, R^3 = 3,5-Me_2–C_6H_3 (**h**), R^1 = H, R^2 = Cl, R^3= 2,5-Me_2–C_6H_3 (**i**), **V**, R^1 = R^2 = Cl, R^3 = Me (**a**), R^1 = R^2 = H, R^3 = Me (**b**), R^1 = R^2 = H, R^3 = 4-Cl-C_6H_4, R^1 = NO_2 (**c**), R^2 = H, R^3 = Me (**d**).

Let us examine a characteristic ^{1}H NMR spectrun by an example of 4-(4-methylphenyl)-2-(2-nitro-5-chlorophenyl)phthalazin-1(2*H*)-one (**IVd**) (DMSO-d_6). Alongside a singlet of a methyl group at 2.43 ppm there are two doublets in the region 7.3–7.6 ppm corresponding to a *para*-substituted phenyl in the position *4* of the phthalazinone. The spin system of the 2-(2-nitrophenyl) ring gives rise to three well-resolved signals: a doublet H$^{6'}$ with a coupling constant of 1.9 Hz at 7.97 ppm, a doublet of doublets H$^{4'}$, J =8.7 and 1.9 Hz, at 7.77 ppm, and a doublet H$^{3'}$, J 8.7 Hz, at 8.17 ppm. In its turn the spin system of the phthalazinone ring is also represented by three signals: one-proton multiplets at 7.81 and 8.42 ppm, and a two-proton multiplet in the region 7.90–8.01 ppm. An interesting feature of the spectra of these compounds is the location of one proton signal of the phthalazinone ring in an uncommonly weak field. Although the *ortho*-nitro group in the benzene ring is known to possess a strong deshielding effect the chemical shift of H$^{3'}$ proton is by 0.25 ppm smaller than that of the phthalazinone proton. Therewith this feature is characteristic of virtually all 2-(2-nitrophenyl)phthalazin-1-one save 2-(2-nitro-5-chlorophenyl)- and 2-(2,4-dinitrophenyl)-4-methyl-1,2-dihydro-1-phthalazinones (**IVb** and **Vd**). In the spectrum of compound **IVb** the most downfield signal is that of H^4 proton of phthalazinone, and in the spectrum of **Vd** the combined effect of two nitro groups in the side phenyl ring transfers the signals of protons H$^{3'}$ and H$^{5'}$ to the region 8.7–8.8 ppm.

The most downfield proton signal of the phthalazinone is apparently that of the proton in the position *8* of the heterocycle as has been proved by an experiment with a lanthanide shift-reagent, Eu(fod)$_3$ complex. Inasmuch as the most favorable for complexing the shift-reagent in this case is the carbonyl group of the phthalazinone, it is presumable that the strongest change in the chemical shift should suffer the signal of the proton in the position *8*.

The experiment with 2-(2-nitro-5-chlorophenyl)-4-methyl-1,2-dihydrophthalazin-1-one (**IVa**) in $CDCl_3$ showed that at the growing concentration of Eu(fod)$_3$ the proton signal at 8.48 ppm displaced downfield by more than 0.5 ppm. Based on the findings obtained we attributed this downfield signal to H^8 proton both in this and the other analogous compounds.

The developed method of the synthesis of phthalazin-1(2*H*)-ones is more efficientthan those previously applied [7–10]. By examples of preparation of compounds of this series with versatile substituents including alkyl, aryl, or hydrogen in the position *4* and various 2-nitrophenyl substituents in the position *2* we demonstrated that the cyclization in a mixture of concentrated sulfuric acid–ethanol was a simple laboratory procedure giving high yields of the target products.

EXPERIMENTAL

Melting points were measured on a Boëtius heating block. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker AMX-400 (400 MHz) using as internal references the signals of residual protons (^{1}H) and carbon nuclei (^{13}C) of deuterated solvents. IR spectra were recorded on a spectrometer Shimadzu FTIR 8400S from pellets with KBr. The reaction progress was monitored by TLC on Silufol UV-254 plates (development under UV-irradiation). All solvents used in the study were purified by standard procedures [11].

2-Nitro-5-chlorophenylhydrazine (IIa). To a solution of 100 g (0.495 mol) of 1,2-dinitro-4-chlorobenzene in 800 ml of ethanol was added at stirring 60 g (1.20 mol) of hydrazine hydrate. The solution turned dark-red, and gas liberation started. The reaction mixture was stirred at room temperature for 1 h, and gradual crystallization occurred in theis period. Then the solution was filtered, the precipitate was washed on the filter with ethanol (3×100 ml) and dried in air. Yield 61 g (62%), red crystals, mp 137–139°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.81 s (NH_2), 6.62 d (H^4, J_{HH} 9.0 Hz), 7.69 s (H^6), 8.04 d (H^3, J_{HH} 9.0 Hz), 8.92 s (NH).

2-Nitro-4,5-dichlorophenylhydrazine (IIb) was similarly prepared from 50 g (0.211 mol) of 1,2-dinitro-4,5-dichlorobenzene and 27 g (0.450 mol) of hydrazine hydrate. Yield of crude substance 38.5 g. After recrystallization from ethanola yield 34.25 g (73%), red crystals, mp 175–177°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.55 s (NH_2), 7.83 s (ArH), 8.08 s (ArH), 9.13 s (NH).

2-(2-Nitrophenyl)phthalazin-1(2*H*)-ones IV and V. A solution of 0.060 mol of 2-acylbenzoic acid and 0.057 mol of an appropriate hydrazine was heated at reflux in a mixture of of 80 ml of ethanol and 40 ml of 96% sulfuric acid. On completion of the reaction (TLC monitoring) the mixture was poured on 300 g of crushed ice, the precipitate was filtered off, ground with 5% aqueous NaOH and filtered off again, then it was thoroughly washed with water, dried, and recrystallized.

4-Methyl-2-(2-nitro-5-chlorophenyl)-1,2-dihydrophthalazin-1(2*H*)-one (IVa). A mixture of 9.8 g of 2-acetylbenzoic acid (**IIIa**) and 10.7 g of 2-nitro-5-

chlorophenylhydrazine (**IIa**) was boiled for 1 h. Yield 12.6 g (70%), mp 168–170°C (chloroform–ethanol). IR spectrum, ν, cm^{-1}: 1670, 1604, 1527, 1350, 1334, 1326, 1172, 1142, 773, 753, 690. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.64 s (CH_3), 7.52 d ($H^{4'}$, *J* 8.6 Hz), 7.70 s ($H^{6'}$), 7.78–7.94 m (H^{5-7}), 8.04 d ($H^{3'}$, *J* 8.6 Hz), 8.48 d (H^{8}, *J* 7.8 Hz). Found, %: C 57.10; H 3.12; N 13.49. $C_{15}H_{10}ClN_3O_3$. Calculated , %: C 57.07; H 3.19; N 13.31.

2-(2-Nitro-5-chlorophenyl)-1,2-dihydrophthalazin-1(2*H*)-one (IVb). A mixture of 9.0 g of 2-formylbenzoic acid (**IIIb**) and 10.7 g of 2-nitro-5-chlorophenylhydrazine (**IIa**) was boiled for 1 h. Yield 7.7 g (45%), mp 175–177°C (chloroform–ethanol). IR spectrum, ν, cm^{-1}: 1663, 1595, 1525, 1343, 752. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.75 d.d ($H^{4'}$, *J* 8.8 and 2.1 Hz), 7.84 d ($H^{6'}$, *J* 2.1 Hz), 7.91 m (H^{7}), 7.97–8.05 m ($H^{5,6}$), 8.16 d ($H^{3'}$, *J* 8.8 Hz), 8.31 d (H^{8}, *J* 7.6 Hz), 8.58 s (H^{4}). Found, %: C 55.59; H 2.53; N 14.15. $C_{14}H_8ClN_3O_3$. Calculated , %: C 55.74; H 2.67; N 13.93.

2-(2-Nitro-5-chlorophenyl)-4-phenyl-1,2-dihydrophthalazin-1(2*H*)-one (IVc). A mixture of 13.6 g of 2-benzoylbenzoic acid (**IIIc**) and 10.7 g of 2-nitro-5-chloro-phenylhydrazine (**IIa**) was boiled for 1 h. Yield 12.4 g (58%), mp 137–139°C (chloroform–ethanol). IR spectrum, ν, cm^{-1}: 1672, 1599, 1587, 1536, 1472, 1348, 1326, 1137, 739, 692. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.53–7.69 m (4-phenyl), 7.75–7.84 m ($H^{5,4'}$), 7.92–8.04 m ($H^{6,7,6'}$), 8.19 d ($H^{3'}$, *J* 8.8 Hz), 8.42 m (H^{8}). Found, %: C 63.51; H 3.23; N 11.35. $C_{20}H_{12}ClN_3O_3$. Calculated , %: C 63.59; H 3.20; N 11.12.

2-(2-Nitro-5-chlorophenyl)-4-(4-tolyl)-1,2-dihydrophthalazin-1(2*H*)-one (IVd). A mixture of 14.4 g of 2-(4-methylbenzoyl)benzoic acid (**IIId**) and 10.7 g of 2-nitro-5-chlorophenylhydrazine (**IIa**) was boiled for 1 h. Yield 13.4 g (60%), mp 184–186°C (chloroform–ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.43 s (CH_3), 7.36 d (H^{m} Tol, *J* 7.9 Hz), 7.52 d (H° Tol, *J* 7.9 Hz), 7.77 d.d ($H^{4'}$, *J* 8.7 and 1.9 Hz), 7.81 m (H^{5}), 7.90–8.01 m ($H^{6,7}$), 7.97 d ($H^{6'}$, *J* 1.9 Hz), 8.17 d ($H^{3'}$, *J* 8.7 Hz), 8.42 m (H^{8}). Found, %: C 64.24; H 3.48; N 10.92. $C_{21}H_{14}ClN_3O_3$. Calculated , %: C 64.38; H 3.60; N 10.72.

2-(2-Nitro-5-chlorophenyl)-4-(4-chlorophenyl)-1,2-dihydrophthalazin-1(2*H*)-one (IVe). A mixture of 15.6 g of 2-(4-chlorobenzoyl)benzoic acid (**IIIe**) and 10.7 g of 2-nitro-5-chlorophenylhydrazine (**IIa**) was boiled for 1 h. Yield 12.4 g (53%), mp 190–192°C (chloroform–ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.61 d (H° 4-ClC_6H_4, *J* 7.9 Hz), 7.69 d (H^{m} 4-ClC_6H_4, *J* 7.9 Hz), 7.75–7.83 m ($H^{5,4'}$), 7.94–8.04 m ($H^{6,7,6'}$), 8.18 d ($H^{3'}$, *J* 8.8 Hz), 8.42 m (H^{8}). Found, %: C 58.24; H 2.70; N 10.40. $C_{20}H_{11}Cl_2N_3O_3$. Calculated , %: C 58.27; H 2.69; N 10.19.

2-(2-Nitro-5-chlorophenyl)-4-(4-ethylphenyl)-1,2-dihydrophthalazin-1(2*H*)-one (IVf). A mixture of 15.2 g of 2-(4-ethylbenzoyl)benzoic acid (**IIIf**) and 10.7 g of 2-nitro-5-chlorophenylhydrazine (**IIa**) was boiled for 1.5 h. Yield 8.1 g (35%), mp 218–220°C (chloroform–ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.24 t ($CH_2C\underline{H}_3$, *J* 7.4 Hz), 2.69 q ($C\underline{H}_2CH_3$, *J* 7.4 Hz), 7.42 d (H^{m} 4-EtC_6H_4, *J* 7.4 Hz), 7.57 d (H° 4-EtC_6H_4, *J* 7.4 Hz), 7.79–7.88 m ($H^{5,4'}$), 7.96–8.11 m ($H^{6,7,6'}$), 8.21 d ($H^{3'}$, *J* 8.6 Hz), 8.41 m (H^{8}). Found: C 65.00; H 3.87; N 10.57. $C_{22}H_{16}ClN_3O_3$. Calculated , %: C 65.11; H 3.97; N 10.35.

4-(3,4-Dimethylphenyl)-2-(2-nitro-5-chlorophenyl)-1,2-dihydrophthalazin-1(2*H*)-one (IVg). A mixture of 15.2 g of 2-(3,4-dimethylbenzoyl)benzoic acid (**IIIg**) and 10.7 g of 2-nitro-5-chlorophenylhydrazine (**IIa**) was boiled for 1.5 h. Yield 8.6 g (37%), mp 238–240°C (chloroform–ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.31 s (2Me), 7.30–7.44 m ($Me_2C_6H_3$), 7.78–7.87 m ($H^{5,4'}$), 7.94–8.10 m ($H^{6,7,6'}$), 8.20 d ($H^{3'}$, *J* 8.8 Hz), 8.39 m (H^{8}). Found: C 64.97; H 3.81; N 10.56. $C_{22}H_{16}ClN_3O_3$. Calculated , %: C 65.11; H 3.97; N 10.35.

4-(2,4-Dimethylphenyl)-2-(2-nitro-5-chlorophenyl)-1,2-dihydrophthalazin-1(2*H*)-one (IVh). A mixture of 15.2 g of 2-(2,4-dimethylbenzoyl)benzoic acid (**IIIh**) and 10.7 g of 2-nitro-5-chlorophenylhydrazine (**IIa**) was boiled for 1.5 h. Yield 8.8 g (38%), mp 204–206°C (chloroform–ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.09 s (4-CH_3), 2.37 s (2-CH_3), 7.14–7.25 m ($Me_2C_6H_3$), 7.32 m (H^{5}), 7.83 d.d ($H^{4'}$, *J* 8.8 and 2.0 Hz), 7.92–8.01 m ($H^{6,7}$), 8.04 d ($H^{6'}$, *J* 2.0 Hz), 8.21 d ($H^{3'}$, *J* 8.8 Hz), 8.40 m (H^{8}). Found, %: C 65.10; H 3.89; N 10.52. $C_{22}H_{16}ClN_3O_3$. Calculated , %: C 65.11; H 3.97; N 10.35.

4-(2,5-Dimethylphenyl)-2-(2-nitro-5-chlorophenyl)-1,2-dihydrophthalazin-1(2*H*)-one (IVi). A mixture of 15.2 g of 2-(2,5-dimethylbenzoyl)benzoic acid (**IIIi**) and 10.7 g of 2-nitro-5-chlorophenylhydrazine (**IIa**) was boiled for 1.5 h. Yield 10.9 g (47%), mp 205–207°C (chloroform–ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.13 s (5-CH_3), 2.38 s (2-CH_3), 7.12–7.24 m ($Me_2C_6H_3$), 7.37 m (H^{5}), 7.77 d.d ($H^{4'}$, *J* 8.9 and 2.2 Hz), 7.83 d ($H^{6'}$, *J* 2.2 Hz), 7.86–7.93 m ($H^{6,7}$), 8.15 d ($H^{3'}$, *J* 8.9 Hz), 8.42 m (H^{8}). Found, %:

C 65.07; H 3.91; N 10.54. $C_{22}H_{16}ClN_3O_3$. Calculated, %: C 65.11; H 3.97; N 10.35.

2-(4,5-Dichloro-2-nitrophenyl)-4-methyl-1,2-dihydrophthalazin-1(2*H*)-one (Va). A mixture of 9.8 g of 2-acetylbenzoic acid (**IIIa**) and 12.7 g of 2-nitro-5-chlorophenylhydrazine (**IIb**) was boiled for 1 h. Yield 12.4 g (62%), mp 205–207°C (chloroform–ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.64 s (CH_3), 7.92 m (ArH), 8.00–8.09 m ($H^{5-7, 6'}$), 8.34 d (H^8, *J* 7.7 Hz), 8.41 C ($H^{3'}$). Found, %: C 51.39; H 2.39; N 11.97. $C_{15}H_9Cl_2N_3O_3$. Calculated , %: C 51.45; H 2.59; N 12.00.

4-Methyl-2-(2-nitrophenyl)-1,2-dihydrophthalazin-1(2*H*)-one (Vb). A mixture of 9.8 g of 2-acetylbenzoic acid (**IIIa**) and 8.8 g of 2-nitrophenylhydrazine (**IIc**) was boiled for 1.5 h. Yield 9.6 g (60%), mp 195–197°C (chloroform–ethanol). IR spectrum, ν, cm^{-1}: 1668, 1533, 1356, 1340, 1175, 777, 687. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.62 s (CH_3), 7.62–8.02 m ($H^{5-7, 4'-6'}$), 8.10 d ($H^{3'}$, *J* 7.9 Hz), 8.32 d (H^8, *J* 7.5 Hz). Found, %: C 63.81; H 3.82; N 15.14. $C_{15}H_{11}N_3O_3$. Calculated , %: C 64.05; H 3.94; N 14.94.

2-(2-Nitrophenyl)-4-(4-chlorophenyl)-1,2-dihydrophthalazin-1(2*H*)-one (Vc). A mixture of 15.6 g of 2-(4-chlorobenzoyl)benzoic acid (**IIIe**) and 8.7 g of 2-nitrophenylhydrazine (**IIc**) was boiled for 1 h. Yield 6.0 g (55%), mp 167–169°C (ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.52–8.01 m [$H^{5-7, 4'-6'}$, 4-(4-chlorophenyl)], 8.09 d.d ($H^{3'}$, *J* 8.0 and 1.2 Hz), 8.43 m (H^8). Found, %: C 63.41; H 3.29; N 11.33. $C_{20}H_{12}ClN_3O_3$. Calculated , %: C 63.59; H 3.20; N 11.12.

2-(2,4-Dinitrophenyl)-4-methyl-1,2-dihydrophthalazin-1(2*H*)-one (Vd). A mixture of 9.9 g of acetylbenzoic acid (**IIIa**) and 11.4 g of 2,4-dinitrophenylhydrazine (**IId**) was boiled for 1.5 h in a mixture of 40 ml of ethanol and 40 ml of 96% sulfuric acid. Yield 9.9 g (54%), mp 244–246°C (DMF). IR spectrum, ν, cm^{-1}: 3073, 1671, 1608, 1540, 1530, 1350, 1337, 773. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.66 s (CH_3), 7.94 m (H^7), 8.00–8.06 m ($H^{5,6}$), 8.09 d ($H^{6'}$, *J* 8.9 Hz), 8.36 d (H^8, *J* 7.5 Hz), 8.72 d.d ($H^{5'}$, *J* 8.9 and 1.8 Hz), 8.81 d ($H^{3'}$, *J* 1.8 Hz). Found, %: C 55.05; H 3.00; N 17.34. $C_{15}H_{10}N_4O_5$. Calculated , %: C 55.22; H 3.09; N 17.17.

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