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Synthesis and Transformation of 1-Monosubstituted Tetrazoles to Pyrimidinones, Benzoxazoles and Quinazolinediones Through 1,4-Disubstituted Tetrazolium Salts

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Synthesis and some new transformations of 1-aryltetrazoles into other heterocycles through 1,4-disubstituted tetrazolium salts are described. 1-Aryltetrazoles, quaternized with *tert*-butanol and diacetone alcohol in perchloric acid media, gave pure 1,3- or 1,4-disubstituted tetrazolium salts or their mixtures. 1,3-Disubstituted tetrazolium salts are slowly converted into the corresponding 1,4-salts under dissolving in perchloric acid. 1,4-Disubstituted tetrazolium salts are recyclized to 2-alkylaminobenzoxazoles, 3-monosubstituted 2,4-quinazolinediones and mixtures of di- and tetrahydropyrimidin-2(1H)-ones in basic conditions.

Key words: tetrazoles, quaternization, tetrazolium salts, 2-aminobenzoxazoles, 2,4-quinazolinediones, dihydropyrimidin-2(1H)-one, tetrahydropyrimidin-2(1H)-one, crystal structure

Recently an increasing interest has been directed to investigation of various tetrazolium salts, which may be used for producing the N-substituted heterocyclic carbenes, bipolar ionic systems, different active tetrazolines and other heterocyclic compounds [1–3]. This interest is conditioned also by advances in elaboration of new convenient methods for synthesis of the tetrazolium salts [4–9]. The structure of products of transformations of the tetrazolium salts depend substantially on the nature and the position of substituents in the tetrazole cycle. As a rule, 1,3- and 2,3-disubstituted tetrazolium salts generate triazene structures [10], whereas 1,4-salts give tetrazolines, carbodiimides and products of their further transformations, including aziridines, hydantoin derivatives and iminodihydrotetrazines [11,12].

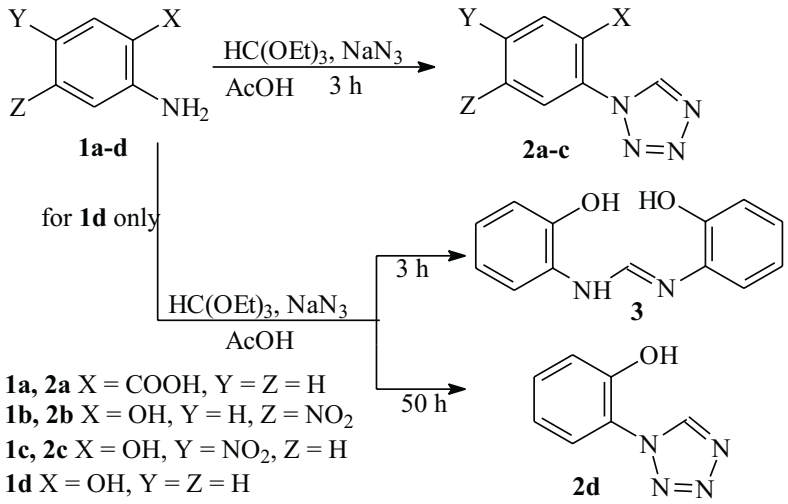
Here, we report on new types of conversion of tetrazolium salts, namely, recyclization of 1,4-disubstituted tetrazolium salts, having some functional groups into 2,4-quinazolinediones, 2(1H)-pyrimidinones and 2-aminobenzoxazoles. For this purpose, a synthesis of a number of hitherto unknown 1-aryltetrazoles was performed and the reactions of their quaternization were studied. Some transformations of the obtained polyfunctional 1,4-disubstituted tetrazolium salts were also investigated.

RESULTS AND DISCUSSION

1-Monosubstituted tetrazoles: Several methods for the synthesis of 1-monosubstituted tetrazoles have been reported [1–3]. Heterocyclization of primary amines with triethylorthoformate and sodium azide seems to be the most convenient method [13–15]. It is applicable to the synthesis of tetrazoles, using aliphatic, aromatic and heterocyclic amines of different structure. However, this reaction has several restrictions. Some low basic amines, for example 2,4-dinitroaniline, are not susceptible to heterocyclization [15]. In the case of thiosemicarbazide and o-phenylenediamine, condensation with triethylorthoformate, leading to formation of aminothiodiazole or benzimidazole, has been observed [14,15].

The behaviour of o-substituted anilines in the reaction of heterocyclization has been studied in this paper. Anthranilic acid **1a** was found to react with triethylorthoformate and sodium azide in acetic acid (70–80°C, 3 h) giving 1-(o-carboxyphenyl)tetrazole **2a** (Scheme 1). Similarly, nitroaminophenols **1b** and **1c** produce tetrazoles **2b, c**. In the case of o-aminophenol (**1d**) as a product of reaction N,N′-di(o-hydroxyphenyl)amidine (**3**) was isolated in 55% yield. Tetrazole **2d** was obtained in low yield (12%) after longer reaction time (50 h).

Scheme 1

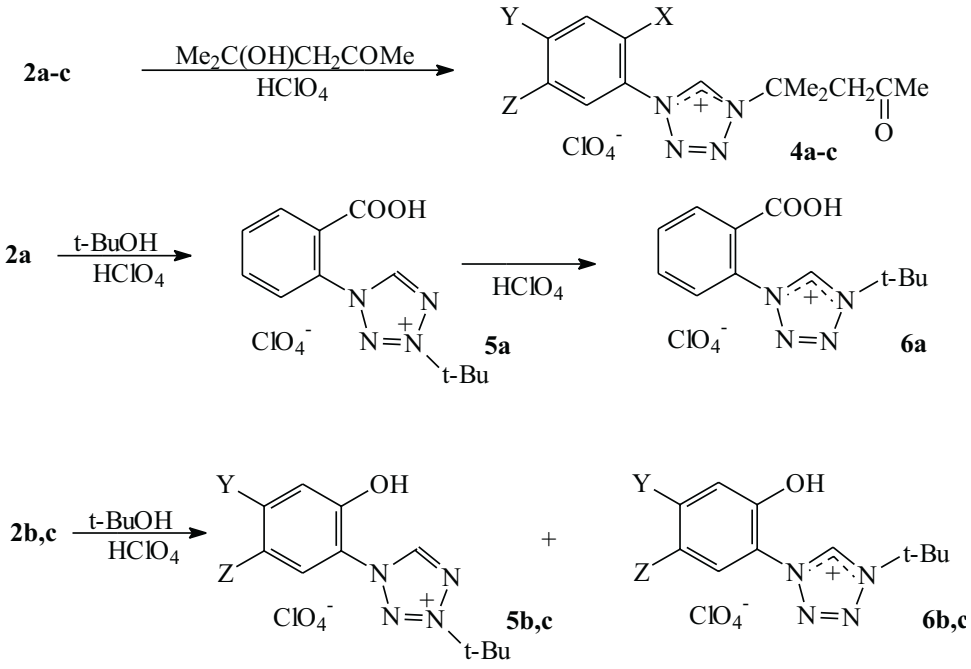


The obtained data confirm the previously proposed mechanism for heterocyclization of primary amines, which includes generation of N,N′-disubstituted amidines followed by nucleophilic attack of azide ion and formation of 1-substituted tetrazoles [13]. The distinction in the behaviour of investigated aminophenols is due to different electron effects of the substitutents. Thus, a strong mesomeric effect of

hydroxyl group prevent nucleophilic attack on amidine carbon atom of **3**. Introduction of nitro group characterized by strong electron-withdrawing inductive and mesomeric effects increases the positive charge on amidine carbon atom, resulting in rising of its reactivity in nucleophillic substitution.

1,4-Disubstituted tetrazolium salts: One of the methods widely used for the synthesis of tetrazolium salts is quaternization of tetrazoles [1–3], including exhaustive alkylation in acidic media [5–8]. The latter process has some advantages. In contrast to quaternization in neutral conditions, this method allows one to introduce some bulky substituents, particularly CR_3 groups, to N-positions of the tetrazole cycle. This is impossible when quaternization proceeds under neutral conditions with alkyl halides, alkyl sulphates, oxonium salts and other alkylating agents. At the same time, quaternization in acidic media has been studied only for a limited number of alkyl- and phenyltetrazoles [5-8]. We have investigated the quaternization of polyfunctional 1-aryltetrazoles with *tert*-butanol and diacetone alcohol in the presence of perchloric acid (Scheme 2).

Scheme 2



4a X = COOH, Y = Z = H; **4b** X = OH, Y = H, Z = NO_2; **4c** X = OH, Y = NO_2, Z = H.
5b, 6b Y = H, Z = NO_2; **5c, 6c** Y = NO_2, Z = H.

The exhaustive alkylation of substituted 1-aryltetrazoles with diacetone alcohol, independently on the nature of initial tetrazole and concentration of acid within the range of 62–72 wt %, results in formation of individual 1,4-disubstituted tetrazolium salts **4**. On the contrary, selectivity of *tert*-butylation depends substantially on both these factors. Thus, *tert*-butylation of tetrazole **2a** in 72% perchloric acid proceeds selectively on $N_{(3)}$ atom, giving 1,3-disubstituted tetrazolium salt **5a**. The decrease of the acid concentration up to 62% leads to formation of mixtures of tetrazolium salts **5a** and **6a** (molar ratio 1:2, yield 63%). In the case of tetrazoles **2b** and **2c,** mixtures of 1,3- and 1,4-disubstituted tetrazolium salts were obtained upon *tert*-butylation regardless of the concentration of perchloric acid. The experimental results obtained along with the data of our earlier investigations [5–7] allow one to propose the following mechanism of the described processes. Under acidic conditions 1-aryltetrazoles undergo protonation at the most nucleophilic $N_{(4)}$ atom, resulting in formation of 1-aryl-4H-tetrazolium cations [2,16,17]. In turn, upon the action of acid, alcohols generate the corresponding carbocations, which attack tetrazolium cations on the $N_{(3)}$ atom leading to formation of 1,3-disubstituted tetrazolium salts. The interaction of two cations seems to be unusual. However, according to quantum-chemical calculations of electron structure of 1-alkyl- and 1-aryl-4H-tetrazolium cations, the positive charge localizes in $N_{(1)}$–$C_{(5)}$–$N_{(4)}$ fragment, whereas $N_{(2)}$ and $N_{(3)}$ atoms are characterized by negative π-charges [6]. The decrease of acidity leads to incomplete protonation of 1-monosubstituted tetrazoles and, as a result, to formation of isomeric 1,4-disubstituted salts. Such process takes place upon *tert*-butylation of 1-alkyl- and 1-phenyltetrazoles in 40% $HClO_4$ and 48% HBF_4 [5,6].

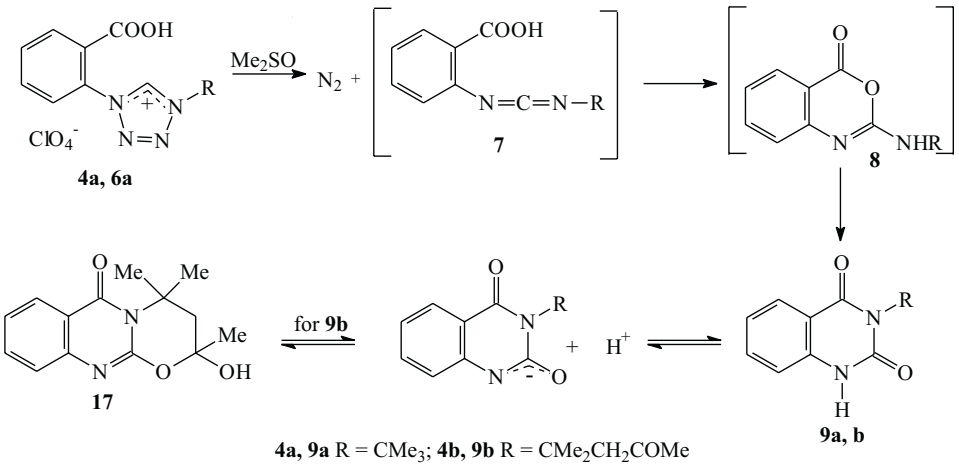
The increasing of the reaction time (> 12 h) leads to formation of mixtures of 1,3- and 1,4-disubstituted tetrazolium salts. Analogous transformation occurs on long standing of individual 1,3-disubstituted salts in perchloric acid. These data suggest that isomerization of 1,3-salts to 1,4-isomers proceeds under acidic conditions. The driving forces of this process are probably the larger thermodynamic stability of 1,4-isomers [6,18] and their lower solubility in acidic media compared with 1,3-disubstituted ones. Isomerization can occur under highly acidic conditions only where the generation of carbocation R^+ is possible at the expense of heterolysis of exocyclic $N_{(3)}$–R bond, where R = *t*-Bu, CMe_2CH_2COMe. Obviously, the isomerization rate is depending on the acidity of media and the nature of substituent R. For R = *t*-Bu the complete isomerization requires approximately 4 days. In the case of R = CMe_2CH_2COMe the rate of isomerization is higher and 1,3-disubstituted salts formed under quaternization of 1-monosubstituted tetrazoles with diacetone alcohol convert completely into the corresponding 1,4-isomers after 12 h. The observed isomerization processes have been used for the synthesis of 1,4-disubstituted salts **6** starting from individual 1,3-disubstituted salts **5** or mixtures of isomeric salts.

Ring transformation of 1,4-disubstituted tetrazolium salts: According to spectral characteristics, the obtained 1,4-disubstituted tetrazolium salts have a labile hydrogen atom H_c at the carbon atom of the tetrazole ring. The chemical shifts of these hydrogen atoms in ^1H NMR spectra undergo a downfield shift comparing to

analogous chemical shifts for initial tetrazoles. Thus, chemical shift of H_c for salt **4b** appears at 10.75 ppm, whereas tetrazole **2b** shows this one at 9.39 ppm under the same conditions. The relatively high lability of H_c may be the reason of the ability of 1,4-disubstituted salts to decompose under the action of nucleophiles. We have revealed, that 1,4-disubstituted salts **4** and **6** decompose in the presence of dimethylsufoxide (DMSO) with evolution of nitrogen and formation of 3-monosubstituted 2,4-quinazolinediones **9** or 2-alkylaminobenzoxazoles **11** (Schemes 3 and 4). Probably, DMSO, similarly to other nucleophiles [11,19] splits out hydrogen atom H_c and the tetrazole ring undergoes a fragmentation resulting in formation of nitrogen and carbodiimides **7, 10,** intramolecular cyclization of which may proceed by interaction of carbodiimide carbon atom with hydroxyl and carboxyl groups. In the first case, a stable fused aromatic benzoxazole system is formed. The attack of carbodiimide by carboxyl group leads to formation of cyclic O-benzoylisourea **8**, which isomerizes giving 2,4-quinazolinedione **9.** The literature data on interaction of carbodiimides with carbon acids and phenols [20,21] are in agreement with the proposed mechanisms.

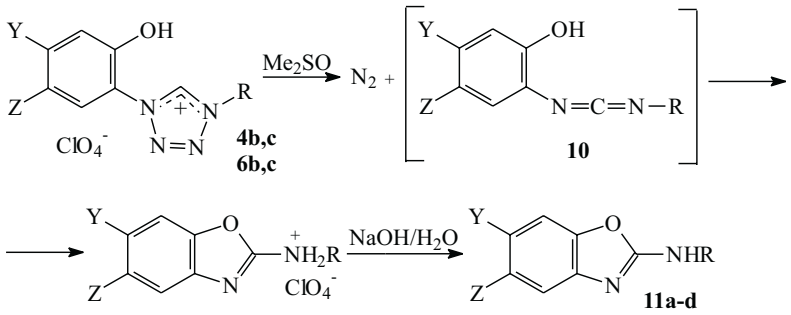
We studied also the behaviour of other 1,4-substituted tetrazolium perchlorates **12** [7]. 1-Phenyl-4-(2-methylpentanon-4-yl-2)tetrazolium perchlorate **12a** was found to convert in DMSO solution into two isomeric pyrimidinones – 3,4-dihydro-4,4,6-trimethyl-1-phenylpyrimidin-2(1H)-one **15a** and 3,4,5,6-tetrahydro-4,4-dimethyl-1-phenyl-6-methylidenpyrimidin-2(1H)-one **16a** (the molar ratio of **15a:16a,** determined by ^{1}H NMR data amounts to 6:1) (Scheme 5). According to ^{1}H NMR data, H_c atom of the salt **12b** is less labile than that one in salt **12a.** Thus, the chemical shift of H_c atoms in ^{1}H NMR spectra of salts **12b** and **12a** appear at 10.11 and 10.73 ppm in

Scheme 3



4a, 9a R = CMe_3; **4b, 9b** R = CMe_2CH_2COMe

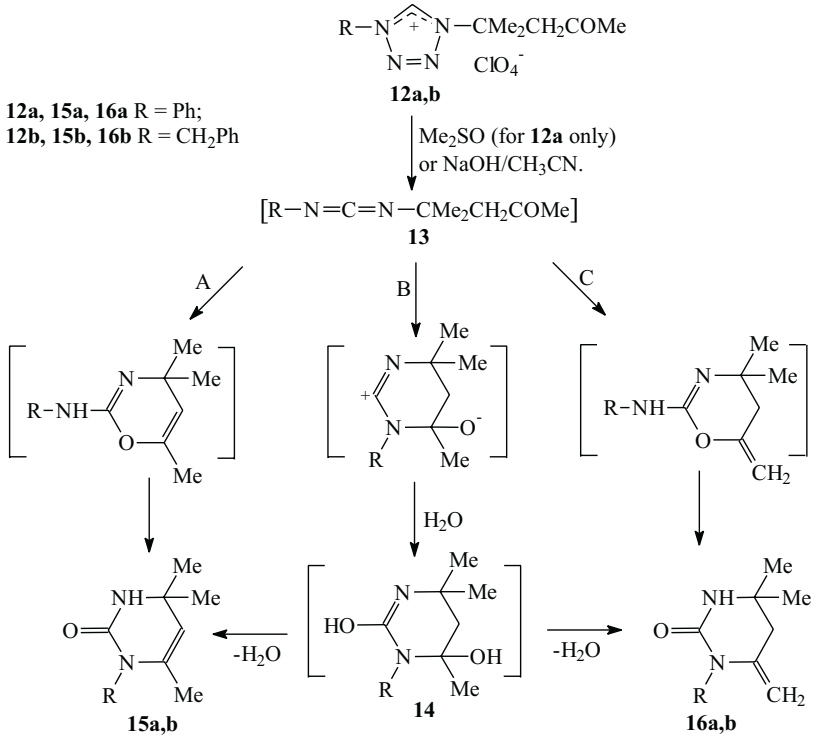
Scheme 4



11a, R = CMe_3, Y = H, Z = NO_2; **11b,** R = CMe_3, Y = NO_2, Z = H;
11c, R = CMe_2CH_2COMe, Y = H, Z = NO_2;
11d, R = CMe_2CH_2COMe, Y = NO_2, Z = H.

CD_3CN. Probably for this reason salt **12b** is stable in DMSO solution and its decomposition proceeds under the action of strong bases only, for example, of sodium hydroxide. In this case the mixture of isomeric pyrimidinones **15b**, **16b** (molar ratio 1.8:1) is formed. In these conditions salt **12a** was found to yield pyrimidinones **15a** and **16a** (molar ratio 4.4:1).

Scheme 5



The formation of pyrimidinones **15** and **16** is accompanied by intramolecular cyclization of intermediate carbodiimide **13.** This process may be accomplished by attack of carbodiimide by enol forms of keton (routes A, C) or by attack of C=O group by carbodiimide nitrogen atom (route B). In the latter case, the unstable intermediate **14** is formed, dehydration of which leads to isomeric compounds **15** and **16** with predominance of **15** according to Zaitsev rule.

Identification of products: All the compounds obtained, excluding **9a** [22] and **15a** [23], were not described previously. The physical and chemical characteristics of **9a** and **15a** are in agreement with the literature data [22,23]. Strong absorption bands are observed in the region of 950–1100 cm^{-1} of IR spectra of 1R-tetrazoles **2**, which are characteristic of stretching-deformation vibrations of the tetrazole ring. The absorptions of stretching vibrations of C–H_c bonds are located in the typical for N-substituted tetrazoles region, *i.e.* about 3100 cm^{-1}. The chemical shifts of H_c, which appear at 9.30–9.80 ppm, are characteristic of 1-monosubstituted tetrazoles.

The compounds **4–6** were characterized as 1,3- and 1,4-disubstituted salts, according to ^{1}H NMR chemical shifts of hydrogen atom H_c. The latter corresponds to well-known literature data on related tetrazolium salts [5–7]. The chemical shifts of H_c for 1,3-disubstituted tetrazolium salts are observed at 9.8–10.4 ppm. At the same time, analogous signals for1,4-disubstituted tetrazolium salts appear at 10.5–10.9 ppm.

The ^{13}C NMR data of quinazoline ring of compounds **9a** and **9b** are similar. However, in spectra of **9b** chemical shifts of some carbon atoms are shifted by 2.7–7.7 ppm to a lower field and the chemical shift of C=O group is observed at 94.3 ppm. At the same time, chemical shift of C=O group of compounds **11c,d** appears at 210 ppm. The strong absorption band at 1724 cm^{-1}, which is attributed to free aliphatic carbonyl group is observed in IR spectra of crystalline **9b** in nujol. The present data indicate the possibility of intramolecular cyclization of quinazolinedione **9b** in solution. 3-Monosubstituted 2,4-quinazolinediones are known to be a strong N-H acids [24]. Under their dissociation the negative charge is localized on $N_{(1)}$–$C_{(2)}$=O fragment of the molecule. The attack of aliphatic C=O group by the latter fragment leads to cyclic acetal **17**. In similar manner γ- and δ-hydroxylaldehydes and ketones undergo cyclization giving cyclic acetals and ketals [25].

Spectral characteristics of **11a–d** correspond to well-known literature data on related 2-aminobenzoxazoles [26,27]. Thus, the strong absorption bands of C=N bonds are observed at 1660–1670 cm^{-1} in IR spectra of **11**, the typical bands of $C_{(7a)}$ and $C_{(2)}$ cycle atoms appear at 165–167 and 150–155 ppm in their ^{13}C NMR spectra correspondingly.

The structure proposed for **15b** was confirmed by X-ray crystallographic study. As shown by X-ray analysis, the molecule of **15b** has some peculiarities of spatial structure (Figure 1). The phenyl ring is planar, the r.m.s. deviation of ring atoms from the least-square plane through them is 0.003(2) Å. The planar fragment of pyrimidine is formed by the atoms of double bond, namely, $N_{(1)}$, $C_{(4)}$, $C_{(5)}$ and $C_{(6)}$. The r.m.s. deviation of these atoms from the least-square plane through them is 0.007(2) Å. The di-

hedral angle between the mentioned above planes is 89.16(9)°. The bond distances and angles in the phenyl and pyrimidine fragments are consistent with those observed previously [28]. Inspection of the packing of the molecules reveals the following features. Firstly, the molecules in the crystal are combined to dimers by hydrogen bonds: $d[N_{(3)}\cdots O_{(2)}]$ = 2.933(2), $d[N_{(3)}–H_{(3)}]$ = 0.91(3), $d[H_{(3)}\cdots O_{(2)}]$ = 2.02(2) Å, $\omega[N_{(3)}–H_{(3)}\cdots O_{(2)}]$ = 176(2)°. Secondly, only van der Waals interactions take place between these dimers.

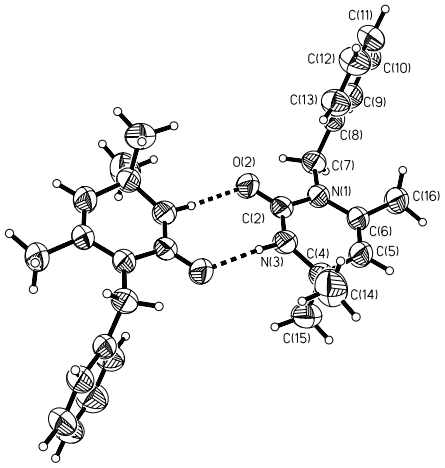


Figure 1. A fragment of the crystal structure **15b** showing hydrogen bonds (dashed lines) in molecular dimer.

EXPERIMENTAL

General. M.p.'s were determined in capillary tubes and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Tesla BS 567A spectrometer at operating frequencies of 100.028 and 25.142 MHz correspondingly with hexamethyldisiloxane as internal reference and hexadeuteriuodimethylsulfoxide or trideuteriuoacetonitrile as solvent. IR spectra were measured with FT-IR "Spectrum 1000" Perkin-Elmer spectrophotometer.

1-Aryltetrazoles 2a–d (General procedure): The glacial acetic acid (50 ml) was added with stirring to the suspension of primary amine **1** (100 mmol), sodium azide (7.8 g, 120 mmol) and triethylorthoformate (22 ml, 150 mmol). A mixture was stirred at 70–80°C for 3 h. Then hydrochloric acid (120 mmol) was added and mixture was evaporated *in vacuo*. The residue was stirred with water (50 ml). The obtained precipitate **2a,b,c** was recrystallized from ethanol. In the case of heterocyclization of **1d,** the residue was recrystallized from ethanol and **3** was obtained. For the synthesis of **2d,** the initial reaction mixture was stirred at 70–80°C for 50 h.

2a: M.p. 204–6°C. Yield 69%. ^{1}H NMR (DMSO-d_6), δ: 9.81 (s, 1H, H_c), 8.05–8.15 (m, 1H, Ph), 7.71–7.88 (m, 3H, Ph). IR (cm^{-1}): 3135 ($HC_{tetrazole}$), 1700 (C=O), 1590, 1490 ($C{=}C_{arom}$), 1250 (C–O), 1200 (C–N), 1165, 1096, 1080 ($HC_{tetrazole}$), 995, 970 (HC_{arom}), 890 (OH), 790, 755 (HC_{arom}). Anal. (%). Calcd. for $C_8H_6N_4O_2$ (190.05) : C 50.51; H 3.18; N 29.47. Found: C 50.72; H 3.02; N 29.32.

2b: Dec 205°C Yield 80%. ^{1}H NMR (CD_3CN), δ: 9.39 (s, 1H, H_c), 8.57 (d, 1H, Ph), 8.26 (dd, 1H, Ph), 7.29 (d, 1H,Ph). IR (cm^{-1}): 3172 ($HC_{tetrazole}$), 1598, 1450 ($C{=}C_{arom}$), 1410 (OH), 1340 (NO_2), 1300, 1280 (C–N), 1200 (C–O), 1100, 1074, 955 ($HC_{tetrazole}$), 940, 885 (HC_{arom}), 835 (NO_2), 740, 715 ($C{=}C_{arom}$). Anal. (%). Calcd. for $C_7H_5N_5O_3$ (207.04) : C 40.57; H 2.43; N 33.82. Found: C 40.74; H 2.52; N 33.52.

2c: Dec 220°C. Yield 90%. ^{1}H NMR (CD_3CN), δ: 9.48 (s, 1H, H_c), 7.90–7.99 (m, 3H, Ph). IR (cm^{-1}): 3090 ($HC_{tetrazole}$), 1595, 1450 ($C{=}C_{arom}$), 1385 (OH), 1340 (NO_2), 1274, 1220 (C–N), 1200 (C–O), 1105, 1040, 995 ($HC_{tetrazole}$), 930, 880 (HC_{arom}), 815 (NO_2), 740 (HC_{arom}). Anal. (%). Calcd. for $C_7H_5N_5O_3$ (207.04) : C 40.57; H 2.43; N 33.82. Found: C 40.69; H 2.60; N 33.91.

2d: M.p. 124–6°C. Yield 12%. ^{1}H NMR (CD_3SOCD_3), δ: 9.75 (s, 1H, H_c), 6.95–7.69 (m, 4H, Ph). IR (cm^{-1}): 3135 ($HC_{tetrazole}$), 1700 (C=O), 1590, 1490 ($C{=}C_{arom}$), 1250 (C–O), 1200 (C–N), 1165, 1096, 1080 ($HC_{tetrazole}$), 995, 970 (HC_{arom}), 890 (OH), 790, 755 (HC_{arom}). Anal. (%). Calcd. for $C_7H_6N_4O$ (162.05) : C 51.83; H 3.73; N 34.56. Found: C 51.69; H 3.62; N 34.71.

3: Dec 160°C. Yield 55%. ^{1}H NMR (CD_3COCD_3), δ: 8.50–11.30 (br s, 3H, HO, HN), 7.02–7.45 (m, 6H, Ph), 7.14 (s, 1H, CH), 6.70–6.91 (m, 2H, Ph). IR (cm^{-1}): 1636 (C=N), 1602 ($C{=}C_{arom}$), 1520 (NH), 1488 ($C{=}C_{arom}$), 1346, 1315 (OH), 1282 (C–N), 1230 (C–O), 1176 (C–N), 1109, 1007, 854, 752, 640 (HC_{arom}). Anal. (%). Calcd. for $C_{13}H_{12}N_2O_2$ (228.09) : C 68.39; H 5.30; N 12.28. Found: C 68.66; H 5.68; N 12.01.

Tetrazolium salts 4a–c, 5a–c, 6b,c. (General procedure): A solution of **2a–c** (60 mmol) and 2-methylpentan-4-on-2-ol (70 mmol) in perchloric acid (72%, 25 ml, 300 mmol) was kept at room temperature for 12 h. Then water (50 ml) was added. The solid residue was precipitated on cooling the formed soluton to 0°C. Recrystallization of crude product from ethanol yielded crystals of pure salts **4a–c.**

Quaternization of **2a** with 1,1-dimethylethanol according to described above procedure yielded crystals of pure salts **5a**. Quaternization of **2b,c** with 1,1-dimethylethanol according to this procedure yielded the mixtures of salts **5** and **6** and initial tetrazoles **2** (ratio **5b:6b:2b** = 12.5:1:7.5; **5c:6c:2c** = 3.5:1:2.1). Quaternization of **2c,d** with 1,1-dimethylethanol according to this procedure in 62% $HClO_4$ (48 h) yielded the mixtures of salts **5** and **6** (ratio **5b:6b** = 1:1.7; **5c:6c** = 1.4:1). The total yields of products **5b, 6b** and **5c**, **6c** are 89% and 75%, correspondingly).

4a: Dec 155°C. Yield 67%. ^{1}H NMR (CD_3CN), δ: 10.61(s, 1H, H_c), 8.24–8.35 (m, 1H, Ph), 7.78–8.06 (m, 3H, Ph), 6.22 (br s, 1H, COOH), 3.42 (s, 2H, CH_2CO), 2.12 (s, 3H, MeCO), 1.92 (s, 6H, 2Me). Anal. (%). Calcd. for $C_{14}H_{17}N_4O_7Cl$ (388.08): C 43.29; H 4.41; N 14.43; Cl 9.01. Found: C 43.09; H 4.38; N 14.21; Cl 9.20.

4b: Dec 172°C. Yield 65%. ^{1}H NMR (CD_3CN), δ: 10.75 (s, 1H, H_c), 8.69 (d, 1H, Ph), 8.41 (dd, 1H, Ph), 7.45 (d, 1H, Ph), 3.40 (s, 2H, CH_2CO), 2.10 (s, 3H, CH_3CO), 1.89 (s, 6H, 2Me). Anal. (%). Calcd. for $C_{13}H_{16}N_4O_8Cl$ (391.07): C 39.89; H 4.12; N 14.32; Cl 8.94. Found: C 40.09; H 4.28; N 14.11; Cl 9.10.

4c: Dec 150°C. Yield 78%. ^{1}H NMR (CD_3CN), δ: 10.78 (s, 1H, H_c), 7.95–8.05 (m, 3H, Ph), 3.38 (s, 2H, CH_2CO), 2.10 (s, 3H, MeCO), 1.90 (s, 6H, 2Me). Anal. (%). Calcd. for $C_{13}H_{16}N_4O_8Cl$ (391.07): C 39.89; H 4.12; N 14.32; Cl 8.94. Found: C 39.97; H 4.20; N 14.20; Cl 8.88.

5a: Dec 180°C. Yield 62%. ^{1}H NMR (CD_3CN), δ: 9.80 (s, 1H, H_c), 8.22–8.39 (m, 3H, Ph), 7.80–8.04 (m, 3H, Ph), 1.90 (s, 9H, 3Me). Anal. (%). Calcd. for $C_{12}H_{15}N_4O_6Cl$ (346.07): C 41.61; H 4.37; N 16.19; Cl 10.10. Found: C 41.40; H 4.21; N 16.32; Cl 9.88.

5b: ^{1}H NMR (CD_3CN), δ: 10.09 (s, 1H, H_c), 8.70 (d, 1H, Ph), 8.40 (dd, 1H, Ph), 7.43 (d, 1H, Ph), 1.85 (s, 9H, 3Me).

5c: ^{1}H NMR (CD_3CN), δ: 10.15 (s, 1H, H_c), 7.90–8.10 (m, 3H, Ph), 1.85 (s, 9H, 3Me).

Tetrazolium salts 6a–c (General procedure). A solution or suspension of pure **5a** or mixtures of isomers **5b,c** and **6b,c** (18 mmol) in perchloric acid (72%, 25 ml) was kept at room temperature for 4 days. The solid products **6a–c** were precipitated by adding of water (70 ml) and recrystallized from ethanol.

6a: Dec 176°C. Yield 65%. ^{1}H NMR (CD_3CN), δ: 10.55 (s, 1H, H_c), 8.24–8.38 (m, 1H, Ph), 7.78–8.05 (m, 3H, Ph), 1.85 (s, 9H, 3Me). Anal. (%). Calcd. for $C_{12}H_{15}N_4O_6Cl$ (346.07): C 41.61; H 4.37; N 16.19; Cl 10.10. Found: C 41.33; H 4.29; N 16.09; Cl 10.06.

6b: Dec 172°C. Yield 88%. ^{1}H NMR (CD_3CN), δ: 10.68 (s, 1H, H_c), 8.70 (d, 1H, Ph), 8.40 (dd, 1H, Ph), 7.43 (d, 1H, Ph), 1.85 (s, 9H, 3Me). Anal. (%). Calcd. for $C_{11}H_{14}N_5O_7Cl$ (363.06): C 36.36; H 3.89; N 19.28; Cl 9.63. Found: C 36.53; H 3.78; N 19.10; Cl 9.59.

6c: Dec 150°C. Yield 85%. ^{1}H NMR (CD_3CN), δ: 10.71 (s, 1H, H_c), 7.90–8.10 (m, 3H, Ph), 1.85 (s, 9H, 3Me). Anal. (%). Calcd. for $C_{11}H_{14}N_5O_7Cl$ (363.06): C 36.36; H 3.89; N 19.28; Cl 9.63. Found: C 36.49; H 3.90; N 19.19; Cl 9.66.

Quinazolinediones 9a,b. (General procedure): A solution of **4a** or **6a** (8 mmol) in dimethylsulfoxide (25 ml) was kept at room temperature for 2 h. Colourless solid product **9** was precipitated by adding of water (100 ml) and recrystallized from ethanol.

9a: M.p. 198–200°C, lit. [22], m.p. 198–199°C. Yield 98%. ^{1}H NMR (CD_3SOCD_3), δ: 9.80 (br s, 1H, NH), 8.32 (d, 1H, H_c), 7.88 (dd, 1H, H_c), 7.42 (td, 1H, H_c), 6.91 (td, 1H, H_c), 1.29 (s, 9H, 3Me). ^{13}C NMR (CD_3SOCD_3), δ: 173.1 (C-2), 157.9 (C-4), 147.2 (C-8a), 137.3 (C-8), 134.8 (C-5), 123.5 (C-6, C-7) 118.6 (C-4a), 53.8 (C–N), 33.1 (3Me). IR (cm^{-1}): 3367 (NH), 1655 (C=O), 1580 (C=C), 1520 (C=C). Anal. (%). Calcd. for $C_{12}H_{14}N_2O_2$ (218.11): C 66.02; H 6.47; N 12.84. Found: C 65.89; H 6.39; N 12.77.

9b: M.p. 177–9°C,. Yield 90%. ^{1}H NMR (CD_3SOCD_3), δ: 8.32 (d, 1H, H_c), 7.68–8.04 (m, 2H, H_c), 7.63 (td, 1H, H_c), 7.30 (td, 1H, H_c), 2.37 and 2.32 (two s, 2H, CH_2CO), 1.55 (s, 3H, MeCO), 1.29 and 1.36 (two s, 6H, 2Me). ^{13}C NMR (CD_3SOCD_3), δ: 165.9 (C-2), 155.1 (C-4), 143.2 (C-8a), 137.6 (C-8), 132.0 (C-5), 130.1 (C-7), 128,8 (C-6), 123.6 (C-4a), 94.3 (C=O or O–C–OH), 52.3 (N–C), 49.0 (CH_2), 33.5 (Me), 32.5 and 31.0 (2Me). IR (cm^{-1}): 3224 (NH), 1724 (C=O), 1683 (C=O), 1590 (C=C), 1484 (C=C). Anal. (%). Calcd. for $C_{14}H_{16}N_2O_3$ (260.12): C 64.59; H 6.20; N 10.77. Found: C 64.50; H 6.37; N 10.83.

Benzoxazoles 11a–d. (General procedure): A solution of **4b,c** or **6b,c** (8 mmol) in dimethylsulfoxide (25 ml) was kept at room temperature for 2 h. Solid **11** was precipitated on adding of aqueous sodium hydroxide (9 mmol) and recrystallized from ethanol.

11a: M.p. 178–180°C. Yield 82%. ^{1}H NMR (CD_3SOCD_3), δ: 8.59 (br s, 1H, NH), 8.04–8.23 (m, 2H, H_c), 7.40 (d, 1H, H_c), 1.43 (s, 9H, 3Me). ^{13}C NMR (CD_3SOCD_3), δ: 166.1 (C-2), 155.3 (C-7a), 148.1 (C-3a), 147.9 (C-5), 120.4 (C-6), 113.9 (C-4), 111.9 (C-7), 55.3 (N–C), 32.2 (3Me). IR (cm^{-1}): 3150 (NH), 1662 (C=N), 1584 (C=C), 1521 (NO_2), 1485 (C=C), 1339 (NO_2), 1261 (C–N), 1228 (C–O), 1002 (C–O), 1125 (CMe_3). Anal. (%). calcd. for $C_{11}H_{13}N_3O_3$ (235.10): C 56.15; H 5.57; N 17.87. Found: C 56.31; H 5.69; N 17.70.

11b: M.p. 144–6°C. Yield 90%. ^{1}H NMR (CD_3SOCD_3), δ: 8.58 (br s, 1H, NH), 8.21 (d, 1H, H_c), 8.11 (dd, 1H, H_c), 7.38 (d, 1H, H_c), 1,43 (s, 9H, 3Me). IR (cm^{-1}): 3150 (NH), 1671 (C=N), 1591 (C=C), 1508 (NO_2), 1330 (NO_2), 1280 (C–N), 1220 (C–O), 1060 (C–O), 1120 (CMe_3). Anal. (%). calcd. for $C_{11}H_{13}N_3O_3$ (235.10): C 56.15; H 5.57; N 17.87. Found: C 56.29; H 5.77; N 17.81.

11c: M.p. 120–1°C. Yield 85%. ^{1}H NMR (CD_3SOCD_3), δ: 8.35 (br s, 1H, NH), 7.95–8.10 (m, 1H, H_c), 7.91 (d, 1H, H_c), 7.55 (d, 1H, H_c), 3.07 (s, 2H, CH_2CO), 2.05 (s, 3H, MeCO), 1.45 (s, 6H, 2Me). ^{13}C NMR (CD_3SOCD_3), δ: 210.1 (C=O), 165.8 (C-2), 155.3 (C-7a), 147.9 (C-5, C-3a), 120.5 (C-6), 114.1 (C-4). 111.9 (C-7), 56.5 (N–C), 54.2 (CH_2), 35.4 (Me), 30.6 (2Me). IR (cm^{-1}): 3316 (NH), 1697 (C=O), 1651 (C=N), 1581 (C=C), 1524 (NO_2), 1269 (C–N), 1235 (C–O). Anal. (%). calcd. for $C_{13}H_{15}N_3O_4$ (277.11): C 56.30; H 5.46; N 15.16. Found: C 56.43; H 5.60; N 15.01.

11d: M.p. 125–7°C. Yield 96%. ^{1}H NMR (CD_3SOCD_3), δ: 8.69 (br s, 1H, NH), 8.24 (d, 1H, H_c), 8.12 (dd, 1H, H_c), 7.40 (d, 1H, H_c), 3.08 (s, 2H, CH_2CO), 2.05 (s, 3H, MeCO), 1.45 (s, 6H, $2CH_3$). ^{13}C NMR (CD_3SOCD_3), δ: 210.1 (C=O), 167.3 (C-2), 154.1 (C-3a), 150.3 (C-7a), 144.2 (C-6), 124.6 (C-5), 118.2 (C-4), 108.1 (C-7), 56.7 (N–C), 54.4 (CH_2), 35.4 (Me), 30.7 (2Me). IR (cm^{-1}): 3324 (NH), 1705 (C=O), 1655 (C=N), 1595 (C=C), 1507 (NO_2), 1331 (NO_2), 1289 (C–N), 1255 (C–O), 1202 (CMe_3), 1060 (C–O). Anal. (%). calcd. for $C_{13}H_{15}N_3O_4$ (277.11): C 56.30; H 5.46; N 15.16. Found: C 56.49; H 5.65; N 15.11.

Transformation of salt 12a in dimethylsulfoxide. A solution of **12a** (29 mmol) in dimethylsulfoxide (2 ml) was kept at 50–60°C for 1 h. Then water (10 ml) was added. The obtained precipitate was separated by filtration and then dried (the total yield of **15a** and **16a** is 86%).

Transformation of salts 12a,b by the action of base. The suspension of sodium hydroxide (50 mmol) in acetonitrile was added dropwise to a solution of salt **12** (40 mmol) in acetonitrile (20 ml). The mixture was kept at 60–70°C for 3 h. Then the solvent was evaporated *in vacuo*. The residue was stirred with water (20 ml). Then the obtained precipitate was separated by filtration and dried (the total yield of products **15a**, **16a** and **15b, 16b** are 82% and 74%, correspondingly). An individual compounds **15, 16** were isolated from mixtures by slow crystallization from acetonitrile. The compound **15a,** which is less soluble, is separated in the first fraction of crystalline product and compound **16a** is separated in the last fraction. Upon transformation of salt **12b,** this method allows only the product **15b** to be isolated successively from the corresponding mixture.

15a: M.p. 162–164°C, lit. [23] 163°C. ^{1}H NMR (CD_3SOCD_3), δ: 7.28–7.42 (m, 3H, Ph), 7.10–7.21 (m, 2H, Ph), 5.50 (br s, 1H, NH), 4.72 (s, 1H, CH=), 1.45 (s, 3H, Me), 1.29 (s, 6H, 2Me). ^{13}C NMR (CD_3SOCD_3), δ: 156.8 (C-2), 142.4 (C-6), 130.9, 132.1, 133.5, 135.9 (Ph), 111.1 (C-5), 54.9 (C-4), 35.1 (2Me), 23.5 (Me). IR (cm^{-1}): 3225 (NH), 1699 (C=O), 1660 (C=C), 1240 (C–N). Anal. (%). calcd. for $C_{13}H_{16}N_2O$ (216.13): C 72.18; H 7.46; N 12.96. Found: C 72.30; H 7.59; N 12.68.

15b: M.p. 123–5°C. ^{1}H NMR (CD_3SOCD_3), δ: 7.11–7.36 (m, 5H, Ph), 5.45 (br s, 1H, NH), 4.79 (2H, c, CH_2), 4.59 (1H, c, CH=), 1.73 (s, 3H, Me), 1.18 (s, 6H, 2Me). ^{13}C NMR (CD_3SOCD_3), δ: 157.2 (C-2), 143.9 (C-6), 129.4, 130.0, 132.1, 135.8 (Ph), 110.3 (C-5), 54.6 (C-4), 48.0 (N–CH_2), 35.3 (2Me), 22.5 (Me). IR (cm^{-1}): 3230 (NH), 1650 (C=O), 1610 (C=C), 1260 (C–N). Anal. (%). calcd. for $C_{14}H_{18}N_2O$ (230.13): C 73.00; H 7.88; N 12.17. Found: C 73.19; H 7.67; N 12.19.

16a: M.p. 185–7°C. ^{1}H NMR (CD_3SOCD_3), δ: 7.31–7.45 (m, 3H, Ph), 7.08–7.20 (m, 2H, Ph), 5.50 (br s, 1H, NH), 3.96 (s, 1H, $CH_{2\beta}$=), 3.52 (s, 1H, $CH_{2\alpha}$=), 2.54 (s, 2H, CH_2), 1.28 (s, 6H, 2Me). ^{13}C NMR (CD_3SOCD_3), δ: 156.0 (C-2), 147.7 (C-6), 131.8, 132.7, 133.2, 143.3 (Ph), 94.8 (CH_2=), 52.0 (C-4), 46.2 (N–CH_2), 32,0 (2Me). IR (cm^{-1}): 3210 (NH), 1680 (C=O), 1620 (C=C), 1260 (C–N). Anal. (%). calcd. for $C_{13}H_{16}N_2O$ (216.13): C 72.18; H 7.46; N 12.96. Found: C 72.28; H 7.66; N 13.11.

16b: ^{1}H NMR (CD_3SOCD_3), δ: 7.11–7.36 (m, 5H, Ph), 5.45 (br s, 1H, NH), 4.85 (s, 2H, C$\underline{H_2}$Ph), 4.09 (s, 1H, $CH_{2\beta}$=), 3.98 (s, 1H, $CH_{2\alpha}$=), 2.39 (s, 2H, CH_2), 1.21 (s, 6H, 2Me). ^{13}C NMR (CD_3SOCD_3), δ: 156.8 (C-2), 144.7 (C-6), 129.9, 131.9, 132.1, 142.3 (Ph), 94.0 (CH_2=), 52.1 (C-4), 49.9 (N–CH_2), 46.1 (CH_2), 31.9 (2Me).

X-ray analysis of compound 15b: *Crystal data:* $C_{14}H_{18}N_2O$, triclinic, space group $P\bar{1}$, a = 8.346(2), b = 9.105(2), c = 10.607(3) Å, α = 67.08(2), β = 78.06(2), γ = 63.12(2)°, V = 661.7(3) Å^3, Z = 2, D_c=1.156 g·cm^{-3}, μ = 0.74 cm^{-1}.

Prismatic colourless single crystal (0.78×0.48×0.24 mm) of **15b** was obtained from saturated solution in MeCN. The intensity data were collected with a Nicolet R3m single crystal diffractometer at room temperature using graphite-monochromated MoK_α radiation: ω/2θ scan, $2\theta_{max}$ = 60°, 4254 measured reflections, 3867 independent reflections (R_{int} = 0.0118).

The structure of the compound was solved by direct methods (SHELXS-97 [29]) and anisotropically refined by full-matrix least-squares procedure (SHELXL-97 [29]) for all non-hydrogen atoms. Hydrogen atom positions were located in difference Fourier map and refined isotropically. Isotropic displacement parameters of H-atoms were taken as 1.5 times (for methyl groups) and 1.2 times (for methylene and phenyl groups) equivalent isotropic values of the carrying carbon atoms. Final R1 = 0.0601, wR2 = 0.1757 ($I > 2\sigma(I)$) and R1 = 0.1037, wR2 = 0.2295 (all data); GooF = 1.082.

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