Victoria V. Lipson[a], Irina V. Ignatenko[a], Sergey M. Desenko[b], Svetlana V. Shishkina[b], Oleg V. Shishkin[b], Sergey A. Komykhov[c]*, Natalya V. Logvinenko[c], Valery D. Orlov[c], and Herbert Meier[d]

[a]Antidiabetic Drug Laboratory, V. Danilevsky Institute of Endocrine Pathology Problems, Artema St. 10, 61002 Kharkov, Ukraine
[b]Ukrainian National Academy of Sciences, Institute for Single Crystals, Lenina Av. 60, 61000, Kharkov, Ukraine
[c]Department of Chemistry, Kharkov National University, Svobody Sq. 4, 61077 Kharkov, Ukraine
[d]Institute of Organic Chemistry, University of Mainz, D-55099 Mainz, Germany
Received June 26, 2003

The reaction of 5,7-diphenyl-4,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidine (**1**) with α,β-unsaturated carbonyl compounds **2a-f** led to the formation of the alkylated heterocycles **3a-f** (Figure 1). However, the reaction of 5-methyl-7-phenyl-4,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidine (**5**) with **2a-c** yielded under the same conditions the triazolo[5,1-*b*]quinazolines **6a-c** (Figure 3). In this case, the alkylation is followed by a cyclocondensation. The structure elucidation of the products is based on ir, ms, ^{1}H and ^{13}C nmr measurements and on an X-ray diffraction study.

J. Heterocyclic Chem., **40**, 1081 (2003).

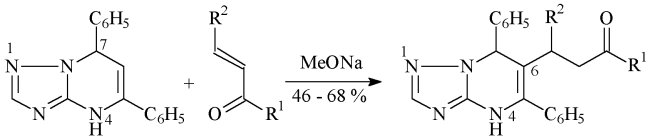
Introduction.

In previous years, fused dihydroazolopyrimidine systems have received considerable attention not only as compounds for pharmacological tests, but also as convenient models for the solution of a number of problems in the field of synthetic chemistry of partially hydrogenated heterocycles. Investigation of their chemical properties, molecular structure and imine - enamine tautomeric equilibrium have been reported recently [1-4].

The 4,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidines **1** and **5** (Figures 1 and 3), which contain an enamine substructure —NH—C(R)=CH—, represent ambident nucleophiles. The nitrogen atom N-4 is their hard and the carbon atom C-6 their soft center. In our previous investigations, we found that alkylation selectively takes place at the N-4 but not at the C-6 atom, when soft electrophiles like CH_3I or hard electrophiles like Me_2SO_4 were used [2,4]. In the present article we report on opposite results when the alkylation of compound **1** or **5** is performed using α,β-unsaturated carbonyl compounds.

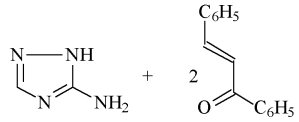
Results and Discussion.

Equimolar amounts of 4,7-dihydro-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidine (**1**) and an α,β-unsaturated carbonyl compound (**2a-f**) were refluxed in methanol in the presence of sodium methoxide. Adducts **3a-f** were formed in yields between 46 and 68 %. The same products were obtained in a one-pot synthesis, when the reaction between one mole of 3-amino-1,2,4-triazole (**4**) and two moles of chalcone was carried out under similar conditions. The formation of **3a** from **4** and **2a** is shown in Figure 1 as an example.



1 **2a-f** **3a-f**

Compound	R^1	R^2	mp [°C]	Yield [%]
3a	C_6H_5	C_6H_5	222 – 224	58
3b	C_6H_5	4-CH_3O-C_6H_4	221	56
3c	C_6H_5	4-Cl-C_6H_4	229	68
3d	C_6H_5	4-F-C_6H_4	250 – 252	67
3e	4-CH_3-C_6H_4	C_6H_5	251	61
3f	C_6H_5	CO-C_6H_5	230 - 232	46



4 **2a**

Figure 1. Alkylation of 4,7-dihydro-5,7-diphenyl-1,2,4-triazolo-[1,5-*a*]pyrimidines.

The structures of the compounds **3a-f** were established by spectroscopic methods. Their ir spectra (potassium bromide pellets) show characteristic absorptions at 3400 - 2850, 1724 - 1684 and 1660 - 1652 cm^{-1} indicating the presence of H-bonding NH groups, C=O and C=C double bonds. High resolution ^{1}H nmr spectra of compounds **3a-f** (Table 1) contain singlets for 2-H, 4-H and 7-H, ABM spin patterns for the side chain on C-6 and a multiplet for the aromatic protons. The ^{13}C nmr spectra of **3a-f** exhibit signals of the side chain, five

signals of the dihydrotriazolopyrimidine scaffold and strongly overlapping signals of the aromatic rings. The signal assignments in Table 2 are based on DEPT measurements.

Finally, the structure of **3a** was confirmed by an X-ray crystal structure analysis. Figure 2 shows a perspective view of the molecule of **3a**. (The numbers used to indicate

Table 1

^{1}H nmr Data of Compounds **3a-f** (δ Values in $(CD_3)_2SO$, TMS as Internal Standard)

Compound	NH	Ar-H	2-H	7-H	Sidechain on C-6 (ABM)			CH_3
	s	m	s	s	C-H	H-C-H	s	
3a	9.75	6.95 – 7.65	[a]	5.70	4.69	3.08	2.68	
3b	9.89	6.77 – 7.65	7.43	5.54	4.36	3.02	2.74	3.68
3c	9.95	6.95 – 7.68	7.45	5.57	4.38	3.07	2.85	
3d	9.93	6.94 – 7.69	7.44	5.56	4.39	3.06	2.83	
3e	9.91	6.93 – 7.68	7.43	5.51	4.40	3.05	2.67	2.23
3f	10.22	7.41 – 7.53	[a]	5.69	4.83	3.23	2.77	

[a] superimposed on the signals of the aromatic protons

Table 2

^{13}C nmr Data of Compounds **3a-f** (δ Values in $(CD_3)_2SO$, TMS as Internal Standard)

	CH_2	CH	C-7	C-6	C-5	C-2	C-3a	CO	Aromat. C [a]	CH_3
3a	40.9	39.5	59.7	108.2	142.1	149.6	148.2	196.6	126.2, 126.3, 126.9, 127.1, 127.5, 128.2, 128.2, 128.4, 128.7, 132.8, 133.9, 135.0, 136.0, 141.0,	
3b	41.1	38.7	59.6	108.5	142.1	149.6	148.2	196.7	127.3, 127.7, 128.1, 128.5, 128.7, 129.0, 129.5, 132.8, 133.1, 133.6, 135.1, 136.0, 157.7	54.9
3c	40.9	38.8	59.7	107.7	142.0	149.7	148.1	196.5	127.4, 127.8, 128.4, 128.5, 128.7, 128.9, 128.9, 129.1, 129.5, 130.9, 133.2, 134.3, 134.9, 135.9	
3d	41.3	38.9	59.9	108.1	142.0	149.7	148.3	196.6	127.3, 127.8, 128.4, 128.7, 128.9, 129.5, 128.8, 129.0, 128.5, 137.3, 160.7	
3e	40.8	39.3	59.7	108.3	142.3	149.7	148.2	196.1	126.4, 127.1, 127.4, 127.7, 128.4, 128.5, 128.7, 129.0, 129.1, 129.5, 133.6, 133.8, 135.1, 141.1, 143.5	21.0
3f	42.8	40.6	60.1	101.4	142.0	149.9	148.0	197.1, 197.9	127.3, 127.7, 127.9, 128.5, 128.6, 128.7, 128.8, 129.0, 129.3, 129.6, 133.3, 134.2, 135.6, 135.7, 136.5	

[a] The signals of the aromatic carbon atoms are strongly superimposed

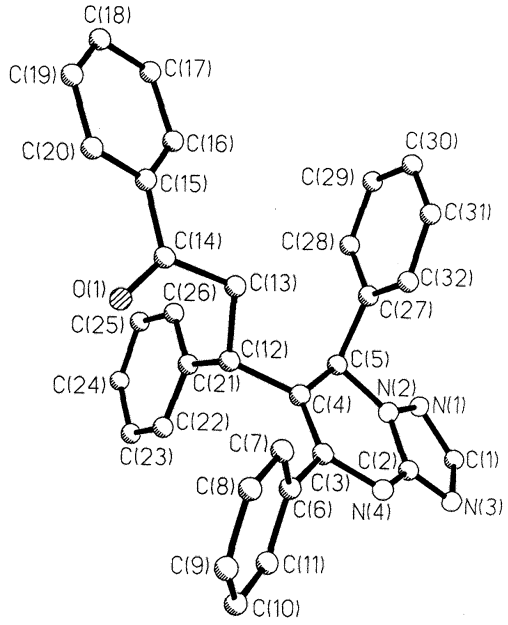


Figure 2. Perspective view of compound **3a**.

Table 3

Bond Lengths [Å] in **3a**

O (1) – C (14)	1.231 (9)	N (1) – C (1)	1.300 (10)
N (1) – N (2)	1.384 (7)	N (2) – C (2)	1.336 (9)
N (2) – C (5)	1.468 (9)	N (3) – C (2)	1.332 (9)
N (3) – C (1)	1.365 (10)	N (4) – C (2)	1.343 (9)
N (4) – C (3)	1.407 (9)	C (3) – C (4)	1.343 (10)
C (3) – C (6)	1.474 (10)	C (4) – C (5)	1.534 (10)
C (4) – C (12)	1.528 (10)	C (5) – C (27)	1.526 (10)
C (6) – C (7)	1.382 (10)	C (6) – C (11)	1.399 (10)
C (7) – C (8)	1.392 (11)	C (8) – C (9)	1.377 (11)
C (9) – C (10)	1.354 (10)	C (10) – C (11)	1.365 (10)
C (12) – C (21)	1.495 (10)	C (12) – C (13)	1.534 (9)
C (13) – C (14)	1.505 (10)	C (14) – C (15)	1.490 (11)
C (15) – C (16)	1.344 (11)	C (15) – C (20)	1.390 (11)
C (16) – C (17)	1.415 (13)	C (17) – C (18)	1.360 (14)
C (18) – C (19)	1.334 (14)	C (19) – C (20)	1.382 (14)
C (21) – C (26)	1.370 (11)	C (21) – C (22)	1.386 (11)
C (22) – C (23)	1.375 (12)	C (23) – C (24)	1.371 (14)
C (24) – C (25)	1.37 (2)	C (25) – C (26)	1.378 (13)
C (27) – C (28)	1.367 (10)	C (27) – C (32)	1.370 (10)
C (28) – C (29)	1.374 (13)	C (29) – C (30)	1.37 (2)
C (30) – C (31)	1.347 (14)	C (31) – C (32)	1.378 (12)

Table 4
Selected Bond (ϖ) and Torsion (τ) Angles for Compound **3a**

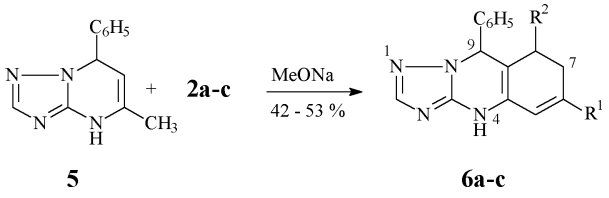
Bond angle	ϖ	Torsion angle	τ
C (4) – C (3) – C (6)	125.5 (7)	C (3) – N (4) – C (2) – N (2)	13 (1)
N (4) – C (3) – C (6)	112.7 (7)	C (5) – N (2) – C (2) – N (4)	-5 (1)
C (3) – C (4) – C (12)	122.8 (7)	C (2) – N (4) – C (3) – C (4)	-9 (1)
C (5) – C (4) – C (12)	114.4 (6)	N (4) – C (3) – C (4) – C (5)	-3 (1)
N (2) – C (5) – C (27)	110.5 (6)	C (6) – C (3) – C (4) – C (12)	-10 (1)
C (27) – C (5) – C (4)	113.2 (6)	C (2) – N (2) – C (5) – C (4)	-6 (1)
C (21) – C 12) – C (4)	108.9 (6)	C (3) – C (4) – C (5) – N (2)	10.0 (9)
C (21) – C (12) – C (13)	114.3 (6)	C (3) – C (4) – C (5) – C (27)	-112.2 (8)
O (1) – C (14) – C (15)	119.2 (7)	C (3) – C (4) – C (12) – C (21)	-118.4 (8)
O (1) – C (14) – C (13)	118.8 (8)	C (3) – C (4) – C (12) – C (13)	112.8 (8)
C (26) – C (21) – C (12)	126.1 (8)	C (4) – C (12) – C (13) – C (14)	-165.7 (7)
C (22) – C (21) – C (12)	116.8 (8)	C (12) – C (13) – C (14) – O (1)	36 (1)
C (28) – C (27) – C (5)	119.6 (8)	O (1) – C (14) – C (15) – C (20)	21 (1)
C (32) – C (27) – C (5)	120.5 (8)	C (13) – C (12) – C (21) – C (26)	21 (1)
C (7) – C (6) – C (3)	121.8 (7)	N (2) – C (5) – C (27) – C (32)	-73.6 (8)
C (11) – C (6) – C (3)	121.1 (7)	C (4) – C (5) – C (27) – C (32)	46.7 (9)
C (16) – C (15) – C (14)	122.8 (8)	C (3) – C (4) – C (12) – H (12)	-4 (1)
C (20) – C (15) – C (14)	118.2 (8)	H (5) – C (5) – C (27) – C (28)	-3 (1)

atoms do not correspond to nomenclature). Selected bond lengths, bond angles and torsion angles are listed in Tables 3 and 4.

The conformation of the dihydropyrimidine ring can be described as flattened boat (puckering coordinates [5]: S = 0.18, Θ = 81.72, Ψ = 18.86); the deviation of the N(4) and C(5) atoms from the plane of the remaining atoms of the ring is –0.11 Å. Essential flattening of the 6-membered ring in this compound as compared to the 5-phenyl-7-tolyl-4,7-dihydro derivative [6,7] is probably caused by considerable strengthening of the 1,2-allyl interactions along the C(4)-C(5) bond. The shortened intramolecular contacts between C(7) and H(12) of 2.74 Å (the van der Waals radii sum is 2.87 Å [8]), between H(5) and C(21) of 2.53 Å, H(5) and C(26) of 2.82 Å, C(27) and C(13) of 3.15 Å and C(27) and H(13b) of 2.65 Å indicate considerable steric strain within the threefold substituted C(3)-C(4)-C(5) fragment. This leads to significant deformations of the exocyclic bond angles at C(3), C(4) and C(5) (Table 3) and to the twist of the substituents at C(3) and C(4) with respect to each other. The C(6)-C(3)-C(4)-C(12) torsion angle amounts to –10(1)° and the C(4)-C(3)-C(6)-C(7) torsion angle amounts to –60(1)° as compared to other 5-phenyl substituted 4,7-dihydrotriazolopyrimidines where the latter torsion angle is about 40° [1,4-6]. The phenyl group on C(12) is turned by 21(1)° relative to the C(12)-C(13) bond (C(13)-C(12)-C(21)-C(26) torsion angle), what probably results from the shortened intramolecular contact of 2.17 Å between H(13b) and H(26). The interaction between the H(13b) and H(16) with a distance of 2.10 Å causes the non-planarity of the benzyl group (the O(1)-C(14)-C(15)-C(20) torsion angle amounts to 21(1)°) and the rotation of the substituent around the C(13)-C(14) bond. (The C(12)-C(13)-C(14)-O(1) torsion angle is 36(1)°). The phenyl group at C(5) has pseudoaxial orientation (the C(3)-C(4)-C(5)-C(27) torsion angle is –112.2(8)°) and is almost coplanar to the H(5) – C(5) bond. The H(5)-C(5)-C(27)-C(28) torsion angle is –3(1)°).

Compound **3a** exists in the crystalline phase as a monohydrate. According to the crystal structure analysis, molecules of **3a**, like other 4,7-dihydroazolopyrimidines [5,8-10], form dimers due to intermolecular hydrogen bonds.

Under the same conditions 4,7-dihydro-5-methyl-7-phenyl-triazolo[1,5-*a*]pyrimidine (**5**) undergoes alkylation at C-6 followed by a cyclocondensation to yield 4,7,8,9-tetrahydro-1,2,4-triazolo[5,1-*b*]quinazolines (**6a-c**, Figure 3).



5 **6a-c**

Compound	R^1	R^2	mp [°C]	Yield [%]
6a	C_6H_5	C_6H_5	240 – 243	53
6b	C_6H_5	4-CH_3O-C_6H_4	243 – 245	42
6c	C_6H_5	4-Cl-C_6H_4	252 - 255	44

Figure 3. Preparation of Compounds **6a-c.**

The structure of compounds **6a-c** was established by spectral methods. The ir spectra prove the absence of a C=O group but the presence of an H-bonding NH-group absorbing at 3300 – 2650 cm^{-1}. The ^1H nmr spectra

(Table 5) of compounds **6a-c** show the absence of a methyl signal but contain singlets for the methine and the NH protons, the methoxy protons of **6b**, and furthermore the four-spin system of the carbocyclic ring. One of the latter four signals is located in the olefinic region at 6.48 ppm, the others are in the region of aliphatic protons. Decoupling of the signal at 6.48 ppm (^4J = 2.4 Hz) leads to the typical spectrum of an ABM system. The ^{13}C nmr spectra (Table 6) confirmed additionally the structure of compounds **6a-c**. (The signal assignment is based on DEPT, HMQC and HMBC experiments).

Table 5

^{1}H nmr Data of the Compounds **6a-c** (δ Values in $(CD_3)_2SO$, TMS as Internal Standard)

Compound	NH	Ar-H	2-H	5-H	7-H	8-H	9-H	OCH_3
	s	m	s	AB XY Spin System			s	s
6a	9.97	6.78 – 7.31	7.55	6.48	3.26/2.61	3.63	6.07	—-
6b	9.94	6.32 – 7.40	7.54	6.48	3.15/2.60	3.57	6.04	3.51
6c	10.01	6.80 – 7.35	7.56	6.48	3.16/2.59	3.64	6.09	—-

Table 6

^{13}C nmr Data of the Compounds **6a-c** (δ Values in $(CD_3)_2SO$, TMS as Internal Standard)

	C-7	C-8	C-9	C-8a	C-5	C-6	C-4a	C-3a	C-2	*o,m*-C(Ar)	*p*-C(Ar)	*i*-C(Ar)
6a	35.7	39.0	63.0	102.5	116.9	136.8	129.2	149.0	149.3	124.6, 126.7, 126.8, 126.9, 127.2, 128.3	125.1, 126.8, 127.6	139.0, 139.3, 142.0
6b [a]	35.9	39.3	63.0	103.3	117.2	137.2	129.3	149.3	149.6	112.7, 124.9, 127.0, 127.5, 128.1, 128.6	127.1, 127.9, 157.0	134.2, 139.3, 139.9
6c	35.6	39.2	63.2	102.5	117.2	137.0	129.9	149.3	149.6	124.9, 127.0, 127.1, 127.6, 128.6, 128.9	127.2, 128.0, 129.6	139.2, 139.7, 141.3

[a] OCH_3 : δ = 54.8

Conclusion.

In contrast to earlier *N*-methylation reactions with CH_3I or $(CH_3O)_2SO_2$ [2,4,11], the reaction of 4,7-dihydro-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidine (**1**) with the enones **2a-f** leads in an alkaline medium to alkylation at C-6. This Michael type addition is followed by a cyclocondensation to 4,7,8,9-tetrahydro-1,2,4-triazolo[5,1-*b*]quinazolines (**6a-c**), provided that a methyl instead of a phenyl group, is present at C-5 of the triazolopyrimidine ring system [12].

EXPERIMENTAL

General.

Melting points were taken on a Kofler melting point apparatus and are uncorrected. Ir spectra were obtained in potassium bromide pellets with a Specord M 82 spectrograph. ^{1}H and ^{13}C nmr spectra were recorded on a Bruker AM 400 spectrometer in $(CD_3)_2SO$. Mass spectra were measured on a Finnigan MAT 95 spectrometer using the field desorption technique. Elemental analyses were obtained using LECO CHNS-900 equipment.

General Procedure for the Alkylation of 4,7-Dihydro-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidine (**1**).

A solution of 0.08 g (1.5 mmol) of sodium methoxide, 0.30 g (1.1 mmol) of 4,7-dihydro-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidine (**1**) and 1.2 mmol of an *α,β*-unsaturated carbonyl compound **2a-f** in 10 mL of methanol was refluxed for 2 h. After cooling, the products **3a-f** were isolated by filtration, washed with methanol, dried and recrystallized from a 2:1 mixture of methanol and dimethylformamide. Yields and melting points are summarized in Figure 1; ^{1}H and ^{13}C nmr spectral data are listed in Tables 1 and 2.

3-(4,7-Dihydro-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidin-6-yl)-1,3-diphenyl-1-propanone (**3a**).

This compound was obtained as colorless crystals: mp 222 – 224 °C; 58 % yield; ir (KBr): 3300 - 2700, 1692, 1652, 1596 cm^{-1}. The fd ms spectrum showed the molecular ion at m/z (%) 483 (100) $[M + H]^+$.

Anal. Calcd. for $C_{32}H_{26}N_4O$ (482.2): C, 79.64; H, 5.43; N, 11.61. Found: C, 79.85; H, 5.77; N, 11.94.

3-(4,7-Dihydro-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidin-6-yl)-3-(4-methoxyphenyl)-1-phenyl-1-propanone (**3b**).

This compound was obtained as colorless crystals: mp 221 °C; yield 56 %; ir (KBr): 3350 – 2700, 1696, 1652, 1600 cm^{-1}. The fd ms spectrum showed the molecular ion at m/z (%) 513 (100) $[M + H]^+$.

Anal. Calcd. for $C_{33}H_{28}N_4O_2$ (512.2): C, 77.32; H, 5.51; N, 10.93. Found: C, 77.27; H, 5.42; N, 11.00.

3-(4-Chlorophenyl)-3-(4,7-dihydro-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidin-6-yl)-1-phenyl-1-propanone (**3c**).

This compound was obtained as colorless crystals: mp 229 °C; yield 68 %; ir (KBr): 3350 – 2650, 1684, 1652, 1596 cm^{-1}. The fd ms spectrum showed molecular ion at m/z (%) 517 (100) $[M + H]^+$.

Anal. Calcd. for $C_{32}H_{25}N_4ClO$ (517.0): C, 74.34; H, 4.87; N, 10.84. Found: C, 74.27; H, 4.82; N, 10.79.

3-(4,7-Dihydro-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidin-6-yl)-3-(4-fluorophenyl)-1-phenyl-1-propanone (**3d**).

This compound was obtained as colorless crystals: mp 250 -252 °C; yield 67 %; ir (KBr): 3350 – 2650, 1684, 1652,1596 cm^{-1}. The fd ms spectrum showed the molecular ion at m/z (%) 501 (100) $[M + H]^+$.

Anal. Calcd. for $C_{32}H_{25}N_4FO$ (500.2): C, 76.78; H, 5.03, N, 11.19. Found: C, 76.66; H, 4.91; N, 10.98.

3-(4,7-Dihydro-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidin-6-yl)-1-(4-methylphenyl)-3-phenyl-1-propanone (**3e**).

This compound was obtained as colorless crystals: mp 251 °C; yield 61 %; ir (KBr): 3350 – 2700, 1692, 1656, 1596 cm^{-1}. The fd ms spectrum showed the molecular ion at m/z (%) 497 (100) $[M + H]^+$.

Anal. Calcd. for $C_{33}H_{28}N_4O$ (496.2): C, 79.81; H, 5.68; N, 11.28. Found: C, 79.78; H, 5.56; N, 11.15.

2-(4,7-Dihydro-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidin-6-yl)-1,4-diphenyl-1,4-butanedione (**3f**).

This compound was obtained as colorless crystals: mp 230 – 232 °C; yield 46 %; ir (KBr): 3350 – 2650, 1684, 1652, 1596 cm^{-1}. The fd ms spectrum showed the molecular ion at m/z (%) 511 (100) $[M + H]^+$.

Anal. Calcd. for $C_{33}H_{26}N_4O_2$ (510.2): C, 77.63; H, 5.13; N, 10.97. Found: C, 77.59; H, 5.06; N, 10.93.

Cyclocondensation of 3-Amino-1,2,4-triazole (**4**) with Two Equivalents of Chalcone (**2a**).

A solution of 0.08 g (1.5 mmol) of sodium methoxide, 0.25 g (3.0 mmol) of 3-amino-1,2,4-triazole (**4**) and 6.2 mmol of chalcone (**2a**) in 10 mL of methanol was refluxed for 4 h. After cooling, the product **3a** was isolated by filtration, washed with methanol, dried and recrystallized from a mixture of methanol and dimethylformamide (2:1). The yield amounted to 52 %.

General Procedure for the Preparation of the Triazolo[5,1-*b*]quinazolines **6a-c**.

A solution of 0.08 g (1.5 mmol) of sodium methoxide, 0.21 g (1.0 mmol) of 4,7-dihydro-5-methyl-7-phenyl-1,2,4-triazolo[1,5-*a*]pyrimidine (**5**) and 1.2 mmol of an α,β-unsaturated carbonyl compound (**2a-c**) in 10 mL of methanol was refluxed for 5 – 10 min. After cooling, the products **6a-c** were isolated by filtration, washed with methanol, dried and recrystallized from a mixture of methanol and dimethylformamide (2:1). The yields and melting points are summarized in Figure 3. The ^1H and ^{13}C nmr spectral data are shown in Tables 5 and 6.

4,7,8,9-Tetrahydro-6,8,9-triphenyl-1,2,4-triazolo[5,1-*b*]quinazoline (**6a**).

This compound was obtained as colorless crystals: mp 240 – 243 °C; yield 53 %; ir (KBr): 3300 – 2650, 1600, 1548 cm^{-1}. The fd ms spectrum showed the molecular ion at m/z (%) 403 (100) $[M + H]^+$.

Anal. Calcd. for $C_{27}H_{22}N_4$ (402.2): C, 80.56; H, 5.51; N, 13.93. Found: C, 80.54; H, 5.42; N, 13.87.

4,7,8,9-Tetrahydro-8-(4-methoxyphenyl)-6,9-diphenyl-1,2,4-triazolo[5,1-*b*]quinazoline (**6b**).

This compound was obtained as colorless crystals: mp 243 -245 °C; yield 42 %; ir (KBr): 3300 – 2650, 1608, 1544 cm^{-1}. The fd ms spectrum showed the molecular ion at m/z (%) 433 (100) $[M + H]^+$.

Anal. Calcd. for $C_{28}H_{24}N_4O$ (432.2): C, 77.75; H, 5.59; N, 12.95. Found: C, 77.74; H, 5.52; N, 12.80.

8-(4-Chlorophenyl)-4,7,8,9-tetrahydro-6,9-diphenyl-1,2,4-triazolo[5,1-*b*]quinazoline (**6c**).

This compound was obtained as colorless crystals: mp 252 -255 °C; yield 44 %; ir (KBr): 3300 – 2700, 1612, 1552 cm^{-1}. The fd ms spectrum showed the molecular ion at m/z (%) 437 (100) $[M + H]^+$.

Anal. Calcd. for $C_{27}H_{21}N_4Cl$ (436.6): C, 74.22; H, 4.84; N, 12.82. Found: C, 74.14; H, 4.76; N, 12.81.

X-Ray Diffraction Study of **3a**.

The crystals of 3-(4,7-dihydro-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidin-6-yl)-1,3-diphenyl-1-propanone (**3a**) $C_{32}H_{26}N_4O \cdot H_2O$ are monoclinic. We found at 293 K: a = 20.54(1), b = 10.460(4), c = 12.777(5), β = 94.01(4)°, V = 2738(2) $Å^3$, space group $P2_1/c$, Z = 8, d_{calc} = 1.192 g/cm^3, μ = 0.075 mm^{-1}, $F(000)$ = 1036. Intensity of 5114 reflections (4869 independent, R_{int} = 0.083) was measured on an automatic four-circles Siemens P3/PC diffractometer (graphite monochromated MoKα radiation, $\Theta/2\ \Theta$ scan, $2\Theta_{max}$ = 50 °). The structure was solved by the direct method using the SHELXTL PLUS 5 package [13]. The profile analysis by the PROFIT [14] program was applied in order to improve the experimental quality. Position of hydrogen atoms were calculated geometrically and refined by "riding" model with $U_{iso} = 1.2\ U_{eq}$. Full-matrix least-squares refinement against F^2 in anisotropic approximation using 4869 reflections was converged to $R1$ = 0.097 (for 1490 reflections with $F > 4\sigma(F)$, $wR2$ = 0.378, S = 1.172.

REFERENCES AND NOTES

[1] G. Fisher, *Adv. Heterocycl. Chem.*, **57**, 81 (1993).

[2] S. M. Desenko, *Chem. Heterocycl. Compd. (Engl. Transl.)*, **31**, 125 (1994).

[3] O. Y. Borbulevych and O. V. Shishkin, *J. Mol. Struct.*, **446**, 11 (1998).

[4] S. M. Desenko, V. D. Orlov and V. V. Lipson, *Khim. Geterotsikl. Soedin.*, 1638 (1990); *Chem. Heterocycl. Compd. (Engl. Transl.)*, **26**, 1362 (1990).

[5] N. S. Zefirov, V. A. Palyulin and E. E. Dashevskaya, *J. Phys. Org. Chem.*, **3**, 147 (1990).

[6] V. D. Orlov, S. M. Desenko, K. A. Potekhin and Y. T. Struchkov, *Khim. Geterotsikl. Soedin.*, 229 (1988); *Chem. Heterocycl. Compd. (Engl. Transl.)*, **24**, 192 (1988).

[7] O. V. Shishkin, S. M. Desenko, V. D. Orlov, S. V. Lindeman and Y. T. Struchkov, *Izv. Akad. Nauk SSSR Ser. Khim.*, 1394 (1994); *Russ. Chem. Bull.*, **43**, 1320 (1994).

[8] Y. V. Zefirov and P. M. Zorky, *Uspekhi Khimii*, **58**, 713 (1989); *Russ. Chem. Rev.*, **58**, 421 (1989).

[9] S. M. Desenko, V. D. Orlov, O. V. Shishkin, K. E. Barykin, S. V. Lindeman and Y. T. Struchkov, *Khim. Geterotsikl. Soedin.*, 1357 (1993); *Chem. Heterocycl. Compd. (Engl. Transl.)*, **29**, 1163 (1993).

[10] O. V. Shishkin, N. V. Getmansky, S. M. Desenko, V. D. Orlov, S. V. Lindeman and Y. T. Struchkov, *Izv. Akad. Nauk SSSR Ser. Khim.*, 1912 (1993); *Russ. Chem. Bull.*, **42**, 1827 (1993).

[11] S. M. Desenko, V. D. Orlov, V. V. Lipson, O. V. Shishkin, S. V. Lindeman and Y. T. Struchkov, *Khim. Geterotsikl. Soedin.*, 1539 (1991); *Chem. Heterocycl. Compd. (Engl. Transl.)*, **27**, 1242 (1991).

[12] See also G. Zigeuner, H. Brunnetti, H. Ziegler and M. Bayer, *Monatsh. Chem.*, **101**, 1767 (1970).

[13] G. M. Sheldrick SHELXTL PLUS 5. PC Version. A system of computer programs for the determination of crystal structure from X-ray diffraction data, Rev. 5.02, Siemens Analytical X-ray Instruments Inc., Germany, (1994).

[14] V. A. Strel'tsov and V. E. Zavodnik, *Kristallografiya*, **34**, 1369 (1989).