Chemistry of Heterocyclic Compounds, Vol. 32, No. 2, 1996

SYNTHESIS AND STRUCTURE OF 3,7-DIHYDRO-2H-1,2,4-TRIAZOLO-[1',5'-*a*']TRIPYRIMIDO[4,5-*d*]BENZO[*b*]PYRANS

**S. M. Desenko, V. D. Orlov, N. V. Getmanskii,
S. A. Komykhov, B. V. Paponov, A. Yu. Kovalevskii,
O. V. Shishkin, and Yu. T. Struchkov***

*The condensation of 5-(2-hydroxyphenyl)-6,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidines with aldehydes yields derivatives of a new heterocyclic system, namely, 3,7-dihydro-2H-1,2,4-triazolo[1',5'-*a*']pyrimido[4,5-*d*]-benzo[*b*]pyran, including the 9-methyl-2,3-diphenyl derivative, whose structure was established by x-ray diffraction structural analysis.*

The presence of an extremely reactive enamine fragment in dihydro derivatives of azolopyrimidines permits their chemical modification, including conversion to new heterocyclic systems. In the present work, we studied the heterocyclization of 5-(2-hydroxyphenyl)-6,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidines (Ia-g) with aldehydes (IIa-h) upon heating solutions of these reagents in DMF at reflux for 10-45 min.

The presence of two potential reaction sites in the dihydropyrimidine ring of I permits the formation of both benzopyran and benzoxazine rings. However, the exclusive formation of benzopyran systems (III) was observed under the reaction conditions. When superbase media (KOH/DMF) were used, which facilitate the participation of the NH group [1], pyrimidine Ia did not react with benzaldehyde but rather underwent heteroaromatization to give a substituted triazolopyrimidine (IV).

The structures of products IIIa-IIIp were established by spectral methods (Tables 1 and 2), while the structure of IIIp was also established by x-ray diffraction structural analysis. Product IV was identical to a sample obtained by the heteroaromatization of dihydroazolopyrimidine systems [2].

The electronic absorption spectra of IIIa-IIIp were analogous on the whole to the spectra of enamine tautomers of dihydroazolopyrimidines [3], while their IR spectra in KBr contain $\nu_{C=C}$ bands at 1655-1675 cm^{-1}. Signals for aromatic protons as well as NH and CH protons are seen in the PMR spectra. Thus, the spectral data indicate the existence of III in the enamine tautomeric form (in the solid phase and in solution in 2-propanol and DMSO-d_6) in contrast to the starting *o*-hydroxyaryl derivatives of dihydro-1,2,4-triazolo[1,5-*a*]pyrimidine I, which exist as mixtures of tautomers A and B [3].

The signals of the methine protons were assigned by comparison of the spectra of IIIe and their deuteroanalog V obtained by the condensation of deuterobenzaldehyde with dihydrotriazolopyrimidine Ia (R = H). The presence of two chiral centers in IIId-IIIp permits the formation of two isomers. Indeed, the spectra of unpurified products IIId-IIIp show doubling of the methine proton signals. The downfield signals with integral intensity 5-15% of the major signals are, in our opinion, signals of the CH group protons of the second diastereomer.

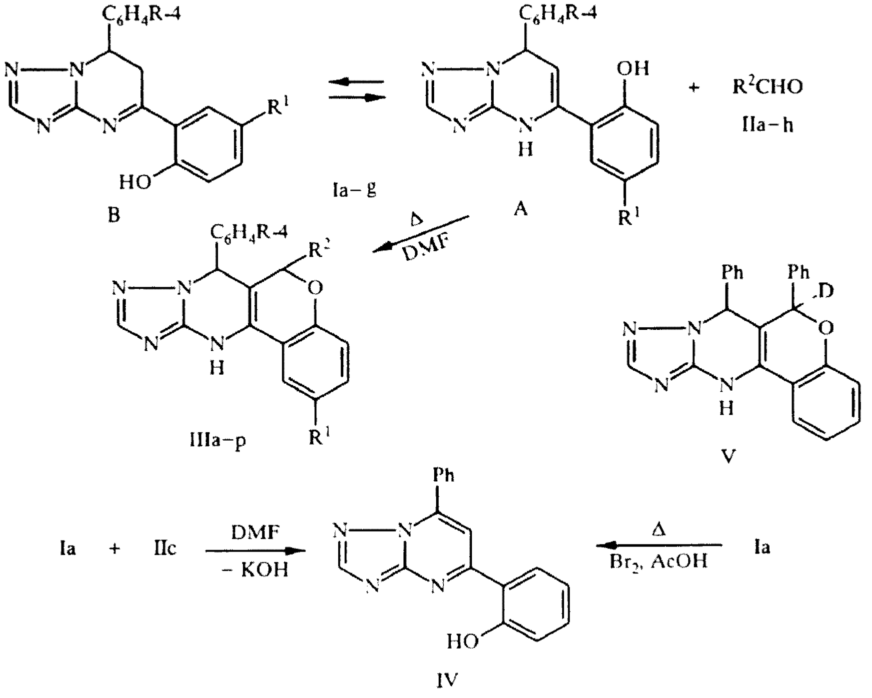
The structure of 9-methyl-2,3-diphenyl-3,7-dihydro-2H-1,2,4-triazolo[1',5'-*a*']pyrimido[4,5-*d*]benzo[*b*]pyran IIIp was also established by x-ray diffraction structural analysis (see Fig. 1 and Tables 3 and 4), which, in particular, showed that this compound has the same *R,R* or *S,S* configuration at $C_{(10)}$ and $C_{(12)}$. Taking account of the PMR spectral features of IIId-IIIp noted above, we may make a general conclusion relative to the analogous configuration of all the isomers formed.

---

*Deceased.

Kharkov State University, 310077 Kharkov and Institute of Heteroorganic Compounds, Russian Academy of Sciences, 117813 Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 240-246, February, 1996. Original article submitted June 28, 1995.

0009-3122/96/3202-0215$15.00



I a $R = R^1 = H$; b $R = MeO$, $R^1 = H$; c $R = Br$, $R^1 = H$; d $R = Me_2N$, $R^1 = H$; e $R = Cl$, $R^1 = H$; f $R = F$, $R^2 = H$; g $R = H$, $R^1 = Me$; II a $R^2 = H$; b $R^2 = Me$; c $R^2 = Ph$; d $R^2 = 4\text{-}MeOC_6H_4$; e $R^2 = 4\text{-}Me_2NC_6H_4$; f $R^2 = 4\text{-}BrC_6H_4$; g $R^2 = 4\text{-}ClC_6H_4$; h $R^2 = 4\text{-}FC_6H_4$; III a $R = R^1 = R^2 = H$; b $R = MeO$, $R^1 = R^2 = H$; c $R = Br$, $R^1 = R^2 = H$; d $R = R^1 = H$, $R^2 = Me$; e $R = R^1 = H$, $R^2 = Ph$; f $R = R^1 = H$, $R^2 = 4\text{-}MeOC_6H_4$; g $R = R^1 = H$, $R^2 = 4\text{-}Me_2NC_6H_4$; h $R = R^1 = H$, $R^2 = 4\text{-}BrC_6H_4$; i $R = MeO$, $R^1 = H$, $R^2 = Ph$; j $R = Br$, $R^1 = H$, $R^2 = Ph$; k $R = MeO$, $R^1 = H$, $R^2 = 4\text{-}MeOC_6H_4$; l $R = Me_2N$, $R^1 = H$, $R^2 = 4\text{-}Me_2NC_6H_4$; m $R = Br$, $R^1 = H$, $R^2 = 4\text{-}BrC_6H_4$; n $R = Cl$, $R^1 = H$, $R^2 = 4\text{-}ClC_6H_4$; o $R = F$, $R^1 = H$, $R^2 = 4\text{-}FC_6H_4$; p $R = H$, $R^1 = Me$, $R^2 = Ph$

The dihydropyrimidine ring has unequally compressed boat conformation (folding parameters [5] $S = 0.16$, $\theta = 69.1°$, $\varphi = 1.4°$), while the pyran ring has distorted sofa conformation (folding parameters $S = 0.44$, $\theta = 51.8°$, $\varphi = 26.7°$). $C_{(3)}$, $C_{(4)}$, $C_{(9)}$, and $O_{(1)}$ are found in a single plane, while $C_{(10)}$ and $C_{(11)}$ extrude from this plane by 0.52 and 0.21 Å, respectively. We should note the considerable compression of the dihydropyrimidine ring in comparison with nonfused analogs of III, namely, 5-phenyl-7-(4'-methylphenyl)-1,2,4-triazolo[1,5-*a*]pyrimidine [6] and 7-methyl-4,7-diphenyl-1,2,4-triazolo[1,5-*a*]-pyrimidine [7], which is probably related to interaction of the two condensed partially hydrogenated heterocycles. $C_{(10)}$ and $C_{(12)}$ extrude in opposite directions from the mean square plane of $N_{(1)}$, $N_{(2)}$, $N_{(3)}$, $C_{(1)}$, $C_{(2)}$, $C_{(3)}$, $C_{(11)}$ by −0.23 and 0.16 Å, respectively. The conjugated system is somewhat decompressed (the $C_{(11)}-C_{(3)}-C_{(4)}-C_{(9)}$ torsion angle is −10.6(4)°), which is probably a result of short intramolecular contacts: $H_{(5)}\cdots H_{(4N)}$ 2.11(1) Å (sum of the van der Waals radii 2.32 Å [8]), $H_{(5)}\cdots H_{(4)}$ 2.61(1) Å (sum of the van der Waals radii 2.66 Å [8]), $C_{(5)}\cdots N_{(4N)}$ 2.69(1) Å (sum of the van der Waals radii 2.87 Å [8]). However, the bond lengths $C_{(3)}-C_{(4)}$ 1.472(4) Å and $O_{(1)}-C_{(9)}$ 1.376(4) Å indicate conjugation between the unshared electron pair of $O_{(1)}$ and the π systems of the $C_{(4)}-C_{(9)}$ benzene ring and triazolopyrimidine fragment. The phenyl substituents at $C_{(10)}$ and $C_{(12)}$ has pseudoaxial orientation (torsion angles $C_{(3)}-C_{(11)}-C_{(12)}-C_{(20)}$, −112.9(3)°; $C_{(3)}-C_{(11)}-C_{(12)}-H_{(12)}$, 125(2)°; $C_{(3)}-C_{(11)}-C_{(10)}-C_{(14)}$, −99.9(3)°; $C_{(3)}-C_{(11)}-C_{(10)}-H_{(10)}$, 138(2)°) and are located on opposite sides of the mean square plane $N_{(1)}$, $N_{(2)}$, $N_{(3)}$, $C_{(1)}$, $C_{(2)}$, $C_{(3)}$, $C_{(11)}$ (the angles between this plane and bonds $C_{(12)}-C_{(20)}$ and $C_{(10)}-C_{(14)}$ are −59.3° and 69.3°, respectively).

Centrosymmetric dimers are formed in the crystal of IIIp due to $N_{(4)}H\cdots N_{(3')}$ hydrogen bonds [H···N, 1.97(1) Å; N−H···N', 167.9°].

EXPERIMENTAL

X-Ray Diffraction Structural Analysis of IIIp. The unit cell parameters of monoclinic crystals of IIIp at 20°C are as follows: $a = 10.702(4)$, $b = 7.774(2)$, $c = 24.340(9)$ Å, $\beta = 96.32(2)°$, $V = 2013(2)$ Å^3, $d_{calc} = 1.246$ g/cm^3, space

TABLE 1. Physical Indices of IIIa-IIId, IIIf-IIIj, IIIp, IV, and V*

Compound	Found N, %	Empirical formula	Calculated N, %	mp, °C	IR spectrum,	UV spectrum, λ_{max} ($\varepsilon \cdot 10^{-3}$)	Yield, %
IIIa	18,8	$C_{18}H_{14}N_4O$	18,5	314...316	1675	282 (5,1), 294 (4,7), 318 (5,2)	62
IIIb	16,7	$C_{19}H_{16}N_4O_2$	16,9	261...263	1673	282 (5,4), 294 (4,9), 317 (5,2)	55
IIIc	14,5	$C_{18}H_{13}N_4OBr$	14,7	256...258	1672	285(3,9), 295 (4,5), 315 (4,3)	65
IIId	17,4	$C_{19}H_{16}N_4O$	17,7	246...248	1655	285 sh., 294 (3,4), 315 (3,5)	37
IIIf	13,4	$C_{25}H_{20}N_4O_2$	13,7	244....247	1658	283 (5,4), 296 (5,4), 319 (4,4)	36
IIIg	16,3	$C_{26}H_{23}N_5O$	16,6	240...242	1660	297 (11,1)	
IIIh	12,2	$C_{24}H_{17}N_4OBr$	12,3	265...267	1660	287 (4,5), 297 (5,1), 321 (4,1)	24
IIIi	13,9	$C_{25}H_{20}N_4O_2$	13,7	208...210	1665	284 (5,5), 296 (5,6), 321 (5,5)	33
IIIj	12,0	$C_{24}H_{17}N_4OBr$	12,3	254...256	1663	287 (4,7), 297 (5,4), 321 (4,6)	44
IIIp	14,1	$C_{25}H_{20}N_4O$	14,3	240...242	1675	285 sh., 298 (9,3), 320 sh.	40
IV	19,1	$C_{17}H_{12}N_4O$	19,4	187...190	—	261 (23,4), 317 (18,6)	61
V	14,5	$C_{24}H_{17}N_4OD$	14,8	227...230	1670	285 sh., 296 (4,7), 320 (3,9)	55

---

*Products IIIe, IIIk-IIIo were described in our previous work [4].

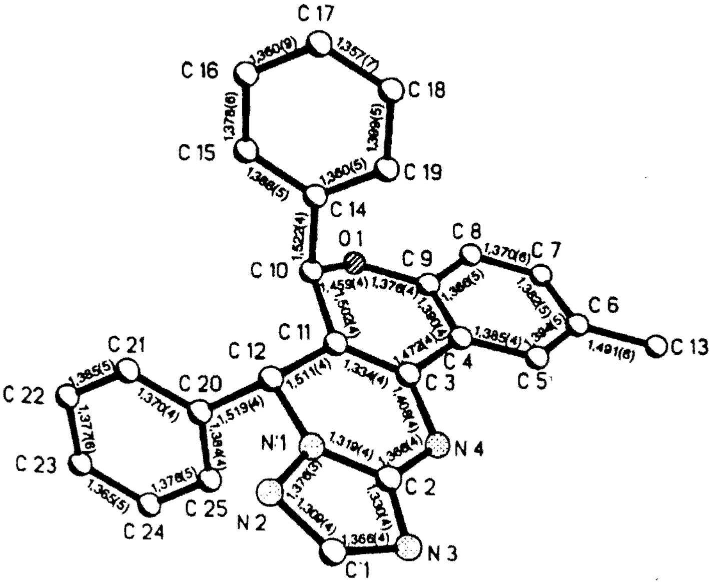


Fig. 1. Structure and bond lengths of IIIp without hydrogen atoms.

group $P2_1/c$, $Z = 4$. The unit cell parameters and intensities of 1737 reflections with $F > 6\sigma(F)$ were measured on a Siemens P3/PC automatic diffractometer using $\lambda MoK\alpha$ radiation, graphite monochromator, and $\theta/2\theta$ scanning; $2\theta_{max} = 60°$).

The structure was solved by the direct method using the SHELXTL PLUS program package [9]. The positions of the hydrogen atoms were found in the electron density difference map. Refinement by the full-matrix method of least squares anisotropically for the nonhydrogen atoms and isotropically for the hydrogen atoms gave $R = 0.043$ ($R_w = 0.049$, $S = 1.62$). The coordinates of the nonhydrogen atoms are given in Table 4.

TABLE 2. Chemical Shifts δ (ppm) and Coupling Constants *J* (Hz) of IIIa-IIIp, IV, and V

Compound	H_{Ar} m	$H_{heterocycle\ fragments}$				CH_3
		triazole CH (1H, s)	pyran CH (1H)	dihydropyrimidine		
				CH (1H, s)	NH (1H, s)	
IIIa	6,9...7,7	7,69	4,18 d; 4,71 d*	6,10	10,3	
IIIb	6,7...7,6	7,64	4,67 d; 4,20 d*	6,04	10,2	3,72 (3H, s)
IIIc	6,8...7,7	7,67	4,70 d; 4,20 d*	6,14	10,3	
IIId	7,2...7,4	7,65	4,48 q 4,91 q	A†: 6,13 B†: 6,18	10,2 10,2	2,26 (3H, d, *J* = 6,4) 0,55 (3H, d, *J* = 6,6)
IIIe	6,3...7,8	7,66	5,37 s 5,90 s	A: 5,63 B: 6,19	10,5	
IIIf	6,8...7,8	7,66	5,34 s 5,84 s	A: 5,59 B: 6,13	10,5	3,72 (3H, s) 3,56 (3H, s)
IIIg	7,6...7,8	7,66	5,25 s	A: 5,56	10,5	2,86 (6H, s)
IIIh	6,7...7,9	7,66	5,38 s 5,89 s	A: 5,69 B: 6,15	10,5	
IIIi	6,7...8,8	7,64	5,38 s 5,86 s	A: 5,57 B: 6,10	10,5	3,75 (3H, s) 3,54 (3H, s)
IIIj	6,7...7,6	7,67	5,39 s 5,88 s	A: 5,67 B: 6,21	10,5	
IIIk	6,7...7,7	7,65	5,33 s 5,80 s	A: 5,55 B: 6,11	10,5	3,74 (3H, s) 3,71 (3H, s) 3,57 (3H, s) 3,55 (3H, s)
III*l*	6,6...7,4	7,63	5,28 s	A: 5,42	10,6	2,78 (6H, s) 2,70 (6H, s)
IIIm	6,7...7,7	7,80	5,39 s 5,87 s	A. 5,73 B: 6,19	10,6	
IIIn	6,7...7,6	7,68	5,41 s 5,90 s	A: 5,74 B: 6,21	10,6	
IIIo	6,7...7,6	7,70	5,41 s 5,90 s	A: 5,70 B: 6,20	10,6	
IIIp	6,6...7,4	7,65	5,34 s	5,63	10,4	2,26 (3H, s)
IV	7,0...8,3	—	—	—	12,3(OH)	
V	6,7...7,4	7,66	— —	A: 5,63 B: 6,28	10,5 10,4	

---

*J = 13.5-13.8 Hz.

†A) *R,R(S,S)*-isomer, B) *R,S(S,R)*-isomer.

The IR spectra of IIIa-IIIp, IV, and V were taken on a Specord 75 IR spectrometer in KBr pellets. The electronic absorption spectra were taken in 2-propanol on a Specord M-40 spectrophotometer (c = (2-5)·10^{-5} mole/liter). The PMR spectra were taken for solutions in DMSO-d_6 on a Gemini-200 spectrometer with TMS as the internal standard. The reaction course and purity of the products were monitored by thin-layer spectrometry on Silufol UV-254 plates using 10:1 benzene–DMF as the eluent. Starting reagents Ia-Ig were prepared previously [3]. The nitrogen content in the products obtained corresponded to the calculated values (see Table 1).

3-Phenyl-3,7-dihydro-2H-1,2,4-triazolo[1′,5′-*a*′]pyrimido[4,5-*d*]benzo[*b*]pyran (IIIa). Method A. A solution of 0.5 g (1.7 mmole) Ia and 0.1 g (3.3 mmoles) paraformaldehyde in 1 ml DMF was heated at reflux for 30 min. Then, 20 ml benzene was added and the solution was cooled to give 0.32 g IIIa, which was filtered off and recrystallized from 1:10 benzene–DMF.

Analogously, IIIb and IIIc were obtained from the reaction of paraformaldehyde with Ib and Ic, respectively, while IIId was obtained from Ia and metaldehyde.

Method B. A sample of 0.4 g (10 mmoles) ground NaOH was added to a suspension of 0.5 g (1.7 mmole) Ia and 0.1 g (3.3 mmole) paraformaldehyde in 1 ml DMF. The mixture was heated at reflux for 5 min and cooled. Water was added. The mixture was neutralized by adding dilute hydrochloric acid. Filtration gave 0.4 g (78%) IIIa.

2-Phenyl-3-(4-methoxyphenyl)-3,7-dihydro-2H-1,2,4-triazolo[1′,5′-*a*′]pyrimido[4,5-*d*]benzo[*b*]pyran (IIIi). The reaction of 0.5 g (1.6 mmole) Ib and 0.17 g (0.16 ml, 1.6 mmole) benzaldehyde IIc in 0.3 ml DMF according to procedure A gave IIIi, which was recrystallized from 1:20 benzene–DMF.

TABLE 3. Some Bond (ω) and Torsion Angles (τ) in IIIp

Angle	ω	Angle	ω
$N_{(2)}$—$N_{(1)}$—$C_{(2)}$	110,0(2)	$N_{(1)}$—$C_{(2)}$—$N_{(4)}$	121,2(2)
$C_{(2)}$—$N_{(1)}$—$C_{(12)}$	127,8(2)	$C_{(4)}$—$C_{(3)}$—$C_{(11)}$	120,3(3)
$C_{(1)}$—$N_{(3)}$—$C_{(2)}$	100,5(2)	$C_{(3)}$—$C_{(4)}$—$C_{(9)}$	117,0(3)
$C_{(9)}$—$O_{(1)}$—$C_{(10)}$	118,2(2)	$O_{(1)}$—$C_{(9)}$—$C_{(4)}$	122,3(3)
$N_{(1)}$—$C_{(2)}$—$N_{(3)}$	111,7(3)	$C_{(3)}$—$C_{(11)}$—$C_{(10)}$	121,2(3)
$N_{(4)}$—$C_{(3)}$—$C_{(11)}$	121,4(3)	$C_{(5)}$—$C_{(4)}$—$C_{(9)}$	118,5(3)
$O_{(1)}$—$C_{(10)}$—$C_{(11)}$	111,9(2)	$C_{(5)}$—$C_{(6)}$—$C_{(7)}$	117,4(3)
$C_{(3)}$—$C_{(11)}$—$C_{(12)}$	124,5(2)	$C_{(4)}$—$C_{(5)}$—$C_{(6)}$	122,2(3)
$N_{(1)}$—$C_{(12)}$—$C_{(11)}$	106,4(2)	$C_{(7)}$—$C_{(8)}$—$C_{(9)}$	120,0(3)
$N_{(1)}$—$N_{(2)}$—$C_{(1)}$	100,8(2)	$C_{(6)}$—$C_{(7)}$—$C_{(8)}$	121,8(3)
$C_{(2)}$—$N_{(4)}$—$C_{(3)}$	117,5(2)	$C_{(7)}$—$C_{(8)}$—$C_{(9)}$	120,0(3)
$N_{(2)}$—$C_{(1)}$—$N_{(3)}$	117,1(3)		
Angle	**τ**	**Angle**	**τ**
$C_{(12)}$—$N_{(1)}$—$C_{(2)}$—$N_{(4)}$	3,4(4)	$C_{(3)}$—$C_{(4)}$—$C_{(9)}$—$O_{(1)}$	0,1(4)
$N_{(1)}$—$C_{(2)}$—$N_{(4)}$—$C_{(3)}$	6,0(4)	$C_{(4)}$—$C_{(9)}$—$O_{(1)}$—$C_{(10)}$	23,9(4)
$C_{(2)}$—$N_{(4)}$—$C_{(3)}$—$C_{(11)}$	-6,1(4)	$C_{(9)}$—$O_{(1)}$—$C_{(10)}$—$C_{(11)}$	-35,0(4)
$N_{(4)}$—$C_{(3)}$—$C_{(11)}$—$C_{(12)}$	-3,0(5)	$O_{(1)}$—$C_{(10)}$—$C_{(11)}$—$C_{(3)}$	25,2(4)
$C_{(3)}$—$C_{(11)}$—$C_{(12)}$—$N_{(1)}$	10,4(4)	$C_{(10)}$—$C_{(11)}$—$C_{(3)}$—$C_{(4)}$	-3,2(5)
$C_{(11)}$—$C_{(12)}$—$N_{(1)}$—$C_{(2)}$	-10,5(4)	$C_{(11)}$—$C_{(3)}$—$C_{(4)}$—$C_{(9)}$	-10,6(4)

TABLE 4. Coordinates of the Non-Hydrogen Atoms ($\times 10^4$) and Hydrogen Atoms ($\times 10^3$) in IIIp

Atom	x	y	z	Atom	x	y	z
$N_{(1)}$	3486(2)	2965(3)	3899(1)	$C_{(21)}$	2505(3)	2944(3)	2437(1)
$N_{(2)}$	4025(2)	1358(3)	3905(1)	$C_{(22)}$	2988(4)	3070(5)	1934(2)
$N_{(3)}$	4825(2)	2954(3)	4648(1)	$C_{(23)}$	4097(4)	3941(5)	1898(2)
$N_{(4)}$	3549(2)	5476(3)	4431(1)	$C_{(24)}$	4710(3)	4663(5)	2362(2)
$O_{(1)}$	724(2)	7692(3)	3321(1)	$C_{(25)}$	4224(3)	4554(4)	2862(2)
$C_{(1)}$	4792(3)	1441(5)	4362(1)	$H_{(4N)}$	402(2)	615(4)	473(1)
$C_{(2)}$	3958(2)	3849(4)	4336(1)	$H_{(1)}$	536(3)	44(4)	450(1)
$C_{(3)}$	2524(3)	6109(4)	4076(1)	$H_{(5)}$	287(3)	812(3)	499(1)
$C_{(4)}$	1967(3)	7763(4)	4214(1)	$H_{(7)}$	49(3)	1194(4)	449(1)
$C_{(5)}$	2280(3)	8650(4)	4704(1)	$H_{(8)}$	-2(3)	1049(4)	363(1)
$C_{(6)}$	1750(3)	10239(4)	4808(2)	$H_{(10)}$	99(2)	567(3)	288(1)
$C_{(7)}$	889(3)	10916(5)	4401(2)	$H_{(12)}$	186(3)	259(3)	342(1)
$C_{(8)}$	543(3)	10057(5)	3916(2)	$H_{(13A)}$	242(3)	1044(4)	564(1)
$C_{(9)}$	1080(3)	8477(4)	3820(1)	$H_{(13B)}$	292(3)	1182(4)	533(1)
$C_{(10)}$	886(3)	5834(4)	3282(1)	$H_{(13C)}$	150(3)	1181(4)	548(1)
$C_{(11)}$	2042(2)	5223(4)	3634(1)	$H_{(15)}$	-73(3)	396(4)	262(1)
$C_{(12)}$	2557(3)	3535(4)	3450(1)	$H_{(16)}$	-256(3)	245(4)	279(1)
$C_{(13)}$	2106(4)	11188(6)	5334(2)	$H_{(17)}$	-320(3)	276(4)	366(1)
$C_{(14)}$	-300(3)	4904(4)	3411(1)	$H_{(18)}$	-202(3)	425(5)	438(1)
$C_{(15)}$	-993(3)	3988(5)	2993(2)	$H_{(19)}$	-21(3)	560(4)	423(1)
$C_{(16)}$	2076(4)	3146(5)	3094(2)	$H_{(21)}$	175(3)	230(4)	246(1)
$C_{(17)}$	2475(4)	3232(6)	3605(3)	$H_{(22)}$	252(3)	261(4)	161(1)
$C_{(18)}$	1823(4)	4134(5)	4019(2)	$H_{(23)}$	443(3)	387(4)	154(2)
$C_{(19)}$	-707(3)	4959(5)	3920(2)	$H_{(24)}$	542(3)	531(5)	236(1)
$C_{(20)}$	3115(3)	3672(4)	2904(1)	$H_{(25)}$	467(3)	508(3)	322(1)

Products IIIe-IIIh and IIIi-IIIp were obtained from the corresponding I and II by analogous procedures.

7-Phenyl-5-(2-hydroxyphenyl)-1,2,4-triazolo[1,5-*a*]pyrimidine (IV). Method A. A sample of 0.4 g (10 mmoles) ground NaOH was added to a suspension of 0.5 g (1.7 mmoles) Ia and 0.18 g (0.17 ml, 1.7 mmole) benzaldehyde in 1 ml

DMF. The mixture was heated for 15 min and cooled. Water was added and the mixture was neutralized by adding dilute hydrochloric acid. The separated mass was mixed with 20 ml acetone and filtered to give 0.3 g IV.

Method B. A solution of 0.5 g (1.7 mmole) Ia and 0.1 ml (2 mmoles) bromine in 1 ml acetic acid was heated to reflux, cooled, mixed with 20 ml water, and filtered to give 0.32 g (65%) IV, which was recrystallized from 2-propanol.

The present work was carried out with support from the Soros International Program for Supporting Education in the Exact Sciences, International Vozrozhdenie Fund (Grant 046), Russian Fund for Basic Research (Project 94-03-8338), and International Science Fund (Grant M04000).

REFERENCES

1. A. F. Pozharskii, Theoretical Basis of Heterocyclic Chemistry [in Russian], Khimiya, Moscow (1985), p. 145.
2. S. M. Desenko, V. D. Orlov, and V. V. Lipson, Khim. Geterotsikl. Soedin., No. 12, 1638 (1990).
3. S. M. Desenko, V. D. Orlov, N. V. Getmanskii, and S. A. Komykhov, Khim. Geterotsikl. Soedin., No. 10, 1353 (1993).
4. S. M. Desenko, V. D. Orlov, N. V. Getmanskii, B. V. Paponov, and S. A. Komykhov, Khim. Geterotsikl. Soedin., No. 10, 1433 (1993).
5. N. S. Zefirov, V. A. Palyulin, and E. E. Dashevskaya, J. Phys. Org. Chem., 3, 143 (1990).
6. V. D. Orlov, S. M. Desenko, K. A. Potekhin, and Yu. T. Struchkov, Khim. Geterotsikl. Soedin., No. 2, 229 (1988).
7. O. V. Shishkin, S. M. Desenko, V. D. Orlov, S. V. Lindeman, and Yu. T. Struchkov, Izv. Rossiisk. Akad. Nauk, Ser. Khim., No. 8, 1394 (1994).
8. Yu. V. Zefirov and P. M. Zorkii, Usp. Khim., 58, 713 (1989).
9. G. M. Sheldrick, SHELXTL PLUS PC Version. A System of Computer Programs for the Determination of Crystal Structure from X-Ray Diffraction Data. Rev. February 4, 1992.