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Bromination–Dehydrobromination of 4-Aryl-5-nitro-6-phenyl-3,4-dihydropyrimidin-2(1*H*)-ones

V. F. Sedova, Yu. V. Gatilov, and O. P. Shkurko

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia
e-mail: oshk@nioch.nsc.ru

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Abstract—Depending on the conditions, bromination of 4-aryl-5-nitro-6-phenyl-3,4-dihydropyrimidine-2(1*H*)-ones and subsequent dehydrobromination gives either 4-aryl-5-nitro-6-phenylpyrimidin-2(1*H*)-ones or their mixtures with the corresponding 4-aryl-5-bromo-6-methoxy-5-nitro-6-phenyltetrahydropyrimidin-2-ones which are formed as two diastereoisomers.

Some 4-aryl-5-nitro-3,4-dihydropyrimidin-2(1*H*)-ones exhibit an appreciable biological activity, specifically as calcium channel modulators [1]. We recently found that several 4-aryl-5-nitro-6-phenyl-3,4-dihydropyrimidin-2(1*H*)-one derivatives show a high antiarrhythmic activity [2]. According to the data of [3], the stability of the heterocyclic fragment in 1,4(or 3,4)-dihydropyrimidines and structurally related 1,4-dihydropyridines to aromatization is important for their biological activity. Therefore, it seemed to be reasonable to examine the behavior of 4-aryl-5-nitro-6-phenyl-3,4-dihydropyrimidin-2(1*H*)-ones **I** in dehydrogenation and oxidation reactions which could result in aromatization of the heteroring.

The present communication reports on the bromination and subsequent dehydrobromination of dihydropyrimidinones **Ia**–**Ic**. This two-step technique is widely used for aromatization of dihydropyrimidinones [4]. Here, the first step (i.e., bromination) is usually determining. It was shown that the ease of bromination of 4,6-diphenyldihydropyrimidin-2-ones depends on the substituent in position *5* of the heteroring. The bromination of 4,6-diphenyldihydropyrimidin-2-ones having such substituent in position *5* as ethoxycarbonyl, aroxy, or nitro group requires more severe conditions as compared to the corresponding 5-unsubstituted and 5-alkyl derivatives [4–6]. For example, compound **Ia** undergoes bromination with bromine in boiling acetic acid, and the subsequent dehydrobromination yields pyrimidinone **IIa** [5].

Taking into account these findings, we performed bromination of 3-chlorophenyl derivative **Ib** on heating in acetic acid, and the bromination product was isolated and treated with pyridine in boiling methanol. As a result, we obtained 4-(3-chlorophenyl)-5-nitro-6-phenylpyrimidin-2(1*H*)-one (**IIb**) in good yield (Scheme 1). Unlike compounds **Ia** and **Ib**, 4-(4-methoxyphenyl)-5-nitro-6-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (**Ic**) readily reacted with an equimolar amount of bromine both in acetic acid and in chloroform at room temperature. However, the reaction involved only the methoxyphenyl group to give 4-(3-bromo-4-methoxyphenyl)-5-nitro-6-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (**Id**). This is consistent with published data on ready bromination of *para*-substituted anisoles [7]. The subsequent bromination of compound **Id** with an equimolar amount of bromine in acetic acid on heating, followed by dehydrobromination, afforded a mixture of products containing 4-(3-bromo-4-methoxyphenyl)-5-nitro-6-phenylpyrimidin-2(1*H*)-one (**IId**) and dibromo derivatives (according to the data of elemental analysis and mass spectrometry). We succeeded in isolating compound **IId** and a mixture of dibromo derivatives, but we failed to separate the latter into inidividual components. The absence in that mixture of compounds like **I** and **II** with a dibromomethoxyphenyl group ($[M]^+$ 481 and 479, respectively) suggests that the addition of bromine occurred at the double $C^5=C^6$ bond in the heteroring.

We also made an attempt to effect bromination under milder conditions, in chloroform at room temperature. There are no published data on the behavior of diarylpyrimidinones **I** under these conditions, while

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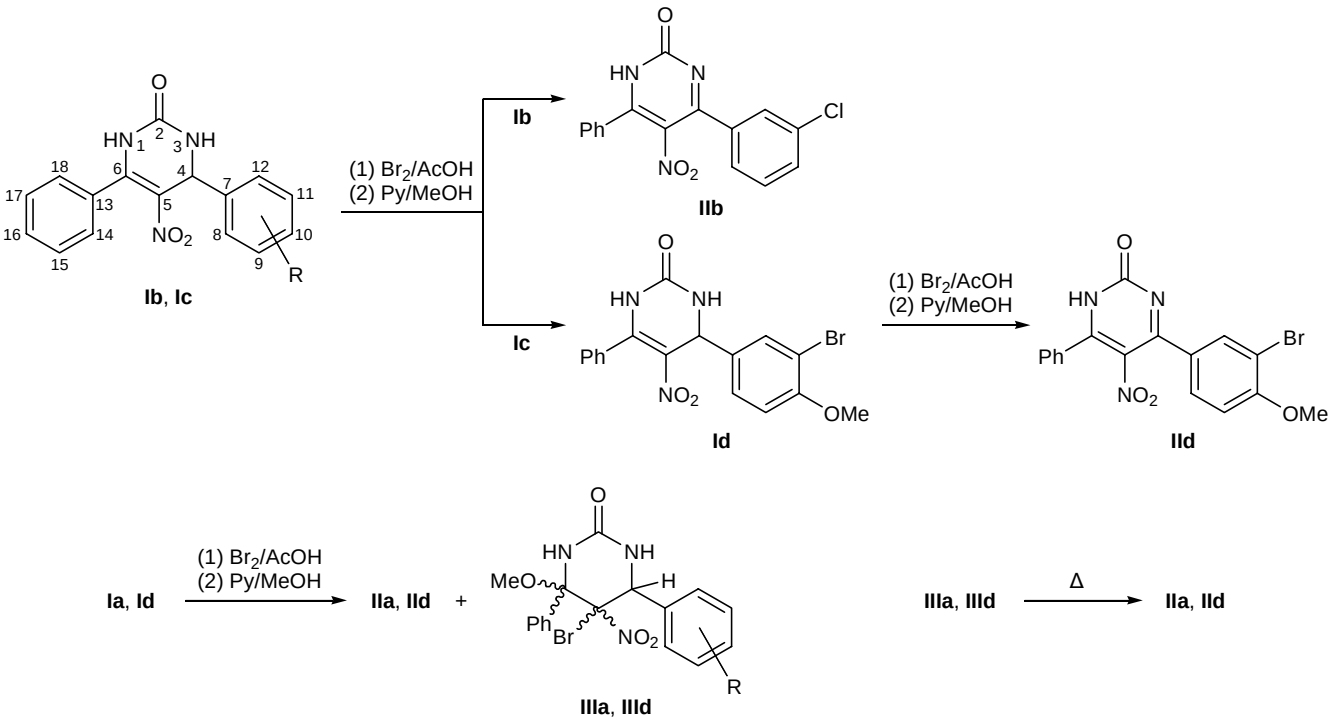
Scheme 1.



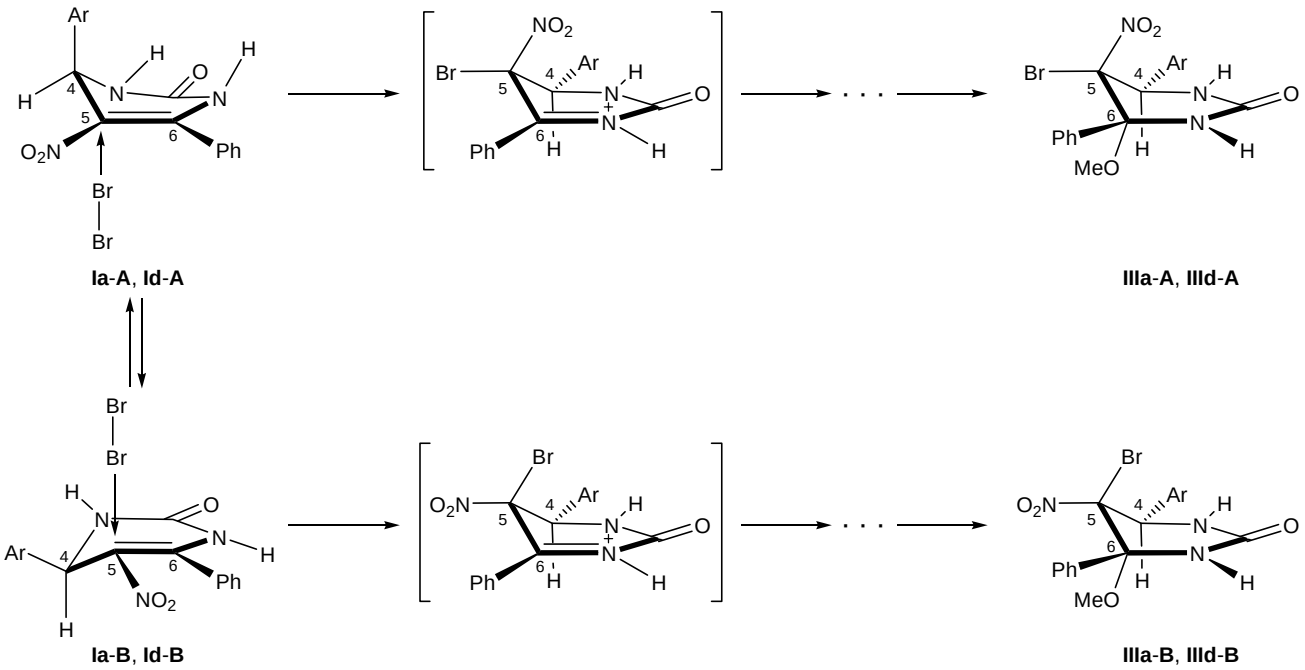
structurally related 4-aryl-6-methyl-5-nitro-3,4-dihydropyrimidin-2(1*H*)-ones are known to undergo bromination mainly at the 6-methyl group [8]. The bromination of compounds **Ia** and **Id** in chloroform, followed by dehydrobromination, afforded in each case two products, pyrimidinone **IIa** or **IId** and bromine-containing tetrahydropyrimidinone **IIIa** or **IIId**. Compound **Ib** failed to react under the same conditions.

In the IR spectra of **IIIa** and **IIId**, stretching vibrations of the carbonyl groups appear at 1689 and 1676 cm^{-1}. The molecular ion peak in the mass spectrum of **IIIa** is a doublet with *m*/*z* 405/407 ($C_{17}H_{16}BrN_3O_4$), while compound **IIId** shows a triplet with *m*/*z* 513/515/517 ($C_{18}H_{17}Br_2N_3O_5$). The presence of bromine atoms and methoxy group in molecules **IIIa** and **IIId** also follows from the analytical data and ^1H and ^{13}C NMR spectra. Compound **IIIa** is converted into pyrimidinone **IIa** on heating to 230°C; first, the initial compound changes its color (presumably due to elimination of hydrogen bromide), and methanol is then released.

The formation of substituted 5-bromo-6-alkoxy(or hydroxy)-5,6-dihydropyrimidines in the bromination is well known for pyrimidin-2-ones [9], 1,2-dihydropyrimidin-2-ylmethylene(cyano)acetic acid esters [10], and uracils [11]. The presence of bromine and methoxy group in positions *5* and *6*, respectively, of the hexahydropyrimidine ring in compounds **III** was confirmed by the ^{13}C NMR spectra and by the calculation of the chemical shifts of C^5 and C^6 according to the additivity scheme. Analysis of the ^1H and ^{13}C NMR spectra of **IIIa** and **IIId** showed that these compounds are approximately equimolar mixtures of two diastereoisomers.

By analogy with 4-(*o*-nitrophenyl)- and 4-(*m*-fluorophenyl)-5-nitro-6-phenyl-3,4-dihydropyrimidin-2(1*H*)-ones [12], compounds **Ia** and **Id** are likely to exist mainly in a *flattened boat* conformation with pseudoaxial 4-aryl group which declines over the $C^2N^3C^5C^6$ plane (conformer **A**; Scheme 2). Taking into account the high conformational mobility of the heteroring (according to the PM3 calculations, the activation enthalpy $\Delta H^{\neq}$ for ring inversion in isolated molecule **Ia** is 1.67 kJ/mol; for the solvated molecule, the corresponding value should be slightly greater), some equilibrium amount of the second conformer (**B**) should be present in solution. Conformer **B** also has a *flattened boat* structure, but the 4-aryl group therein is oriented equatorially. Analysis of the steric models of conformers **A** and **B** showed that, under conditions of kinetic control, attack by bromine molecule on the

Scheme 2.



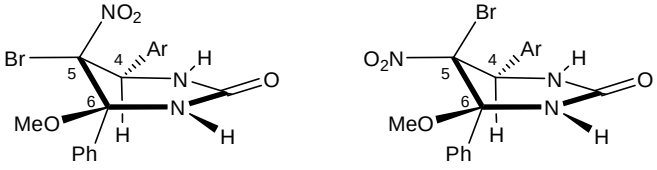
double bond can occur only from the spatially accessible *exo* side of the heteroring. Rehybridization of the C^5 atom from sp^2 to sp^3 leads to distortion of the heteroring, so that the bromine atom and 4-aryl group in conformer **A** occupy equatorial positions while the nitro group and 4-H become axial. Conformer **B** is characterized by the opposite orientation of substituents at C^5. Both structures are then stabilized via addition of bromide ion at position *6* of the heteroring.

6-Methoxytetrahydropyrimidin-2-one **III** is formed by heating of intermediate 5,6-dibromo derivative in boiling methanol in the presence of pyridine. Presumably, in the two cases derivatives with axial methoxy group on C^6 are mainly formed. The orientation of the methoxy and phenyl groups on C^6 can be judged on the basis of the data reported for hydrogenated pyrimidinones; in keeping with these data, phenyl group tends to occupy equatorial position while hydroxy or alkoxy group is usually oriented axially due to its anomeric effect [13–16].

While elucidating the structure of diastereoisomers **III**, we also considered published data for tetrahydropyrimidin-2-ones which were found to exist in a *distorted boat* conformation with the base formed by the $N^1N^3C^4C^6$ atoms of the pyrimidine ring [13, 14]. The orientation of substituents in position *4* of the pyrimidine ring in compounds **IIIa** and **IIId** follows from the ^{1}H NMR spectra. The spectra contain two singlets from 4-H at δ 5.57 and 6.03 ppm for compound **IIIa** and δ 5.55 and 5.98 ppm for **IIId** ($^3J_{3,4} \approx 0$ Hz); therefore, the 4-H atom in both diastereoisomers is axial [13] and the 4-aryl group occupies equatorial position. Such orientation of the aryl group is typical of phenyl-substituted cyclohexanes, cyclohexanones [17], and tetrahydropyrimidin-2-ones (thiones) [13–15].

In keeping with the above stated, the most probable structures of compounds **IIIa** and **IIId** are diastereoisomeric configurations **A** and **B**. We calculated by the AM1, PM3, and HF/3-21G methods the thermodynamic stabilities ΔH_f of four diastereoisomers **A–D** of **IIIa** with axial hydrogen atom and equatorial phenyl group on C^4. The following ΔH_f values were obtained for diastereoisomers **A–D**, respectively, kJ/mol: AM1: 66.94, 67.15, 73.47, 84.85; PM3: –56.07, –50.92, –47.61, –49.50; HF/3-21G: 0.00, 0.79, 28.49, 31.17 (E = –3669.576144 a.u.). These data are consistent with the greater thermodynamic stability of diastereoisomers **A** and **B**, as compared to diastereoisomers **C** and **D** in which the 6-methoxy group is equatorial while the 6-Ph group is axial.

Thus the bromination of compounds **Ia**, **Ib**, and **Id** with bromine in acetic acid on heating and the sub-



sequent dehydrobromination occurs selectively to give pyrimidinones **IIa**, **IIb**, and **IId**. When the bromination of compounds **Ia** and **Id** is carried out under milder conditions (in chloroform at room temperature), the subsequent dehydrobromination involves only a part of the products while the others are converted into stable bromine-containing tetrahydropyrimidin-2-ones **IIIa** and **IIId**. Stable 5-bromo-5-nitrotetrahydropyrimidin-2-ones were isolated for the first time as mixtures of two diastereoisomers.

EXPERIMENTAL

The IR spectra were recorded in KBr on a Bruker Vector-22 spectrometer. The UV spectra of solutions in ethanol were measured on a Specord M-40 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were obtained on Bruker AC-200 and AM-400 spectrometers using DMSO-d_6 as solvent and reference. The mass spectra (electron impact, 70 eV) were run on a Finnigan MAT 8200 instrument with direct sample admission into the ion source. The purity of the products was checked by TLC on Silufol UV-254 plates using $CHCl_3$ as eluent; spots were visualized under UV light.

5-Nitro-4,6-diphenyl-3,4-dihydropyrimidin-2(1*H*)-one (Ia) was synthesized according to the procedure reported in [5]. ^{13}C NMR spectrum (100 MHz), δ_C, ppm: 54.31 (C^4), 122.54 (C^5), 126.50 (Ph), 127.79 (C^9, C^{11}), 128.17 (C^{10}), 128.49 (Ph), 128.94 (Ph), 129.93 (Ph), 132.56 (C^{13}), 142.29 (C^7), 149.71 (C^6), 150.43 (C^2).

4-(3-Chlorophenyl)-5-nitro-6-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (Ib) and 4-(4-methoxyphenyl)-5-nitro-6-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (Ic) were prepared as described in [2]. ^{13}C NMR spectrum of **Ic** (50 MHz), δ, ppm: 53.62 (C^4); 55.06 (OMe); 114.10 (C^9, C^{11}); 122.86 (C^5); 127.53, 127.58, 128.23, 129.64 (C_{arom}); 132.49 (C^{13}); 134.29 (C^7); 148.99 (C^6); 150.26 (C^{10}); 158.99 (C^2).

4-(3-Chlorophenyl)-5-nitro-6-phenylpyrimidin-2(1*H*)-one (IIb). A solution of 1.1 g (7 mmol) of bromine in 5 ml of acetic acid was added to a solution of 2.0 g (6 mmol) of compound **Ib** in 20 ml of acetic acid, and the mixture was heated for 1 h under reflux. The mixture was poured into 200 ml of water, and the yellow precipitate was filtered off and washed with water and methanol. Methanol, 20 ml, and pyridine, 3 ml, were added to the product, the mixture was heated for 4 h under reflux, poured into 100 ml of water, and acidified with 10% hydrochloric acid, and the precipitate was filtered off and washed with water and ethanol. Yield 1.4 g (70%), mp 226–228°C (from EtOH). UV spectrum, λ_{max}, nm (log ε): 249 (4.17), 297 (3.99). IR spectrum, ν, cm^{-1}: 1656 (C=O), 1528 (NO_2, asym.), 1328 (NO_2, sym.). Mass spectrum, *m*/*z* (I_{rel}, %): 329 (24.2) and 327 (69.8) $[M]^+$, 312 (1.5) and 310 (4.3) [*M* – OH], 301 (6.9) and 299 (28.6) [*M* – CO], 292 (24.0), 140 (20.1), 138 (63.1), 115 (26.2), 113 (11.0), 111 (28.3), 104 (100.0), 81 (43.3), 77 (60.3). Found, %: C 58.78; H 3.05; Cl 10.20; N 12.83. $[M]^+$ 327.0401. $C_{16}H_{10}ClN_3O_3$. Calculated, %: C 58.63; H 3.08; Cl 10.82; N 12.82. *M* 327.0410.

4-(3-Bromo-4-methoxyphenyl)-5-nitro-6-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (Id). A solution of 2.15 g (13 mmol) of bromine in 5 ml of chloroform was added dropwise with stirring at room temperature to a suspension of 3.25 g (10 mmol) of compound **Ic** in 25 ml of chloroform. The mixture was stirred for 12 h, and the precipitate was filtered off and washed with chloroform. Methanol, 15 ml, and pyridine, 2.5 ml, were added to the product, the mixture was heated for 1.5 h under reflux, and the precipitate was filtered off and washed with water and methanol. Yield 2.2 g (55%), mp 208–210°C (from EtOH). UV spectrum, λ_{max}, nm (log ε): 228 (4.31), 346 (3.89). IR spectrum, ν, cm^{-1}: 1693 (C=O), 1496 (NO_2, asym.), 1303 (NO_2, sym.). ^{1}H NMR spectrum (400 MHz), δ, ppm: 3.86 s (3H, OMe), 5.62 d (1H, 4-H, ^3J = 3.5 Hz), 7.18 d (1H, *m*-H, ^3J = 8.5 Hz), 7.42 d.d (1H, *o*-H, ^3J = 8.5, ^4J = 2 Hz), 7.43–7.60 m (5H, Ph), 7.62 d (1H, *o*-H, ^4J = 2 Hz), 8.38 d (1H, 3-H, ^3J = 3.5 Hz), 10.14 s (1H, 1-H). ^{13}C NMR spectrum (100 MHz), δ_C, ppm: 53.19 (C^4); 56.32 (OMe); 110.67 (C^9); 113.02 (C^{11}); 122.23 (C^5); 126.85, 127.74, 128.47, 129.96 (C_{arom}); 131.18 (C^8); 132.39 (C^{13}); 135.93 (C^7); 149.66 (C^6); 150.25 (C^{10}); 155.18 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 405 (7.8) and 403 (8.5) $[M]^+$, 388 (86.4) and 386 (86.7) [*M* – OH], 357 (100), 355 (81.9), 308 (8.8), 277 (15.3), 218 (38.3), 171 (42.9), 117 (7.8), 104 (20.4), 103 (5.8), 102 (5.1), 77 (15.4). Found, %: C 51.03; H 3.54; Br 19.80; N 10.43. $[M]^+$ 403.0185. $C_{17}H_{14}BrN_3O_4$. Calculated, %: C 50.51; H 3.49; Br 19.77; N 10.40. *M* 403.0168.

4-(3-Bromo-4-methoxyphenyl)-5-nitro-6-phenylpyrimidin-2(1*H*)-one (IId). A solution of 1.0 g (6 mmol) of bromine in 7 ml of acetic acid was added dropwise with stirring at room temperature to a suspension of 2.0 g (5 mmol) of compound **Id** in 20 ml of acetic acid. The mixture was stirred for 12 h at room temperature, heated for 0.5 h under reflux, cooled, and poured into 300 ml of water. The yellow precipitate was filtered off, washed with water, and dried on

a filter. Methanol, 15 ml, and pyridine, 2.2 ml, were added to the product, the mixture was heated for 0.5 h under reflux and cooled, and the precipitate was filtered off and washed in succession with ethanol, 10% hydrochloric acid, water, and ethanol again. Yield 1.6 g, mp 195–260°C; recrystallization from dioxane gave 1.0 g (50%) of compound **IId** with mp 270–272°C. UV spectrum, λ_{max}, nm (logε): 207 (4.51), 240 sh (4.18), 316 (4.08). IR spectrum, ν, cm^{-1}: 1654 (C=O), 1519 (NO_2, asym.), 1356 (NO_2, sym.). ^{1}H NMR spectrum (200 MHz), δ, ppm: 3.93 s (3H, OMe), 7.25 d (1H, 11-H, ^3J = 8.7 Hz), 7.51–7.62 m (6H, 12-H, C_6H_5), 7.85 d (1H, 8-H, ^4J = 2.1 Hz), 11.17 br.s (1H, NH). ^{13}C NMR spectrum (50 MHz), δ_C, ppm: 56.66 (OMe); 110.72 (C^9); 112.62 (C^{11}); 127.23 (C^5); 127.40, 128.27, 128.58, 128.66 (C_{arom}); 131.02 (C^{13}); 132.33 (C^7); 132.67 (C^8); 152.29 (C^6); 156.17 (C^4); 157.64 (C^{10}); 169.20 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 403 (26.8) and 401 (24.8) $[M]^+$, 388 (7.2) and 386 (7.5) [*M* – Me], 375 (7.1) and 373 (9.0) [*M* – CO], 357 (13.5) and 355 (11.2) [*M* – NO_2], 242 (11.0), 240 (12.0), 214 (14.8), 212 (13.8), 122 (13.8), 105 (100), 104 (39.1), 77 (80.9). Found, %: C 50.52; H 3.19; Br 20.10; N 10.17. $[M]^+$ 401.0017. $C_{17}H_{12}BrN_3O_4$. Calculated, %: C 50.76; H 3.01; Br 19.87; N 10.45. *M* 401.0011.

By diluting the dioxane mother liquor with water we isolated a mixture of mono- and dibromo-substituted compounds (according to the mass spectral data).

5-Bromo-6-methoxy-5-nitro-4,6-diphenyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (IIIa) (a mixture of stereoisomers A and B). A solution of 2.7 g (17 mmol) of bromine in 10 ml of chloroform was added to a suspension of 4.4 g (15 mmol) of compound **Ia** in 40 ml of chloroform. The mixture was stirred for 10 h at room temperature and was left to stand for 10 days. A solid gradually separated from the solution; it was filtered off, washed with chloroform, and dispersed in 50 ml of methanol, 4 ml of pyridine was added, and the mixture was kept for 24 h and was then heated for 5 h under reflux. The precipitate was filtered off, washed in succession with 10% hydrochloric acid, water, and methanol, and dissolved in hot methanol, the solution was cooled, and the product was precipitated with water, filtered off, and dried in air. Yield of diastereoisomer mixture **IIIa-A**/**IIIa-B** 2.4 g (40%), mp 214–216°C (from MeOH). IR spectrum, ν, cm^{-1}: 1689, 1676 sh (C=O); 1560 (NO_2, asym.); 1339 (NO_2, sym.). ^{1}H NMR spectrum (400 MHz), δ, ppm: 3.20 s and 3.25 s (3H, OMe), 5.57 s and 6.03 s (1H, 4-H), 7.35–7.51 m (20H, Ph), 7.66 s and 7.72 s (1H, 3-H), 8.43 s and 8.62 s (1H, 1-H). ^{13}C NMR spectrum (100 MHz), δ_C, ppm: 49.90 and 51.22 (OMe); 58.40 and 62.34 (C^4); 89.16 and 90.87 (C^6); 105.76 and 106.67 (C^5); 127.58, 127.78, 127.88, 128.06, 128.82, 128.91, 128.97, 129.15, 129.19, 129.42, 129.75, 129.92 (C_{arom}); 132.11 and 132.39 (C^{13}); 134.21 and 134.59 (C^7); 153.75 and 154.15 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 407 (4.9) and 405 (4.1) $[M]^+$, 375 (2.0) and 373 (1.6) [*M* – MeOH], 329 (34.6) and 327 (35.9) [*M* – MeOH – NO_2], 294 (23.2) [*M* – MeOH – Br], 278 (14.5), 253 (6.9), 251 (7.9), 249 (10.4), 247 (20.1), 218 (12.5), 171 (10.5), 162 (59.9), 136 (100), 134 (11.8), 132 (19.7), 105 (32.6), 104 (49.9), 103 (7.8), 102 (14.4), 77 (37.9). Found, %: C 50.20; H 3.85; Br 19.35; N 10.25. $[M]^+$ 405.0321. $C_{17}H_{16}BrN_3O_4$. Calculated, %: C 50.26; H 3.97; Br 19.67; N 10.34. *M* 405.0324.

The methanol–pyridine filtrate was poured into 150 ml of water, and the precipitate was filtered off, washed in succession with water, 10% hydrochloric acid, water again, and methanol, and dried in air to isolate 1.6 g (36%) of compound **IIa**, mp 249–250°C (from EtOH); published data [5]: mp 248–251°C.

5-Bromo-4-(3-bromo-4-methoxyphenyl)-6-methoxy-5-nitro-6-phenyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (IIId) (a mixture of stereoisomers A and B) was synthesized as described above for compound **IIIa**. A mixture of 1.0 g (2.5 mmol) of compound **Id** and 0.5 g (3 mmol) of bromine in 8 ml of chloroform was stirred for 3 days at room temperature. Treatment of the mixture afforded 0.2 g (15%) of a mixture of diastereoisomers **IIId-A** and **IIId-B** with mp 205–206°C (from EtOH–dioxane). IR spectrum, ν, cm^{-1}: 1689, 1675 sh (C=O); 1560 (NO_2, asym.); 1330 (NO_2, sym.). ^{1}H NMR spectrum (200 MHz), δ, ppm: 3.18 s and 3.23 s (3H, OMe), 3.84 s (6H, OMe), 5.55 s and 5.98 s (1H, 4-H), 7.07 d and 7.12 d (1H, 11-H, $^3J_{11,12}$ = 4.3 Hz), 7.30–7.48 m (6H, 12-H, C_6H_5), 7.57 d and 7.68 d (1H, 8-H, $^4J_{8,12}$ = 2 Hz), 7.75 s and 7.81 s (1H, 3-H), 8.50 s and 8.68 s (1H, 1-H). ^{13}C NMR spectrum (50 MHz), δ_C, ppm: 49.87 and 51.19 (6-OMe); 56.26 (10-OMe); 57.36 and 61.21 (C^4); 89.11 and 90.80 (C^6); 105.81 and 106.43 (C^5); 109.65 and 109.90 (C^9); 111.78 and 112.00 (C^{11}); 127.53, 127.83, 128.83, 128.85, 129.72, 130.26, and 130.65 (C_{arom}); 132.03 and 132.31 (C^{13}); 133.51 and 134.20 (C^7); 153.66 and 154.09 (C^2); 155.99 (C^{10}). Mass spectrum, *m*/*z* (I_{rel}, %): 517 (2.1), 515 (3.9), 513 (2.3) $[M]^+$, 439 (8.2), 437 (15.6) i 435 (9.2) [*M* – MeOH – NO_2], 404 (6.5) and 402 (5.7) [*M* – MeOH – Br], 359 (6.0), 357 (12.0) and

355 (5.3), 242 (12.7) and 240 (11.7), 215 (6.1) and 213 (7.4), 214 (11.2) and 212 (10.7), 162 (64.0), 136 (100), 134 (9.4), 132 (4.0), 105 (43.0), 104 (46.0), 103 (9.3), 102 (8.1), 77 (44.6). Found, %: C 42.58; H 3.53; Br 29.70; N 7.73. $[M]^+$ 512.9532. $C_{18}H_{17}Br_2N_3O_5 \cdot 0.25C_4H_8O_2$. Calculated, %: C 42.47; H 3.57; Br 29.75; N 7.82. *M* 512.9536.

From the methanol–pyridine filtrate we isolated 0.65 g (64%) of compound **IId**, mp 269–271°C (from dioxane).

Thermal decomposition of compound IIIa. A 30-mg portion of compound **IIIa** was heated for 5 min at 230°C. The resulting melt was recrystallized from ethanol. The product was identical to **IIa** in the melting point (248–251°C) and IR spectrum [5].

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