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OXIDATIVE BROMINATION OF IMIDAZOHETEROCYCLE BROMOHYDRATES*

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The behavior of imidazo[1,2-a]pyridinium, imidazo[1,2-a]pyrimidinium, and imidazo[2,1-b]thiazolium bromides derivatives in oxidative bromination reactions has been studied. It has been established that reaction products structures and their yields depend on the properties of the substituents in the bicycle and the oxidant concentration.

Keywords: bromohydrates, imidazoheterocycles, oxidative bromination.

It is known [1,2] that the attack of electrophilic agents predominantly proceeds on the imidazole ring of imidazoheterocycles*. Among such reactions there is considerable interest in bromination because bromine-substituted imidazo[1,2-*a*]pyridines, imidazo[1,2-*a*]pyrimidines, and imidazo[2,1-*b*]thiazoles have found use as physiologically active substances [3]

Most frequently bromination of the starting bases is carried out by bromine in chloroform [4], in acetic acid [5] or with the help of such brominating agents as *N*-bromosuccinimide and *N*-bromoacetamide in ethanol or carbon tetrachloride [6]. Interesting is the method of synthesis of bromo-substituted imidazoheterocycles by treating bromohydrates of the starting bases with an oxidizing agent. Note that carrying out this type of reaction in dimethyl sulfoxide, the solvent also acts as oxidant [7]. We have used hydrogen peroxide as oxidant in our work on the synthesis of bromo-substituted imidazo[1,2-*a*]pyridines [8, 9] and also sodium nitrite in glacial AcOH (in particular in the synthesis of 5-bromo-6-(bromomethyl)imidazo[2,1-*b*]thiazole [10]).

Earlier [8, 11] we have synthesized bromides of imidazo[1,2-*a*]pyridinium, imidazo[1,2-*a*]pyrimidinium, and imidazo[2,1-*b*]thiazolium derivatives by interaction of the corresponding 2-aminoheterocycles with mono- or dihalo ketones. The reaction products were isolated as the salts **1a-g** and converted into the dehydrated salts **2a-g**.

*The term imidazoheterocycles means bicyclic heterosystems, one of the rings of which is imidazole (for example, imidazopyridine, imidazopyrimidine, and imidazothiazole).

*Dedicated to the illustrious life of Academician M.O. Lozinskii.

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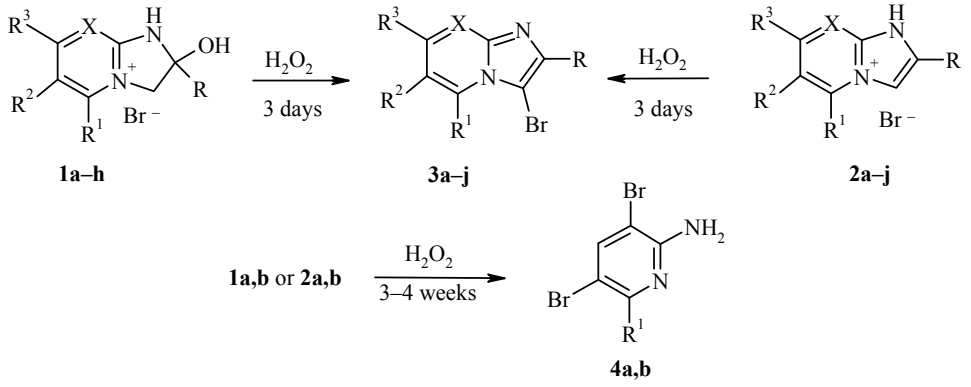
In the present work a study of the behavior of compounds **1** and **2** in the oxidative bromination reaction is described. For a more complete study of the reaction we have also synthesized salts containing aryl substituents in position 2 of the imidazo[1,2-*a*]pyridinium ring. On quaternization of 2-aminopyridine with substituted phenacyl bromides the salt **1** was isolated only in the case of interaction with *p*-bromophenacyl bromide. In reaction with *p*-methyl- and *p*-methoxy-substituted phenacyl bromides, mixtures of the salts **1** and **2** were formed, from which the dehydrated salts **2h-j** were isolated after short boiling in glacial AcOH.

Compounds **2h-j** were described earlier [12] however oxidative bromination with them was not carried out.

Bromo-substituted imidazo[1,2-*a*]pyridines **3a-d,g** and imidazo[1,2-*a*]pyrimidines **3e,f** were obtained by reaction of hydrogen peroxide with bromides **1a-g** or salts **2a-g**.

The reaction proceeded in high yield and the end product was crystallized from solution in analytically pure state as colorless crystals.

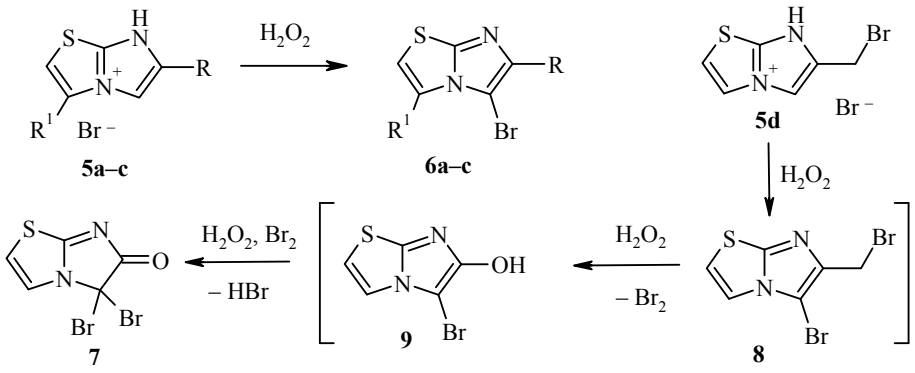


1–3 a–f R = $BrCH_2$, **a–c** X = CH, **a** $R^1 = R^2 = R^3$ = H, **b** R^1 = Me, $R^2 = R^3$ = H, **c** $R^1 = R^3$ = H, R^2 = Cl, **d** X = CBr, $R^1 = R^3$ = H, R^2 = Br, **e,f** X = N, **e** $R^1 = R^2 = R^3$ = H, **f** $R^1 = R^3$ = Me, R^2 = H; **1–3 g** R = Me, X = CBr, $R^1 = R^3$ = H, R^2 = Br; **1–3 h** X = CH, R = 4-BrC_6H_4, $R^1 = R^2 = R^3$ = H; **2, 3 i,j** X = CH, $R^1 = R^2 = R^3$ = H, **i** R = 4-MeC_6H_4, **j** R = 4-$MeOC_6H_4$; **4a** R^1 = H, **b** R^1 = Me

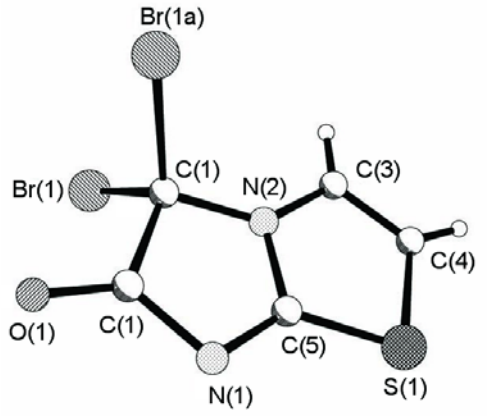
The high yields (91-93%) of products **3a-d** were found both when using salts of the type **1a-d** (15% H_2O_2) and when using dehydrated salts **2a-d** (30% H_2O_2). Products **3h-j** (yields 50-70%) were obtained from compounds **1h**, **2h-j** and from mixture of salts **1i** and **2i**, **1j** and **2j**. This fact may be explained by steric hindrance caused by substituents for bromine atom to attack the ring.

Solid product began to precipitate from the reaction mixture already after a few hours but the reaction was completed in 3 days. A spot of an alternative product appeared on a chromatogram on increasing time. For example, after separation of **3a** or **3b,** 2-amino-3,5-dibromopyridines **4a** and **4b** were isolated in 5 and 6% yield respectively from the reaction mixture after 3-4 weeks. These compounds have been synthesized previously by other methods [13]. Use of other oxidizing agents, such as sodium nitrite in glacial AcOH, potassium permanganate in weakly acidic media, or cerium(IV) salts also led to compounds **3** [8]. However, in contrast to hydrogen peroxide, the yields of final products were lower, the reaction times were longer, and additional purification was required. We suggest that salts **2** in solution exist in equilibrium with small amount of the free base and hydrobromic acid, the latter of which reacts with the oxidizing agent to produce free bromine which then reacts with the base. The characteristic signals of the 3-CH_2 protons and also those of the NH and OH groups of salts **1** or the CH and NH groups of salts **2** are absent in the ^{1}H NMR spectra of compounds **3**. In the ^{13}C NMR spectra of compounds **3,** the signal of the CBr group carbon was observed in the 90-96 ppm region. Signals ascribed to the carbon of the CH_2Br group (compounds **3a-f**) were observed in the 24.8-26.1 ppm range. The signals of the remaining protons and carbon nuclei of the heterocyclic ring agree with the proposed structure.

The course of oxidative bromination of imidazo[2,1-*b*]thiazole derivatives **5a-d** and structures of the products obtained **6a-d** depend on the nature of substituents on the starting compounds [8-11, 14]. Thus, bromination of compounds **5a-c** with a methyl group in position 3 or 6 proceeds with 30% H_2O_2 at 10-15°C with yields of ~70%. Structures of the obtained products correspond to 5-bromo-6-methylimidazo[2,1-*b*]thiazole (**6a)** and 5-bromo-3,6-dimethylimidazo[2,1-*b*]thiazole (**6b)** which have been synthesized earlier by other methods [14]. In the case of bromide **5c,** 5-bromo-6-bromomethyl-3-methylimidazo[2,1-*b*]thiazole (**6c**) should be separated immediately as it appeared because of the formation of a solid precipitate which prevented the reaction in the whole volume. Oxidative bromination of compound **5d** occurred twice with the formation of 5,5-dibromoimidazo[2,1-*b*]-thiazol-6(5*H*)-one (**7**), the structure of which was confirmed by X-ray structural analysis.



5, 6 a,b R = Me, **a** R^1 = H, **b** R^1 = Me; **c** R = CH_2Br, R^1 = Me



Structure of compound **7** by X-ray crystallographic data.

It may be suggested that the reaction proceeds *via* a stage of compound **8** formation, which is not precipitated from solution but is further oxidized. This was confirmed when compound **8**, synthesized earlier by another method [10], after suspending in 15% hydrogen peroxide at a temperature of 10-15°C was dissolved slowly and after a day yellow needles of the imidazothiazolone **7** were formed**.** It may be suggested that the excess hydrogen peroxide oxidizes the CH_2Br group into a carboxyl group to form the *N*-oxide and more bromine. The carboxyl group is easily decarboxylated, as can be seen by formation of carbon dioxide bubbles, while the *N*-oxide is isomerized to form the 2-hydroxy derivative **9.** The C=C bond in the imidazole ring adds bromine and immediately loses HBr to give the product **7** which is readily crystallized. Other products of oxidation and bromination of unestablished structure remained in solution.

Thus it has been shown that imidazo[1,2-*a*]pyridinium and imidazo[1,2-*a*]pyrimidinium bromides are converted in high yields under the influence of hydrogen peroxide to the corresponding 3-bromo-2-bromo-

methylimidazo[1,2-*a*]pyridines or 3-bromo-2-bromomethylimidazo[1,2-*a*]pyrimidines. This reaction is of a general nature in the synthesis of this class of products. The behavior of 3R-6R'-7*H*-imidazo[2,1-*b*]thiazolium bromohydrates is different in the oxidative bromination reaction. While the 3- and 6-methyl derivatives gave the expected 5-bromoimidazo[2,1-*b*]thiazoles, the compounds unsubstituted in positions 3 and 6 unexpectedly formed 5,5-dibromoimidazo[2,1-*b*]thiazol-6(5*H*)-one.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded in 1:1 DMSO-d_6–CCl_4 solution with TMS as internal standard with a Varian Mercury 400 spectrometer (400 and 100 MHz respectively). Elemental analysis was performed with a Vario MICRO Cube analyzer. A Boetius PHMK apparatus (VEB Analytic, Dresden, Germany) was used to determine the melting points (uncorrected). The course of reactions and the purity of synthesized products were monitored by TLC on Silufol UV-254 plates with 9:1 chloroform–methanol solvents system.

2-(4-Bromophenyl)-2-hydroxy-2,3-dihydro-1*H*-imidazo[1,2-*a*]pyridinium Bromide (1h). *p*-Bromophenacyl bromide (2.78 g, 0.01 mol) in AcOEt (15 ml) was added with stirring to a solution of 2-aminopyridine (0.94 g, 0.01 mol) in AcOEt (10 ml). The mixture was kept at room temperature for 2 days. The precipitate was filtered off, washed with acetone and ether, and dried in air. Yield 82%. The melting point was not determined – the compound was readily dehydrated. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.65 (1H, d, ^2J = 15.0) and 4.85 (1H, d, ^2J = 15.0, 3-CH_2); 7.12 (1H, m, H-6); 7.55 (1H, br. s, NH); 7.65 (2H, d, ^3J = 7.6, H Ar); 7.68 (1H, d, ^3J = 8.6, H-8); 8.04 (2H, d, ^3J = 7.6, H Ar); 8.11 (1H, dd, ^3J = 6.7, ^3J = 8.6, H-7); 8.43 (1H, d, ^3J = 6.5, H-5); 10.21 (1H, s, OH). Found, %: C 42.07; Br 43.07; N 7.57. $C_{13}H_{12}Br_2N_2O$. Calculated, %: C 41.97; Br 42.95; N 7.53.

Compounds 3a-g (General Method). Salts **1a-h** [8, 11] or **2a-h** [8, 11] (0.01 mol) were dissolved in hydrogen peroxide (5 ml, 15 or 30% respectively) and kept at room temperature. After three days a colorless precipitate was filtered off, washed with water, dried and recrystallized from ethanol.

3-Bromo-2-bromomethylimidazo[1,2-*a*]pyridine (3a). Yield 93%; mp 146-147°C (mp 146°C [8]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.67 (2H, s, CH_2Br); 6.93 (1H, t, ^3J = 7.1, H-6); 7.28 (1H, dd, ^3J = 9.2, ^3J = 7.6, H-7); 7.59 (1H, d, ^3J = 9.2, H-8); 8.06 (1H, d, ^3J = 6.8, H-5). ^{13}C NMR spectrum, δ, ppm: 25.5 (CH_2Br); 94.6 (C-3); 113.9 (C-6); 117.6 (C-8); 124.6 (C-7); 125.9 (C-5); 140.7 (C-2); 145.0 (C-8a). Found, %: C 33.29; H 2.06; N 9.58; Br 55.03. $C_8H_6Br_2N_2$. Calculated, %: C 33.14; H 2.09; N 9.66; Br 55.11.

3-Bromo-2-bromomethyl-5-methylimidazo[1,2-*a*]pyridine (3b). Yield 92%; mp 132-133°C (mp 132°C [8]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.95 (3H, s, 5-CH_3); 4.70 (2H, s, CH_2Br); 6.75 (1H, d, ^3J = 7.2, H-6); 7.28 (1H, dd, ^3J = 8.5, ^3J = 7.2, H-7); 7.45 (1H, d, ^3J = 8.5, H-8). ^{13}C NMR spectrum, δ, ppm: 20.8 (5-CH_3); 26.1 (CH_2Br); 93.3 (C-3); 114.9 (C-8); 116.3 (C-6); 125.8 (C-7); 136.6 (C-2); 141.9 (C-5); 143.4 (C-8a). Found, %: C 35.59; H 2.58; N 9.28; Br 52.61. $C_9H_8Br_2N_2$. Calculated, %: C 35.56; H 2.65; N 9.22; Br 52.57.

3-Bromo-2-bromomethyl-6-chloroimidazo[1,2-*a*]pyridine (3c). Yield 91%; mp 162-163°C (mp 162°C [11]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.72 (2H, s, CH_2Br); 7.39 (1H, d, ^3J = 8.0, H-7); 7.65 (1H, d, ^3J = 8.0, H-8); 8.45 (1H, d, ^4J = 1.9, H-5). ^{13}C NMR spectrum, δ, ppm: 25.1 (CH_2Br); 95.6 (C-3); 118.5 (C-8); 121.6 (C-6); 122.5 (C-7); 127.1 (C-5); 141.8 (C-2); 143.4 (C-8a). Found, %: C 29.78; H 1.61; Br 49.14; Cl 11.03; N 8.96. $C_8H_5Br_2ClN_2$. Calculated, %: C 29.62; H 1.55; Br 49.26; Cl 10.93; N 8.64.

3,6,8-Tribromo-2-bromomethylimidazo[1,2-*a*]pyridine (3d). Yield 92%; mp 192°C (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.69 (2H, s, CH_2Br); 7.79 (1H, s, H-7); 8.47 (1H, s, H-5). ^{13}C NMR spectrum, δ, ppm: 24.7 (CH_2Br); 97.5 (C-3); 107.4 (C-8); 112.0 (C-6); 124.4 (C-7); 130.8 (C-5); 141.4 (C-2); 142.3 (C-8a). Found, %: C 21.72; H 1.00; Br 71.69; N 6.52. $C_8H_4Br_4N_2$. Calculated, %: C 21.46; H 0.90; Br 71.38; N 6.26.

3-Bromo-2-bromomethylimidazo[1,2-*a*]pyrimidine (3e). Yield 56%; mp 210°C (mp 210°C [8]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.74 (2H, s, CH_2Br); 7.04 (1H, dd, ^3J = 4.4, ^3J = 6.4, H-6); 8.56 (1H, d, ^3J = 4.4, H-7); 8.88 (1H, dd, ^3J = 6.4, ^4J = 1.8, H-5). ^{13}C NMR spectrum, δ, ppm: 25.0 (CH_2Br); 93.7 (C-3); 110.6 (C-6); 133.2 (C-2); 142.1 (C-5); 147.7 (C-7); 151.4 (C-8a). Found, %: C 29.03; H 1.84; N 14.53; Br 54.98. $C_7H_5Br_2N_3$. Calculated, %: C 28.90; H 1.73; N 14.44; Br 54.93.

3-Bromo-2-bromomethyl-5,7-dimethylimidazo[1,2-*a*]pyrimidine (3f). Yield 89%; mp 194-195°C (mp 194-195°C [9]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.57 (3H, s, CH_3); 2.66 (3H, s, CH_3); 4.67 (2H, s, CH_2Br); 6.83 (1H, s, H-6). ^{13}C NMR spectrum, δ, ppm: 19.9 (5-CH_3); 24.4 (7-CH_3); 25.9 (CH_2Br); 91.3 (C-3); 112.0 (C-6); 142.3 (C-2); 145.4 (C-5); 148.6 (C-7); 160.6 (C-8a). Found, %: C 34.00; H 2.88; N 13.12; Br 50.21. $C_9H_2Br_2N_3$. Calculated, %: C 33.89; H 2.84; N 13.17; Br 50.10.

3,6,8-Tribromo-2-methylimidazo[1,2-*a*]pyridine (3g). Yield 89%; mp 117-119°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.40 (3H, s, 2-CH_3); 7.68 (1H, s, H-5); 8.36 (1H, s, H-7). ^{13}C NMR spectrum, δ, ppm: 13.7 (2-CH_3); 95.4 (C-3); 106.3 (C-8); 111.2 (C-6); 124.7 (C-7); 129.4 (C-5); 141.1 C-2); 143.2 (C-8a). Found, %: C 26.27; H 1.50; Br 64.69; N 7.52. $C_8H_5Br_3N_3$. Calculated, %: C 26.05; H 1.37; Br 64.99; N 7.56.

Compounds 3h-j (General Method). 15% Hydrogen peroxide (5 ml) was added to salt (**1h, 2h-j)** or a mixture of salts (**1i** and **2i**, or **1j** and **2j**) (0.01 mol) and the mixture was kept for 3 days at room temperature. The colorless precipitate was filtered off, washed with water, and dried. Compound **3d** was recrystallized, compounds **3i** and **3j** were sublimed.

3-Bromo-2-(4-bromophenyl)imidazo[1,2-*a*]pyridine (3h). Yield 70%; mp 156-157°C (Et_2O) (mp 156-157°C [12]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.09 (1H, m, H-6); 7.36 (1H, t, ^3J = 7.1, H-7); 7.62 (3H, m, H Ar, H-8); 8.04 (2H, d, ^3J = 8.0, H Ar); 8.33 (1H, d, ^3J = 7.6, H-5).

3-Bromo-2-(4-methylphenyl)imidazo[1,2-*a*]pyridine (3i). Yield 57%; mp 109-110°C (subl.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.40 (3H, s, CH_3); 7.03 (1H, t, ^3J = 7.0, H-6); 7.25 (2H, m, H Ar); 7.32 (1H, dd, ^3J = 8.0, ^3J = 7.1, H-7); 7.57 (1H, d, ^3J = 8.0, H-8); 7.97 (2H, d, ^3J = 8.0, H Ar); 8.28 (1H, d, ^3J = 7.6, H-5). Found, %: C 58.64; H 3.97; Br 27.92; N 9.83. $C_{14}H_{11}BrN_2$. Calculated, %: C 58.56; H 3.86; Br 27.83; N 9.76.

3-Bromo-2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine (3j). Yield 53%; mp 102-103°C (subl.) (mp 101-103°C [12]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.84 (3H, s, OCH_3); 7.00 (2H, m, H Ar); 7.04 (1H, m, H-6); 7.32 (1H, dd, ^3J = 8.0, ^3J = 7.1, H-7); 7.57 (1H, d, ^3J = 8.0, H-8); 8.02 (2H, d, ^3J = 8.0. H Ar); 8.29 (1H, d, ^3J = 7.6, H-5). Found, %: C 55.89; H 3.72; Br 26.66; N 9.31. $C_{14}H_{11}BrN_2O$. Calculated, %: C 55.47; H 3.66; Br 26.36; N 9.24.

Compounds 4a,b (General Method). After isolation of product **3a** or **3b**, the solution was kept for 3 weeks. After 3 weeks the precipitate was filtered off, dried, and recrystallized.

3,5-Dibromopyridin-2-amine (4a). Yield 5%; mp 105°C (75% EtOH) (mp 105°C [13]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.21 (2H, s, NH_2); 7.77 (1H, s, H-6); 7.87 (1H, s, H-4).

3,5-Dibromo-6-methylpyridin-2-amine (4b). Yield 6%; mp 144°C (EtOH) (mp 144°C [13]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.35 (3H, s, CH_3); 6.06 (2H, br. s, NH_2); 7.60 (1H, s, H-4).

Compounds 6a,b (General Method). 15% Hydrogen peroxide (5 ml) was added to salt **5a** [9, 14] (0.01 mol) or salt **5b** [11] (0.01 mol) and kept at 10-15°C. The precipitate formed over a day was filtered off, washed, and recrystallized.

5-Bromo-6-methylimidazo[2,1-*b*]thiazole (6a). Yield 86%; mp 93°C (xylene) (mp 93°C [14]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.22 (3H, s, CH_3); 7.24 (1H, d, ^3J = 4.5, H-2); 7.60 (1H, d, ^3J = 4.5, H-3).

5-Bromo-3,6-dimethylimidazo[2,1-*b*]thiazole (6b). Yield 79%; mp 95-96°C (subl.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.19 (3H, s, CH_3); 2.59 (3H, s, CH_3); 6.78 (1H, s, H-2). ^{13}C NMR spectrum, δ, ppm: 13.5 (6-CH_3); 14.6 (3-CH_3); 91.0 (C-5); 108.3 (C-2); 129.2 (C-3); 142.0 (C-6); 148.8 (C-7a). Found, %: Br 34.86; N 12.78; S 14.36. $C_7H_7BrN_2S$. Calculated, %: Br 34.57; N 12.12; S 13.87.

5-Bromo-6-bromomethyl-3-methylimidazo[1,2-*b*]thiazole (6c). 30% Hydrogen peroxide (5 ml) was added to salt **5c** [9] (3.13 g, 0.01 mol) at room temperature. The precipitate was filtered off, dried, and recrystallized. Yield 78%; mp 118-119°C (MeCN). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.58 (3H, s, 3-CH_3); 4.60 (2H, s, CH_2Br); 7.00 (1H, s, H-2). ^{13}C NMR spectrum, δ, ppm: 14.5 (3-CH_3); 26.3 (CH_2Br); 93.6 (C-5); 109.9 (C-2); 129.2 (C-3); 141.8 (C-6); 149.9 (C-7a). Found, %: C 27.38; H 2.05; Br 51.62; N 8.86; S 10.04. $C_7H_6Br_2N_2S$. Calculated, %: C 27.12; H 1.95; Br 51.55; N 9.04; S 10.34.

5,5-Dibromoimidazo[2,1-*b*]thiazol-6(5*H*)-one (7). 15% Hydrogen peroxide (15 ml) was added to salt **5d** [9] (2.98 g, 0.01 mol) and the mixture was kept at 10-15°C. After a day the precipitate was filtered off, dried,

and recrystallized. Yield 34%; mp 160-161°C (MeCN). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.22 (1H, d, ^3J =4.5, H-2); 8.15 (1H, d, ^3J = 4.5, H-3). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 50.4 (C-5); 112.2 (C-2); 123.5 (C-3); 169.0 (C-6); 153.7 (C-7a). Found, %: C 20.16; H 0.65; Br 53.48; N 9.48; S 10.44. $C_5H_2Br_2N_2OS$. Calculated, %: C 20.16; H 0.60; Br 53.63; N 9.40; S 10.76.

Crystallographic Analysis of Compound 7. Rhombic crystals, $C_5H_2Br_2N_2OS$, at 20°C a = 16.356(7), b = 7.046(2), c = 7.023(3) Å, V = 809.4(5) Å^3, M_r = 297.97, Z = 4, space group Pnma, d_{calc} = 2.445 g/cm^3, μ(MoKα) 10.212 mm^{-1}, F(000) = 560. The elemental cell parameters and the intensities of 2332 reflections (1228 independent, R_{int} = 0.060) were measured on an automatic four-circle Siemens P3/PC diffractometer (MoKα radiation, graphite monochromator, θ/2θ scanning, $2\theta_{max}$ = 60°). The structure was determined by direct methods using the SHELXTL of program suite [15]. The hydrogen positions were determined from difference syntheses of electron densities and refined in the isotropic approximation. The absorptions were refined semi-empirically from Ψ-scanning data (T_{min} = 0.0380, T_{max} = 0.04415). The structure was refined with respect to F^2 in full-matrix least-squares analysis in the anisotropic approximation for non-hydrogen atoms to wR_2 = 0.0797 for 1228 reflections (R_1 = 0.048 for 831 reflexions with F>4σ(F), S = 0.933). Complete data for the structure have been deposited in the Cambridge Crystallographic Data Center (CCDC 148666).

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