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AROMATIC DERIVATIVES OF 1H-2,3-DIHYDROPYRAZOLO[4,5-b]-1,5-DIAZEPINE

V. D. Orlov, Kh. Kiroga, and N. N. Kolos

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Aromatic derivatives of 1H-2,3-dihydropyrazole[4,5-b]-1,5-diazepine were obtained by the reaction of 1-phenyl-3-methyl-4,5-diaminopyrazole with chalcones and acetylarenes, catalyzed by acetic or sulfuric acid. The seven-membered ring in these compounds has a conformation of the boat type. The IR, UV, PMR, and mass spectra of the compounds are discussed.

It is known [1, 2] that the reaction of α,β-unsaturated ketones of the aromatic series (chalcones, their vinylogs) with 1,2-diamines under the conditions of base or acid catalysis leads to the formation of dihydrodiazepine systems. The aim of the present work was to study the reaction of aromatic ketones with 1-phenyl-3-methyl-4,5-diaminopyrazole (I), a convenient method for the synthesis of which was proposed in [3]. It was found that the initial components were recovered unchanged when alcohol solutions of the diamine (I) and chalcones, containing catalytic amounts of triethylamine, were boiled. Prolonged boiling (6-8 h) of the same compounds in pure triethylamine led to small yields (~20%) of compounds (II), but the process was accompanied by considerable resin formation. At the same time the reaction of the diamine (I) with chalcones took place smoothly when their methanol solutions were boiled for 1-3 h with catalytic amounts of acetic acid; 2,4-diaryl-6-methyl-8-phenyl-1H-2,3-dihydropyrazolo[4,5-b]-1,5-diazepines (IIa-c, e-m) were obtained (Table 1).

A second method for the synthesis of dihydrodiazepine derivatives is based on the reaction of 1,2-diamines with acetylarenes [4]. It was found that even the diamine (I) reacts with 4-R-acetophenones when their methanol solutions are boiled in the presence of catalytic amounts of concentrated sulfuric acid. The 2,4-diaryl-2,6-dimethyl-8-phenyl-1H-2,3-dihydropyrazolo[4,5-b]-1,5-diazepines (IIIa, b, d-g) were obtained (Table 1).

Compounds (II, III) were crystalline substances with colors ranging from light-yellow to orange-red. The fact that they belong to the dihydrodiazepines was confirmed by elemental analysis and spectral data. Thus, the electronic absorption spectra are typical of dihydro-

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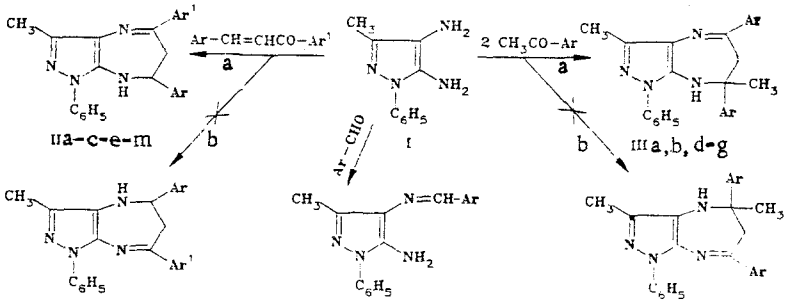
TABLE 1. Derivatives of 1H-2,3-Dihydropyrazolo[4,5-b]-1,5-diazepine (II, III)

Compound	mp, °C	UV spectrum, λ_{max}, nm ($\varepsilon \cdot 10^3$)	ν_{NH}, cm^{-1}	N found, %	Molecular formula	N calculated, %	Boiling time, h	Yield, %
IIa	178	355 (12,02), 265 (17,65), 251 (18,92)	3366	15,0	$C_{25}H_{22}N_4$	14,8	2,5	76
IIb	185—186	356 (11,99), 265 (18,61), 248 (20,51)	3181	14,5	$C_{26}H_{24}N_4$	14,3	2	75
IIc	158	357 (13,09), 269 (21,99), 247 (24,08)	3365	13,5	$C_{25}H_{21}N_4O$	13,7	4	75
IIe	220—221	356 (12,79), 265 (19,67), 247 (20,35)	3181	13,5	$C_{26}H_{24}ClN_4$	13,6	1	85
IIf	202—204	349 (12,81), 267 (20,0), 230 (24,19)	3183	12,5	$C_{25}H_{21}BrN_4$	12,3	1	80
IIg	233—234	352 (12,46), 269 (26,44), 246 (22,55)	3181	16,8	$C_{25}H_{21}N_5O_2$	16,6	1	74
IIh	162—163	353 (13,28), 267 (20,0), 252 (20,31)	3357	14,5	$C_{26}H_{24}N_4$	14,3	2	75
IIi	168	353 (14,02), 275 (19,03), 246 (16,67)	3373	13,6	$C_{26}H_{24}N_4O$	13,7	4	73
IIj	143—145	362 (13,44), 267 (19,09), 253 (19,76)	3383	13,5	$C_{25}H_{21}ClN_4$	13,6	1,5	82
IIk	156	365 (14,66), 268 (21,2), 252 (20,9)	3389	12,4	$C_{25}H_{21}BrN_4$	12,3	1,5	80
III	153—154	429 (12,19), 260 (18,90), 252 (20,85)	3365	16,7	$C_{25}H_{21}N_5O_2$	16,6	1,5	83
IIm	202	363 (14,47), 272 (22,29), 246 (23,26)	3165	12,3	$C_{25}H_{20}Cl_2N_4$	12,5	2,5	75
IIIa	146—148	352 (10,0), 269 (14,5), 246 (15,04)	3203	14,0	$C_{26}H_{24}N_4$	14,3	2,5	66
IIIb	93	350 (13,72), 271 (18,62), 245 (18,1)	3210	13,3	$C_{23}H_{28}N_4$	13,3	3	48
IIId	232—233	357 (21,9), 289 (19,4), 239 (29,7)	3193*	19,7	$C_{26}H_{26}N_6$	19,9	2,5	67
IIIe	103	360 (13,9), 272 (17,6), 240 (17,3)	3189	13,6	$C_{26}H_{22}Cl_2N_4$	13,7	2	74
IIIf	113	361 (13,8), 273 (17,5), 247 (17,1)	3216	10,3	$C_{26}H_{22}Br_2N_4$	10,2	2	70
IIIg	233—234	418 (14,1), 266 (27,7)	3350	17,6	$C_{26}H_{22}N_6O_4$	17,4	1,5	75

*ν_{NH_2} values 3313 and 3393 cm^{-1}.

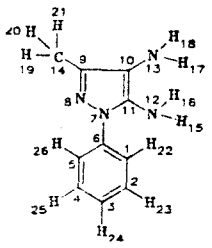


II—IV a, h—l R=H, b R=CH$_3$, c R=OCH$_3$, d R=NH$_2$, e R=Cl, f R=Br, g R=NO$_2$, a-g R^1=H, h R^1=CH$_3$, i R^1=OCH$_3$, j R^1=Cl, k R^1=Br, l R^1=NO$_2$, m R=R^1=Cl; Ar=C$_6$H$_4$R-*p*, Ar^1=C$_6$H$_4$R^1-*p*

diazepine structures [5]; the most long-wave band has medium intensity (log ε ~ 4.0-4.2) and λ_{max} 350-360 nm. The PMR spectra of compounds (II) contain signals for the protons of the $CHCH_2$ fragment, while the spectra of compounds (III) contain signals for the protons of the methylene group.

The IR spectra of compounds (II) and (III) are rather unusual. On the spectrograms measured in the solid phase there is a narrow peak in the region of 3365-3383 cm^{-1} (as a rule, in the compounds with R = H) or a broadened band shifted into the region of 3165-3216 cm^{-1} (Table 1). On the other hand, the IR spectra of these compounds measured in carbon tetrachloride solutions contain a doublet of narrow bands in the region of 3350-3420 cm^{-1}. (The frequency difference for these peaks amounts to 45-50 cm^{-1}.) Similar splitting of the

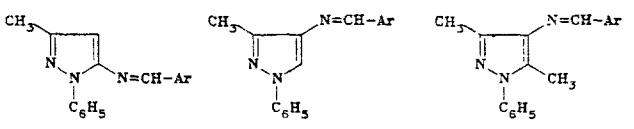
TABLE 2. Distribution of the Effective Charges in the Diamine (I)

Compound	Atom	q	Atom	q	Atom	q
	$C_{(1)}$	−0,080	$C_{(10)}$	0,045	$H_{(19)}$	0,052
	$C_{(2)}$	0,031	$C_{(11)}$	0,147	$H_{(20)}$	0,015
	$C_{(3)}$	−0,037	$N_{(12)}$	−0,220	$H_{(21)}$	0,006
	$C_{(4)}$	0,008	$N_{(13)}$	−0,232	$H_{(22)}$	0,032
	$C_{(5)}$	−0,035	$C_{(14)}$	−0,089	$H_{(23)}$	−0,023
	$C_{(6)}$	0,137	$H_{(15)}$	0,092	$H_{(24)}$	0,019
	$N_{(7)}$	−0,119	$H_{(16)}$	0,093	$H_{(25)}$	0,021
	$N_{(8)}$	−0,108	$H_{(17)}$	0,069	$H_{(26)}$	0,003
E_{tot} = 126,40 a.u.	$C_{(9)}$	0,120	$H_{(18)}$	0,058		

ν_{NH} bands in the transition from the solid phase to solutions was also observed in the IR spectra of derivatives of 1H-2,3-dihydrobenzo[b]-1,5-diazepines and was explained by the existence of intramolecular hydrogen bonds. It is possible that the effect observed in the present case is similar in nature. It should be noted that the IR spectra of all the compounds (II) and (III) contain fairly strong ν_{CH} bands (2900-3050 cm^{-1}) typical of alicyclic CH bonds.

The nonequivalence of the amino groups in the diamine (I) gives rise to two probable directions for its reaction with ketones. At the same time chromatographic (TLC) and spectral (UV, IR, PMR, and mass spectra) control confirms the individuality of the obtained compounds and makes it possible to assign them to one series of isomers. The exception is the nitro derivative (III), which according to the PMR spectra represents a mixture of two isomeric dihydropyrazolodiazepines, which could not be separated, in a ratio of 3:1.

It is known [6] that 1-phenyl-3-methyl-4-aminopyrazole has the characteristics of aromatic amines; in particular, it reacts readily with aromatic aldehydes, forming azomethines. The existence of amine—imine tautomerism was proposed for the amino group at position 5 of the pyrazole ring, and this explains the formation both of the azomethines and of the addition products in the reaction of 1-phenyl-3-methyl-5-aminopyrazole with aldehydes [7]. The diamine (I) was brought into reaction with acetoacetic ester, and it was shown that the amino group at position 4 takes part in the formation of an azomethine bond [8]. Data on the basicity of the isomeric 4- and 5-aminopyrazoles [9] demonstrate the higher basicity of the amino group at position 4 compared with the amino group at position 5. Our CNDO/2 calculation of the electron density distribution in the molecule of the diamine (I) (Table 2) confirms that with the simultaneous presence of the two amino groups the amino group at position 4 has higher basicity. In addition, it is known [10] that the azomethine condensation is favored by the enhanced basicity of the amine. Together these data make it possible to suppose that the reactions of the diamine (I) with ketones take place by path a (see the scheme).



Va,g VIg VIIa,g

g Ar=$C_6H_4NO_2$-p

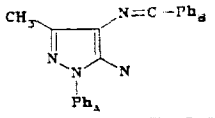
Similar questions about the direction of the processes arose earlier during investigation of the reactions of ketones with 4,5-diamino-1,3-dimethyluracil [2] and 4-phenyl-1,2-diamino-imidazole [10]. They were solved by analysis of the electronic absorption spectra of model azomethine systems. In the present work, therefore, we undertook a synthesis of monoazomethines on the basis of the derivatives of benzaldehyde and the diamine (I) (IVa, c-e) and also on the basis of 1-phenyl-3-methyl-5(4)-aminopyrazoles (Va, g, VIg) and 1-phenyl-3,5-dimethyl-4-aminopyrazoles (VIIa, g) and recorded their electronic absorption spectra (Table 3).

TABLE 3. Electronic Absorption Spectra of the Azomethines (IV-VII) (in Methanol)

Compound	λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)
IVa	368 (10,3), 272 (20,0), 237 (18,8)
IVc	362 (13,8), 299 (25,1), 235 (18,6)
IVe	376 (11,0), 277 (22,9), 240 (19,0)
IVg	417 (18,9), 279 (12,8), 249 (18,5)
Va*	332 (4,9), 250 (15,4)
Vg*	362 (2,7), 254 (17,0)
VIg*	377 (19,0), 280 (14,5)
VIIa*	329 (3,5), 269 (7,0)
VIIg	368 (16,3), 263 (17,0)

*In ethanol.

TABLE 4. Data from Calculation of the UV Spectrum of the Planar Model of the Molecule



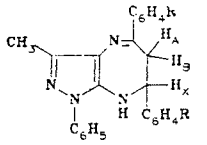
Electronic transition	Band	Calculation E, eV	Calculation f	Experiment E, eV	Experiment f	L, % N	L, % Pyr	L, % C=N	L, % Ph_A	L, % Ph_B	Δq, e N	Δq, e Pyr	Δq, e C=N	Δq, e Ph_A	Δq, e Ph_B
0→1	1	3,38	0,62	3,37	0,21	15,4	30,0	32,0	1,1	21,4	−0,25	−0,33	0,33	0,02	0,23
0→2		4,21	0,07			16,1	40,6	8,5	30,8	4,0	−0,28	−0,20	−0,05	0,53	−0,005
0→3		4,43	0,003			2,4	6,1	8,7	0,11	82,6	−0,04	−0,09	−0,02	0,0	0,15
0→4	2	4,48	0,11	4,56	0,59	5,8	14,4	0,7	78,4	0,6	−0,10	−0,21	0,003	0,31	0,003
0→5		4,88	0,04			11,1	26,2	7,3	51,3	4,1	−0,22	−0,46	−0,08	−0,78	−0,02

From the data in Table 3 it is seen that the electronic absorption spectra of the monoazomethines (IV) are similar to the spectra of the dihydropyrazolodiazepines having related p,π-systems [compounds (IIa, i, j, l), Table 1]. From this it follows that one and the same amino group, situated at position 4 of the diamine (I), takes part in the formation of the azomethine bond in compounds of both series.

The azomethines (V-VII) obtained from the monoaminopyrazoles absorb in a more short-wave region than the remaining compounds, and this may be due to the absence of the adjacent electron-donating amino group. Substantial changes are observed in the spectra of compounds (Va, g); the long-wave absorption band has low intensity and undergoes the largest hypsochromic shift. In the spectra of compounds (VIg) and (VIIa, g), however, the observed hypsochromic shift, due to the absence of the amino group at position 5 [for example, about the spectrum of compound (III) Table 1], is close in value to the λ_{max} value in the spectra of benzylideneaniline and its o-amino derivative (~50 nm [11]). Thus, together the obtained data confirm that compounds (II, III) are formed by path a.

This conclusion is also consistent with the calculation of the characteristics of the electronic transitions in the planar model of the molecule of (IVa) (the transition energy, E; the oscillator force, f; the localization of the transition, L; the change in electron density at the fragments, Δq). [Its π system corresponds to the main chromophoric group of the investigated compounds (II, III).] The calculation was made by the LCAO-MO SCF-CI method in the PPP version with the use of the localization criteria of the electronic transitions [12] (Table 4). The long-wave absorption band in the calculated spectrum is a one-electron π—π*-transition, localized on the N—Pyr—N=C—Ph_B fragment. The transition is accompanied by substantial transfer of electron density (0.58 e) from the amino group and the pyrazole ring to the benzylideneaniline fragment. The calculation predicts a hypsochromic shift of the long-wave absorption band with the introduction of electron-donating groups R^1 and a bathochromic shift with the introduction of electron-withdrawing groups R^1, and this is fully consistent with experiment (Table 1). The calculation also predicts an insignificant effect from the phenyl radical attached to the pyrazole on the long-wave absorption of the

TABLE 5. PMR Spectra of Compounds (IIa-c, e-i, k-m)



Compound	Chemical shift, δ, ppm					J_{AB}, Hz	J_{BX}, Hz	J_{AX} Hz	$\theta_{AX}°$	$\theta_{BX}°$
	H_B	H_A	H_X	NH	CH_3					
IIa	3,21	3,53	4,58	4,64	2,47	−15,5	7,5	0,5	155	72
IIb	3,18	3,56	4,54	4,63	2,48	−15,6	7,5	1,5	155	63
IIc	3,16	3,56	4,52	4,61	2,46	−15,4	7,4	1,4	154	64
IIe	3,24	3,50	4,62	4,66	2,46	−15,4	7,6	2,0	156	59
If	3,24	3,49	4,61	4,66	2,46	−15,4	6,8	1,8	150	60
IIg	3,32	3,61	4,88	4,95	2,46	−15,0	6,7	2,2	149	57
IIh	3,18	3,54	4,58	4,63	2,48	−15,4	7,5	1,56	155	62
IIi	3,16	3,52	4,57	4,62	2,46	−15,5	7,4	1,5	154	63
IIj	3,22	3,49	4,62	4,72	2,46	−15,4	7,0	1,9	151	60
IIk	3,19	3,49	4,60	4,72	2,46	−15,4	7,0	2,0	151	55
IIl*	3,16	3,81	5,02	5,05	2,34	−15,3	6,4	1,1	147	67
IIm	3,29	3,69	4,95	4,27	2,28	−15,6	6,7	1,5	149	63
**	3,19	3,41	4,61	4,67	2,44	−15,6	6,2	2,5	146	55
***	2,90	3,08	4,99	3,85	—	−13,6	8,9	3,5	168	48
	3,07	3,27	4,76	4,92	—	−16,6	7,2	2,23	135	100

*Mixture of isomers.
**2,4-Diphenyl-2,3-dihydrobenzodiazepine.
***2,4,7-Triphenyl-5H-3,4-dihydroimidazo[1,2-b]-1,2,4-triazepine.

molecule of (IVa) and substantial localization of the 0 → 4 electronic transition, which corresponds to the second experimentally observed absorption band, on this radical.

It should also be noted that the long-wave absorption band is sensitive to conformational changes in the chromophore. Thus, the inclusion of the chromophore in the seven-membered dihydrodiazepine ring gives rise to a small hypsochromic shift [about the spectra of compounds (IIa, i, j) and (IVa, c, e) in Tables 1 and 3]. For the same reason a similar effect is observed with the introduction of the bulky methyl group at position 2 of the seven-membered heterocycle [compound (III)].

Analysis of a Dreiding model of the (IIa) molecule shows that the seven-membered ring must exist in a single preferred boat conformation, similar to that in the molecules of 2,4,7-triaryl-5H-3,4-dihydroimidazo[1,2-b]-1,2,4-triazepines [10]. The rigid structure of the bicycle in the molecules of (II) explains the multiplicity of the signals for the protons of the CH_2—CH fragment observed in the spectra of these compounds (an octet or sextet and a quartet, respectively). The chemical shifts of these protons and also δ_{NH} (Table 5) change little, but these changes are similar to the change in the inductive effect of the substituents R and R^1 introduced into the aromatic radicals. It is therefore natural that the signals for the protons of the heterocycle in compounds (IIg) and IIl), containing a nitrophenyl radical at position 2 or 4, are shifted downfield by the largest amount.

The vicinal constants J_{AX} and J_{BX} in the series of compounds (II) also change little, which in our opinion indicates the absence of conformational rearrangements during substitution in the aromatic rings. The electronegativity of the groups R and R^1 probably play a major role in the variation of these constants. Attention is drawn to the fact that one of the vicinal constants (J_{BX}) is of the J_{aa} type. From this it follows that the aryl radical at position 2 is equatorial.

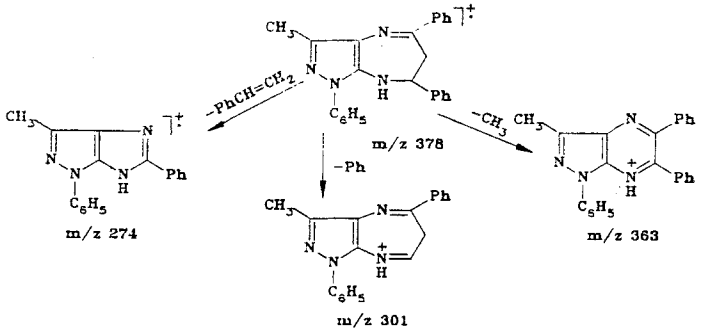
The PMR characteristics of two other related heterocyclic systems are given in Table 5 for comparison. It is clearly seen that annellation of the seven-membered heterocycle with the benzene, imidazole, and pyrazole rings is reflected significantly both in the chemical shifts and in the constants of the H_A, H_B, and H_X protons. These changes are due to some degree to the different polarizations of the compared conjugated systems. However, in our opinion the main role here is played by differences in the conformations of the seven-membered heterocycles. An important argument in favor of such a conclusion is provided by the substantial changes in the geminal constants J_{AB}. This is indicated also by the fact that the sizes of the dihedral angles θ_{AX} and θ_{BX}, calculated from the constants J_{AX} and J_{BX}

TABLE 6. Mass Spectra of Pyrazolo[4,5-b]-1H-2,3-dihydro-1,5-diazepines (IIa) and (IIIa)

Compound	m/z values (intensities, %)
IIa	378 (M^+, 45), 363 (35), 301 (15), 274 (7), 268 (12), 253 (7), 230 (5), 187 (6), 165 (6), 159 (6), 132 (5), 104 (24), 103 (50), 91 (11), 89 (9), 78 (12), 77 (100), 76 (12)
IIIa	392 (M^+, 100), 377 (35), 336 (5), 301 (7), 288 (5), 275 (9), 274 (13), 273 (8), 259 (6), 258 (25), 222 (7), 221 (38), 206 (5), 196 (6), 180 (9), 130 (10), 129 (8), 128 (5), 119 (10), 118 (15), 117 (7), 115 (6), 105 (5), 104 (42), 103 (50), 102 (6), 91 (14), 78 (11), 77 (75)

by means of the Karplus equation [13] and amounting to 55-72 and 146-155°, also differ appreciably from the corresponding angles in the molecules of derivatives of dihydrobenzodiazepines (~48 and ~168° [13]) and dihydroimidazotriazepines (~100 and ~135° [10]).

The mass spectra were measured for compounds (IIa) and (IIIa) (Table 6) and contained molecular ion peaks with high intensities. The main fragmentation paths largely coincide and are given for the case of (IIa):



Three main processes are observed, i.e., the elimination of the methyl group, leading to contraction of the ring (m/z 363), removal of the phenyl radical from position 2, and elimination of the styrene fragment (m/z 274). The subsequent fragmentation processes are due largely to the disintegration of the intermediate pyrazoloimidazole bicycle.

The chemical characteristics of dihydropyrazolodiazepine (IIa) were studied. This compound is not reduced by sodium borohydride, is not oxidized by $K_2S_2O_8$, and does not react with acetic anhydride, although all these reactions take place with 2,4-diphenyl-2,3-dihydro-1H-1,5-benzodiazepine. The first two facts demonstrate the stability of the seven-membered ring in (IIa). Acylation is difficult on account, probably, of steric hindrances created by the phenyl radical at position 8. This experimental fact can also serve as indirect evidence for reaction by path a. Additions of hydrochloric acid to the alcohol solutions of the dihydropyrazolodiazepines (IIa, c) lead to the formation of their salt forms. The question of the position of protonation in these compounds was solved by comparison of the electronic absorption spectra of the base and its salt form. The significant bathochromic shift observed during protonation [$\Delta\lambda_{max}$ 48 and 50 nm for (IIa) and (IIc), respectively] can only be explained by the fact that salt formation takes place at the azomethine nitrogen atom ($N_{(5)}$). The combination of its electron pair leads to an increase in the π-electron interactions, flattening of the chromophoric system, and consequently deeper absorption. Interaction at the $N_{(1)}$, $N_{(7)}$, and $N_{(8)}$ atoms of the bicycle should either not have a significant effect on the spectra ($N_{(7)}$) or be accompanied by a hypsochromic shift ($N_{(1)}$ and $N_{(8)}$). The highest basicity at the $N_{(5)}$ atom is probably determined not only by the enhanced electron density but also by the greater accessibility of its unshared electron pair for attack by the proton.

EXPERIMENTAL

The IR spectra were recorded in tablets with potassium bromide on a Specord IR-75 spectrophotometer. The electronic absorption spectra were measured in methanol with the substances at concentrations of $(2 - 3)\cdot10^{-5}$ M on a Specord UV-vis spectrophotometer. The

PMR spectra were recorded in deuterochloroform on a Varian XL-100 instrument with TMS as internal standard. The mass spectra were obtained on a Varian MAT CH-6 instrument at 70 eV. The individualities of the compounds were monitored by TLC on Silufol UV-254 plates with chloroform as eluent.

6-Methyl-2,4,8-triphenyl-1H-2,3-dihydropyrazolo[4,5-b]-1,5-diazepine (IIa). A solution of 0.6 g (3.2 mmole) of 1-phenyl-3-methyl-4,5-diaminopyrazole and 0.66 g (3.2 mmole) of the chalcone in 15 ml of methanol with the addition of 1 ml of acetic acid was boiled for 2 h 30 min. After cooling, the reaction mixture was neutralized to pH 7 with ammonia and left at 0°C for 1 h. The precipitate was filtered off. The yield was 0.92 g (76%); mp 178°C (1:2 hexane–benzene). Compounds (IIb, c, e-m) were obtained similarly with variation of the boiling times of the solutions.

2,6-Dimethyl-2,4,8-triphenyl-1H-2,3-dihydropyrazolo[4,5-b]-1,5-diazepine (IIIa). To a solution of 0.6 g (3.2 mmole) of 1-phenyl-3-methyl-4,5-diaminopyrazole and 0.77 g (6.4 mmole) of acetophenone in 15 ml of methanol we added two or three drops of concentrated sulfuric acid. The mixture was boiled for 2 h 30 min and neutralized to pH 7 with ammonia. The crystals which separated were filtered off. The yield was 0.83 g (66%); mp 146-148°C (from a 1:2 mixture of hexane and benzene). Compounds (IIIb, d-g) were obtained similarly.

1-Phenyl-3-methyl-4-benzylideneamino-5-aminopyrazole (IVa). A solution of 0.6 g (3.2 mmole) of the diamine (I) and 0.34 g (3.2 mmole) of benzaldehyde in 15 ml of methanol with the addition of four or five drops of acetic acid was boiled for 1 h. The solution was concentrated to two thirds of the volume and cooled. The precipitate was filtered off. The yield was 0.7 g (80%); mp 160°C. Compounds (IVc, e, g, Va, g, VIg, VIIa, g) were obtained similarly.

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