Base-catalyzed intramolecular heterocyclization of *o*-alkynylbenzhydrazides

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The reaction of methyl *o*-(2-R-ethynyl)benzoates with hydrazine affords either fused 4-R-methylphthalazin-1-ones or 2-amino-3-R-methylideneisoindolin-1-ones. The latter are on treatment with KOH undergo recyclization into the corresponding 4-R-methylphthalazin-1-ones.

Key words: *o*-alkynylbenzhydrazides, cross-coupling, heterocyclization, recyclization, isoindolinones, phthalazinones.

Accessibility and high synthetic potential of aromatic acetylenes determine increasing interest of chemists in this class of compounds.[1] Vicinal functionally substituted arylacetylenes play a special role. They are highly reactive building blocks in the synthesis of annelated heterocycles, which are promising structures in the search for biologically active compounds.[1,2] From the fundamental point of view, they are convenient models for studying the cyclization rules: the dependence of the heterocyclization direction on internal and external factors (nature of substituents, substrate structure, electronic and steric effects).

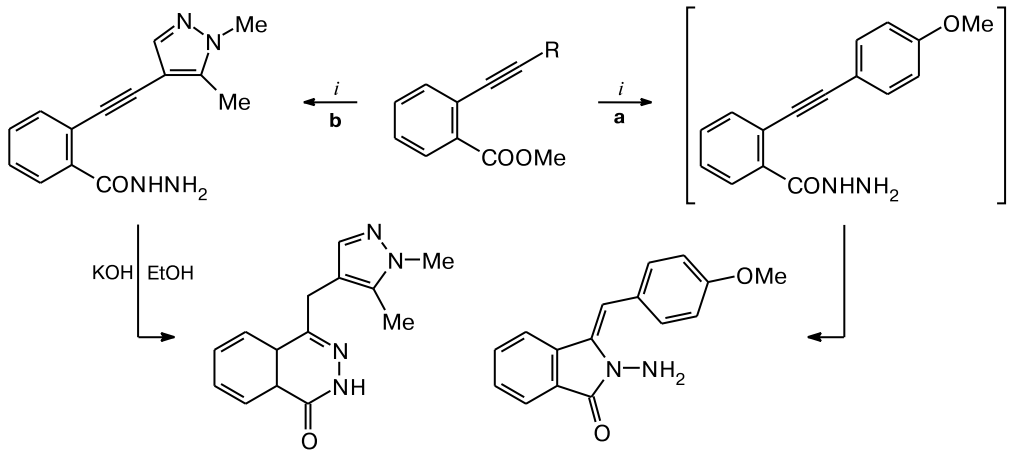
We are carrying out systematic studied of the reactivity of vicinal hydrazides of alkynylbenzoic[3—6] and alkynylpyrazolecarboxylic acids.[7,8] Among advantages of the chosen substrates, we consider the presence of two electrophilic centers (α- and β-carbon atoms of the triple bond) and two nucleophilic centers (amine and amide nitrogen atoms of the hydrazide groups), which provide multichannel transformations.

In fact, the study of the reactivity of vicinal alkynylpyrazolecarboxhydrazides showed that the intramolecular addition of the functional group follows several directions and depends on the nature of the substituent at the carbon atom of the triple bond.[7,8]

We have recently published the data on the unusual intramolecular heterocyclization of *o*-alkynylbenzhydrazides[5] (Scheme 1).

The formation of 2-amino-3-(4-methoxybenzylidene)-isoindolin-1-one (see Scheme 1, route *a*) is quite predictable: it is the product of the nucleophilic attack of the

Scheme 1



R = 4-$MeOC_6H_4$ (**a**), 1,5-dimethylpyrazol-4-yl (**b**)

i. NH_2NH_2, EtOH.

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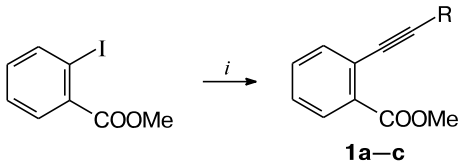
α-carbon atom of the triple bond by the N-anion generated from the amide moiety under basic conditions. In the case of the pyrazole analog (see Scheme 1, route *b*), the pyridazinone cycle was formed unexpectedly and formally represented the result of the attack of the α-carbon atom of the triple bond by the amine nitrogen atom followed by prototropic isomerization. Similar cyclization to benzopyridazinones has earlier been observed only under neutral conditions,[3–8] where the amine nitrogen atom was a stronger nucleophile than the amide nitrogen atom. We assumed that 4-[(1,5-dimethyl-1*H*-pyrazol-4-yl)methyl]-phthalazin-1(2*H*)-one[5] is formed due to the rearrangement of intermediate *N*-aminolactam (see Scheme 1, route *b*).

To confirm or reject this assumption, we decided to study this recyclization in more detail, extending the set of acetylene substituents in the series of *o*-alkynylbenzhydrazides.

The starting compounds, *viz.*, esters of *o*-alkynylbenzoic acids **1a—c**, were synthesized by the reaction of methyl *o*-iodobenzoate with the corresponding alk-1-ynes under the Sonogashira reaction conditions[9] (using the system $Pd(PPh_3)_2Cl_2$—CuI—NEt_3), and the yields of products **1a**—**c** were 68—77% (Scheme 2).

Scheme 2



1a—c

R = 2-pyridyl (**a**), 4-$Me_2NC_6H_4$ (**b**), C(OH)Me_2 (**c**)

i. HC≡CR, $[Pd(PPh_3)]_2Cl_2$, CuI, Et_3N.

Depending on the substrate structure, the reaction of ethynylbenzoates **1a—c** with hydrazine hydrate in boiling ethanol affords either the corresponding *N*-amino-γ-lactams **2b—c**, or benzopyridazinones **3a** (Scheme 3).

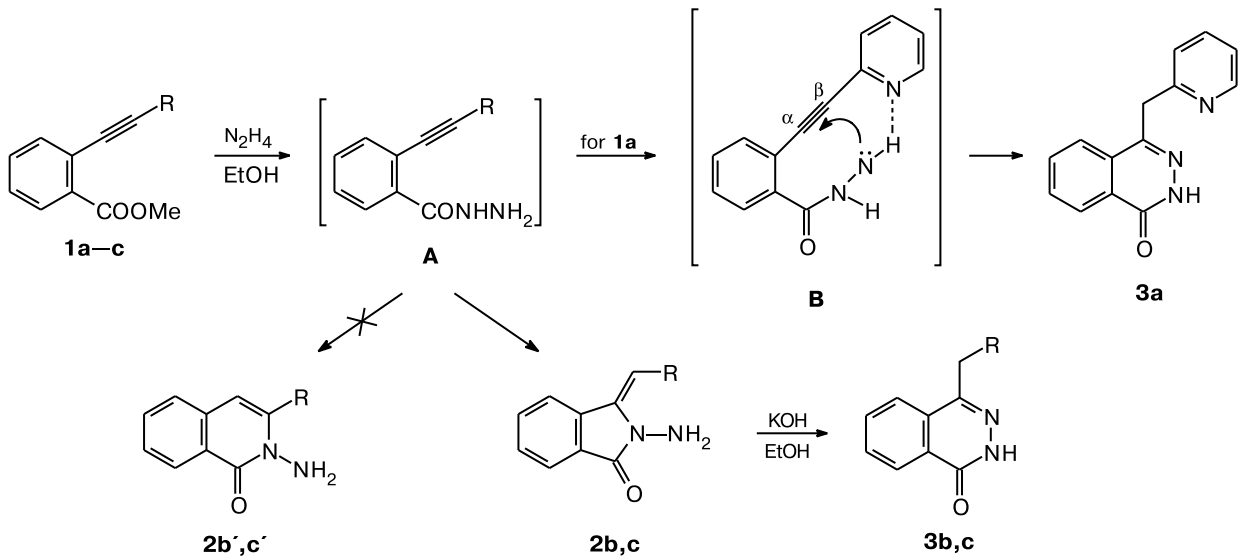
The choice of the structure of the products formed between five- (**2b**,**c**) and six-membered (**2b´**,**c´**) *N*-aminolactams cannot be done on the basis of the ^1H NMR spectra, since the chemical shifts for the *exo*- and *endo*-methine protons are similar.

The structures of lactams were determined from the difference in stretching vibration frequencies of the carbonyl groups (ν(CO)) for the isomeric five- and six-membered rings in the IR spectra. It is known[10,11] that an increase in the strain on going from the six- to five-membered ring increases ν(CO) by 30—35 cm^{-1}. In the known δ-lactams the stretching vibration frequency of the C=O group is 1660—1680 cm^{-1}, whereas in γ-lactams it is at least 1695—1700 cm^{-1}. For the products synthesized, the ν(CO) values in the IR spectra are 1706—1716 cm^{-1}, which indicates unambiguously the *N*-amino-γ-lactam structure of **2b**,**c**. The substantiality of this approach is confirmed by our preliminary report[6] on the structure for the methoxy derivative determined from the 2D NMR data, which established its structure as γ-lactam.

Another additional confirmation of the correct structure determination is the fact that the synthesized *N*-aminolactams **2b**,**c** on heating with KOH yield phthalazinones **3b**,**c** (43—67%). Note that the six-membered *N*-aminolactams **2b´**,**c´** do not interact with alkalis. This simultaneously confirm our assumption about the recyclization of five-membered isoindolinones to phthalazinones.

The result of the reaction of the 2-pyridyl-substituted ester derivative **1a** with hydrazine was unexpected: the

Scheme 3



1a—c **A** **B** **3a** **2b´,c´** **2b,c** **3b,c**

R = 2-pyridyl (**a**), 4-$Me_2NC_6H_4$ (**b**), C(OH)Me_2 (**c**)

major reaction product was the corresponding benzopyridazinone **3a** (70%), which is the net result of the attack of the α-carbon atom of the triple bond by the amine nitrogen atom, which is a weaker nucleophile than the N-anion formed by the action of KOH.

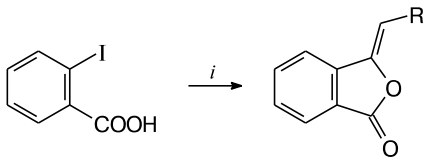
We believe that in this case the mechanism of the product formation is different and is not due to the rearrangement of a possible intermediate aminolactam, because it has previously been shown[5] that five-membered lactam bearing the electron-withdrawing substituent (NO_2 group) cannot be transformed into six-membered diazinone even on heating with KOH.

It can be assumed that the formation of the "anomalous" product from compound **1a** is due to the specific conformation of intermediate hydrazide in which the hydrogen atom of the terminal amino group of the hydrazide moiety is bound to the nitrogen atom of the pyridine moiety by the hydrogen bond. This approaches the terminal nitrogen atom to the α-carbon atom of the triple bond and thus favors six-membered ring (diazinone) (see Scheme 3, intermediate **B**). It should be noted that available published method for the synthesis of similar compounds require high temperatures (200 °C)[12] or the use of absolute media and organometallic compounds.[13]

Since chemists pay great attention to phthalazinones as promising compounds in the search for biologically active compounds,[12–16] we studied in comparison the above described method and another approach to these derivatives, namely, through the corresponding phthalides. We aimed at revealing which of these methods is preferable from the preparative point of view. It is known that the reaction of hydrazine with 3-benzylidenephthalides affords phthalazinones.[17]

The starting phthalides **5a—e** were synthesized by the known method using the Castro reaction[18] (Scheme 4).

Scheme 4



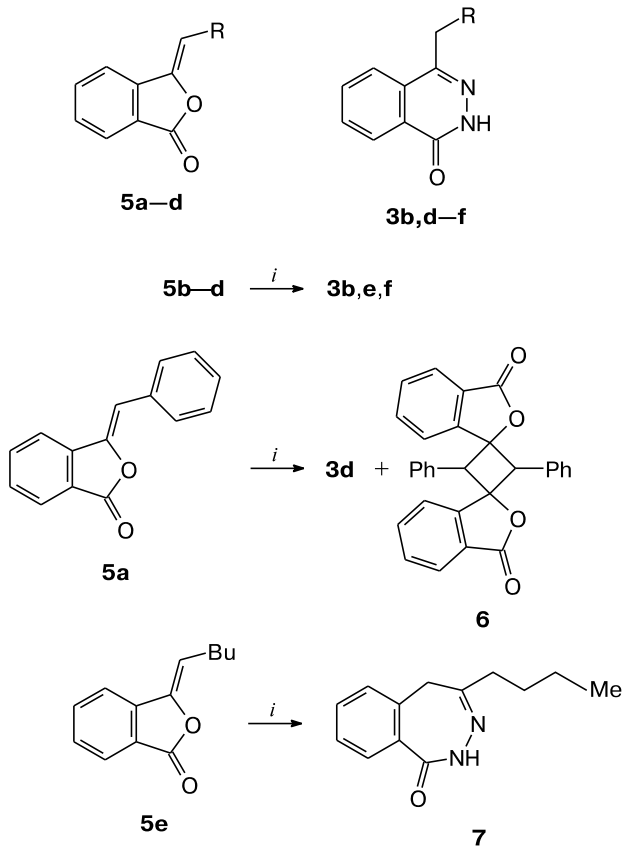
5a—e

R = Ph (**a**), 4-$Me_2NC_4H_6$ (**b**), CH_2OPh (**c**), 4-BrC_6H_4 (**d**), Bu (**e**)

i. CuC≡CR, DMF.

Phthalides **5a—e** reacted with hydrazine hydrate in ethanol following two routes (Scheme 5). In the case of derivatives **5a—d**, as should be expected, phthalazinones **3** were obtained in 67—87% yields. Note that the cyclodimer of benzylidenephthalide **6** is probably formed due to cyclization upon the storage of the mother liquor of compound **3d** (*cf.* Ref. 19). In

Scheme 5



R = Ph (**5a**, **3d**), 4-$Me_2NC_6H_4$ (**5b**, **3b**), CH_2OPh (**5c**, **3e**), 4-BrC_6H_4 (**5d, 3f**), Bu (**5e**)

i. NH_2NH_2, EtOH

the case of the butyl derivative **5e**, diazepinone **7** was formed (72%).

A comparison of the methods for synthesis of phthalazinones from acid esters and phthalides as the starting compounds shows that they are approximately equivalent for the aromatic derivatives. At the same time, the "phthalide" method gives diazepinones in the case of the aliphatic derivatives.

Thus, the reaction of methyl *o*-alkynylbenzoates with hydrazine hydrate in ethanol affords either the corresponding pyridazinones, or the intramolecular cyclization products, *viz.*, *N*-amino-γ-lactams. The latter are treated with a stronger bas (KOH) and rearranged into benzodiazinones (except for substrates with the withdrawing groups). The recyclization found can serve as an alternative method for the synthesis of phthalazinones of a wide range of pharmacological effect.

Experimental

The IR spectra of the new compounds were recorded on a Vector-22 spectrometer in KBr pellets. NMR spectra were

measured on Bruker AV-300 (300.13 MHz) and Bruker AV-400 (400.13 MHz) spectrometers in $CDCl_3$. High-resolution mass spectra were obtained on a DFS spectrometer (Thermo Electron Corporation) using direct inlet (ionization temperature of the chamber was 220—270 °C, ionization voltage 70 eV). Silica gel 60 (70—230 μm, Merck) was used for column chromatography. The reaction was monitored by TLC on Silufol UV-254 plates (Merck).

Methyl 2-(2-pyridylethynyl)benzoate (1a). A solution of 2-bromopyridine (1.58 g, 10 mmol), CuI (0.02 g), $Pd(PPh_3)_2Cl_2$ (0.04 g), PPh_3 (0.02 g), Et_3N (3 mL), and methyl 2-ethynylbenzoate (1.76 g, 11 mmol) in toluene (40 mL) was stirred at 70 °C for 8 h under argon until the starting bromide disappeared (TLC monitoring, eluent CH_2Cl_2). After the end of the reaction, the mixture was filtered through a small Al_2O_3 layer, and the filtrate was concentrated *in vacuo*. The residue was chromatographed on a column with Al_2O_3 (80×20 mm) and SiO_2 (20×20 mm, eluent benzene). Product **1a** was obtained in a yield of 1.64 g (70%), n_D^{20} =1.5125. IR (KBr), ν/cm^{-1}: 2223 (C=O), 1728 (C≡C). ^{1}H NMR, δ: 3.94 (s, 3 H, OCH_3,); 7.32—7.35 (m, 1 H, γ-H(Py)); 7.37—7.52 (m, 2 H, H(4), H(5)); 7.56—7.59 (m, 1 H, β-H(Py)); 7.56 (m, 1 H, H(10)); 7.64—7.66 (m, 1 H, H(3)); 7.69—7.72 (m, 1 H, β-H(Py)); 7.97 (d, 1 H, H(6), J = 7.9 Hz); 8.60—8.62 (m, 1 H, α-H(Py)). ^{13}C NMR, δ: 51.83; 87.46; 92.80; 122.45; 124.80; 127.08; 128.14; 130.08; 130.37; 131.37; 134.02; 135.66; 143.10; 149.67; 165.89. MS, *m/z*: [M$^+$], found 237.0784, calculated 237.0786, $C_{15}H_{11}NO_2$.

Compounds **1b**,**c** were obtained similarly.

Methyl 2-[(4-dimethylaminophenyl)ethynyl]benzoate (1b), 76% yield, m.p. 88—89 °C. IR (KBr), ν/cm^{-1}: 2220 (C=O), 1715 (C≡C). ^{1}H NMR ($CDCl_3$), δ: 2.98 (s, 6 H, $N(CH_3)_2$); 3.94 (s, 3 H, OCH_3); 6.67 (d, 2 H, *o*-H, J = 8.9 Hz); 7.29 (d, 1 H, H(5)); 7.44—7.57 (m, 3 H, H(4), *m*-H); 7.57—7.60 (m, 1 H, H(3)); 7.91 (d, 1 H, H(6), J = 7.6 Hz). ^{13}C NMR, δ: 39.75; 51.66; 86.16; 95.63; 111.01; 111.31; 124.21; 126.49; 129.95; 131.11; 132.19; 132.53; 133.13; 149.84; 166.59. MS, *m/z*: [M$^+$], found 279.1366, calculated 279.1363, $C_{15}H_{11}NO_2$.

Methyl 2-(3-hydroxy-3-methylbutynyl)benzoate (1c). The yield of **1c** was 77%, n_D^{20} = 1.5512 (*cf.* Ref. 20: n_D^{20} = 1.5505).

4-(2-Pyridylmethyl)phthalazin-1(2*H*)-one (3a). $NH_2NH_2 \cdot H_2O$ (84 mg, 1.68 mmol) was added to a solution of ester **1a** (200 mg, 0.84 mmol) in ethanol (5 mL), and the mixture was refluxed for 8 h (TLC monitoring, eluent CH_2Cl_2—AcOEt). The mixture was cooled to 25 °C, the precipitate that formed was filtered off through an Al_2O_3 layer (10×10 mm), and the filtrate was evaporated and recrystallized from ethyl acetate. Product **3a** was obtained in a yield of 70 mg (70%), m.p. 236—238 °C. IR (KBr), ν/cm^{-1}: 1668 (C=O). ^{1}H NMR, δ: 4.48 (s, 2 H, CH_2); 7.10—7.11 (m, 1 H, H(7)); 7.22 (d, 1 H, H(5), J = 7.7 Hz); 7.53—7.55 (m, 1 H, H(6)); 7.69—7.92 (m, 3 H, β-H, γ(Py)); 8.52 (m, 1 H, H(8)); 8.53—8.54 (m, 1 H, α-H); 11.3 (br.s, 1 H, NH). ^{13}C NMR, δ: 41.78; 121.74; 123.05; 125.67; 126.71; 128.07; 129.81; 131.23; 133.36; 136.60; 145.66; 149.30; 157.72; 160.73. MS, *m/z*: [M$^+$], found 237.0820, calculated 237.0897, $C_{14}H_{11}N_3O$.

2-Amino-3-(4-dimethylaminobenzylidene)isoindolin-1-one (2b). 80% $NH_2NH_2 \cdot H_2O$ (36 mg, 0.72 mmol) was added to a solution of ester **1b** (100 mg, 0.36 mmol) in ethanol (5 mL), and the mixture was refluxed for 8 h (TLC monitoring, eluent CH_2Cl_2—AcOEt). The mixture was cooled to 25 °C, and the precipitate that formed was filtered off and recrystallized from ethanol (5 mL). Product **2b** was obtained in a yield of 70 mg (70%), m.p. 136—137 °C. IR (KBr), ν/cm^{-1}: 1700 (C=O). ^{1}H NMR, δ: 2.96 (s, 6 H, $N(CH_3)_2$); 4.38 (s, 2 H, NH_2); 6.67 (s, 1 H, =CH); 6.73 (d, 2 H, *o*-H, J = 8.9 Hz); 7.39—7.42 (m, 1 H, H(6)); 7.49 (d, 2 H, *m*-H, J = 8.9 Hz); 7.52—7.55 (m, 1 H, H(5)); 7.68 (d, 1 H, H(4), J = 6.9 Hz); 7.82 (d, 1 H, H(7), J = 7.5 Hz). ^{13}C NMR, δ: 40.18; 108.79; 111.40; 118.91; 121.76; 122.93; 126.08; 128.08; 131.35; 1.65; 136.61; 149.77; 166.88. MS, *m/z*: [M$^+$], found 279.1366, calculated 279.1374, $C_{17}H_{17}N_3O$.

2-Amino-3-(2-hydroxy-2-methylpropylidene)isoindolin-1-one (2c) was synthesized similarly to **2b**. The yield of product **2c** was 0.54 g (60%), m.p. 146—147 °C. IR (KBr), ν/cm^{-1}: 1700 (C=O). ^{1}H NMR, δ: 1.57 (s, 6 H, $(CH_3)_2$); 1.73 (s, 1 H, OH); 5.2 (br.s, NH_2); 5.91 (s, 1 H, =CH); 7.44—7.45 (m, 1 H, H(6)); 7.57—7.58 (m, 2 H, H(4), H(5)); 7.80 (d, 1 H, H(7), J = 8.4 Hz). ^{13}C NMR, δ: 32.04; 68.48; 116.39; 118.85; 122.74; 125.81; 128.67; 132.16; 132.62; 136.05; 167.16. MS, *m/z*: [M$^+$], found 218.1048, calculated 218.1050, $C_{12}H_{14}N_2O_2$.

4-(4-Dimethylaminobenzyl)phthalazin-1(2*H*)-one (3b). ***A.*** KOH (8 mg, 0.14 mmol) was added to a solution of hydrazide **2b** (40 mg, 0.14 mmol) in ethanol (8 mg, 0.14 mmol), and the mixture was refluxed for 8 h (TLC monitoring, eluent AcOEt). The mixture was cooled to 25 °C, and the precipitate that formed was filtered off and recrystallized from ethanol. Product **3b** was obtained in a yield of 27 mg (67%), m.p. 254—255 °C. IR (KBr), ν/cm^{-1}: 1657 (C=O). ^{1}H NMR, δ: 2.88 (s, 6 H, $N(CH_3)_2$); 4.18 (s, 2 H, CH_2); 6.66 (d, 2 H, *o*-H, J = 8.64 Hz); 7.11 (d, 2 H, *m*-H, J = 8.64 Hz); 7.68—7.71 (m, 3 H, H(5), H(6), H(7)); 8.42—8.43 (m, 1 H, H(8)); 10.2 (br.s, 1 H, NH). ^{13}C NMR, δ: 41.26; 115.21 118.62; 124.62; 125.71; 126.31; 127.63; 128.12; 130.25; 133.87; 138.43; 143.26; 148.81; 166.57. MS, *m/z*: [M$^+$], found 279.1366, calculated 279.1363, $C_{17}H_{17}N_3O$.

B. Compound **3b** was obtained in 87% yield from compound **5e** (see the synthesis of compound **7**).

4-(2-Hydroxy-2-methylpropyl)phthalazin-1(2*H*)-one (3c) was obtained similarly to **3b** in a yield of 60 mg (43%), m.p. 178—179 °C. IR (KBr), ν/cm^{-1}: 1649 (C=O). ^{1}H NMR, δ: 1.35 (s, 6 H, $C(CH_3)_2$); 3.10 (s, 2 H, CH_2); 3.43 (s, 1 H, OH); 7.77—7.87 (m, 3 H, H(5), H(6), H(7)); 8.46—8.48 (m, 1 H, H(8)); 10.4 (br.s, 1 H, NH). ^{13}C NMR, δ: 29.92; 42.36; 70.84; 125.52; 127.08; 128.03; 130.55; 131.62; 133.54; 145.98; 136.61; 149.77; 159.98. MS, *m/z*: [M$^+$], found 218.1048, calculated 218.1038, $C_{12}H_{14}N_2O_2$.

Compounds **3d**—**f** were synthesized similarly to compound **7** (see below).

4-Benzylphthalazin-1(2*H*)-one (3d) in 83% yield, m.p. 203—204 °C (see Ref. 3: m.p. 197—198 °C). The benzylidenephthalide, *viz.*, 2,2′-(1,3-dihydroxy-2,4-diphenylcyclobutane-1,3-diyl)dibenzoic acid di-γ-lactone **6**, was isolated from the mother liquor. The yield was 12%, m.p. 280—282 °C (*cf.* Ref. 19: m.p. 294—296 °C).

4-(2-Phenoxyethyl)phthalazin-1(2*H*)-one (3e), 67% yield, m.p. 149—150 °C (*cf.* Ref. 4: m.p. 156—157 °C).

4-(4-Bromobenzyl)phthalazin-1(2*H*)-one (3f), 67% yield, m.p. 230—231 °C (*cf.* Ref. 6: m.p. 229—230 °C).

3-(2-Phenoxyethylidene)isobenzofuran-1(3*H*)-one (5b). A solution of 2-iodobenzoic acid (1.24 g, 5 mmol) and copper phenoxymethylacetylenide (1.17 g, 6 mmol) in DMF (20 mL) was refluxed for 40 min under argon (TLC monitoring, eluent CH_2Cl_2). The cooled reaction mixture was diluted with dichloromethane (25 mL), washed with 25% aqueous NH_3 (5×20 mL) to remove copper(I) salts, and water (50 mL), and dried with an-

hydrous Na_2SO_4. The solution was passed through an Al_2O_3 layer (80×25 mm, eluent CH_2Cl_2). The solvent was removed *in vacuo*, and the residue was recrystallized from hexane. The yield of product **5b** was 79%, m.p. 92—93 °C. IR (KBr), ν/cm^{-1}: 1795 (C=O). ^{1}H NMR, δ: 5.01 (d, 2 H, CH_2, J = 6.7 Hz); 5.83 (t, 1 H, =CH, J = 6.7 Hz); 6.95—6.98 (m, 3 H, *m*-H, *p*-H); 7.29—7.31 (m, 2 H, *o*-H); 7.55—7.56 (m, 1 H, H(5)); 7.67—7.71 (m, 2 H, H(4), H(6)); 7.93 (d, 1 H, H(7), J = 8.3 Hz). ^{13}C NMR, δ: 61.88; 103.31; 114.48; 120.30; 121.03; 124.58; 125.42; 129.47; 130.35; 134.50; 138.71; 146.90; 157.95; 166.14. MS, *m/z*: [M$^+$], found 252.0781, calculated 252.0780, $C_{16}H_{12}O_3$.

Compounds **5a,c—e** were synthesized similarly.

3-Pentylideneisobenzofuran-1(3*H*)-one (5c), 72% yield, m.p. 40—40.5 °C. IR (KBr), ν/cm^{-1}: 1725 (C=O). ^{1}H NMR, δ: 0.94 (t, 3 H, CH_3, J = 7.3 Hz); 1.36—1.42 (m, 2 H, δ-CH_2); 1.68—1.70 (m, 2 H, β-CH_2); 2.52 (t, 2 H, α-CH_2, J = 7.8 Hz); 6.24 (s, 1 H, =CH); 7.34 (d, 1 H, H(4), J = 7.8 Hz); 7.43—7.45 (m, 1 H, H(6)); 7.63—7.66 (m, 1 H, H(5)); 8.23 (d, 1 H, H(7), J = 9.2 Hz). ^{13}C NMR, δ: 13.63; 21.97; 28.83; 33.08; 102.71; 119.94; 124.84; 127.38; 129.37; 134.54; 137.45; 158.16; 163.03. MS, *m/z*: [M$^+$], found 202.0988, calculated 202.0991, $C_{13}H_{14}O_2$.

3-(4-Dimethylaminobenzylidene)isobenzofuran-1(3*H*)-one (5e), 67% yield, m.p. 195—196 °C. IR (KBr), ν/cm^{-1}: 1765 (C=O). ^{1}H NMR, δ: 3.01 (s, 6 H, N(CH_3)$_2$); 6.35 (s, 1 H, =CH); 6.71 (d, 2 H, *o*-H, J = 8.9 Hz); 7.40—7.70 (m, 5 H, H_{arom}); 7.87—7.88 (m, 1 H, H(7)). ^{13}C NMR, δ: 40.03; 90.38; 108.20; 111.68; 119.67; 126.42; 129.49; 131.54; 134.61; 138.30; 151.20; 154.68; 162.66; 167.37. MS, *m/z*: [M$^+$], found 265.1097, calculated 265.1099, $C_{17}H_{15}NO_2$.

3-Benzylideneisobenzofuran-1-(3*H*)-one (5a). The yield of **5a** was 73%, m.p. 101—102 °C (*cf.* Ref. 17: m.p. 90—92 °C).

3-(4-Bromobenzylidene)isobenzofuran-1-(3*H*)-one (5d). The yield of product **5d** was 78%, m.p. 151—152 °C (*cf.* Ref. 21: m.p. 154—155 °C).

4-Butyl-2*H*-benzo[*d*][1,2]diazepin-1(5*H*)-one (7). 80% $NH_2NH_2 \cdot H_2O$ (25 mg, 0.5 mmol) was added to a solution of phthalide **5e** (50 mg, 0.25 mmol) in ethanol (6 mL), and the mixture was refluxed for 2 h (TLC monitoring, eluent CH_2Cl_2—AcOEt). The mixture was cooled to 25 °C and filtered through an Al_2O_3 layer (15×10 mm), the solvent was evaporated, and the precipitate was recrystallized from hexane. The yield was 38 mg (72%), m.p. 71—72 °C. IR (KBr), ν/cm^{-1}: 1652 (C=O). ^{1}H NMR, δ: 0.85 (t, 3 H, CH_3, J = 7.2 Hz); 1.21—1.23 (m, 2 H, γ-CH_2); 1.52—1.55 (m, 2 H, β-CH_2); 2.40 (t, 2 H, α-CH_2, J = 7.4 Hz); 3.57 (s, 2 H, CH_2); 7.19—7.39 (m, 2 H, H(6), H(7)); 7.51—7.52 (m, 1 H, H(8)); 7.98 (d, 1 H, H(9), J = 6.9 Hz); 8.4 (br.s, 1 H, NH). ^{13}C NMR, δ: 13.57; 22.04; 27.92; 36.98; 37.89; 24.67; 126.96; 127.51; 130.67; 131.15; 133.06; 136.95; 165.97. MS, *m/z*: [M$^+$], found 216.1257, calculated 216.1256, $C_{13}H_{16}N_2O$.

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