Synthesis and chemical transformations of partially hydrogenated [1,2,4]triazolo[5,1-*b*]quinazolines

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The reaction of 5-methyl-7-phenyl-4,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidine with α,β-unsaturated carbonyl compounds in MeOH in the presence of MeONa affords partially hydrogenated aryl-substituted [1,2,4]triazolo[5,1-*b*]quinazolines. Hydrolysis, oxidation, reduction, and alkylation of 5,6,8-triphenyl-5,6,7,10-tetrahydro[1,2,4]triazolo[5,1-*b*]quinazoline were studied. The structure of one oxidation product, *viz.*, 7-hydroxy-5,6,8-triphenyl-6,7-dihydro[1,2,4]triazolo[5,1-*b*]quinazoline, was established by X-ray diffraction.

Key words: partially hydrogenated [1,2,4]triazolo[5,1-*b*]quinazolines, synthesis, chemical properties, X-ray diffraction study.

Partially hydrogenated quinazoline systems have attracted interest from both fundamental and applied points of view. Most structures of this type belong to so-called drug-like molecules or are present in natural biologically active compounds, for example, in alkaloids.[1] Adenosine uptake inhibitors (potent vasodilators and antiaggregants)[2,3] and carbocyclic purine analogs exhibiting antimetabolic activity were found in the azoloquinazoline series.[4] At the same time, these compounds are convenient models for elucidating some questions of theoretical organic chemistry, in particular, the characteristic features of the three-dimensional and electronic structures of partially hydrogenated nitrogen-containing heterocycles, their stability, and reactivity.

There are two main procedures for the formation of azoloquinazoline systems. The most widely used procedure is based on the construction of the pyrimidine ring in reactions of α-aminoazole derivatives with carbonyl 1,3-bielectrophiles containing a partially or completely hydrogenated carbocycle.[5—12] A nontrivial procedure has been developed earlier for the assembly of 2-methyl-5,10-diphenyl-5,10-dihydro[1,2,4]triazolo[5,1-*b*]quinazolines based on the cascade reaction giving rise to both the triazole and quinazoline fragments.[13] However, the pyrimidine ring closure in this process is also preceded by the formation of the aminotriazole fragment. An alternative approach to the desired compounds is associated with the formation of the five-membered azole ring based on the already present quinazoline moiety, but this method is synthetically more limited.[14] Recently,[15] we have described yet another procedure for the synthesis of [1,2,4]triazolo[5,1-*b*]quinazolines, which differs from the above-mentioned methods in that the carbocycle closure occurs on the basis of the already present partially hydrogenated 5-methyl-7-phenyl-1,2,4-triazolo[1,5-*a*]pyrimidine system with the involvement of 1,3-diaryl-2-propen-1-ones in an alcoholic medium in the presence of MeONa.

The aim of the present study was to extend the range of carbonyl 1,3-bielectrophiles, which react with 5-methyl-7-phenyl-4,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidine (**1**) to give partially hydrogenated [1,2,4]triazolo[5,1-*b*]quinazoline systems (Scheme 1), and to study the chemical behavior of the latter in hydrolysis, oxidation, reduction, and alkylation reactions.

It was found that refluxing of equimolar amounts of carbonyl 1,3-bielectrophiles **2a,b**, **4**, **6**, **9**, and **11** with dihydrotriazolo[1,5-*a*]pyrimidine **1** in an MeOH medium in the presence of MeONa for a short period (5—7 min) afforded [1,2,4]triazolo[5,1-*b*]quinazoline systems with different degrees of saturation of the quinazoline fragment (see Scheme 1). For example, the reactions of dihydroazoloazine **1** with Mannich base hydrochlorides **2a,b** and benzylideneacetone (**4**) give tetrahydrotriazolo[5,1-*b*]quinazolines **3a,b** and **5**, respectively. Under analogous conditions, the reactions of azoloazine **1** with dibenzoylethylene (**6**), 2,3-dibromo-1,3-diphenylpropan-1-one (**9**), and 1,3-diphenylpropyn-1-one (**11**) produce dihydro derivatives **7** and **10**. It should be noted that cyclocondensation involving dibenzoylethylene (**6**) gave triazoloquinazoline **7** along with dibenzoylethane (**8**).

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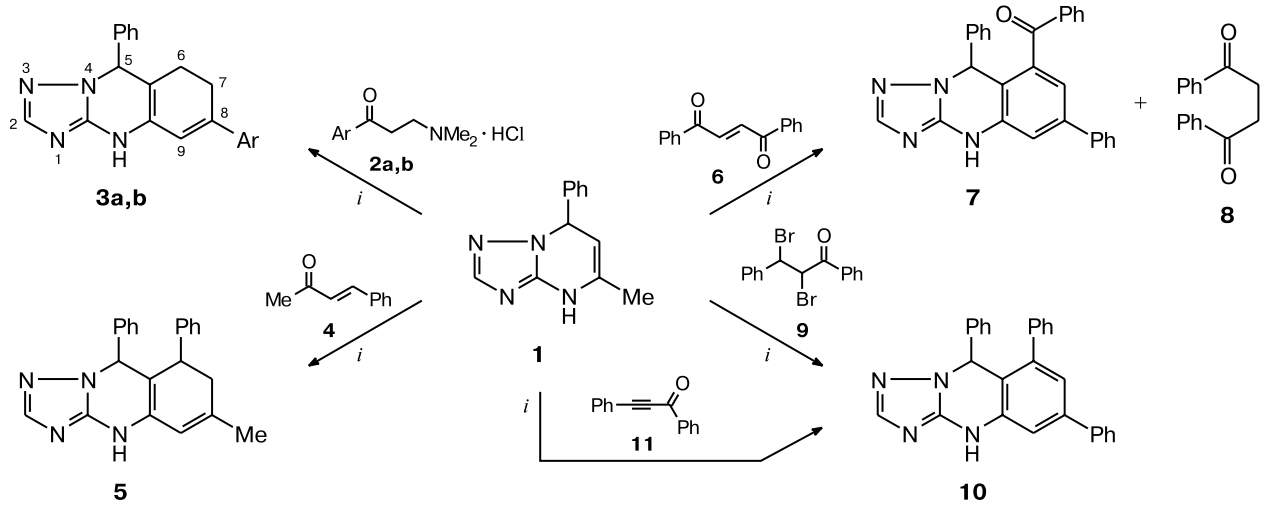
Scheme 1



i. MeONa, MeOH.

2, 3: Ar = Ph (**a**), 4-BrC_6H_4 (**b**)

The formation of the same product **10** in the reactions of azoloazine **1** with both dibromo derivative **9** and propynone **11** is, apparently, attributed to the fact that cyclization is preceded by dehydrobromination of compound **9** giving rise to propynone **11** in a basic medium.

The structures of compounds **3a,b**, **5**, **7**, and **10** were established by spectroscopic methods. In the IR spectra of all the compounds under consideration, the most characteristic absorption bands at 3376—2650 cm^{-1} belong to the associated NH group. The IR spectrum of compound **7** shows also an intense band of the C=O group at 1660 cm^{-1}. The ^1H NMR spectra of both tetrahydro- (**3**, **5**) and dihydrotriazolo[5,1-*b*]quinazolines (**7**, **10**) are characterized by the presence of signals for the aryl protons and the H(2), H(5), H(9), and NH protons. However, substantial differences are observed in the resonance region of aliphatic protons. Tetrahydrotriazoloquinazolines are characterized by a five- (**3a,b**) or four-spin (**5**) system of signals for the protons of the cyclohexadiene ring. By contrast, these signals are absent in the spectra of dihydrotriazolo[5,1-*b*]quinazolines **7** and **10**. It should be noted that the H(9) proton in the spectra of compounds **3a,b** appears as a broadened singlet (δ 6.13—6.18) due to coupling with the protons of the CH_2 groups. In the spectrum of compound **5**, the signal for H(9) is additionally complicated by allylic coupling with the protons of the Me group. The assignment of the signals in the spectrum of this compound was made based on the NOE experiment, which demonstrated that irradiation of the methyl protons causes a response of the C(7)H_2 and H(9) protons, which indicates that they are spatially close to the Me group.

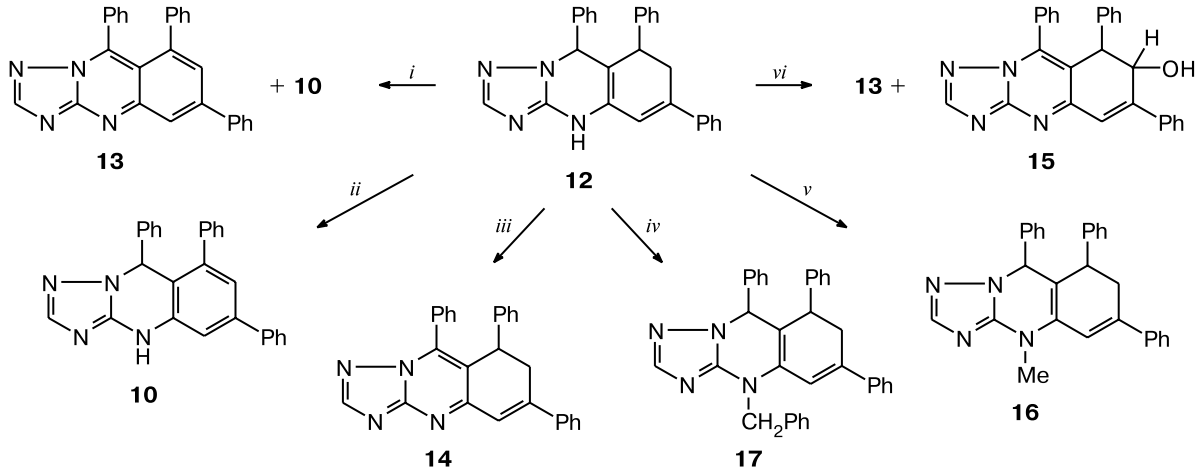
The structures of triazolo[5,1-*b*]quinazolines **3a,b**, **5**, **7**, and **10** provide evidence that the formation of the carbocycle in these compounds occurs as a result of the attack of the β-carbon atom of 1,3-bielectrophiles **2a,b**, **4**, **6**, **9**, and **11** on the C(6) reaction center in dihydroazoloazine **1**, while the carbonyl group attacks the methyl group in the same compound. This is consistent with the pathway of the reaction of dihydro-1,2,4-triazolo[1,5-*a*]pyrimidines with benzylideneacetophenones described earlier.[15]

We studied the chemical properties of partially hydrogenated triazoloquinazolines, such as the ability to undergo hydrolysis, oxidation, reduction, and alkylation (Scheme 2), using 5,6,8-triphenyl-5,6,7,10-tetrahydro[1,2,4]triazolo[5,1-*b*]quinazoline (**12**) as an example. The synthesis of this compound has been described recently.[15]

It appeared that compound **12**, unlike dihydrotriazolopyrimidine **1** studied earlier,[16] is stable to aqueous and alcoholic solutions of HCl (1 : 1). Even prolonged refluxing of triazoloquinazoline **12** under the above-mentioned conditions did not lead to hydrolysis of this compound.

In a Pr^iOH—KOH medium, compound **12** is oxidized, the reaction being accompanied by aromatization of the cyclohexadiene fragment and the hydrogenated pyrimidine ring to give a mixture of compounds **10** and **13**. An analogous situation was also observed upon prolonged refluxing (1.5—2 h) of tetrahydro derivative **12** in an MeOH—MeONa mixture or in DMF under conditions of free access of atmospheric oxygen. The physicochemical and spectroscopic characteristics of compound **10** are completely identical to those of the condensation product

Scheme 2



Reagents and conditions: *i*. Pr^{i}OH—KOH or MeOH—MeONa or DMF; *ii*. Br_2, AcOH; *iii*. NBS or $NaNO_2$, AcOH; *iv*. $PhCH_2Cl$, Pr^{i}OH—KOH; *v*. MeI, Pr^{i}OH—KOH; *vi*. SeO_2, AcOH.

of azoloazine **1** with compounds **9** and **11**. Product **13** was identified as 5,6,8-triphenyl[1,2,4]triazolo[5,1-*b*]quinazoline based on the fact that its mass spectrum has a molecular ion peak at *m/z* 398, which indicates that the formation of compound **13** is accompanied by a decrease in the molecular weight by four units, and taking into account that the ^{1}H NMR spectrum shows signals for only aromatic protons.

The presence of the partially hydrogenated hetero- and carbocycles in structure **12** opens the possibility for the selective transformation of each fragment into the aromatic system. We revealed the differences in the pathways of oxidation of compound **12** with reagents of different nature. For example, the reaction with NBS in an alcohol or with $NaNO_2$ in an AcOH medium afforded product **14**. In the IR spectrum of this compound, an absorption band characteristic of the associated NH group is absent. In the ^{1}H NMR spectrum, the signals for the NH and H(5) protons are also absent. However, the spectrum shows the resonance of a four-spin system of the H(6), C(7)H_2, and H(9) protons. Consequently, the partially hydrogenated structure of the carbocycle in compound **14** is retained.

In the reaction with Br_2 in AcOH, tetrahydrotriazoloquinazoline **12** is transformed into dihydro derivative **10**. However, oxidation with SeO_2 gave rise to two compounds (**13** and **15**). The mass spectrum of product **15** shows a molecular ion peak at *m/z* 416, which indicates that the formation of this compound is accompanied by an increase in the molecular weight by 14 units. The ^{1}H NMR spectrum of compound **15** shows, along with the singlet for the H(2) proton and the multiplet for the aromatic protons, a doublet and a doublet of doublets for the H(6) and H(7) protons, respectively, and a doublet for the proton of the OH group, which disappears upon the deuterium exchange with CD_3OD. An additional splitting of the signal for the H(7) proton (^3J = 2.0 Hz) occurs due to coupling with the geminal OH group. The structure of compound **15** was unambiguously established by X-ray diffraction (Fig. 1). In molecule **15**, the triazolopyrimidine bicyclic fragment is planar to within 0.01 Å. The cyclohexadiene ring adopts a distorted sofa conformation (the puckering parameters: S = 0.65, Θ = 53.5°, Ψ = 28.3°).[17] The deviations of the C(6) and C(7) atoms from the mean plane through the other atoms of the ring are 0.83 and 0.37 Å, respectively. The substituents at the C(5) and C(6) atoms are in a *trans*-di-

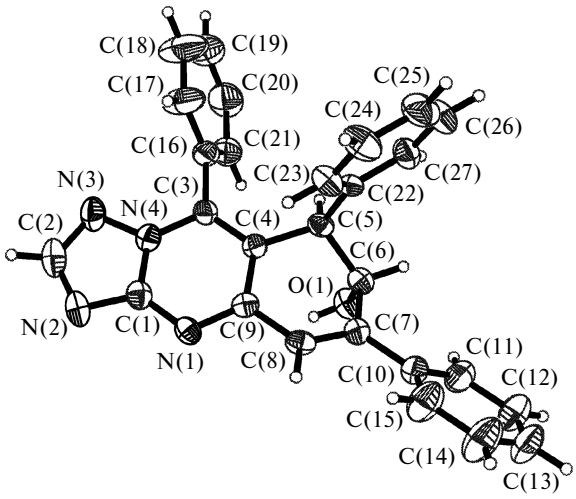


Fig. 1. Molecular structure of compound **15**.

axial orientation (C(9)—C(4)—C(5)—C(22), −88.4(4)°; C(4)—C(5)—C(6)—O(1), 73.3(4)°).

Repulsion between the phenyl rings at the C(3) and C(5) atoms (shortened intramolecular contacts: C(21)...H(5), 2.72 Å; C(16)...H(5), 2.71 Å; C(4)...H(23), 2.60 Å; C(9)...H(23), 2.84 Å; C(27)...H(6), 2.68 Å (the sum of the van der Waals radii is 2.87 Å);[17] C(17)...N(3), 3.15 Å (3.21 Å)) causes a noticeable deformation of the C(4)—C(3)—C(16) bond angle (128.2(4)°) and a rotation of the substituents relative to the plane of the bicyclic fragment (C(4)—C(3)—C(16)—C(21), 70.0(6)°; C(4)—C(5)—C(22)—C(23), 15.8(5)°). The shortened contacts C(11)...H(6) (2.69 Å), C(15)...H(8) (2.69 Å), C(6)...H(11) (2.67 Å), C(8)...H(15) (2.70 Å) (the sum of the van der Waals radii is 2.87 Å), H(11)...H(6) (2.31 Å), and H(8)...H(15) (2.23 Å) (the sum of the van der Waals radii is 2.34 Å) are responsible for distortion of the conjugation between the C(7)=C(8) bond and the π system of the phenyl ring at the C(17) atom due to rotation of the substituent about the C(7)—C(10) bond (the C(8)—C(7)—C(10)—C(15) torsion angle is −28.7(6)°). In the crystal structure, the molecules are linked to each other by the intermolecular H(1O)...N(1′ hydrogen bond ($1 - x$, y, $1.5 - z$) (H...N′, 2.20 Å; O—H...N′, 171.5°) to form dimers.

Unlike its synthetic precursor **1**, triazoloquinazoline **12** is not reduced with $NaBH_4$ in an alcoholic medium. Apparently, this is due to the fact that reduction of 4,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidines occurs through the preliminary transformation into the imine form,[18] which is impossible for compound **12**.

Alkylation of compound **12** with MeI or BnCl in a Pr^iOH—KOH solution affords *N*-methyl- and *N*-benzyl-substituted compounds **16** and **17**, respectively. The mass spectra of the reaction products show molecular ion peaks at *m/z* 416 (**16**) and 492 (**17**). The ^1H NMR spectra confirm the presence of the methyl and benzyl groups in compounds **16** and **17**, respectively, and the retention of the partially hydrogenated pyrimidine and cyclohexadiene systems.

A comparison of the results of our study with the data on the chemical transformations of 4,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidines[16,18] shows that the loss of one of the centers of electrophilic attack, *viz.*, the C(6) atom in the pyrimidine ring, in partially hydrogenated [1,2,4]triazolo[5,1-*b*]quinazolines compared to triazolopyrimidines eliminates an alternative in the direction of alkylation reactions, resulting in another pathway of the reaction with $NaNO_2$ in an acidic medium and incapability of such compounds to be reduced with $NaBH_4$ in alcohols. At the same time, the presence of the partially hydrogenated pyrimidine and cyclohexadiene rings in tetrahydro[1,2,4]triazolo[5,1-*b*]quinazolines opens wide possibilities for their selective reactions with various oxidizing reagents.

Experimental

The ^1H NMR spectra were recorded on a Bruker AC-300 (299.95 MHz) spectrometer in DMSO-d_6 with Me_4Si as the internal standard. The IR spectra were measured on a Specord M-82 instrument (KBr pellets). The mass spectra of compounds **7**, **13**, and **15** were obtained on a Finnigan MAT INCOS-50 instrument (70 eV). The positive- and negative-ion mass spectra of compounds **3a**,**b**, **5**, **10**, **14**, **16**, and **17** were measured on an MSBC SELMI spectrometer (10 μCi^{252} Cf source) at an accelerating voltage of ±20 kV. The compositions of the reaction mixtures and the purity of the reaction products were checked by TLC on Silufol UV-254 plates ($CHCl_3$—MeOH, 9 : 1, as the eluent). The melting points were measured on a Kofler hot-stage apparatus.

The synthesis of 2,3-dibromo-1,3-diphenylpropan-1-one (**9**) has been described earlier.[19] 1,3-Diphenylpropyn-1-one (**11**) was prepared according to a known procedure.[20]

5,8-Diphenyl-5,6,7,10-tetrahydro[1,2,4]triazolo[5,1-*b*]quinazoline (3a). A solution of MeONa (0.08 g, 1.5 mmol), azoloazine **1** (0.21 g, 1 mmol), and *N*,*N*-dimethylaminopropiophenone hydrochloride (**2a**) (0.21 g, 1 mmol) in MeOH (10 mL) was refluxed for 5—7 min until a finely dispersed precipitate of quinazoline **3a** was obtained. The precipitate was purified by recrystallization from a 1 : 2 DMF—MeOH mixture. Compound **3a** was obtained in a yield of 0.2 g (60%), m.p. 260—263 °C. Found (%): C, 77.25; H, 5.50; N, 17.15. $C_{21}H_{18}N_4$. Calculated (%): C, 77.30; H, 5.52; N, 17.18. IR, ν/cm^{-1}: 3220—2850, 1616, 1552. ^1H NMR, δ: 9.49 (br.s, 1 H, NH); 7.51 (s, 1 H, C(2)H); 7.17—7.49 (m, 10 H, H arom.); 6.13 (br.s, 1 H, C(9)H); 5.87 (s, 1 H, C(5)H); 3.26 and 2.79 (both m, 2 H, C(7)H_2); 2.57 and 2.18 (both m, 2 H, C(6)H_2). MS, *m/z*: 327 $[M + H]^+$, 325 $[M - H]^-$.

8-(4-Bromophenyl)-5-phenyl-5,6,7,10-tetrahydro[1,2,4]triazolo[5,1-*b*]quinazoline (3b) was synthesized analogously to compound **3a** from azoloazine **1** and 1-(4-bromophenyl)-3-(*N*,*N*-dimethylamino)propan-1-one hydrochloride (**2b**). The yield was 58%, m.p. 255—257 °C (DMF—MeOH, 1 : 2). Found (%): C, 62.19; H, 4.15; Br, 19.69; N, 13.78. $C_{21}H_{17}BrN_4$. Calculated (%): C, 62.22; H, 4.20; Br, 19.75; N, 13.83. IR, ν/cm^{-1}: 3252—2880, 1620, 1552. ^1H NMR, δ: 9.50 (br.s, 1 H, NH); 7.52 (s, 1 H, C(2)H); 7.17—7.51 (m, 9 H, H arom.); 6.18 (br.s, 1 H, C(9)H); 5.83 (s, 1 H, C(5)H); 3.23 and 2.86 (both m, 2 H, C(7)H_2); 2.72 and 2.20 (both m, 2 H, C(6)H_2). MS, *m/z*: 406 $[M + H]^+$, 404 $[M - H]^-$.

8-Methyl-5,6-diphenyl-5,6,7,10-tetrahydro[1,2,4]triazolo[5,1-*b*]quinazoline (5) was synthesized analogously to compound **3a** from azoloazine **1** and benzylideneacetone (**4**). The yield was 45%, m.p. 258—259 °C (DMF—MeOH, 1 : 2). Found (%): C, 77.68; H, 5.92; N, 16.43. $C_{22}H_{20}N_4$. Calculated (%): C, 77.65; H, 5.88; N, 16.47. IR, ν/cm^{-1}: 3208—2880, 1608, 1552. ^1H NMR, δ: 9.69 (br.s, 1 H, NH); 7.44 (s, 1 H, C(2)H); 6.07—6.83 (m, 10 H, H arom.); 5.78 (s, 1 H, C(5)H); 5.32 (m, 1 H, C(9)H); 4.01 (m, 1 H, C(6)H); 3.09 and 2.82 (both m, 2 H, C(7)H_2); 1.71 (s, 1 H, Me). MS, *m/z*: 341 $[M + H]^+$, 339 $[M - H]^-$.

6-Benzoyl-5,8-diphenyl-5,10-dihydro[1,2,4]triazolo[5,1-*b*]quinazoline (7) was synthesized analogously to compound **3a** from azoloazine **1** and dibenzoylethylene (**6**). The yield was 36%, m.p. 282—284 °C (DMF—MeOH, 1 : 2). Found (%): C, 78.56; H, 4.71; N, 13.01. $C_{28}H_{20}N_4O$. Calcu-

lated (%): C, 78.50; H, 4.67; N, 13.08. IR, ν/cm^{-1}: 3220—2680, 1660, 1608, 1572. ^{1}H NMR, δ: 10.95 (br.s, 1 H, NH); 7.63 (s, 1 H, C(2)H); 6.98—7.62 (m, 17 H, H arom.); 6.87 (s, 1 H, C(5)H). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 428 $[M]^+$ (95).

After separation of quinazoline **7**, the reaction mixture was concentrated to one-half of the initial volume. Dibenzoylethane (**8**) was isolated from the residue. The yield was 32%, m.p. 142—143 °C (*cf.* lit. data[21]: m.p. 145 °C).

5,6,8-Triphenyl-5,10-dihydro[1,2,4]triazolo[5,1-*b*]quinazoline (10). ***A.*** Compound **10** was synthesized analogously to compound **3a** from azoloazine **1** and 2,3-dibromo-1,3-diphenylpropan-1-one (**9**). The yield was 28%, m.p. 263—265 °C (DMF—MeOH, 1 : 2).

B. Compound **10** was prepared analogously to compound **3a** from azoloazine **1** and 1,3-diphenyl-2-propyn-1-one (**11**). The yield was 43%.

C. A solution of Br_2 (0.24 g, 1.5 mmol) in AcOH (3 mL) was added to a solution of tetrahydrotriazoloquinazoline **12** (0.4 g, 1 mmol) in AcOH (3 mL). The reaction mixture was stirred for 1 h and poured into water. Compound **10** was filtered off. The yield was 0.29 g (72%). Found (%): C, 80.67; H, 4.90; N, 14.25. $C_{27}H_{20}N_4$. Calculated (%): C, 81.00; H, 5.00; N, 14.00. IR, ν/cm^{-1}: 3376—2880, 1628, 1568. ^{1}H NMR, δ: 10.67 (br.s, 1 H, NH); 7.55 (s, 1 H, C(2)H); 6.54—7.67 (m, 17 H, H arom.); 6.63 (s, 1 H, C(5)H). MS, *m/z*: 401 $[M + H]^+$, 399 $[M - H]^-$.

5,6,8-Triphenyl[1,2,4]triazolo[5,1-*b*]quinazoline (13). ***A.*** Tetrahydrotriazoloquinazoline **12** (0.4 g, 1 mmol) was refluxed in a 5% KOH solution in Pr^{i}OH (10 mL) for 2 h. The reaction mixture was neutralized with AcOH and poured into water. The precipitate that formed was recrystallized from a 1 : 2 DMF—Pr^{i}OH mixture. Yellow crystals of triazoloquinazoline **13** with m.p. 295—297 °C and compound **10** were successively isolated in yields of 0.14 g (34%) and 0.25 g (63%), respectively.

Compound **13**. Found (%): C, 81.54; H, 4.57; N, 14.15. $C_{27}H_{18}N_4$. Calculated (%): C, 81.41; H, 4.52; N, 14.07. IR, ν/cm^{-1}: 1596, 1576. ^{1}H NMR, δ: 8.76 (s, 1 H, C(2)H); 7.07—8.35 (m, 17 H, H arom.). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 398 $[M]^+$ (100).

B. A mixture of compound **12** (0.4 g, 1 mmol) and MeONa (0.08 g, 1.5 mmol) in MeOH (10 mL) was refluxed for 1.5 h, neutralized with AcOH, and poured into water. The precipitate that formed was recrystallized from a 1 : 2 DMF—MeOH mixture. Triazoloquinazoline **13** and compound **10** were isolated in yields of 0.19 g (48%) and 0.2 g (50%), respectively.

C. A solution of compound **12** (0.8 g, 2 mmol) was refluxed in DMF (5 mL) for 1.5 h. Then MeOH (10 mL) was added. Triazoloquinazoline **13** and compound **10** were successively isolated in yields of 0.22 g (54%) and 0.16 g (41%), respectively.

5,6,8-Triphenyl-6,7-dihydro[1,2,4]triazolo[5,1-*b*]quinazoline (14). ***A.*** A mixture of tetrahydrotriazoloquinazoline **12** (0.4 g, 1 mmol) and NBS (0.36 g, 2 mmol) in Pr^{i}OH (10 mL) was refluxed for 1.5 h and cooled. Compound **14** was isolated in a yield of 0.3 g (76%), m.p. 220—223 °C. Found (%): C, 81.11; H, 5.05; N, 14.12. $C_{27}H_{20}N_4$. Calculated (%): C, 81.00; H, 5.00; N, 14.00. IR, ν/cm^{-1}: 3056, 1612, 1592, 1576. ^{1}H NMR, δ: 8.43 (s, 1 H, C(2)H); 7.27—7.64 (m, 10 H, H arom.); 6.89—7.17 (m, 5 H, H arom.); 7.21 (dd, 1 H, C(9)H, ^4J = 2.1 Hz, ^4J = 0.7 Hz); 4.40 (dd, 1 H, C(6)H, ^3J = 7.0 Hz, ^3J = 0.2 Hz); 3.39 (br.ddd, 1 H, C(7)H, ^2J = −17.6 Hz, ^3J = 7.0 Hz, ^4J = 2.1 Hz); 3.20 (br.dd, 1 H, C(7)H, ^3J = 0.2 Hz, ^4J = 0.7 Hz). MS, *m/z*: 401 $[M + H]^+$, 399 $[M - H]^-$.

B. Sodium nitrite (0.21 g, 3 mmol) was added portionwise (0.05 g) to a solution of compound **12** (0.4 g, 1 mmol) in AcOH (5 mL). Once liberation of gaseous products ceased, the reaction mixture was poured into water and compound **14** was filtered off. The yield was 0.21 g (53%).

7-Hydroxy-5,6,8-triphenyl-6,7-dihydro[1,2,4]triazolo[5,1-*b*]quinazoline (15). Selenium dioxide (0.26 g, 2.5 mmol) was added to a solution of compound **12** (0.8 g, 2 mmol) in AcOH (10 mL). The reaction mixture was stirred at ~20 °C for 6 h and mixed with water (50 mL). An amorphous precipitate was filtered off and recrystallized from a 1 : 20 Pr^{i}OH—hexane mixture. First, compound **15** was isolated in a yield of 0.21 g (25%) with m.p. 275—278 °C, and then triazoloquinazoline **13** was isolated in a yield of 0.37 g (46%).

Compound **15**. Found (%): C, 78.05; H, 4.86; N, 13.54. $C_{27}H_{20}N_4O$. Calculated (%): C, 77.88; H, 4.81; N, 13.46. IR, ν/cm^{-1}: 3148, 1612, 1600, 1532. ^{1}H NMR, δ: 8.49 (s, 1 H, C(2)H); 6.90—7.67 (m, 16 H, H arom.); 5.83 (d, 1 H, C(6)H, J = 6.4 Hz); 4.79 (dd, 1 H, C(7)H, ^3J = 6.4 Hz, ^2J = 2.0 Hz); 4.44 (d, 1 H, C(7)OH, ^2J = 2.0 Hz). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 416 $[M]^+$ (25).

10-Methyl-5,6,8-triphenyl-5,6,7,10-tetrahydro[1,2,4]triazolo[5,1-*b*]quinazoline (16). Compound **12** (0.4 g, 1 mmol) and MeI (0.28 g, 2 mmol) were added to a 3% KOH solution in Pr^{i}OH. The reaction mixture was kept for 1 h and poured into water. The precipitate that formed was filtered off. Compound **16** was obtained in a yield of 0.25 g (61%), m.p. 190—192 °C (from Pr^{i}OH). Found (%): C, 81.25; H, 5.83; N, 13.57. $C_{28}H_{24}N_4$. Calculated (%): C, 80.77; H, 5.77; N, 13.46. IR, ν/cm^{-1}: 3068, 3028, 1656, 1572. ^{1}H NMR, δ: 7.60 (s, 1 H, C(2)H); 6.81—6.89 (m, 11 H, H arom.); 7.25—7.42 (m, 5 H, H arom.); 6.11 (s, 1 H, C(5)H); 3.66 (dd, 1 H, C(6)H, ^3J = 8.3 Hz, ^3J = 2.8 Hz); 3.15 (br.ddd, 1 H, C(7)H, ^2J = −16.8 Hz, ^3J = 8.3 Hz, ^4J = 2.2 Hz); 2.63 (dd, 1 H, C(7)H, ^2J = −16.8 Hz, ^3J = 2.8 Hz); 3.59 (s, 3 H, Me). MS, *m/z*: 417 $[M + H]^+$, 415 $[M - H]^-$.

10-Benzyl-5,6,8-triphenyl-5,6,7,10-tetrahydro[1,2,4]triazolo[5,1-*b*]quinazoline (17) was synthesized analogously to compound **16** from triazoloquinazoline **12** and benzyl chloride. The yield was 53%, m.p. 180—183 °C (from Pr^{i}OH). Found (%): C, 83.02; H, 5.76; N, 11.51. $C_{34}H_{28}N_4$. Calculated (%): C, 82.93; H, 5.69; N, 11.38. IR, ν/cm^{-1}: 3060, 3028, 2872, 1656, 1568. ^{1}H NMR, δ: 7.63 (s, 1 H, C(2)H); 6.70—6.85 (m, 11 H, H arom.); 7.15—7.47 (m, 10 H, H arom.); 6.15 (s, 1 H, C(5)H); 5.36 and 5.43 (both d, 1 H each, NCH_2, ^2J = −16.8 Hz); 3.66 (dd, 1 H, C(6)H, ^3J = 2.3 Hz, ^3J = 8.0 Hz); 3.09 (br.ddd, 1 H, C(7)H, ^2J = −16.5 Hz, ^3J = 8.1 Hz, ^4J = 1.3 Hz); 2.62 (br.dd, 1 H, C(7)H, ^2J = −16.5 Hz, ^3J = 2.8 Hz). MS, *m/z*: 493 $[M + H]^+$, 491 $[M - H]^-$.

X-ray diffraction study of compound 15. Single crystals of compound **15** were grown by crystallization from a 1 : 20 Pr^{i}OH—hexane mixture. The unit cell parameters and intensities of 3775 reflections (3703 independent reflections, R_{int} = 0.08) were measured on an automated four-circle Siemens P3/PC diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, 20 °C, θ/2θ-scanning technique, $2\theta_{max}$ = 50°). Crystals of **15** are monoclinic: a = 28.340(1) Å, b = 13.136(4) Å, c = 12.437(5) Å, β = 114.11(3)°, V = 4226(3) Å^3, M_r = 416.47, Z = 8, space group $C2/c$, d_{calc} = 1.309 g cm^{-3}, μ(Mo-Kα) = 0.082 mm^{-1}, F(000) = 1744. The structure was solved by direct methods with the use of the SHELXTL program package.[22] The

positions of the H atoms were located from difference electron density maps and refined using a riding model with $U_i = 1.2U_{eq}$ of the corresponding pivot nonhydrogen atoms. The structure was refined by the full-matrix least-squares method against F^2 with anisotropic displacement parameters for nonhydrogen atoms to $wR_2 = 0.107$ using 3637 reflections ($R_1 = 0.061$ based on 1534 reflections with $F > 4\sigma(F)$, GOF = 0.947). The complete X-ray diffraction data were deposited with the Cambridge Structural Database.

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