# Reactions of 3-amino-1,2,4-triazoles with cinnamic aldehydes

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The reaction of 3-amino- and 3-amino-5-methylthio-1,2,4-triazoles with cinnamaldehyde takes two directions to form mixtures of 5-[*N*-(3-phenylpropenylideneamino)]-1*H*-1,2,4-triazoles and 5-phenyl-4,5,6,7-tetrahydro[1,2,4]triazolo[1,5-*a*]pyrimidin-7-ols.

**Key words:** 3-amino-1,2,4-triazoles, cinnamic aldehydes, heterocyclization, tetrahydro-[1,2,4]triazolo[1,5-*a*]pyrimidin-7-ols, X-ray diffraction analysis.

It is well known that pyrimidine systems can be synthesized based on the reactions of amidine or guanidine derivatives with α,β-unsaturated carbonyl compounds, but despite considerable amount of publications devoted to this subject, the reactions of cinnamaldehyde with the nitrogen-containing binucleophiles indicated are dealt with in only few works.[1—6] It was shown that the cyclizations of this aldehyde with form-, acet-, and benzamidines furnish 6-hydroxy-1,4,5,6-tetrahydropyrimidines, which in aprotic solvents in the presence of molecular sieves undergo dehydration to the corresponding 2-substituted 1,4- or 1,6-dihydropyrimidines.[1,2] In those cases when the guanidine fragment is a part of the α-aminoazole, for example, aminotetrazole and 2-aminobenzimidazole, the partially hydrogenated azolopyrimidines were not obtained in the reactions with cinnamaldehyde, the process stopped at the stage of azomethines.[3—6] If the molecules of heterocyclic binucleophiles are unsymmetric, for instance, 3-amino-1,2,4-triazole and its 5-substituted derivatives, which have not been earlier studied in such reactions, an ambiguity arises in the direction of electrophilic attack of the endocyclic reaction centers by the unsaturated aldehyde, that in the case of cyclization allows one to suggest a possibility to obtain isomeric azoloazines. In the present work we study direction of the reaction of 3-amino- (**1**) and 3-amino-5-methylthio-1,2,4-triazole (**2**) with cinnamic (**3a**) and *p*-nitrocinnamic (**3b**) aldehydes.

It was found that a short-time (5—10 min) reflux of equimolar amounts of aminotriazoles **1** and **2** with aldehydes **3a**,**b** in DMF or Pr$^i$OH affords the Schiff bases **4a**,**b** and **5a**,**b** (Scheme 1). However, in Pr$^i$OH when a catalytic amount of piperidine is present, both amines with cinnamaldehyde (**3a**) during the same period of time give mixtures of bicyclic products **6a**, **7a** and azomethines **4a**, **5a** with predominance of the latter. At the same time, the presence in the reaction mixture of the starting aminotriazoles was also found. When the refluxing time of aminotriazoles **1** and **2** with aldehyde **3a** in alcohol or DMF is increased, the process is accompanied by considerable resinification. The yields of compounds **6** and **7** can be considerably increased and the formation of azomethines **4a** and **5a** can be avoided by running the reaction under milder conditions, in an acetone—piperidine solvent mixture. No cyclization products with *p*-nitrocinnamic aldehyde (**3b**) were obtained in the experiments described above. It should be noted that hydroxy-derivatives **6** and **7** are stable to the thermal dehydration upon a short-time reflux (30 min) in toluene or DMF, as well as to the action of polyphosphoric acid and prolonged (25 h) reflux in acetonitrile when molecular sieves 4 Å are present, which considerably distinguishes them from the monocyclic structural analogs, 6-hydroxy-1,4,5,6-tetrahydropyrimidines.[1,2]

The structures of compounds **4**—**7** are confirmed by spectroscopic methods. The structure of hydroxy derivative **7a** is also confirmed by X-ray diffraction analysis. The IR spectra of azomethines **4a**,**b** exhibit a set of absorption bands characteristic of the structure with developed system of conjugate C=C and C=N bonds (see Ref. 7). The $^1$H NMR spectra contain all the groups of signals, confirming the structures of compounds **4** and **5** as 5-[*N*-(3-arylpropenylideneamino)]-1*H*-1,2,4-triazoles.

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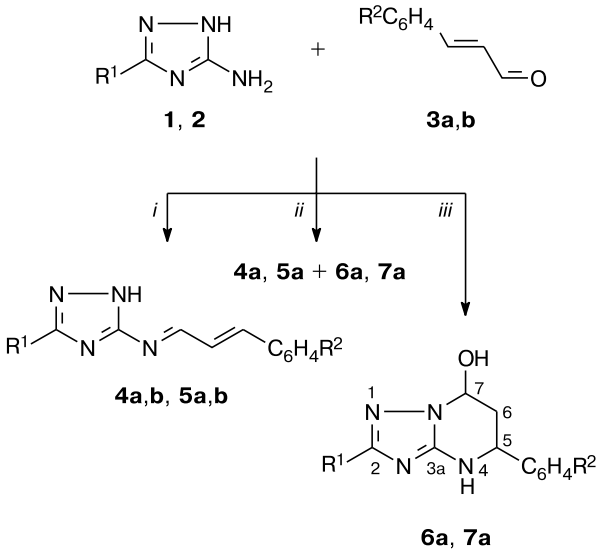
**Scheme 1**




$R^1$ = H (**1**, **4**, **6**), SMe (**2**, **5**, **7**), $R^2$ = H (**3a**—**7a**), 4-$NO_2$ (**3b**—**5b**)

*i.* $Pr^iOH$ or DMF; *ii.* $Pr^iOH$—piperidine; *iii.* $Me_2CO$—piperidine.

In the mass spectra of compounds **6a** and **7a**, there are present the peaks of molecular ions $[M]^+$ (216 and 262, respectively), which is an evidence that during their formation, cinnamaldehyde is added to the molecules of amines **1** and **2** without elimination of water.

The IR spectra of 7-hydroxytriazolopyrimidines **6a** and **7a** differ from the spectra of azomethines by the presence of intensive and broad absorption bands in the region 3264—3256 and 3140—2928 $cm^{-1}$ typical of associated NH and OH groups.[7] Due to the extremely low solubility of compounds under consideration in the solvents commonly used in IR spectroscopy, it has proved impossible to confirm the presence of a hydroxy group in their structures by this method.

The $^1H$ NMR spectra of compounds **6a** and **7a**, in addition to the signals for the protons of the phenyl ring, exhibit the multiplets for the methine and methylene protons of the partially hydrogenated pyrimidine ring. The NH and OH groups are found in the forms of a broad singlet $\delta_{NH}$ 6.84—7.64 and doublet $\delta_{OH}$ 6.75—6.99, which disappear when methanol-$d_4$ is present, causing the multiplicity of the signals for the neighboring CH groups to change. However, the data do not allow us to chose between triazolo[1,5-*a*]- and triazolo[4,3-*a*]pyrimidine systems and C(5)- or C(7)-placement of the OH group in the bicycle.

The $^{13}C$ NMR spectra of compounds **6a** and **7a** exhibit signals, the comparison of which with the $\delta$ $^{13}C$ values for triazolo[1,5-*a*]- and triazolo[4,3-*a*]pyrimidines reported in the literature,[8] as well as with the spectrum of 7-phenyl-4,5,6,7-tetrahydro-1,2,4-triazolo[1,5-*a*]pyrimidin-5-one described by us earlier[9], allows us to substantiate the assignment of compounds **6a** and **7a** to triazolo[1,5-*a*]-pyrimidine series and somewhat preferable placement of the hydroxy group on the atom C(7). However, only X-ray diffraction analysis of 2-methylthio-5-phenyl-4,5,6,7-tetrahydro-1,2,4-triazolo[1,5-*a*]pyrimidin-7-ol **7a** unambiguously confirmed structures of the cyclocondensation products (Fig. 1, Table 1 and 2).

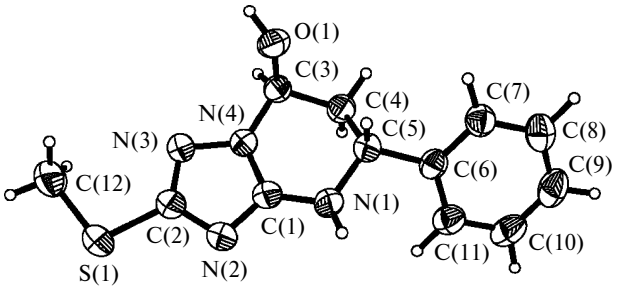



**Fig. 1.** Molecular structure of compound **7a** with the numeration used in the X-ray analysis.

In the independent part of the unit cell of the crystal **7a**, there are two molecules (**A** and **B**), which are a pair of enantiomers. The tetrahydropyrimidine ring in both molecules is in the half-chair conformation (the folding parameters[10]: $S = 0.78$, $\theta = 31.1°$, $\psi = 23.0°$ for molecule **A** and $S = 0.79$, $\theta = 30.3°$, $\psi = 22.8°$ for **B**). The deviations of atoms C(4) and C(5) from the mean-square plane of other atoms in the ring are −0.46 and 0.28 Å for molecule **A** and 0.46 and −0.28 Å for molecule **B**, respectively. The

**Table 1.** Bond distances (*d*) in the molecule of **7a**

| Bond | *d*/Å | Bond | *d*/Å |
|---|---|---|---|
| S(1A)—C(2A) | 1.748(2) | S(1A)—C(12A) | 1.795(3) |
| N(1A)—C(1A) | 1.348(2) | N(1A)—C(5A) | 1.460(2) |
| N(2A)—C(1A) | 1.334(2) | N(2A)—C(2A) | 1.361(2) |
| N(3A)—C(2A) | 1.318(2) | N(3A)—N(4A) | 1.388(2) |
| N(4A)—C(1A) | 1.339(2) | N(4A)—C(3A) | 1.454(2) |
| O(1A)—C(3A) | 1.405(2) | C(3A)—C(4A) | 1.522(2) |
| C(4A)—C(5A) | 1.535(2) | C(5A)—C(6A) | 1.520(2) |
| C(6A)—C(11A) | 1.390(3) | C(6A)—C(7A) | 1.395(3) |
| C(7A)—C(8A) | 1.379(3) | C(8A)—C(9A) | 1.374(3) |
| C(9A)—C(10A) | 1.375(3) | C(10A)—C(11A) | 1.392(3) |
| S(1B)—C(2B) | 1.747(2) | S(1B)—C(12B) | 1.788(3) |
| N(1B)—C(1B) | 1.349(2) | N(1B)—C(5B) | 1.465(2) |
| N(2B)—C(1B) | 1.325(2) | N(2B)—C(2B) | 1.355(3) |
| N(3B)—C(2B) | 1.324(3) | N(3B)—N(4B) | 1.383(2) |
| N(4B)—C(1B) | 1.348(2) | N(4B)—C(3B) | 1.451(2) |
| O(1B)—C(3B) | 1.403(2) | C(3B)—C(4B) | 1.522(2) |
| C(4B)—C(5B) | 1.533(2) | C(5B)—C(6B) | 1.519(2) |
| C(6B)—C(11B) | 1.383(3) | C(6B)—C(7B) | 1.385(3) |
| C(7B)—C(8B) | 1.389(3) | C(8B)—C(9B) | 1.375(4) |
| C(9B)—C(10B) | 1.361(4) | C(10B)—C(11B) | 1.396(3) |

**Table 2.** Bond angles (φ) in the structure of **7a**

| Angle | φ/deg | Angle | φ/deg | Angle | φ/deg |
|---|---|---|---|---|---|
| C(2A)—S(1A)—C(12A) | 101.2(1) | N(3B)—C(2B)—N(2B) | 116.1(2) | C(11A)—C(6A)—C(5A) | 122.8(2) |
| C(1A)—N(2A)—C(2A) | 102.0(2) | N(2B)—C(2B)—S(1B) | 119.5(2) | C(8A)—C(7A)—C(6A) | 121.3(2) |
| C(1A)—N(4A)—N(3A) | 109.4(1) | O(1B)—C(3B)—C(4B) | 110.3(2) | C(8A)—C(9A)—C(10A) | 120.0(2) |
| N(3A)—N(4A)—C(3A) | 124.1(1) | C(3B)—C(4B)—C(5B) | 111.3(1) | C(6A)—C(11A)—C(10A) | 119.9(2) |
| N(2A)—C(1A)—N(1A) | 127.4(2) | N(1B)—C(5B)—C(4B) | 107.8(2) | C(1B)—N(1B)—C(5B) | 117.5(2) |
| N(3A)—C(2A)—N(2A) | 116.3(2) | C(11B)—C(6B)—C(7B) | 119.4(2) | C(2B)—N(3B)—N(4B) | 101.4(2) |
| N(2A)—C(2A)—S(1A) | 118.7(1) | C(7B)—C(6B)—C(5B) | 118.6(2) | C(1B)—N(4B)—C(3B) | 126.2(1) |
| O(1A)—C(3A)—C(4A) | 110.5(1) | C(9B)—C(8B)—C(7B) | 119.5(2) | N(2B)—C(1B)—N(4B) | 110.5(2) |
| C(3A)—C(4A)—C(5A) | 111.7(1) | C(9B)—C(10B)—C(11B) | 120.7(2) | N(4B)—C(1B)—N(1B) | 121.4(2) |
| N(1A)—C(5A)—C(4) | 107.8(2) | C(1A)—N(1A)—C(5A) | 117.6(2) | N(3B)—C(2B)—S(1B) | 124.4(2) |
| C(11A)—C(6A)—C(7A) | 118.3(2) | C(2A)—N(3A)—N(4A) | 101.5(1) | O(1B)—C(3B)—N(4B) | 109.8(1) |
| C(7A)—C(6A)—C(5A) | 118.9(2) | C(1A)—N(4A)—C(3A) | 126.4(1) | N(4B)—C(3B)—C(4B) | 106.4(1) |
| C(9A)—C(8A)—C(7A) | 119.8(2) | N(2A)—C(1A)—N(4A) | 110.8(2) | N(1B)—C(5B)—C(6B) | 111.2(1) |
| C(9A)—C(10A)C(11A) | 120.6(2) | N(4A)—C(1A)—N(1A) | 121.7(2) | C(6B)—C(5B)—C(4B) | 110.9(1) |
| C(2B)—S(1B)—C(12B) | 101.6(1) | N(3A)—C(2A)—S(1A) | 125.1(1) | C(11B)—C(6B)—C(5B) | 121.9(2) |
| C(1B)—N(2B)—C(2B) | 102.6(2) | O(1A)—C(3A)—N(4A) | 109.8(1) | C(6B)—C(7B)—C(8B) | 120.6(2) |
| C(1B)—N(4B)—N(3B) | 109.4(2) | N(4A)—C(3A)—C(4A) | 106.2(1) | C(10B)—C(9B)—C(8B) | 120.4(2) |
| N(3B)—N(4B)—C(3B) | 124.3(1) | N(1A)—C(5A)—C(6A) | 111.5(1) | C(6B)—C(11B)—C(10B) | 119.4(2) |
| N(2B)—C(1B)—N(1B) | 128.0(2) | C(6A)—C(5A)—C(4A) | 110.5(1) | | |

hydroxy group is in the axial position (the torsional angle C(1)—N(4)—C(3)—O(1) is −98.1(2)° (**A**), 97.0(2)° (**B**)). The phenyl substituent has the equatorial orientation (the torsional angle C(1)—N(1)—C(5)—C(6) is −164.0(2)° in molecule **A** and 164.9(2)° in molecule **B**) and is turned with respect to the N(1)—C(5) bond (the torsional angle N(1)—C(5)—C(6)—C(11) is 18.8(2)° in molecule **A** and −30.1(2)° in molecule **B**). It can be suggested that the turn of the phenyl substituent is due to the repulsion between atoms of the partially hydrogenated pyrimidine ring and the aromatic ring (shortened intramolecular contacts H(1N)...C(11) are 2.77 (**A**), 2.83 Å (**B**) and H(11)...N(1) are 2.52 (**A**), 2.55 Å (**B**), the sum of the Van der Waals radii[11] is 2.87 and 2.66 Å, respectively). The methyl group of the methylsulfanyl substituent is virtually coplanar with the plane of the triazole ring (the torsional angle C(12)—S(1)—C(2)—N(3) is −3.7(2)° (**A**), 5.2(2)° (**B**)).

The nitrogen atom N(1) has a trigonal pyramidal configuration. The sum of the bond angles centered on this atom is 350° in both molecules.

The molecules of **7a** in the crystal form a three-dimensional netting due to the intermolecular hydrogen bonds N(1a)—H(1Na)...O(1a)′ (−*x*, 0.5 + *y*, 0.5 − *z*), H...O 2.04 Å, N—H...O 177°; N(1b)—H(1Nb)...O(1b)′ (1 − *x*, 0.5 + *y*, 1.5 − *z*), H...O 2.01 Å, N—H...O 176°; O(1a)—H(1Oa)...N(3a)′ (−*x*, 1 − *y*, −*z*) H...N, 1.86 Å, O—H...N 172°; O(1b)—H(1Ob)...N(3b)′ (1 − *x*, 1 − *y*, 1 − *z*) H...N 1.91 Å, O—H...N 174°.

In conclusion, the structure of compounds **4**—**7** confirm that the reaction of 3-amino-1,2,4-triazole (**1**) and 3-amino-5-methylthio-1,2,4-triazole (**2**) with cinnamaldehyde takes both possible directions of the attack by the ambident binucleophile on the carbonyl group of the unsaturated aldehyde. And only one of them corresponding to the reaction of the carbonyl carbon with the N(2)-reaction center in the molecule of aminoazole results in the formation of partially hydrogenated triazolo[1,5-*a*]pyrimidine system.

## Experimental

$^1$H and $^{13}$C NMR spectra were recorded on a Varian Mercury 400 spectrometer (400.448 MHz for $^1$H, 100.702 MHz for $^{13}$C) in DMSO-$d_6$ with $SiMe_4$ as an internal standard. IR spectra were recorded on a Specord M-82 spectrometer in KBr pellets. Mass spectra of compounds **4a**, **6a**, and **7a** were obtained on a Varian 1200 L instrument with direct injection of the sample into the ions source (EI, 70 eV). Melting points were measured on a Kofler stage.

**5-[*N*-(*E*)-3-Phenylprop-2-en-1-ylideneamino]-1*H*-1,2,4-triazole (4a).** A mixture of aminotriazole **1** (0.42 g, 5 mmol) with cinnamaldehyde (**3a**) (0.66 g, 5 mmol) in Pr$^i$OH (3 mL) was refluxed for 10 min, a yellow amorphous precipitate was filtered off, washed with Pr$^i$OH, and recrystallized from MeOH. The yield of azomethine **4a** was 0.4 g (40%), m.p. 203—205 °C (from MeOH). The starting aminotriazole **1** (0.23 g, 55%) was isolated from the reaction mixture after evaporation of Pr$^i$OH. The synthesis of compound **4b**, as well as azomethines **5a**,**b** from aminotriazole **2** was performed similarly. When the reaction was run in DMF, the refluxing time was 5 min, azomethines **4a** (38%) and **5b** (21%) were isolated using MeOH.

Compound **4a**. Found (%): C, 66.95; H, 4.54; N, 28.38. $C_{11}H_{10}N_4$. Calculated (%): C, 66.67; H, 5.05; N, 28.28. IR, ν/cm$^{-1}$: 3392, 3372, 3276, 1560, 1496. $^1$H NMR, δ: 13.99 (br.s, 1 H, NH); 8.95 (d, 1 H, CH, *J* = 9.4 Hz); 7.68—7.23 (m, 6 H, 1 H, C(3)H and 5 H, $H_{arom}$); 7.20 (d, 1 H, CH, *J* = 16.0 Hz);

6.88, 6.77 (both dd, 1 H each, CH, $J$ = 9.4 Hz, $J$ = 16.0 Hz). MS, $m/z$ ($I_{rel}$ (%)): 198 $[M]^+$ (82), 171 (15), 155 (18), 129 (25), 121 (100), 84 (58), 77 (33).

**5-[*N*-(*E*)-3-(4-Nitrophenyl)prop-2-en-1-ylideneamino]-1*H*-1,2,4-triazole (4b).** Orange crystals, the yield was 57%, m.p. 269—272 °C (decomp.) (from MeOH). Found (%): C, 54.51; H, 3.28; N, 28.89. $C_{11}H_9N_5O_2$. Calculated (%): C, 54.32; H, 3.70; N, 28.81. IR, ν/cm$^{-1}$: 3140, 3108, 3024, 2904, 1600, 1524, 1340. $^1$H NMR, δ: 14.07 (br.s, 1 H, NH); 9.01 (d, 1 H, CH, $J$ = 9.3 Hz); 8.29—7.97 (dd, 4 H, $H_{arom}$, $J$ = 8.7 Hz); 8.26 (s, 1 H, C(3)H); 7.68 (d, 1 H, CH, $J$ = 15.6 Hz); 7.40, 7.35 (both dd, 1 H each, CH, $J$ = 9.3 Hz, $J$ = 15.6 Hz).

**3-Methylthio-5-[*N*-(*E*)-3-phenylprop-2-en-1-ylideneamino]-1*H*-1,2,4-triazole (5a).** Yellow crystals, the yield was 32%, m.p. 173—175 °C (decomp.) (from MeOH). Found (%): C, 59.26; H, 4.50; N, 23.00; S, 13.20. $C_{12}H_{12}N_4S$. Calculated (%): C, 59.01; H, 4.92; N, 22.95; S, 13.11. IR, ν/cm$^{-1}$: 3384, 3280, 2928, 1584, 1560, 1496. $^1$H NMR, δ: 13.79 (br.s, 1 H, NH); 8.92 (d, 1 H, CH, $J$ = 9.4 Hz); 7.71—7.26 (m, 5 H, $H_{arom}$); 7.20 (d, 1 H, CH, $J$ = 16.0 Hz); 6.77, 6.68 (both dd, 1 H each, CH, $J$ = 9.4 Hz, $J$ = 16.0 Hz); 2.34 (s, 3 H, SMe).

**3-Methylthio-5-[*N*-(*E*)-3-(4-nitrophenyl)prop-2-en-1-ylideneamino]-1*H*-1,2,4-triazole (5b).** Orange crystals, the yield was 18%, m.p. 195—198 °C (decomp.) (from MeOH). Found (%): C, 50.05; H, 3.50; N, 24.30; S, 11.08. $C_{12}H_{11}N_5O_2S$. Calculated (%): C, 49.83; H, 3.81; N, 24.22; S, 11.07. IR, ν/cm$^{-1}$: 3200, 3076, 1600, 1520, 1348. $^1$H NMR, δ: 14.10 (br.s, 1 H, NH); 8.98 (d, 1 H, CH, $J$ = 9.2 Hz); 8.30—7.99 (dd, 4 H, $H_{arom}$, $J$ = 8.8 Hz); 7.68 (d, 1 H, CH, $J$ = 15.8 Hz); 7.40, 7.35 (dd, 1 H, CH, $J$ = 9.2 Hz, $J$ = 15.8 Hz); 2.45 (s, 3 H, SMe).

**5-Phenyl-4,5,6,7-tetrahydro[1,2,4]triazolo[1,5-*a*]pyrimidin-7-ol (6a).** ***A.*** A mixture of aminotriazole **1** (0.42 g, 5 mmol) with aldehyde **3a** (0.66 g, 5 mmol), piperidine (0.15 mL) in Pr$^i$OH (3 mL) was refluxed for 5 min, a yellow precipitate of azomethine **4a** (0.34 g, 34%) was filtered off. Triazolo[1,5-*a*]pyrimidin-7-ol **6a** was isolated from a cooled filtrate as colorless precipitate, which was recrystallized from Pr$^i$OH. The yield of compound **6a** was 0.27 g (27%), m.p. 237—238 °C. Full evaporation of Pr$^i$OH from the reaction mixture left after isolation of products **4a** and **6a** gave an oil, from which the starting aminotriazole **1** was isolated (0.15 g, 36%) using MeOH. Compounds **5a** (the yield was 30%) and **7a** were synthesized similarly from aminopyrazole **2**.

***B.*** A mixture of aminotriazole **1** (0.42 g, 5 mmol) with aldehyde **3a** (0.66 g, 5 mmol), piperidine (0.15 mL) in $Me_2CO$ (5 mL) was refluxed for 5 min, cooled, compound **6a** was filtered off (0.43 g, 43%) as colorless crystals. The amorphous residue obtained after full evaporation of $Me_2CO$ from the filtrate was treated with MeOH to yield the starting aminotriazole **1** (0.22 g, 52%). Compound **7a** was synthesized similarly from aminotriazole **2**.

For compound **6a** found (%): C, 61.07; H, 5.54; N, 25.89. $C_{11}H_{12}N_4O$. Calculated (%): C, 61.11; H, 5.56; N, 25.93. IR, ν/cm$^{-1}$: 3256, 3140—2932, 1612. $^1$H NMR, δ: 7.43—7.33 (m, 6 H, 1 H, C(2)H, 5 H, $H_{arom}$); 6.84 (br.s, 1 H, NH); 6.75 (d, 1 H, OH, $J$ = 5.6 Hz); 5.54 (m, 1 H, C(7)H); 4.68 (m, 1 H, C(5)H); 2.03 (m, 2H, $CH_2$). $^{13}$C NMR, δ: 38.7 (C(6)); 50.1 (C(5)); 73.9 (C(7)); 126.7, 127.6, 128.5, 141.8 ($C_{arom}$); 148.9 C(2); 153.6 (C(3a)). MS, $m/z$ ($I_{rel}$ (%)): 216 $[M]^+$ (100), 198 (30), 171 (15), 132 (45), 105 (80), 84 (30), 77 (50).

**2-Methylthio-5-phenyl-4,5,6,7-tetrahydro[1,2,4]triazolo-[1,5-*a*]pyrimidin-7-ol (7a).** Colorless crystals, the yield was 23% (method ***A***), 37% (method ***B***), m.p. 212—214 °C (from Pr$^i$OH). Found (%): C, 54.93; H, 5.30; N, 21.40; S, 12.19. $C_{12}H_{14}N_4OS$. Calculated (%): C, 54.96; H, 5.34; N, 21.37; S, 12.21. IR, ν/cm$^{-1}$: 3264, 3128—2928, 1612. $^1$H NMR, δ: 7.64 (br.s, 1 H, NH); 7.30—7.38 (m, 5 H, $H_{arom}$); 6.99 (d, 1 H, OH, $J$ = 5.8 Hz); 5.86 (m, 1 H, C(7)H); 4.63 (m, 1 H, C(5)H); 2.43 (s, 3 H, SMe); 1.99 (m, 2 H, $CH_2$). $^{13}$C NMR, δ: 39.6 (C(6)); 50.5 (C(5)); 74.5 (C(7)); 94.9 (SMe); 127.4, 128.4, 129.3, 142.4 ($C_{arom}$); 155.2 (C(2)); 158.2 (C(3a)). MS, $m/z$ ($I_{rel}$ (%)): 262 $[M]^+$ (100), 233 (24), 217 (84), 130 (36), 117 (22), 105 (20).

**X-ray diffraction study of compound 7a.** Crystals of compound **7a** are monoclinic, $C_{12}H_{14}N_4OS$, at 20 °C $a$ = 21.281(2) Å, $b$ = 9.240(1) Å, $c$ = 13.921(1) Å, β = 108.09(1)°, $V$ = 2602.0(4) Å$^3$, $M_r$ = 262.33, $Z$ = 8, the space group is $P2_1/c$, $d_{calc}$ = 1.339 g cm$^{-3}$, μ(Mo-Kα) = 0.243 mm$^{-1}$, $F$(000) = 1104. Parameters of the unit cell and intensities of 16758 reflections (7542 were independent, $R_{int}$ = 0.067) were measured on a Xcalibur-3 diffractometer (Mo-Kα irradiation, a CCD detector, a graphite monochromator, ω-scanning, $2\theta_{max}$ = 60°). The structure was decoded by direct method using the SHELXTL program package.[12] Positions of hydrogen atoms were found from the differential synthesis of electron density and refined isotropically. The structure was refined on $F^2$ by full-matrix least-squares method in anisotropic approximation for nonhydrogen atoms to $wR_2$ = 0.183 on 7482 reflections ($R_1$ = 0.058 on 4343 reflections with $F > 4\sigma(F)$, $S$ = 0.977). The atom coordinates and full tables of bond distances and bond angles were deposited with the Cambridge Structural Database (CCDC 685602).

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