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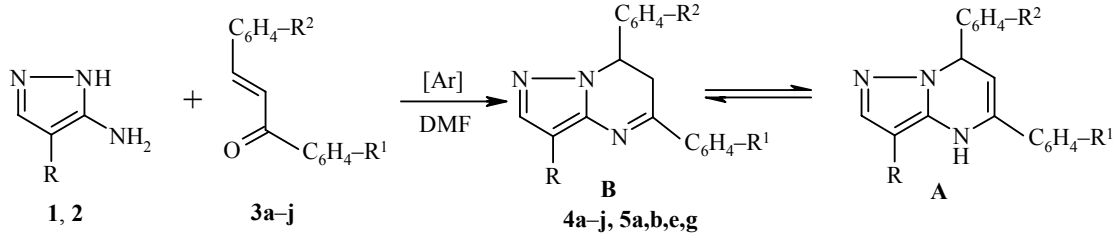
SYNTHESIS AND TAUTOMERISM OF 5,7-DIARYL-3-CYANO- AND 5,7-DIARYL-3-ETHOXYCARBONYL-4,7(6,7)-DIHYDRO-PYRAZOLO[1,5-*a*]PYRIMIDINES

V. V. Lipson[1], S. M. Desenko[2], V. V. Borodina[1], and M. G. Shirobokova[1]

The cyclocondensation of 3-amino-4-cyanopyrazole and 3-amino-4-ethoxycarbonylpyrazole with 1,3-diaryl-2,3-propen-1-ones gives the corresponding 3-substituted 5,7-diaryl-4,7(6,7)-dihydro-pyrazolo[1,5-a]pyrimidines. Their tautomeric composition in solution has been investigated by ^{1}H NMR.

Keywords: dihydropyrazolo[1,5-*a*]pyrimidine system, synthesis, imino–enamine tautomerism.

We previously obtained aryl derivatives of 2-methyl- and 2-phenyldihydropyrazolo[1,5-*a*]pyrimidines by the cyclocondensation of 5-substituted 3-aminopyrazoles with α,β-unsaturated ketones and showed that these compounds exist both in the solid phase and in solution mainly in the imine 6,7-dihydro form [1-3]. In a continuation of these investigations, with the aim of clarifying the influence of substituents in the pyrazole fragment on the the state of the imine–enamine tautomeric equilibrium of dihydropyrazolopyrimidines, 5,7-diaryl-3-cyano- and 5,7-diaryl-3-ethoxycarbonyldihydropyrazolo[1,5-*a*]pyrimidines have been synthesized and the tautomeric state of their solutions have been studied.



1, **4**, **6** R = CN; **2**, **5**, **7** R = COOEt; **a**, **f–i** R^1 = H, **b** R^1 = 4-Cl, **c** R^1 = 4-Me, **d**, **j** R^1 = 4-OMe, **e** R^1 = 4-NMe_2; **a–e** R^2 = H, **f** R^2 = 4-Br, **g** R^2 = 4-Cl, **h** R^2 = 2,4-$(Cl)_2$, **i** R^2 = 4-F, **j** R^2 = 4-OMe

[1]V. Danilevsky Institute of Endocrine Pathology Problems, Academy of Medical Sciences of Ukraine, Kharkiv 61002; e-mail: lipson@ukr.net. [2]STC Institute of Single Crystals, Kharkiv 61001, Ukraine. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1824-1832, December, 2007. Original article submitted August 27, 2004; revision submitted November 26, 2007.

The desired compounds **4a-j** and **5a,b,e,g** were obtained by boiling equimolar quantities of 3-amino-4-cyanopyrazole **1** or 3-amino-4-ethoxycarbonylpyrazole **2** with α,β-unsaturated ketones **3a-j** in DMF for 15-20 min in an atmosphere of argon. In the case of free access to the oxygen of the air the formation was observed of dihydro derivatives **4a,c,g** or **5a,b,e,g** mixed with their heteroaromatic analogs **6a,c,g** or **7a,b,g** respectively.

The structures of the synthesized compounds were demonstrated by spectral methods (Tables 1-3) and the nitrogen contents were confirmed by elemental analysis (Table 1). In the IR spectra of 3-cyano-pyrazolo[1,5-*a*]pyrimidines **4a-j** and **6a,c,g** the most characteristic was the absorption band for the CN group at 2256-2268 cm^{-1}. The significant differences informative for differentiating structures **4** and **6** were observed in them only when dihydro products **4** in the solid phase were in the enamine 4,7-dihydro form **A**. Bands were

TABLE 1. Characteristics of Compounds **4a-j**, **5a,b,e,g**, **6a,c,g**, and **7a,b,g**

Com-pound	Empirical formula	Found N, % / Calculated N, %	mp, ° C	IR, spectrum ν, cm^{-1}	Yield, %
4a	$C_{19}H_{14}N_4$	18.82 / 18.79	170-172	2268, 1592	75* 34*[2]
4b	$C_{19}H_{13}ClN_4$	16.78 / 16.84	202-203	2258, 1586	66
4c	$C_{20}H_{19}N_4$	17.73 / 17.78	142-144	2262, 1592	72* 57*[2]
4d	$C_{20}H_{16}N_4O$	17.15 / 17.07	187-190	3320, 2264, 1668	47
4e	$C_{21}H_{19}N_5$	20.68 / 20.53	198-200	2260, 1610	50
4f	$C_{19}H_{13}BrN_4$	14.94 / 14.85	235-237	3248, 2258, 1670	64
4g	$C_{19}H_{13}ClN_4$	16.88 / 16.84	220-221	3272, 2256, 1672, 1592	64* 27*[2]
4h	$C_{19}H_{12}Cl_2N_4$	15.17 / 15.26	240-243	3248, 2264, 1676, 1596	68
4i	$C_{19}H_{13}FN_4$	17.80 / 17.83	200-201	3256, 2260, 1672, 1592	64
4j	$C_{21}H_{18}N_4O_2$	15.71 / 15.64	150-152	2263, 1628	43
5a	$C_{21}H_{19}N_3O_2$	12.06 / 12.17	84-86	3421, 1680	67* 23*[2]
5b	$C_{21}H_{18}ClN_3O_2$	11.12 / 11.07	98	3423, 1678	85* 63*[2]
5e	$C_{23}H_{24}N_4O_2$	14.37 / 14.43	131-134	3425, 1698	45
5g	$C_{21}H_{18}ClN_3O_2$	11.02 / 11.07	122-124	3423, 1682	82* 66*[2]
6a	$C_{19}H_{12}N_4$	18.87 / 18.91	195-196	2258, 1646	45
6c	$C_{20}H_{13}N_4$	18.09 / 18.12	197-199	2261, 1608	29
6g	$C_{19}H_{11}ClN_4$	16.89 / 16.94	256-258	2256, 1616	51
7a	$C_{21}H_{17}N_3O_2$	12.28 / 12.24	96-98	1688	53
7b	$C_{21}H_{16}ClN_3O_2$	11.17 / 11.13	102	1690	17
7g	$C_{21}H_{16}ClN_3O_2$	11.09 / 11.13	182-184	1694	13

* In an argon atmosphere.

*[2] With free access to oxygen of the atmosphere.

present in the spectrum for the vibrations of NH and C=C fragments of the dihydropyrimidine ring with ν 3248-3320 and 1668-1676 cm^{-1} respectively. Therefore, according to the IR spectra, pyrazolopyrimidines **4d,f-i** exist in the dihydro form **A** in the solid phase. In the spectra of the imine tautomers **B** (compounds **4a-c,e,j**) and heteroaromatic derivatives **6a,c,g** a set of absorption bands was noted characteristic of condensed azoloazine systems containing several C=N bonds [1, 3].

In the IR spectra of ethoxycarbonylpyrazolopyrimidines **5a,b,e,g** there were characteristic absorption bands for NH and –C=O at 3421-3425 and 1678-1698 cm^{-1} respectively. In the spectra of their heteroaromatic analogs **7a,b,g** the vibrations of the NH group were absent.

The most complete information on the structure of the compounds under consideration was given by their ^{1}H NMR spectra (Tables 2 and 3). The spectra of the hetaryl derivatives **6a,c,g** (Table 2) contain three groups of signals, multiplet for the protons of the aryl substituents, and singlets for the 2-CH and 6-CH fragments of the pyrazole and pyrimidine rings. In the spectra of products **7a,b,g** signals of the ethoxy groups were also present in addition to those indicated above. For compounds **6a,c,g** and **7a,b,g**, as might have been expected, the resonance of the methine protons is observed at lower field in comparison with the corresponding signals in the spectra of dihydrocompounds **4a-j** and **5a,b,e,g** (Tables 2, 3).

The ^{1}H NMR spectra made it possible to estimate the equilibrium tautomeric composition of solutions of dihydro derivatives **4a-j** and **5a,b,e,g** (Table 3). The spectra of the dihydro forms **A** and **B** of compounds **4a-j**, **5a,b,e,g** differ essentially in the region of resonance of the azomethine and aliphatic protons. For the tautomeric forms **A** of carbonitriles **4a-j** the presence of a singlet for NH and two doublets for =CH–CH– fragment of the pyrimidine ring are characteristic. In the case of the enamine form of the ethoxycarbonyl derivatives **5a,b,e,g** the singlet of the NH proton was absent, probably due to exchange. Indirect proof of the presence of the NH group is the additional splitting of the 6-CH signal with $^4J \sim 1.3$-2.0 Hz. This splitting disappears on adding deuteromethanol to solutions of ethoxycarbonyl derivatives **5a,b,e,g**.

In the spectra of imine tautomers **B** of compounds of the **4** and **5** series the signal for the azomethine group was absent, but the resonance of the $–CH_2–CH–$ protons was displayed as an ABX or an A_2X system. In the presence of a mixture of tautomers **A** and **B** the spectrum is a superposition of the signals of both forms. Comparison of the integral intensities of the corresponding groups of signals enabled estimation of the tautomeric composition of the compounds being investigated in solution (Table 3). From the data obtained it

TABLE 2. ^{1}H NMR Spectra of Compounds **6a,c,g** and **7a,b,g**

Com-pound	Chemical shifts, δ, ppm (*J*, Hz)*			
	2-CH (1H, s)	H_{arom}	H-6 (1H, s)	Signals of substituents*[2]
6a	8.37	7.40-8.25 (10H, m)	7.51	—
6c	8.80	7.42 (2H, d); 8.32 (2H, d), *J* = 8.4; 7.64-8.18 (5H, m)	8.08	2.43 (3H, s)
6g	8.80	7.70 (2H, d); 8.20 (2H, d), *J* = 8.4; 7.58-8.38 (5H, m)	8.10	—
7a	8.62	7.41-8.32 (10H, m)	7.25	4.44 (2H, q); 1.47 (3H, t)
7b	8.60	7.53-7.62 (5H); 8.08 (2H, d); 8.27 (2H, d), *J* = 7.8	7.26	4.48 (2H, q); 1.47 (3H, t)
7g	8.59	7.33-7.62 (9H, m)	7.26	4.52 (2H, q); 1.51 (3H, t)

* The spectra of compounds **6a** and **7a,b,g** were recorded in $CDCl_3$, and of compounds **6c,g** in DMSO-d_6.

*[2] For compounds **7a,b,g** *J* = 7.0 Hz in the ethyl fragment.

follows that in $CDCl_3$ solutions the cyano derivatives **4a-e** are in the imine 6,7-dihydro form **B**, but the ethoxycarbonyl derivatives **5a,b,g** are in the enamine 4,7-dihydro form **A** within the limits of sensitivity of NMR spectroscopy. A mixture of **A** and **B** forms was noted in $CDCl_3$ for compounds **4i** and **5e**.

In DMSO-d_6 cyano derivatives **4a-j** and their ethoxycarbonyl analogs **5a,b,e** form a mixture of 4,7- and 6,7- dihydro forms, but compound **5g** is present exclusively in tautomeric form **A**.

It was shown previously that a decisive influence on the tautomeric composition of dihydroazolopyrimidines is exerted by the nature of the annelated azole ring [4, 5]. The equilibrium concentration of the imine form **B** increases in the series of dihydro derivatives tetrazolo[1,5-*a*]- ≤ 1,2,4-triazolo-[1,5-*a*]- < 1,2,3-triazolo[1,5-*a*]pyrimidine < pyrimido[1,2-*a*]benzimidazole < imidazo[1,2-*a*]pyrimidine ≤ pyrazolo[1,5-*a*]pyrimidine in accordance with the fall in electron-withdrawing properties of the azole fragment [4-6]. Consequently, the introduction of the electron-withdrawing cyano or ethoxycarbonyl groups into the pyrazole ring must lead to growth of the equilibrium concentration of tautomer **A**. In reality the presence of the enamine tautomeric form in solution was noted for all compounds of the **4** and **5** series, while for the close structural analogs reported in the literature [3], 2-methyl-6,7(4,7)-dihydropyrazolo[1,5-*a*]pyrimidines, the tautomeric form **A** is encountered in only 40% of cases.

In the series of ethoxycarbonyl derivatives **5** an additional factor stabilizing dihydroform **A** is an intramolecular hydrogen bond involving the NH proton of the dihydropyrimidine ring and the carbonyl oxygen atom of the ethoxycarbonyl group. This leads to a markedly higher concentration of the enamine form **A** in the case of compounds **5a,b,e,g** in comparison with compounds **4a,b,e,g**.

In the series of carbonitriles **4** the influence of the solvent on the position of the tautomeric equilibrium is displayed in its displacement in the direction of the NH forms in the proton-withdrawing DMSO in comparison with $CDCl_3$, which is explained by the formation of NH···DMSO hydrogen bonds. In the case of the ethoxycarbonyl derivatives of **5** on the other hand, on going from $CDCl_3$ to DMSO-d_6 a displacement of the equilibrium takes place in the direction of form **B**, which is caused by competition between DMSO molecules and ethoxycarbonyl groups binding with the NH proton of the enamine form.

In addition to the factors enumerated above the substituents R^1 and R^2 proved to have a significant influence on the position of the imine–enamine equilibrium. For example, in the case of compound **4a** ($R^1 = R^2 = H$) the content of form **A** in DMSO did not exceed 10%, while in solutions of the methoxy-substituted compounds **4d,j** (**d** R^1 = 4-OMe, R^2 = H; **j** $R^1 = R^2$ = 4–OMe) the ratio between the concentrations of forms **A** and **B** levels off. Growth of the concentration of dihydro form **A** in comparison with **4a** is also observed in the case of the halo-substituted **4b,f,g,i** (see Table 3).

EXPERIMENTAL

The IR spectra were recorded on a Specord M-82 spectrometer in KBr disks. The ^1H NMR spectra of compounds **4a-j** and **6a,c,g** were taken on a Varian 200 (200 MHz) spectrometer, of compounds **5a,b,e,g,** and **7a,b,g** on a Varian VX-300 (300 MHz) spectrometer, internal standard was TMS. A check on the composition of reaction mixtures and the purity of the substances obtained was carried out by TLC on Silufol UV 254 plates, eluent was chloroform–methanol, 5:1.

3-Cyano-5,7-diphenyl-6,7-dihydropyrazolo[1,5-*a*]pyrimidine (4a). A mixture of amine **1** (0.22 g, 2 mmol) and 1,3-diphenyl-2-propen-1-one **3a** (0.42 g, 2 mmol) in DMF (1 ml) was boiled for 20 min in an atmosphere of argon, cooled, and water (7-10 ml) added. The mixture was extracted with chloroform, the extract was dried over anhydrous Na_2SO_4, the excess solvent was removed under reduced pressure, the residue, a light-yellow oil, was crystallized from methanol, and compound **4a** (0.45 g) was filtered off.

Compounds **4b-j** were obtained analogously.

TABLE 3. ^{1}H NMR Spectra of Compounds **4a-j**, **5a,b,e,g**

Com-pound	Solvent	Tautomer	Chemical shifts, δ, ppm (*J*, Hz)*					Tautomer content, %
			NH (1H, br. s)*[2]	2-H (1H, s)	7-H (1H)	6-H (1H, d) for **A**, (2H) for **B**	Signals of substituent *[2]	
1	2	3	4	5	6	7	8	9
4a	DMSO-d_6	**B**	—	8.10	5.85 (dd, J_{AX} = 6.0, J_{BX} = 7.4)	3.80 (dd, J_{BX} = 7.4); 3.73 (dd, J_{AX} = 6.0), J_{AB} = -18.0	—	90
	DMSO-d_6	**A**	10.10	7.67	6.16 (d, J = 3.9)	5.23 (^{4}J = 1.3)	—	10
	$CDCl_3$	**B**	—	8.04	5.64 (t, J_{A2X} = 6.8)	3.58 (d, J_{A2} = -17.6)	—	100
4b	DMSO-d_6	**B**	—	8.10	5.04 (dd, J_{AX} = 6.5, J_{BX} = 7.5)	3.83 (dd, J_{BX} = 7.5); 3.75 (dd, J_{AX} = 6.5), J_{AB} = -16	—	20
	DMSO-d_6	**A**	10.17	7.80	6.16 (d, J_{AB} = 4.7)	5.2 (J_{AB} = 4.7)	—	80
	$CDCl_3$	**B**	—	8.02	5.63 (dd, J_{AX} = 6.3, J_{BX} = 7.8)	3.56 (dd, J_{BX} =7.8); 3.50 (dd, J_{AX} = 6.3), J_{AB} = -17.8	—	100
4c	DMSO-d_6	**B**	—	8.11	5.83 (t, J_{A2X} = 6.5)	3.72 (d, J_{A2} = -17.3)	2.36 (3H, s)	30
	DMSO-d_6	**A**	10.1	7.81	6.15 (d, J_{AB} = 3.9)	5.19 (J_{AB} = 3.9)	2.32 (3H, s)	70
	$CDCl_3$	**B**	—	8.05	5.72 (t, J_{A2X} = 6.5)	3.45 (d, J_{A2} = -17.3)	2.36 (3H, s)	100
4d	DMSO-d_6	**B**	—	8.07	5.81 (t, J_{A2X} = 6.5)	3.70 (d, J_{A2} = -16.8)	3.82 (3H, s)	50
	DMSO-d_6	**A**	10.06	7.79	6.13 (d, J_{AB} = 4.4)	5.13 (J_{AB} = 4.4)	3.77 (3H, s)	50
	$CDCl_3$	**B**	—	8.06	5.59 (t, J_{A2X} = 6.8)	3.51 (d, J_{A2} = -16.6)	3.87 (3H, s)	100
4e	DMSO-d_6	**B**	—	8.00	5.77 (dd, J_{AX} = 7.3, J_{BX} = 5.0)	3.68 (dd, J_{BX} = 5.0); 3.59 (dd, J_{AX} = 7.3), J_{AB} = -17.5	2.96	90
	DMSO-d_6	**A**	9.94	7.78	6.11 (d, J_{AB} = 3.6)	5.06 (J_{AB} = 3.6)	2.91	10
	$CDCl_3$	**B**	—	7.74	5.55 (t, J_{A2X} = 6.6)	3.48 (d, J_{A2} = -16.6)	3.07 (6H, s)	100
4f	DMSO-d_6	**B**	—	8.11	5.83 (t, J_{AX} = 5.8, J_{BX} = 7.7)	3.79 (dd, J_{BX} = 7.7); 3.68 (dd, J_{AX} = 5.8), J_{AB} = -18.5	—	20
	DMSO-d_6	**A**	10.07	7.77	6.19 (d, J_{AB} = 3.6)	5.20 (J_{AB} = 3.6)	—	80
4g	DMSO-d_6	**B**	—	8.08	5.85 (dd, J_{AX} = 6.2, J_{BX} = 6.8)	3.78 (dd, J_{BX} = 6.8); 3.72 (dd, J_{AX} = 6.2), J_{AB} = -17.8	—	20
	DMSO-d_6	**A**	10.12	7.79	6.20 (d, J_{AB} = 4.0)	5.22 (J_{AB} = 4.0)	—	80
4h	DMSO-d_6	**B**	—	8.10	6.09 (dd, J_{AX} = 6.6, J_{BX} = 8.2)	3.92 (dd, J_{BX} = 8.2); 3.56 (dd, J_{AX} = 6.6), J_{AB} = -18.1	—	10
	DMSO-d_6	**A**	10.30	7.78	6.51 (d, J_{AB} = 3.7)	5.13 (J_{AB} = 3.7)	—	90
4i	DMSO-d_6	**B**	—	8.10	5.84 (t, J_{AX} = 7.4, J_{BX} = 7.6)	3.83 (dd, J_{BX} = 7.6); 3.65 (dd, J_{AX} = 7.4), J_{AB} = -18.0	—	20
	DMSO-d_6	**A**	10.18	7.80	6.20 (d, J_{AB} = 3.6)	5.23 (J_{AB} = 3.6)	—	80
	$CDCl_3$	**B**	—	8.09	5.61 (dd, J_{AX} = 5.8, J_{BX} = 7.8)	3.58 (dd, J_{BX} = 7.8); 3.51 (dd, J_{AX} = 5.8), J_{AB} = -18.1	—	10
	$CDCl_3$	**A**	10.24	7.58	6.10 (d, J_{AB} = 3.7)	5.14 (^{4}J = 1.6)	—	90

TABLE 3. (continued)

1	2	3	4	5	6	7	8	9
4j	DMSO-d_6	**B**	—	8.07	5.72 (t, $J_{AX} = J_{AB} = 7.2$)	—*[3]	3.70 (3H, s), 3.85 (3H, s)	55
	DMSO-d_6	**A**	10.0	7.75	6.07 (d, $J = 4.0$)	5.01 ($^4J = 2.0$)	3.75 (3H, s), 3.80 (3H, s)	45
5a	DMSO-d_6	**B**	—	8.64	5.75 (dd, J_{AX} =5.8, $J_{BX} = 5.0$)	3.88 (dd, $J_{BX} = 5.0$); 3.76 (dd, $J_{AX} = 5.8$), $J_{AB} = -17.2$	4.30 (2H, q), 1.33 (3H, t)	28
	DMSO-d_6	**A**	—*[4]	8.31	6.18 (d, $J_{AB} = 4.0$)	5.34 ($^4J = 2.0$)	4.25 (2H, q), 1.29 (3H, t)	72
	$CDCl_3$	**A**	—*[4]	7.70	6.15 (d, $J_{AB} = 3.8$)	5.17 ($J_{AB} = 3.8$)	4.30 (2H, q), 1.33 (3H, t)	100
5b	DMSO-d_6	**B**	—	8.64	5.80 (t, $J_{A2X} = 6.6$)	3.67 (d, $J_{A2} = -16.8$)	4.27(2H, q), 1.32 (3H, t)	5
	DMSO-d_6	**A**	—*[4]	8.43	6.17 (d, $J_{AB} = 4.0$)	5.35 ($^4J = 1.8$)	4.24 (2H, q), 1.28 (3H, t)	95
	$CDCl_3$	**A**	—*[4]	7.71	6.13 (d, $J_{AB} = 4.1$)	5.14 ($^4J = 2.0$)	4.25 (2H, q), 1.30 (3H, t)	100
5e	DMSO-d_6	**B**	—	8.51	5.72 (dd, J_{AX} =7.9, $J_{BX} = 4.3$)	3.66 (dd, $J_{BX} = 4.3$); 3.46 (dd, J_{AX} =7.9), $J_{AB} = -17.6$	4.28 (2H, q), 1.33 (3H, t), 2.99 (3H, s)	14
	DMSO-d_6	**A**	—*[4]	7.65	6.13 (d, $J_{AB} = 4.2$)	5.16 ($^4J = 1.9$)	4.22 (2H, q), 1.29 (3H, t), 2.85 (3H, s)	86
	$CDCl_3$	**B**	—	8.01	5.58 (t, $J_{A2X} = 6.3$)	3.46 (d, $J_{A2} = -17.6$)	4.45 (2H, q), 1.47 (3H, t), 3.08 (6H, s)	20
	$CDCl_3$	**A**	—*[4]	7.70	6.10 (d, $J_{AB} = 3.5$)	5.03 ($J_{AB} = 3.5$)	4.37 (2H, q), 1.37 (3H, t), 3.05 (6H, s)	80
5g	DMSO-d_6	**A**	—*[4]	7.68	6.22 (d, $J_{AB} = 4.0$)	5.33 ($^4J = 1.4$)	4.24 (2H, q), 1.29(3H, t)	100
	$CDCl_3$	**A**	—*[4]	7.71	6.12 (d, $J_{AB} = 3.6$)	5.03 ($J_{AB} = 3.6$)	4.30 (2H, q), 1.37 (3H, t)	100

* Signals of the protons of the aryl fragments of compounds **4a-j** and **5a,b,e,g** were observed in the 6.85-8.20 ppm region.

*[2] In the ethyl fragment of all compounds **5** $J = 7.6$ Hz.

*[3] Signals of the 6-CH_2 protons of compound **4j** were overlapped by the signals of the OCH_3 group.

*[4] Signals of the NH group were absent due to the formation of an intramolecular H bond.

3-Ethoxycarbonyl-5,7-diphenyl-4,7-dihydropyrazolo[1,5-*a*]pyrimidine (5a). A mixture of amine **2** (0.16 g, 1 mmol) and compound **3a** (0.21 g, 1 mmol) in DMF (0.5 ml) was boiled for 20 min in an atmosphere of argon, cooled, and water (7-10 ml) was added. The mixture was extracted with chloroform, the extract dried, and the excess solvent was removed under reduced pressure. The oily residue was dissolved with heating in 2-propanol (5 ml), and the solution left for 3 days at –5 to 0°C. Compound **5a** (0.23 g) was filtered off.

Compounds 5b,e,g were obtained analogously.

3-Cyano-5,7-diphenylpyrazolo[1,5-*a*]pyrimidine (6a). A mixture of amine **1** (0.11 g, 1 mmol) and compound **3a** (0.21 g, 1 mmol) in DMF (0.5 ml) was boiled for 15 min under conditions of free access to the oxygen of the air, cooled, methanol (5-7 ml) was added, the mixture was kept at a temperature below 0°C for 1 day, and compound **6a** (0.13 g) was filtered off. In addition the dihydro derivative **4a** (0.1 g) was isolated from the filtrate.

Compounds 6c,g were obtained analogously.

3-Ethoxycarbonyl-5,7-diphenylpyrazolo[1,5-*a*]pyrimidine (7a). A mixture of amine **2** (0.32 g, 2 mmol) and compound **3a** (0.42 g, 2 mmol) in DMF (1 ml) was boiled for 15 min under conditions of free access to the oxygen of the air, cooled, 2-propanol (10 ml) was added, the mixture was kept at a temperature below 0°C for 1 day, and compound **7a** (0.35 g) was filtered off. In addition the dihydro derivative **5a** (0.1 g) was recovered from the filtrate.

Compounds 7b,g were obtained analogously.

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