Synthesis of 3-arylazo-1*H*-pyridazin-4-ones from difluoroboron chelates of 1,3-diketones*

*I. V. Kravtsov, P. A. Belyakov, S. V. Baranin, and V. A. Dorokhov**

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 5328. E-mail: vador@ioc.ac.ru

A convenient method for the synthesis of 6-R-3-arylazo-1*H*-pyridazin-4-ones from difluoroboron chelates of acetylacetone and aroylacetones was developed. The method is based on the ability of the methyl group of the chelates to react with two equivalents of a diazonium salt.

Key words: 1,3-diketones, difluoroboron chelates, diazonium tetrafluoroborate, 3-arylazo-1*H*-pyridazin-4-one.

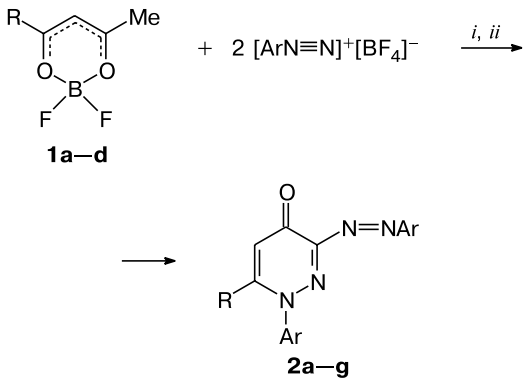
In our previous studies[1,2] of using boron chelates of 1,3-diketones in the synthesis of nitrogen-containing heterocyclic compounds, we have proposed novel routes to 5-aroylmethylpyrazoles and pyrazolo[1,5-*c*]pyrimidines *via* reactions of amide acetals with β-diketone difluoroboron chelates at their exocyclic methyl group followed by heterocyclization of the condensation products under the action of binucleophilic reagents (hydrazines, thiosemicarbazide, and aminoguanidine).

Apparently, electrophilic reagents other than amide acetals (*e.g.*, diazonium salts) can also be used in reactions with β-diketone difluoroboron chelates (for a preliminary communication, see Ref. 3). It is well known that diazonium salts react with acetylacetone at position 3 to give 3-arylhydrazonopentane-2,4-dione.[4] Azo coupling with aroylacetones occurs analogously. We found, however, that condensation of difluoroboron complexes of the above β-diketones involves two equivalents of a diazonium salt.

The reaction proceeds at ~0 °C in methanol—sulfolane (1 : 1) in the presence of sodium acetate. The resulting dark red crystalline complexes decompose on reflux in pyridine—butanol (3 : 1) to give 3-arylazo-1*H*-pyridazin-4-one derivatives (**2a—g**) identified by spectroscopic methods (Scheme 1). Note that in a reaction with one equivalent of the aryldiazonium salt, the monocoupling product cannot be isolated and half the starting chelate **1** remains nonconsumed.

Compounds **2** are orange-red solids that are poorly soluble in most organic solvents (except for compounds **2a,e**, which are well soluble in chloroform, benzene, ethyl acetate, and ethanol but insoluble in hexane and diethyl ether). The mass spectra of the pyridazinones obtained show molecular ion peaks M^+. The azo coupling reaction is possible in two ways *a* and *b* (Scheme 2) leading to the structural isomers of arylazopyridazin-4-ones that differ in the position of the arylazo group: compounds **2** (reaction with two equivalents of aryldiazonium tetrafluoroborate at the methyl group) or **3** (reaction at both the methyl group and the C atom of the methine group of the chelate ring) (see Scheme 2).

Scheme 1



2	R	Ar	2	R	Ar
a	Me	Ph	**e**	Me	4-$MeOC_6H_4$
b	Ph	4-$MeOC_6H_4$	**f**	Ph	4-ClC_6H_4
c	4-ClC_6H_4	4-$MeOC_6H_4$	**g**	4-ClC_6H_4	4-ClC_6H_4
d	2,4-$Me_2C_6H_3$	4-$MeOC_6H_4$			

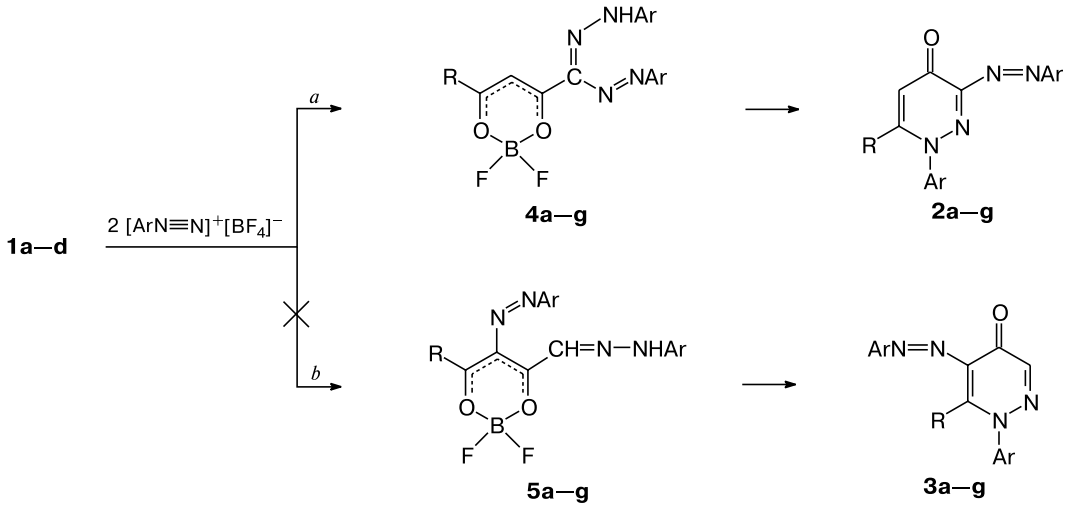
Reagents and conditions: *i*) NaOAc, H_2O, MeOH, sulfolane, 0—2 °C; *ii*) BuOH, pyridine, Δ.

The ^1H and ^{13}C NMR spectra of the pyridazinones obtained contain signals that are consistent in number,

* Dedicated to Academician V. A. Tartakovsky on the occasion of his 75th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1502—1506, August, 2007.

Scheme 2



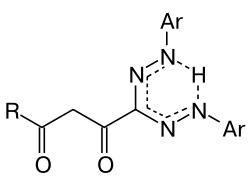
integral intensity ratio, and position with the structures of both isomers **2** and **3**. For instance, the singlets for the protons at δ 6.54—6.80 correspond to the CH proton of the pyridazine ring. The methyl protons in the ^{1}H NMR spectra of the compounds obtained from acetylacetone difluoroboron chelate **1a** and 4-methoxyphenyl- and phenyldiazonium tetrafluoroborates show high-field signals at δ 2.19 and 2.23, respectively. The IR spectra exhibit an absorption band due to the conjugated carbonyl group at ~1630 (in KBr) or ~1620 cm^{-1} (in $CHCl_3$).

However, more detailed studies by 2D ^{1}H—^{1}H and ^{1}H—^{13}C correlation spectroscopy showed that the reaction follows pathway *a* yielding isomers **2a—g**. The NOESY[5] spectrum ($CDCl_3$) of the pyridazinone obtained from chelate **1a** and phenyldiazonium tetrafluoroborate contains two intense cross-peaks due to spatial interactions of the methyl protons at δ 2.19 with the CH proton of the heterocycle at δ 6.66 and with the *ortho*-protons of only one benzene ring at δ 7.39, which corresponds to structure **2a**. The signals in the ^{13}C NMR spectrum were assigned by the HSQC[6] and HMBC methods.[7] It should be noted that the HMBC spectrum shows ^{1}H—^{13}C interactions between the methyl protons and the carbon atom of the CH group of the heterocycle and an interaction of the CH proton of the heterocycle with the carbon atom of the methyl group. Such correlations are possible only for structure **2a**.

Such compounds can arise only from a double attack of the aryldiazonium cation on the same exocyclic methyl group of the chelate. This is indirectly confirmed by the fact that the dibenzoylmethane difluoroboron chelate does not enter into an azo coupling reaction with phenyldiazonium tetrafluoroborate.

Based on the structures of the final pyridazinones, one could assume that intermediate boron complexes have chelate structures **4a—g** (see Scheme 2) rather than **5a—g**. These compounds were precipitated from the reaction mixture by water and washed with hexane. Chelates **4a,b,e** were obtained in the analytically pure state; the other complexes were used in further transformations without additional purification. Compounds **4a,b,e** are poorly soluble in all organic solvents and their mass spectra contain molecular ion peaks M^+. Their ^{11}B NMR spectra show a signal at δ ~0 for the tetracoordinate boron atom. The IR spectra (KBr) of complexes **4a,b,e** exhibit no absorption band of the carbonyl group at 1620—1700 cm^{-1} (which corresponds to *O*,*O*-coordination of the B atom) but contains a wide band at 3300—3600 cm^{-1}.

The structures of intermediate chelates were examined by ^{1}H and ^{13}C NMR spectroscopy with compound **4e** as an example. In the ^{1}H and ^{13}C NMR spectra of this complex, the signals for the protons at δ 3.90 and for the C atom at δ 55.7 of two methoxy groups coincide, which is some evidence for structure **4e**. The signals in the ^{13}C NMR spectrum were assigned by the HSQC and HMBC methods. The HMBC spectrum ($CDCl_3$) shows cross-peaks due to long-range interactions between the protons of the exocyclic methyl group at δ 2.37 and the carbon atom of the CH group of the chelate ring at δ 97.1 and due to interactions of the methyl protons and the CH proton of the chelate ring with the same carbonyl C atom at δ 179.2. The CH proton in the chelate ring at δ 6.83 interacts with two carbonyl C atoms, while the NH proton at δ 16.57 interacts with two quaternary C atoms, one of which is the *ipso*-C atom of the *para*-methoxyphenyl substituents. The observed correlations allow unambiguous assignment of structure **4** to the interme-



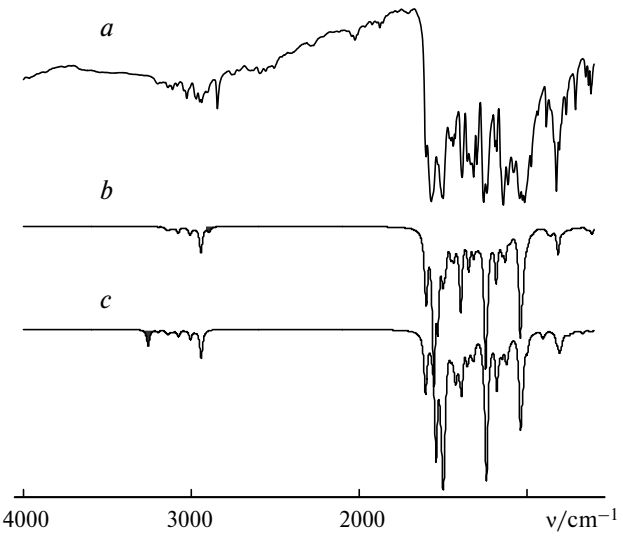


Fig. 1. Experimental IR spectrum of compound **4e** (*a*) and the simulated IR spectra for its cyclic (*b*) and linear structures (*c*). The absorption bands due to the NH stretching vibrations are hatched.

diate. Thus, the corresponding derivatives of 3-(1,3-dioxopropyl)formazan act as chelating ligands in complexes **4**. The presence of the formazan fragment in chelates **4a—g** allows intramolecular hydrogen bonding (IHB) to be formed.

Using attenuated total internal reflection (ATR) IR spectroscopy for chelate **4e**, we excluded the water stretching vibrations. The resulting spectrum contained a set of absorption bands at 2844—3199 cm^{-1}, including a band due to the NH stretching vibrations. To verify the presence of hydrogen bonding, we performed quantum-chemical calculations of the frequencies and energies of the bond vibrations in compound **4e** (see Fig. 1). For a linear structure, the calculated frequency of the NH stretching vibrations is 3255 cm^{-1}, while for a cyclic structure, its value is 2893 cm^{-1}. Therefore, the formazan fragment of chelate **4e** exists in the cyclic form stabilized by an intramolecular hydrogen bond. The presence of this bond can also be responsible for a substantial downfield shift of the signal for the NH proton in the ^1H NMR spectrum.

In contrast to pyridazin-3-one derivatives, isomeric pyridazin-4-ones are probably less accessible and, accordingly, less studied.[8,9] Using the "methodology of chelate organic synthesis",[10,11] we developed a simple and efficient method for the synthesis of novel 3-arylazo-1*H*-pyridazin-4-ones.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker WM-250 instrument (250 and 63 MHz, respectively) at 25 °C. ^{11}B and ^{19}F NMR spectra were recorded on a Bruker AC-200 instrument (64 and 188 MHz, respectively). Mass spectra were recorded on a Kratos MS-30 instrument (EI, 70 eV). ATR studies of compound **4e** were performed on a Shimadzu FTIR-8400S spectrometer (Shimadzu, Japan). Other IR spectra were recorded on a Specord M-82 instrument (KBr).

The geometries were optimized and the vibrational frequencies and energies in the IR spectra were calculated with the PRIRODA program system[12,13] (PBE functional,[14] DFT method, TZ2P basis set).

Tributyl borate was prepared according to a known procedure.[15]

Acetylacetone difluoroboron complex (1a). Boron trifluoride etherate (12.7 mL, 0.1 mol) was slowly added in an inert atmosphere to a solution of acetylacetone (15.4 mL, 0.15 mol) and tributyl borate (13.5 mL, 0.05 mol) in diethyl ether (10 mL). The reaction mixture was kept at room temperature for 16 h. The solvent was removed and the residue was cooled in a freezing chamber. The precipitate that formed was filtered off and washed with light petroleum (10 mL). Recrystallization from diethyl ether gave chelate **1a** (18.5 g, 83%) as white crystals, m.p. 43 °C (*cf.* Ref. 16: m.p. 43 °C (chloroform—ligroin)). ^{11}B NMR (CH_3CN), δ: 0.43.

Aroylacetone difluoroboron chelates 1b—d were prepared according to a known procedure[17] from appropriate aroylacetones and $BF_3 \cdot Et_2O$ in benzene.

Benzoylacetone difluoroboron chelate (1b). Yield 95%, m.p. 155—156 °C (benzene) (*cf.* Ref. 16: m.p. 155 °C (benzene)).

4-Chlorobenzoylacetone difluoroboron chelate (1c). Yield 89%, m.p. 227—228 °C (ethyl acetate) (*cf.* Ref. 18: m.p. 226.5—228 °C).

2,4-Dimethylbenzoylacetone difluoroboron chelate (1d). Yield 84%, m.p. 120—121 °C. Found (%): C, 60.65; H, 5.52. $C_{12}H_{13}BF_2O_2$. Calculated (%): C, 60.55; H, 5.50. MS, *m/z* (I_{rel} (%)): 238 $[M]^+$ (45), 223 (100). ^1H NMR ($CDCl_3$), δ: 2.39, 2.40 (both s, 6 H, $\underline{Me}_2C_6H_3$); 2.59 (s, 3 H, Me); 6.35 (s, 1 H, CH=); 7.14 (m, 2 H, Ar); 7.60 (d, 1 H, Ar, J = 8.3 Hz). ^{11}B NMR (THF), δ: 0.89. IR, ν/cm^{-1}: 3136, 2984, 1616, 1540 (br).

Difluoroboron chelate of 3-(1,3-dioxobutyl)-1,5-diphenylformazan (4a). A solution of NaOAc (82 mg, 5 mmol) in water (2 mL) was added dropwise at 0 °C to a solution of chelate **1a** (0.30 g, 2 mmol) and phenyldiazonium tetrafluoroborate (0.96 g, 5 mmol) in a mixture of sulfolane (5 mL) and methanol (5 mL). Immediately after the first drops of the solution were added, the reaction mixture turned bright red. The solution was stirred at 20 °C for 4 h, kept for 16 h, and then poured into water (100 mL). The precipitate that formed was filtered off, washed with water (50 mL) and hexane, and recrystallized from acetonitrile. The yield of chelate **4a** was 82%, m.p. 188—189 °C. Found (%): C, 57.13; H, 4.22; N, 16.06. $C_{17}H_{15}BF_2N_4O_2$. Calculated (%): C, 57.30; H, 4.21; N, 15.73. MS, *m/z* (I_{rel} (%)): 356 $[M]^+$ (17), 315 (6). ^1H NMR ($CDCl_3$), δ: 2.38 (s, 3 H, Me); 6.86 (s, 1 H, CH=); 7.40—7.80 (m, 10 H, Ar); 16.39 (s, 1 H, NH). ^{11}B NMR ($CHCl_3$), δ: 0.85. IR, ν/cm^{-1}: 3076, 1552, 1500.

Difluoroboron chelate of 3-(1,3-dioxo-3-phenylpropyl)-1,5-bis(4-methoxyphenyl)formazan (4b) was obtained analogously from chelate **1b** (0.42 g, 2 mmol) and 4-methoxyphenyldiazonium tetrafluoroborate (1.11 g, 5 mmol). The yield of chelate **4b** was 73%. Found (%): C, 59.99; H, 4.36; N, 11.52. $C_{24}H_{21}BF_2N_4O_4$. Calculated (%): C, 60.27; H, 4.43; N, 11.71.

MS, *m/z* (I_{rel} (%)): 478 $[M]^+$ (8), 343 (63). ^{1}H NMR (DMSO-d_6), δ: 3.86 (s, 6 H, 2 OMe); 7.12, 7.68, 7.98, 8.22 (all m, 14 H, Ar and CH=); 16.08 (s, 1 H, NH). ^{11}B NMR (CH_3CN), δ: 0—5 (br.s). IR, ν/cm^{-1}: 3048, 2948, 2840, 1600, 1556, 1512.

Difluoroboron chelate of 3-(1,3-dioxobutyl)-1,5-bis(4-methoxyphenyl)formazan (4e) was obtained analogously from chelate **1a** (0.30 g, 2 mmol) and 4-methoxyphenyldiazonium tetrafluoroborate (1.11 g, 5 mmol). The yield of chelate **4e** was 85%, m.p. 194—195 °C. Found (%): C, 54.60; H, 4.52; N, 13.29. $C_{19}H_{19}BF_2N_4O_4$. Calculated (%): C, 54.81; H, 4.57; N, 13.46. MS, *m/z* (I_{rel} (%)): 416 $[M]^+$ (42), 350 (16). ^{1}H NMR ($CDCl_3$), δ: 2.37 (s, 3 H, Me); 3.90 (s, 6 H, 2 OMe); 6.83 (s, 1 H, CH=); 7.02, 7.67 (both d, 2 H each, Ar, J = 9.2 Hz); 16.57 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 24.4 (Me); 55.6 (OMe); 97.1 (C(3)); 115.0 (*m*-C_{Ar}); 121.5 (*o*-C_{Ar}); 135.4 (C(1)); 140.0 (*ipso*-C_{Ar}); 161.0 (*p*-C_{Ar}); 179.2 (C(2)); 188.4 (C(4)). ^{11}B NMR ($CHCl_3$), δ: 0.76. ^{19}F NMR ($CDCl_3$), δ: −140.60. IR, ν/cm^{-1}: 2968, 1604, 1580, 1512.

Difluoroboron chelates **4c,d,g** were obtained analogously from compounds **1b,c,d** and used immediately in subsequent heterocyclization.

1-Aryl-6-R-3-arylazopyridazin-4(1*H*)-ones (2a—g) (general procedure). Chelates **4a—g** were refluxed in a mixture of pyridine (15 mL) and butanol (5 mL) for 4 h. The pyridine was removed and the residue was dissolved in chloroform and passed through a short column with silica gel. The solvent was evaporated and the residue was purified by flash chromatography on Silpearl silica gel with chloroform as an eluent (for pyridazinones **2a,e**); in the other cases, the reaction product was recrystallized from acetonitrile.

6-Methyl-1-phenyl-3-phenylazopyridazin-4(1*H*)-one (2a). Yield 51%, m.p. 225—226 °C. Found (%): C, 70.14; H, 4.85; N, 19.13. $C_{17}H_{14}N_4O$. Calculated (%): C, 70.33; H, 4.86; N, 19.30. MS, *m/z* (I_{rel} (%)): 290 $[M]^+$ (15), 261 (9). ^{1}H NMR ($CDCl_3$), δ: 2.19 (s, 3 H, Me); 6.66 (s, 1 H, H(5)); 7.39 (d, 2 H, Ar); 7.53 (m, 6 H, Ar); 7.95 (d, 2 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 20.8 (Me); 120.6 (C(5)); 123.7 (*o*-$C_{N=NPh}$); 126.4 (*o*-C_{NPh}); 128.8 (*m*-$C_{N=NPh}$); 129.6 (*m*-C_{NPh}); 129.7 (*p*-C_{NPh}); 132.4 (*p*-$C_{N=NPh}$); 141.8 (*ipso*-C_{NPh}); 151.5(C(6)); 152.7 (*ipso*-$C_{N=NPh}$); 159.0 (C(4)); 167.1 (C(3)). IR, ν/cm^{-1}: 3056, 3012, 1636, 1596, 1496; $CHCl_3$: 3072, 3000, 1620, 1596, 1496.

1-(4-Methoxyphenyl)-3-(4-methoxyphenylazo)-6-phenylpyridazin-4(1*H*)-one (2b). Yield 71%, m.p. 220—221 °C. Found (%): C, 69.68; H, 5.00; N, 13.85. $C_{24}H_{20}N_4O_3$. Calculated (%): C, 69.89; H, 4.89; N, 13.58. MS, *m/z* (I_{rel} (%)): 412 $[M]^+$ (15). ^{1}H NMR (DMSO-d_6), δ: 3.68 and 3.87 (both s, 3 H each, 2 OMe); 6.66 (s, 1 H, H(5)); 6.83, 7.14, 7.89 (all d, 2 H each, Ar, J = 8.5 Hz); 7.30 (m, 7 H, Ar). IR, ν/cm^{-1}: 2976, 2840, 1632, 1604, 1580, 1508.

6-(4-Chlorophenyl)-1-(4-methoxyphenyl)-3-(4-methoxyphenylazo)pyridazin-4(1*H*)-one (2c). Yield 58%, m.p. 212—213 °C. Found (%): C, 64.45; H, 4.45; N, 12.58. $C_{24}H_{19}ClN_4O_3$. Calculated (%): C, 64.50; H, 4.29; N, 12.54. MS, *m/z* (I_{rel} (%)): 446 $[M]^+$ (10). ^{1}H NMR (DMSO-d_6), δ: 3.70 and 3.87 (both s, 3 H each, 2 OMe); 6.69 (s, 1 H, H(5)); 6.86, 7.14, 7.31, 7.89 (all d, 2 H each, Ar, J = 8.9 Hz); 7.39 (br.s, 4 H, Ar). IR, ν/cm^{-1}: 2974, 2836, 1628, 1604, 1584, 1508.

6-(2,4-Dimethylphenyl)-1-(4-methoxyphenyl)-3-(4-methoxyphenylazo)pyridazin-4(1*H*)-one (2d). Yield 60%, m.p. 204—205 °C. Found (%): C, 70.66; H, 5.46; N, 12.73. $C_{26}H_{24}N_4O_3$. Calculated (%): C, 70.89; H, 5.49; N, 12.72. MS, *m/z* (I_{rel} (%)): 440 $[M]^+$ (30). ^{1}H NMR (DMSO-d_6), δ: 2.12 and 2.20 (both s, 3 H each, 2 Me); 3.67 and 3.87 (both s, 3 H each, 2 OMe); 6.54 (s, 1 H, H(5)); 6.81, 7.14, 7.89 (all d, 2 H each, Ar, J = 8.9 Hz); 6.97 (br.s, 2 H, Ar); 7.26 (m, 3 H, Ar). IR, ν/cm^{-1}: 2972, 2832, 1628, 1600, 1508.

1-(4-Methoxyphenyl)-3-(4-methoxyphenylazo)-6-methylpyridazin-4(1*H*)-one (2e). Yield 60%, m.p. 160—161 °C. Found (%): C, 64.91; H, 5.13; N, 16.11. $C_{19}H_{18}N_4O_3$. Calculated (%): C, 65.13; H, 5.18; N, 15.99. MS, *m/z* (I_{rel} (%)): 350 $[M]^+$ (18), 231 (25), 216 (22). ^{1}H NMR ($CDCl_3$), δ: 2.20 (s, 3 H, Me); 3.86, 3.88 (both s, 6 H, 2 OMe); 6.67 (s, 1 H, H(5)); 6.98 (m, 4 H, Ar); 7.30 (m, 2 H, Ar); 7.98 (d, 2 H, Ar, J = 8.9 Hz). IR, ν/cm^{-1}: 3060, 3012, 2924, 2836, 1632, 1604, 1580, 1512.

1-(4-Chlorophenyl)-3-(4-chlorophenylazo)-6-phenylpyridazin-4(1*H*)-one (2f). Yield 63%, m.p. 210—211 °C (from ethyl acetate). Found (%): C, 62.82; H, 3.61; N, 12.98. $C_{22}H_{14}Cl_2N_4O$. Calculated (%): C, 62.72; H, 3.35; N, 13.30. MS, *m/z* (I_{rel} (%)): 420 $[M - H]^+$ (16). ^{1}H NMR (DMSO-d_6), δ: 6.76 (s, 1 H, H(5)); 7.36 and 7.41 (both s, 9 H total, Ar); 7.69 and 7.92 (both d, 2 H each, Ar, J = 8.9 Hz). IR, ν/cm^{-1}: 2974, 1636, 1588, 1508.

1,6-Bis(4-chlorophenyl)-3-(4-chlorophenylazo)pyridazin-4(1*H*)-one (2g). Yield 59%, m.p. 233—234°C. Found (%): C, 58.11; H, 2.86; N, 12.27. $C_{22}H_{13}Cl_3N_4O$. Calculated (%): C, 57.98; H, 2.88; N, 12.29. MS, *m/z* (I_{rel} (%)): 454 $[M - H]^+$ (7). ^{1}H NMR (DMSO-d_6), δ: 6.80 (s, 1 H, H(5)); 7.44 (br.s, 8 H, Ar); 7.70 and 7.91 (both d, 2 H each, Ar, J = 8.5 Hz). IR, ν/cm^{-1}: 3048, 1632, 1492.

This work was financially supported by the Russian Academy of Sciences (Basic Research Program of the Presidium of the Russian Academy of Sciences "Development of the Methodology of Organic Synthesis and Creation of Compounds with Valuable Practical Properties").

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Received July 20, 2007