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Halogenation of *N*-Substituted *p*-Quinone Monoimines and *p*-Quinone Monooxime Ethers: XIII.* Specificity of Bromination of *N*-Acetyl(aroyl)-1,4-benzoquinone Monoimines

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Abstract—6-Hydroxy-2-methyl(aryl)-1,3-benzoxazoles were synthesized by bromination of *N*-acetyl(aroyl)-1,4-benzoquinone monoimines.

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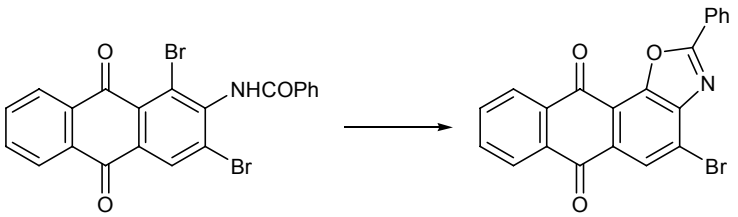
In the preceding communications of this series we described in detail halogenation of *N*-aroyl-1,4-benzoquinone monoimines and their reduction products [1–5], as well as of 4-acetylaminophenols having no other substituents in the benzene ring [6]. Various halogen-containing derivatives were obtained and specificity of halogenation related to the effect of strong electron-withdrawing substituent on the nitrogen atom was revealed. In particular, low stability of intermediate cyclohexene structures [1, 2], halogenation of methyl groups in the quinoid ring, and formation of 5-aroyloxycyclohex-2-ene-1,4-diones [2, 3] were observed.

In keeping with published data, 2-benzoylamino-substituted 1,3-dibromoanthraquinone having a fragment similar to bromine-containing 4-aroylaminophenols is converted into anthroxazole via dehydrobromination on heating [7] (Scheme 1). Analogous transformation of 1,4-naphthoquinone derivative involved dehydrochlorination on heating with acetic anhydride in the presence of traces of sulfuric acid [8] (Scheme 2). In these reactions, the quinoid moiety exerts an activating effect.

Benzoxazoles are also formed by the action of excess bromine on 2,4-bis(acetylamino)phenol [9] (Scheme 3). Benzoxazoles were obtained previously by hydrochlorination of *p*-quinonedipivalimides (among other products) [10] and by treatment of *p*-quinonedibenzimide with sulfuric acid in benzene [11]. The formation of benzoxazoles via hydrochlorination was favored by the presence of chlorine atoms in positions *2* and *6* of the quinoid ring [10] and by acidic conditions [10, 11].

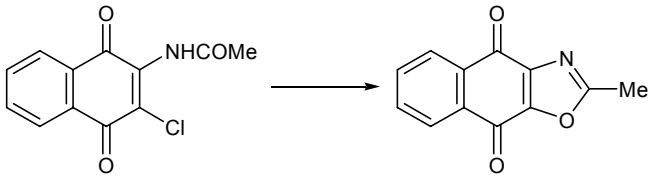
The goal of the present work was to synthesize benzoxazoles from halogen-substituted *N*-acyl-1,4-benzoquinone monoimines. In our previous studies,

Scheme 1.

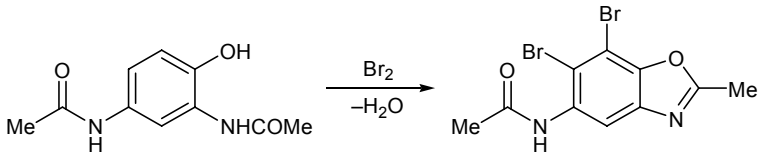


* For communication XII, see [1].

Scheme 2.



Scheme 3.



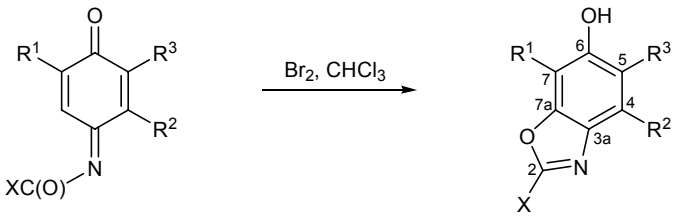
halogenation of various *N*-acetyl(aroyl)-1,4-benzoquinone monoimines gave only halogenated quinone monoimines, aminophenols, cyclohexene structures, and 5-aroyloxycyclohex-2-ene-1,4-diones [1–6], whereas hydrohalogenation of the same substrates afforded the corresponding 1,4-addition products [1–6, 12]. All possible steps in the hydrohalogenation process were examined, while halogenation of *N*-acetyl-(aroyl)-1,4-benzoquinone monoimines having halogen atoms in the quinoid ring was not studied specially.

In this work we performed halogenation of various *N*-acetyl(aroyl)-1,4-benzoquinone monoimines containing one to three halogen atoms in the quinoid ring. *N*-Acetyl(aroyl)-1,4-benzoquinone monoimines **I**–**VII** having one free *ortho* position with respect to the C=N carbon atom reacted with bromine at a molar ratio of 1:5 in chloroform to give benzoxazoles **VIII**–**XIII** (Scheme 4). Bromination of the same compounds in other solvents (dimethylformamide, acetic acid, or dimethylformamide–acetic acid mixture) at different reactant ratios resulted in halogenation of the quinoid ring or did not occur (initial quinone monoimines were recovered from the reaction mixtures), regardless of the conditions.

Benzoxazoles **XVa** and **XVb** were also obtained by bromination of 4-aroylimino-2,6-di-*tert*-butyl-5,5,6-trichlorocyclohex-2-en-1-ones **XIVa** and **XIVb** under similar conditions (Scheme 5). Compounds **XIVa** and **XIVb** are chlorination products of *N*-aroyl-2,6-di-*tert*-butyl-1,4-benzoquinone imines [5]. It should be emphasized that only one *tert*-butyl group was present in molecules **XV**. Analogous replacement of *tert*-butyl group was observed previously in the chlorination of 4-aroylamino-2,6-di-*tert*-butylphenols [5] and in the reaction of 2,6-di-*tert*-butyl-1,4-benzoquinone 4-oxime with S_2Cl_2 in the presence of ethyl(diisopropyl)amine and *N*-chlorosuccinimide in tetrahydrofuran [13].

The structure of benzoxazole derivatives **VIII**–**XIII** and **XV** was proved by their elemental analyses and IR and ^{1}H and ^{13}C NMR spectra. The IR spectra of these compounds contained absorption bands typical of C=N (1610 cm^{-1}) and OH groups (3500 cm^{-1}), while no absorption bands assignable to carbonyl stretching vibration bands were observed (1630–1655 cm^{-1}). The hydroxy proton resonated in the ^{1}H NMR spectra as a broadened singlet at δ 5.83–6.20 ppm, the methyl proton signal was displaced considerably downfield (δ 2.48–3.22 ppm) relative to the corresponding signal

Scheme 4.

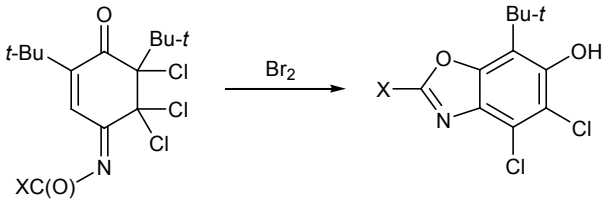


Ia, **Ib**, **IIa**, **IIb**, **IIf**, **IIIa**, **IIIb**, **IVb**, **IVc**, **IVf** **Va**, **Vb**, **Vd**, **Vg**, **VIa**–**VIe**, **VIg**, **VIIa**–**VIIe**, **VIIg**

VIIIa, **VIIIb**, **IXa**, **IXb**, **IXf**, **Xa**, **Xb**, **XIb**, **XIc** **XIf**, **XIIa**–**XIIe**, **XIIg**, **XIIIa**–**XIIIe**, **XIIIg**

I, **VIII**, R^1 = Me, R^2 = R^3 = Cl; **II**, **IX**, R^1 = Me, R^2 = R^3 = Br; **III**, **X**, R^1 = R^3 = Cl, R^2 = Me; **IV**, **XI**, R^2 = Me, R^1 = R^3 = Br; **V**, R^1 = *i*-Pr, R^2 = Me, R^3 = H; **VI**, **XII**, R^1 = *i*-Pr, R^2 = Me, R^3 = Cl; **VII**, **XIII**, R^1 = *i*-Pr, R^2 = Me, R^3 = Br; X = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**), 4-O_2NC_6H_4 (**d**), 3-O_2NC_6H_4 (**e**), 4-Br-3-MeOC_6H_3 (**f**), Me (**g**).

Scheme 5.



XIVa, **XIVb** **XVa**, **XVb**

X = Ph (**a**), 4-MeC_6H_4 (**b**).

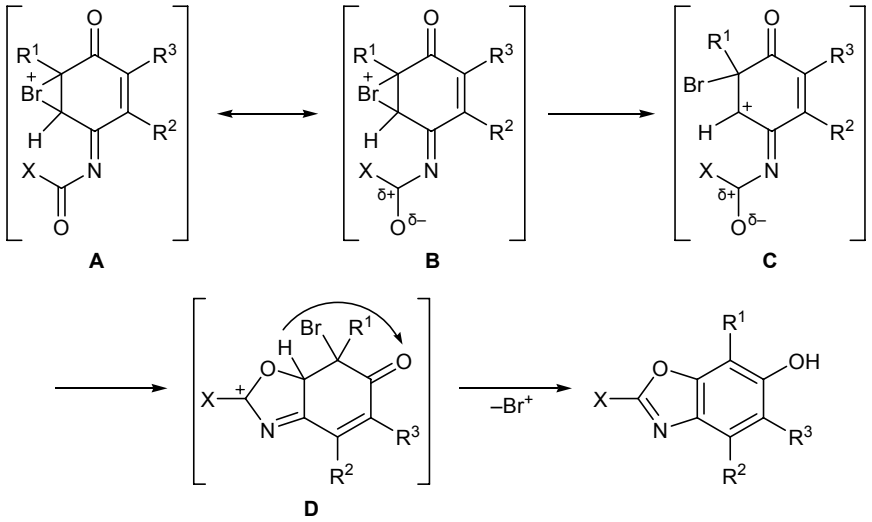
of aminophenols, and no aromatic proton signal was present.

The molecular structure of 5-bromo-6-hydroxy-7-isopropyl-4-methyl-2-(4-nitrophenyl)-1,3-benzoxazol-6-ol (**XIIId**) was unambiguously determined by X-ray analysis (see figure). All non-hydrogen atoms in molecule **XIIId** in crystal (except for methyl carbon atoms in the isopropyl substituent) lie in one plane. Such conformation is stabilized by attractive intramolecular interactions $O^2\cdots H^{8A}$ 2.33 Å (the sum of the van der Waals radii is 2.46 Å [14]), $Br^1\cdots H^{7A}$ 2.85 (3.13 Å), and $Br^1\cdots H^{2A}$ (2.56 Å), which may be regarded as very weak intramolecular hydrogen bonds, taking into account small angles $\angle C^8H^{8A}O^2$ 111°, $\angle C^7H^{7A}Br^1$ 105°, and $\angle O^2H^{2A}Br^1$ 126°. The same factor is responsible for orientation of the isopropyl group which is turned so that the C^8–H^{8A} bond is coplanar to the bicyclic fragment (torsion angle $C^3C^2C^8H^{8A}$ is equal to 0°).

It was presumed previously [10] that the formation of benzoxazoles in the hydrochlorination of *p*-quinonedipivalimides is the result of protonation of the nitrogen atom and subsequent ring closure involving the carbon atom in the *ortho* position with respect to the second C=N carbon atom possessing a partial positive charge. However, the reaction mixture in the bromination of quinone monoimines **I**–**VII** contains no protons. It is known that halogenation of N-substituted 1,4-benzoquinone monoimines involves formation of intermediate halonium ion or carbocation [4, 15]. Bromination of quinone monoimines in the presence of LiCl occurs at the *ortho* position with respect to the carbonyl carbon atom [15]. Taking into account the above stated, we presumed that bromination of quinone monoimines **I**–**VII** in chloroform involves initial formation of bromonium ion **A** which can be converted into tautomer **B** and carbocation **C**; the latter tends to undergo intramolecular cyclization to give intermediate **D** rather than to take up bromide ion (Scheme 6). Prototropic rearrangement and elimination of bromine cation yields final benzoxazole derivative. In polar protic solvents favoring polarization of bromine molecule and protonation of initial quinone monoimine, addition of bromide ion to cation **C** is more advantageous, and quinone monoimines and aminophenols containing additional bromine atoms are formed. Thus the mechanism of formation of benzoxazoles **VIII**–**XIII** and **XV** differs from those proposed in [7–11].

Benzoxazoles were obtained mainly by bromination of quinone monoimines in which only one *meta* position in the quinoid ring was free. As shown previously, halogenation of N-substituted 1,4-benzoquinone monoimines follows different paths including halogen addition at the double C=C bond in the quinoid ring, dehydrohalogenation, hydrohalogenation, prototropic rearrangement, and electrophilic substitution, so that

Scheme 6.

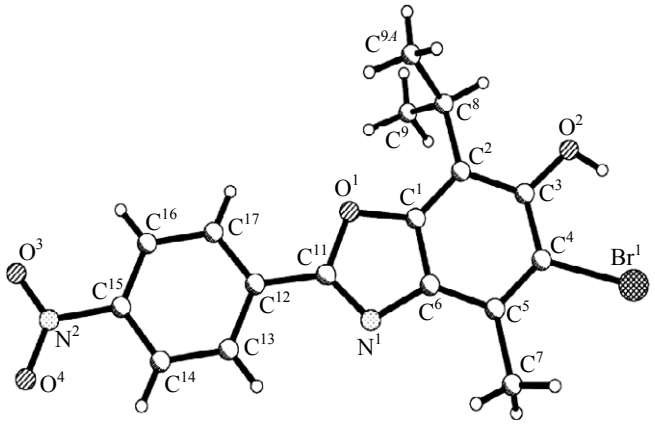


the reaction mixtures are complex multicomponent systems [1–6, 15–17]. As the number of halogen atoms in the quinoid ring increases, further addition of halogen or hydrogen halide becomes more difficult, and more severe conditions are necessary [1–3, 12, 16, 17]. In the bromination of *N*-acetyl(aroyl)-1,4-benzoquinone monoimines having two or more unoccupied positions in the quinoid ring, first addition of bromine molecule and subsequent dehydrohalogenation inevitably produce some amount of hydrogen bromide. As a result, further halogenation or hydrohalogenation of the quinoid ring becomes more favorable than ring closure through the oxygen atom.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were measured from solutions in $CDCl_3$ on a Varian VXR-300 spectrometer (300 and 75.4 MHz, respectively) using tetramethylsilane as reference. The IR spectra were recorded in KBr on a UR-20 spectrometer. The reaction mixtures were analyzed by TLC on Silufol UV-254 plates. Spots were applied from solutions in chloroform, benzene–hexane (10:1) was used as eluent, and components were detected under UV light.

X-Ray analysis of compound XIIId. Monoclinic crystals, $C_{17}H_{15}BrN_2O_4$, with the following unit cell parameters (293 K): a = 9.152(3), b = 6.942(2), c = 13.572(3) Å; β = 100.23(3); V = 848.6(4) Å^3; M_R = 391.22; Z = 2; space group $P2_1/m$; d_{calc} = 1.531 g/cm^3; μ(MoK_α) = 2.445 mm^{-1}; F(000) = 396. The unit cell parameters and intensities of 24333 reflections (2622 independent reflections, R_{int} = 0.029) were measured on an Xcalibur 3 automatic four-circle diffractometer (MoK_α irradiation, CCD detector, graphite monochromator, ω- and φ-scanning, $2\theta_{max}$ = 60°). Empirical absorption corrections (multiscan) were applied using CrysAlis RED software [18]; T_{min} = 0.62, T_{max} = 0.78. The structure was solved by the direct method using SHELX97 [19]. The positions of hydrogen atoms were determined by difference synthesis of electron density and were refined according to the riding model ($U_{iso} = nU_{eq}$; n = 1.5 for methyl and hydroxy groups, n = 1.2 for other hydrogen atoms). The structure was refined with respect to F^2 by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms until wR_2 = 0.069 for 1875 reflections [R_1 = 0.031 for 1684 reflections with $F > 4\sigma(F)$, S = 0.99]. The coordinates of atoms, geometric parameters of the molecule, and crystallographic data were deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 801257).



Structure of the molecule of 5-bromo-7-isopropyl-4-methyl-2-(4-nitrophenyl)-1,3-benzoxazol-6-ol (**XIIId**) according to the X-ray diffraction data.

Initial quinone monoimines **Ia**, **Ib**, **IIa**, **IIb**, **IIIa**, **IIIb**, **IVb**, **IVc** [1], **IIf**, **IVf** [20], **Vg**, **VIg**, **VIIg** [12], **Va**, **Vb**, **Vd**, **VIa**–**VIe**, **VIIa**–**VIIe** [3], **XIVa**, and **XIVb** [5] were synthesized according to known methods; their properties were consistent with published data.

4-Chloro-*N*-(3-chloro-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide (VIc). Yield 88%, mp 114–116°C. ^{1}H NMR spectrum, δ, ppm: 1.05 d [6H, CH(C**H**$_3$)$_2$, J = 6.9 Hz], 2.42 s (3H, 2-Me), 3.00–3.09 m (1H, 5-CH), 6.59 d (1H, 6-H, J = 0.9 Hz), 7.48–7.85 d.d (4H, C_6H_4, J = 9.0 Hz). Found, %: Cl 20.77, 20.95; N 3.84, 4.11. $C_{17}H_{15}Cl_2NO_2$. Calculated, %: Cl 21.09; N 4.17.

***N*-(3-Chloro-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-3-nitrobenzamide (VIe).** Yield 75%, mp 144–145°C. ^{1}H NMR spectrum, δ, ppm: 1.07 d [6H, CH(C**H**$_3$)$_2$, J = 6.9 Hz], 2.46 s (3H, 2-Me), 3.00–3.11 m (1H, 5-CH), 6.64 d (1H, 6-H, J = 0.9 Hz), 7.74 t (1H, 5′-H), 8.26–8.28 d.d (1H, 6′-H, ^3J = 7.8 Hz), 8.47–8.50 d.d (1H, 4′-H, ^3J = 9.0, ^4J = 0.9 Hz), 8.73 d (1H, 2′-H, ^4J = 3.9 Hz). Found, %: Cl 23.95, 24.20; N 4.55, 4.75. $C_{17}H_{15}ClN_2O_4$. Calculated, %: Cl 10.22; N 8.08.

***N*-(3-Bromo-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-chlorobenzamide (VIIc).** Yield 83%, mp 111–112°C. ^{1}H NMR spectrum, δ, ppm: 1.06 d [6H, CH(C**H**$_3$)$_2$, J = 6.9 Hz], 2.47 s (3H, 2-Me), 2.98–3.11 m (1H, 5-CH), 6.58 d (1H, 6-H, J = 1.5 Hz), 7.48–7.84 d.d (4H, C_6H_4, J = 8.7 Hz). Found, %: Br 20.67, 20.85; N 3.48, 3.69. $C_{17}H_{15}BrClNO_2$. Calculated, %: Br 20.99; N 3.68.

***N*-(3-Bromo-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-3-nitrobenzamide (VIIe).**

Yield 68%, mp 149.5–151°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.07 d [6H, CH(C**H**$_3$)$_2$, J = 6.9 Hz], 2.50 s (3H, 2-Me), 3.02–3.14 m (1H, 5-CH), 6.63 d (1H, 6-H, J = 0.9 Hz), 7.74 t (1H, 5′-H), 8.25–8.28 d.d (1H, 6′-H, ^3J = 7.8 Hz), 8.47–8.50 d.d (1H, 4′-H, ^3J = 9.0, ^4J = 1.2 Hz), 8.73 d (1H, 2′-H, ^4J = 3.6 Hz). Found, %: Br 20.47, 20.65; N 7.38, 7.59. $C_{17}H_{15}BrN_2O_4$. Calculated, %: Br 20.42; N 7.16.

6-Hydroxy-2-methyl(aryl)-1,3-benzoxazoles VIII–XIII and XV (*general procedure***).** A solution of 2 mmol of quinone imine **I**–**VII** or cyclohexenone **XIV** in 3 ml of chloroform was heated to 45°C, and 2 ml of a solution of bromine in chloroform was added dropwise under stirring until a substrate-to-bromine ratio of 1:5. The mixture was left to stand for 24 h until complete evaporation, and the precipitate was filtered off, washed with a small amount of acetic acid, and recrystallized from acetic acid.

4,5-Dichloro-7-methyl-2-phenyl-1,3-benzoxazol-6-ol (VIIIa). Yield 84%, mp 150.5–151.5°C. ^{1}H NMR spectrum, δ, ppm: 2.50 s (3H, 7-Me), 5.87 br.s (1H, OH), 7.50–8.28 m (5H, Ph). Found, %: Cl 23.86, 24.15; N 4.37, 4.60. $C_{14}H_9Cl_2NO_2$. Calculated, %: Cl 24.11; N 4.76.

4,5-Dichloro-7-methyl-2-(4-methylphenyl)-1,3-benzoxazol-6-ol (VIIIb). Yield 76%, mp 179–180.5°C. ^{1}H NMR spectrum, δ, ppm: 2.44 s (3H, **Me**C$_6$H$_4$), 2.48 s (3H, 7-Me), 5.88 br.s (1H, OH), 7.32–8.16 d.d (4H, C$_6$H$_4$, J = 7.8 Hz). Found, %: Cl 23.07, 23.35; N 4.61, 4.88. $C_{15}H_{11}Cl_2NO_2$. Calculated, %: Cl 23.01; N 4.55.

4,5-Dibromo-7-methyl-2-phenyl-1,3-benzoxazol-6-ol (IXa). Yield 71%, mp 181–182°C. ^{1}H NMR spectrum, δ, ppm: 2.49 s (3H, 7-Me), 5.84 br.s (1H, OH), 7.52–8.28 m (5H, Ph). Found, %: Br 41.57, 41.82; N 3.00, 3.26. $C_{14}H_9Br_2NO_2$. Calculated, %: Br 41.72; N 3.36.

4,5-Dibromo-7-methyl-2-(4-methylphenyl)-1,3-benzoxazol-6-ol (IXb). Yield 77%, mp 158.5–160°C. ^{1}H NMR spectrum, δ, ppm: 2.44 s (3H, **Me**C$_6$H$_4$), 2.49 s (3H, 7-Me), 5.83 br.s (1H, OH), 7.36–8.18 d.d (4H, C$_6$H$_4$, J = 8.1 Hz). Found, %: Br 40.07, 40.26; N 3.51, 3.82. $C_{15}H_{11}Br_2NO_2$. Calculated, %: Br 40.25; N 3.53.

4,5-Dibromo-2-(4-bromo-3-methoxyphenyl)-7-methyl-1,3-benzoxazol-6-ol (IXf). Yield 81%, mp 189–190°C. ^{1}H NMR spectrum, δ, ppm: 2.49 s (3H, 7-Me), 3.89 s (3H, MeO), 5.87 br.s (1H, OH), 6.93–6.96 d.d (1H, 6′-H, ^3J = 8.7, ^4J = 3.0 Hz), 7.61 br.s (1H, 2′-H, ^4J = 3.0 Hz), 7.63 d (1H, 5′-H, J = 8.7 Hz). Found, %: Br 50.28, 50.43; N 2.79, 3.06. $C_{15}H_{10}Br_3NO_3$. Calculated, %: Br 50.36; N 2.94.

5,7-Dichloro-4-methyl-2-phenyl-1,3-benzoxazol-6-ol (Xa). Yield 68%, mp 152–153.5°C. ^{1}H NMR spectrum, δ, ppm: 2.68 s (3H, 4-Me), 6.02 br.s (1H, OH), 7.53–8.28 m (5H, Ph). Found, %: Cl 23.95, 24.20; N 4.55, 4.75. $C_{14}H_9Cl_2NO_2$. Calculated, %: Cl 24.11; N 4.76.

5,7-Dichloro-4-methyl-2-(4-methylphenyl)-1,3-benzoxazol-6-ol (Xb). Yield 76%, mp 169.5–170°C. ^{1}H NMR spectrum, δ, ppm: 2.46 s (3H, **Me**C$_6$H$_4$), 2.70 s (3H, 4-Me), 6.02 br.s (1H, OH), 7.33–8.19 d.d (4H, C$_6$H$_4$, J = 7.2 Hz). Found, %: Cl 22.77, 22.95; N 4.61, 4.83. $C_{15}H_{11}Cl_2NO_2$. Calculated, %: Cl 23.01; N 4.55.

5,7-Dibromo-4-methyl-2-(4-methylphenyl)-1,3-benzoxazol-6-ol (XIb). Yield 83%, mp 127.5–128.5°C. ^{1}H NMR spectrum, δ, ppm: 2.49 s (3H, **Me**C$_6$H$_4$), 2.88 s (3H, 4-Me), 6.20 br.s (1H, OH), 7.43–8.45 d.d (4H, C$_6$H$_4$, J = 7.2 Hz). Found, %: Br 40.25, 40.51; N 3.28, 3.56. $C_{15}H_{11}Br_2NO_2$. Calculated, %: Br 40.25; N 3.53.

5,7-Dibromo-2-(4-chlorophenyl)-4-methyl-1,3-benzoxazol-6-ol (XIc). Yield 84%, mp 210–212°C. ^{1}H NMR spectrum, δ, ppm: 2.68 s (3H, 4-Me), 6.08 br.s (1H, OH), 7.50–8.18 d.d (4H, C$_6$H$_4$, J = 9.0 Hz). Found, %: Br+Cl 46.48, 46.72; N 3.08, 3.25. $C_{14}H_8Br_2ClNO_2$. Calculated, %: Br+Cl 46.77; N 3.36.

5,7-Dibromo-2-(4-bromo-3-methoxyphenyl)-4-methyl-1,3-benzoxazol-6-ol (XIf). Yield 78%, mp 180.5–182°C. ^{1}H NMR spectrum, δ, ppm: 2.71 s (3H, 4-Me), 3.89 s (3H, MeO), 6.12 br.s (1H, OH), 6.93–6.95 d.d (1H, 6′-H, ^3J = 8.0, ^4J = 3.3 Hz), 7.59 d (1H, 2′-H, ^4J = 3.3 Hz), 7.65 d (1H, 5′-H, J = 9.0 Hz). Found, %: Br 50.41, 50.62; N 2.93, 3.17. $C_{15}H_{10}Br_3NO_3$. Calculated, %: Br 50.36; N 2.94.

5-Chloro-7-isopropyl-4-methyl-2-phenyl-1,3-benzoxazol-6-ol (XIIa). Yield 81%, mp 209–210°C. ^{1}H NMR spectrum, δ, ppm: 1.50 d (6H, CH**Me**$_2$, J = 9.0 Hz), 2.81 s (3H, 4-Me), 3.57–3.73 m (1H, 7-CH), 5.91 br.s (1H, OH), 7.59–8.44 m (5H, Ph). Found, %: Cl 11.77, 11.93; N 4.80, 5.06. $C_{17}H_{16}ClNO_2$. Calculated, %: Cl 11.75; N 4.64.

5-Chloro-7-isopropyl-4-methyl-2-(4-methylphenyl)-1,3-benzoxazol-6-ol (XIIb). Yield 69%, mp 192–193.5°C. ^{1}H NMR spectrum, δ, ppm: 1.48 d (6H, CH**Me**$_2$, J = 6.9 Hz), 2.46 s (3H, **Me**C$_6$H$_4$), 2.76 s (3H, 4-Me), 3.61–3.70 m (1H, 7-CH), 5.88 br.s (1H, OH), 7.37–8.27 d.d (4H, C$_6$H$_4$, J = 7.2 Hz). Found, %:

Cl 11.05, 11.23; N 4.50, 4.79. $C_{18}H_{18}ClNO_2$. Calculated, %: Cl 11.23; N 4.44.

5-Chloro-2-(4-chlorophenyl)-7-isopropyl-4-methyl-1,3-benzoxazol-6-ol (XIIc). Yield 90%, mp 162–164°C. ^{1}H NMR spectrum, δ, ppm: 1.48 d (6H, CH**Me**$_2$, J = 7.8 Hz), 2.68 s (3H, 4-Me), 3.59–3.67 m (1H, 7-CH), 5.98 br.s (1H, OH), 7.51–8.21 d.d (4H, C_6H_4, J = 7.8 Hz). Found, %: Cl 21.10, 21.29; N 4.25, 4.39. $C_{17}H_{15}Cl_2NO_2$. Calculated, %: Cl 21.09; N 4.17.

5-Chloro-7-isopropyl-4-methyl-2-(4-nitrophenyl)-1,3-benzoxazol-6-ol (XIId). Yield 73%, mp 229–230°C. ^{1}H NMR spectrum, δ, ppm: 1.49 d (6H, CH**Me**$_2$, J = 6.9 Hz), 2.67 s (3H, 4-Me), 3.61–3.71 m (1H, 7-CH), 6.08 br.s (1H, OH), 8.38 s (4H, C_6H_4). Found, %: Cl 10.06, 10.34; N 7.92, 8.15. $C_{17}H_{15}ClN_2O_4$. Calculated, %: Cl 10.22; N 8.08.

5-Chloro-7-isopropyl-4-methyl-2-(3-nitrophenyl)-1,3-benzoxazol-6-ol (XIIe). Yield 73%, mp 229–230°C. ^{1}H NMR spectrum, δ, ppm: 1.49 d (6H, CH**Me**$_2$, J = 7.5 Hz), 2.68 s (3H, 4-Me), 3.62–3.73 m (1H, 7-CH), 5.98 br.s (1H, OH), 7.72 t (1H, 5′-H), 8.35–8.38 d.d (1H, 6′-H, ^3J = 7.9 Hz), 8.57 d (1H, 4′-H, ^3J = 7.8 Hz), 9.03 q (1H, 2′-H, ^4J = 3.3 Hz). Found, %: Cl 10.26, 10.53; N 8.24, 8.57. $C_{17}H_{15}ClN_2O_4$. Calculated, %: Cl 10.22; N 8.08.

5-Chloro-7-isopropyl-2,4-dimethyl-1,3-benzoxazol-6-ol (XIIg). Yield 60%, mp 175.5–177°C. ^{1}H NMR spectrum, δ, ppm: 1.43 d (6H, CH**Me**$_2$, J = 6.9 Hz), 2.83 s (3H, 2-Me), 3.22 s (3H, 4-Me), 3.57–3.69 m (1H, 7-CH), 6.17 br.s (1H, OH). Found, %: Cl 14.65, 14.88; N 5.84, 6.03. $C_{12}H_{14}ClNO_2$. Calculated, %: Cl 14.79; N 5.84.

5-Bromo-7-isopropyl-4-methyl-2-phenyl-1,3-benzoxazol-6-ol (XIIIa). Yield 74%, mp 156–157.5°C. ^{1}H NMR spectrum, δ, ppm: 1.52 d (6H, CH**Me**$_2$, J = 6.6 Hz), 3.02 br.s (3H, 4-Me), 3.65–3.75 m (1H, 7-CH), 6.12 br.s (1H, OH), 7.68–8.75 m (5H, Ph). Found, %: Br 22.89, 23.17; N 4.15, 4.26. $C_{17}H_{16}BrNO_2$. Calculated, %: Br 23.08; N 4.05.

5-Bromo-7-isopropyl-4-methyl-2-(4-methylphenyl)-1,3-benzoxazol-6-ol (XIIIb). Yield 72%, mp 163.5–165°C. ^{1}H NMR spectrum, δ, ppm: 1.48 d (6H, CH**Me**$_2$, J = 6.6 Hz), 2.50 br.s (3H, **Me**C_6H_4), 2.91 br.s (3H, 4-Me), 3.64–3.73 m (1H, 7-CH), 6.17 br.s (1H, OH), 7.44–8.48 d.d (4H, C_6H_4, J = 7.8 Hz). Found, %: Br 22.19, 22.38; N 3.56, 3.74. $C_{18}H_{18}BrNO_2$. Calculated, %: Br 22.18; N 3.89.

5-Bromo-2-(4-chlorophenyl)-7-isopropyl-4-methyl-1,3-benzoxazol-6-ol (XIIIc). Yield 81%, mp 168.5–169.5°C. ^{1}H NMR spectrum, δ, ppm: 1.47 d (6H, CH**Me**$_2$, J = 6.9 Hz), 2.71 br.s (3H, 4-Me), 3.60–3.71 m (1H, 7-CH), 6.12 br.s (1H, OH), 7.51– 8.22 d.d (4H, C_6H_4, J = 6.6 Hz). Found, %: Br+Cl 30.10, 30.38; N 3.55, 3.79. $C_{17}H_{15}BrClNO_2$. Calculated, %: Br+Cl 30.30; N 3.68.

5-Bromo-7-isopropyl-4-methyl-2-(4-nitrophenyl)-1,3-benzoxazol-6-ol (XIIId). Yield 85%, mp 230–231°C. ^{1}H NMR spectrum, δ, ppm: 1.49 d (6H, CH**Me**$_2$, J = 7.2 Hz), 2.69 s (3H, 4-Me), 3.62–3.71 m (1H, 7-CH), 5.90 br.s (1H, OH), 8.37 s (4H, C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 17.71 (4-Me), 21.73 (**Me**$_2$CH), 26.93 (**C**HMe$_2$), 111.68 (C^5), 116.41 (C^7), 124.27 ($C^{2'}$, $C^{6'}$), 128.11 ($C^{3'}$, $C^{5'}$), 128.26 (C^4), 132.90 ($C^{1'}$), 135.71 (C^{3a}), 148.06 (C^6), 149.20 ($C^{4'}$), 149.39 (C^{7a}), 159.41 (C^2). Found, %: Br 20.34, 20.51; N 6.97, 7.33. $C_{17}H_{15}BrN_2O_4$. Calculated, %: Br 20.42; N 7.16.

5-Bromo-7-isopropyl-4-methyl-2-(3-nitrophenyl)-1,3-benzoxazol-6-ol (XIIIe). Yield 77%, mp 192–194°C. ^{1}H NMR spectrum, δ, ppm: 1.50 d (6H, CH**Me**$_2$, J = 7.5 Hz), 2.70 s (3H, 4-Me), 3.63–3.72 m (1H, 7-CH), 6.15 br.s (1H, OH), 7.72 t (1H, 5′-H), 8.35–8.38 d.d (1H, 6′-H, ^3J = 9.0 Hz), 8.56 d (1H, 4′-H, ^3J = 7.5 Hz), 9.03 q (1H, 2′-H, ^4J = 3.6 Hz). Found, %: Br 20.15, 20.39; N 6.88, 7.14. $C_{17}H_{15}BrN_2O_4$. Calculated, %: Br 20.42; N 7.16.

5-Bromo-7-isopropyl-2,4-dimethyl-1,3-benzoxazol-6-ol (XIIIg). Yield 59%, mp 138.5–140°C. ^{1}H NMR spectrum, δ, ppm: 1.43 d (6H, CH**Me**$_2$, J = 7.2 Hz), 2.84 br.s (3H, 2-Me), 3.14 br.s (3H, 4-Me), 3.58–3.66 m (1H, 7-CH), 6.10 br.s (1H, OH). Found, %: Br 28.19, 28.47; N 5.03, 5.26. $C_{12}H_{14}BrNO_2$. Calculated, %: Br 28.12; N 4.93.

7-*tert*-Butyl-4,5-dichloro-2-phenyl-1,3-benzoxazol-6-ol (XVa). Yield 68%, mp 189–190°C. ^{1}H NMR spectrum, δ, ppm: 1.67 s (9H, *t*-Bu), 6.12 br.s (1H, OH), 7.52–8.23 m (5H, Ph). Found, %: Cl 21.19, 21.37; N 4.06, 4.58. $C_{17}H_{15}Cl_2NO_2$. Calculated, %: Cl 21.09; N 4.17.

7-*tert*-Butyl-4,5-dichloro-2-(4-methylphenyl)-1,3-benzoxazol-6-ol (XVb). Yield 63%, mp 173–174°C. ^{1}H NMR spectrum, δ, ppm: 1.66 s (9H, *t*-Bu), 2.45 s (3H, **Me**C_6H_4), 6.11 br.s (1H, OH), 7.32–8.12 d.d (4H, C_6H_4, J = 7.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.58 (Me), 30.37 [C(**C**H$_3$)$_3$], 36.41 [**C**(CH$_3$)$_3$], 117.60 (C^6), 119.53 (C^4), 119.63 (C^5), 123.77 (C^7), 127.39 ($C^{3'}$, $C^{5'}$), 129.36 ($C^{2'}$, $C^{6'}$), 134.58 (C^{3a}), 141.92 ($C^{1'}$), 147.99 ($C^{4'}$), 148.06 (C^{7a}), 162.75 (C^2). Found, %: Cl 20.37, 20.55; N 4.16, 4.39. $C_{18}H_{17}Cl_2NO_2$. Calculated, %: Cl 20.24; N 4.00.

REFERENCES

1. Avdeenko, A.P., Konovalova, S.A., and Ludchenko, O.N., *Russ. J. Org. Chem*., 2010, vol. 46, p. 1629.
2. Avdeenko, A.P., Konovalova, S.A., Ludchenko, O.N., Palamarchuk, G.V., and Shishkin, O.V., *Russ. J. Org. Chem*., 2009, vol. 45, p. 1651.
3. Avdeenko, A.P., Konovalova, S.A., and Ludchenko, O.N., *Russ. J. Org. Chem*., 2009, vol. 45, p. 1799.
4. Avdeenko, A.P., Pirozhenko, V.V., Shishkin, O.V., Shishkina, S.V., Konovalova, S.A., and Ludchenko, O.N., *Russ. J. Org. Chem*., 2008, vol. 44, p. 542.
5. Avdeenko, A.P., Pirozhenko, V.V., Shishkin, O.V., Palamarchuk, G.V., Zubatyuk, R.I., Konovalova, S.A., and Ludchenko, O.N., *Russ. J. Org. Chem*., 2008, vol. 44, p. 807.
6. Avdeenko, A.P., Marchenko, I.L., Yusina, A.L., Konovalova, S.A., and Ludchenko, O.N., *Russ. J. Org. Chem*., 2005, vol. 41, p. 1787.
7. Ullmann, F. and Junghans, W., *Justus Liebigs Ann. Chem*., 1913, vol. 399, p. 330.
8. Fries, K. and Ochwat, P., *Ber*., 1923, vol. 56, p. 1291.
9. Heller, G., *J. Prakt. Chem*., 1931, vol. 129, p. 211.
10. Adams, R. and Stewart, J.M., *J. Am. Chem. Soc*., 1952, vol. 74, p. 3660.
11. Adams, R. and Acker, D.S., *J. Am. Chem. Soc*., 1952, vol. 74, p. 5872.
12. Avdeenko, A.P., Konovalova, S.A., Ludchenko, O.N., Ledeneva, O.P., and Vakulenko, A.V., *Russ. J. Org. Chem*., 2011, vol. 47, p. 214.
13. Polo, C., Ramos, V., and Torroba, T., *Tetrahedron*, 1998, vol. 54, p. 223.
14. Zefirov, Yu.V. and Zorkii, P.M., *Usp. Khim*., 1989, vol. 58, p. 713.
15. Avdeenko, A.P., Konovalova, S.A., and Ludchenko, O.N., *Russ. J. Org. Chem*., 2006, vol. 42, p. 683.
16. Avdeenko, A.P. and Konovalova, S.A., *Russ. J. Org. Chem*., 2006, vol. 42, p. 349.
17. Avdeenko, A.P. and Konovalova, S.A., *Russ. J. Org. Chem*., 2006, vol. 42, p. 669.
18. *CrysAlis RED*, *Version 1.171.29.9*, Oxford Diffraction.
19. Sheldrick, G., *Acta Crystallogr., Sect. A*, 2008, vol. 64, p. 112.
20. Avdeenko, A.P., Konovalova, S.A., and Ludchenko, O.N., *Vopr. Khim. Khim. Tekhnol*., 2007, no. 2, p. 21.