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SYNTHESIS OF DIHYDRO DERIVATIVES OF 2-AMINO-4,5,7-TRIARYLIMIDAZO[1,5-*b*]PYRIDAZINE

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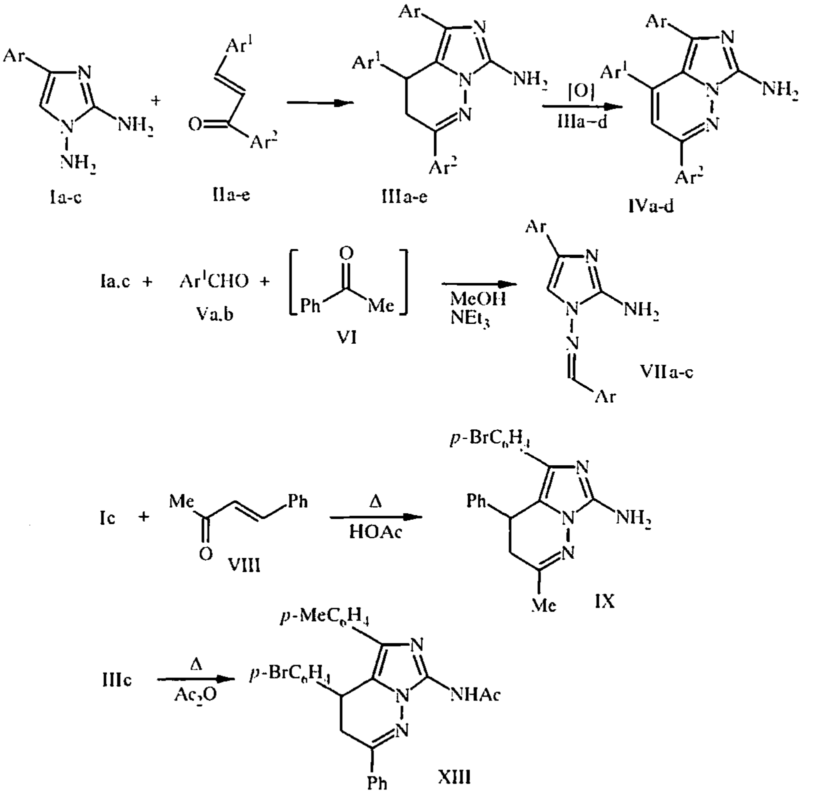
7-Amino-2,4,5-triaryl-3,4-dihydroimidazo[1,5-b]pyridazines have been synthesized by reacting 4-aryl-1,2-diaminoimidazoles with 1,3-diarylpropenones. The structure of one of the products was confirmed by X-ray structural analysis.

As a continuation of investigations on imidazoazine systems [1] possessing high and multiple physiological activity [2,3] the reaction of 1,2-diamino-4-arylimidazoles (Ia-c) with 1,3-diarylpropenones (IIa-e) has been studied. We have established that on carrying out the reaction in methanol under conditions of base



Ia, IIId, IVd, VIIa,b Ar = Ph; Ib, IIIa-c, IVa-c Ar = C_6H_4Me-*p*; Ic, IIIe, VIIc Ar = C_6H_4Br-*p*; IIa, IIIa, IVb, VIIa Ar^1 = Ar^2 = Ph; IIb, IIIb, VIIb Ar^1 = C_6H_4Me-*p*, Ar^2 = Ph; IIc, IIIc, IVc Ar^1 = C_6H_4Br-*p*, Ar^2 = Ph; IId, IIId, IVd Ar^1 = $C_6H_4NO_2$-*p*, Ar^2 = Ph; IIe, IIIe Ar^1 = C_6H_4F-*p*, Ar^2 = C_6H_4OH-*o*; Va Ar^1 = Ph, Vb Ar^1 = C_6H_4OMe-*p*

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TABLE 1. Characteristics of the Compounds Synthesized

Compound	Empirical formula	Found, % / Calculated, %	mp, °C (Lit. mp)	IR spectrum, ν, cm^{-1}		Yield, %
		N		C=N	NH$_2$	
IIIa	$C_{25}H_{22}N_4$	$\frac{14.7}{14.8}$	156	1644	3457, 3290	80
IIIb	$C_{26}H_{24}N_4O$	$\frac{13.8}{13.7}$	153	1640	3424, 3278	72
IIIc	$C_{25}H_{21}N_4Br$	$\frac{12.1}{12.2}$	159	1637	3402, 3278	85
IIId	$C_{24}H_{19}N_5O_2$	$\frac{14.9}{14.8}$	143	1657	3414, 3271	68
IIIe	$C_{24}H_{18}N_4OBrF$	$\frac{11.8}{11.7}$	167	1650	3427, 3291	76
IVa	$C_{25}H_{20}N_4$	$\frac{14.9}{15.0}$	246-247	1612	3403, 3272	56
IVb	$C_{25}H_{19}N_4Br$	$\frac{12.3}{12.2}$	254-255	1619	3407, 3284	52
IVd	$C_{24}H_{17}N_5O_2$	-	317-318 (318 [1])	1640	3447, 3292	75
VIIa	$C_{16}H_{14}N_4$	-	212-213 (213 [1])	1636	3394, 3264	62
VIIb	$C_{17}H_{16}N_4O$	-	214-215 (214 [6])	1636	3400, 3267	66
VIIc	$C_{16}H_{13}N_4Br$	-	197-198 (198 [5])	1640	3400, 3240	61
IX	$C_{19}H_{17}N_4Br$	$\frac{14.8}{14.9}$	228-229	1611	3395, 3272	80
XI	$C_{14}H_{13}N_4Br$	$\frac{17.7}{17.6}$	196-197	1621	3416, 3291	45*^{2}
XII	$C_{19}H_{19}N_4OBr$	$\frac{14.0}{14.0}$	207-208	1618	3407*	29*^{2}
XIII	$C_{27}H_{23}N_4OBr$	$\frac{12.0}{12.1}$	214-215	1614	3310*	91

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* For NH group.

*^{2} Yield of product synthesized by method A.

catalysis (triethylamine or N-methylmorpholine) the products are 7-amino-2,4,5-triaryl-3,4-dihydroimidazo[1,5-b]pyridazines (IIIa-e), while in dimethylformamide, together with compounds IIIa-c, the products of their aromatization (IVa-c) were detected chromatographically. In the case of 4-nitrochalcone IId the corresponding heteroaromatic compound (IVd) was also formed in significant amounts on carrying out the reaction in methanol (ratio of the products IVd : IIId was 2.5 : 1), but in dimethylformamide it was the only product.

Attempts to synthesize compounds III under one-pot conditions by analogy with the synthesis of azoloazine systems [4] using the diamines Ia,c and aromatic aldehydes Va,b, the synthetic precursors of chalcones, and acetophenone (VI) taken in equimolar ratio, were not successful. The sole products in all cases proved to be the hydrazones VIIa-c, which reflects the higher nucleophilicity of the hydrazine amino group of diamines Ia-c.

The structure of the compounds synthesized was in agreement with the results of elemental analysis, and data of ^{1}H NMR and IR spectra (Tables 1 and 2). The structure of dihydroimidazopyridazine IIIb was also confirmed by X-ray structural analysis. The known compounds IVa, VIIa-c were identified by comparing their physicochemical properties with literature data [1,5,6].

In the IR spectra of the compounds IIIa-e (Table 1) absorption bands assigned to the stretching vibrations of the C=N bond (1637-1650) and the NH$_2$ group (3387-3450 and 3270-3291 cm^{-1}) are present, however these bands are also characteristic of the hydrazones VIIa-c.

TABLE 2. ^{1}H NMR Spectral Characteristics of the Compounds Synthesized, δ, ppm, Spin–spin Coupling Constants (*J*), Hz

Compound	4-CH_2 dd	3-CH dd ($J = 2.8$)	NH_2, s	Ar, Ar^1, Ar^2, m	Other protons, s
IIIa	3.15 ($J = 12.0$) 3.33 ($J = 8.1$)	4.95	6.04	7.05-7.89 (14H)	2.26 (CH_3)
IIIb	3.05 ($J = 0.12$) 3.36 ($J = 8.1$)	4.87	5.99	6.93-7.89 (13H)	2.24 (CH_3) 3.78 (OCH_3)
IIIc	3.05 ($J = 12.0$) 3.35 ($J = 8.1$)	4.94	6.07	7.2-7.92 (13H)	2.23 (CH_3)
IIId	3.25 ($J = 14.0$) 3.42 ($J = 8.1$)	5.15	6.21	7.39-8.17 (14H)	—
IIIe	3.18 ($J = 12.0$) 3.45 ($J = 8.1$)	4.85	6.09	6.88-7.49 (12H)	10.22 (OH)
IVd	—	—	6.51	6.86-8.38 (14H)	7.04 (3-H)
VIIa	—	—	6.14	7.49-7.90 (11H)	8.09 (CH=N)
VIIb	—	—	6.07	7.20-8.03 (10H)	3.84 (CH_3) 8.51 (CH=N)
IX	2.57 ($J = 14.0$) 2.90 ($J = 8.1$)	4.69	5.84	7.09-7.42. (9H)	1.97 (CH_3)
XI	—	—	6.01	7.42-7.62 (4H)	6.14 (CH) 2.19 (CH_3) 2.30 (CH_3)
XII	—	—	—	7.54-7.64 (4H)	2.09 (CH_3) 2.19 (CH_3) 2.30 (CH_3) 2.42 (CH_3) 5.47 (CHCO) 6.50 (CH) 13.37 (NH)
XIII	3.30 ($J = 12.0$) 3.45 ($J = 8.1$)	5.11	—	7.80-7.81 (12H)	2.27 (CH_3) 2.37 (CH_3CO)

Clear differences were noted between compounds III and VII in their ^{1}H NMR spectra. The spectra of compounds IIIa-e (in DMSO-d_6) (Table 2) contain signals for an ABX system of protons of the dihydropyridazine ring, absent in spectra of hydrazones VIIa-c, and a multiplet for the protons of the three aromatic nuclei. There was a multiplet signal in the spectra of hydrazones VIIa-c for the protons of two aromatic nuclei and a singlet for the proton on the imidazole ring. Both groups of compounds being considered were characterized by the presence of a broad singlet for the amino group protons in the spectrum; and a singlet signal was observed in the case of hydrazones VIIa-c for the proton of the CH=N group at 8.5-8.7 ppm.

The data of X-ray structural analysis of compound IIIb (Fig. 1, Tables 3, 4) confirm the proposed direction of formation of molecules IIIa-e, i.e. participation of the hydrazine amino group and the carbon atom in position 5 of the imidazole ring in the condensation.

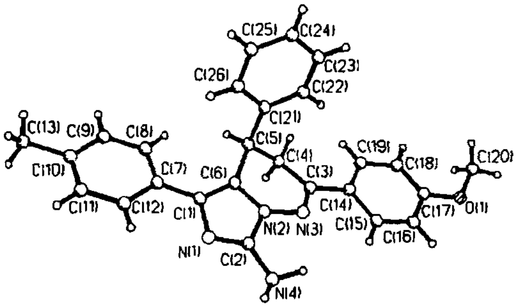

Fig. 1. Structure of compound IIIb.

TABLE 3. Bond Lengths (*d*) in the Compound IIIb Molecule

Bond	*d*, Å	Bond	*d*, Å
$N_{(1)}–C_{(2)}$	1.312(4)	$C_{(10)}–C_{(11)}$	1.375(5)
$N_{(1)}–C_{(1)}$	1.402(4)	$C_{(10)}–C_{(13)}$	1.508(5)
$N_{(2)}–C_{(2)}$	1.358(4)	$C_{(11)}–C_{(12)}$	1.380(5)
$N_{(2)}–C_{(6)}$	1.385(4)	$C_{(14)}–C_{(19)}$	1.381(4)
$N_{(2)}–N_{(3)}$	1.375(3)	$C_{(14)}–C_{(15)}$	1.400(4)
$N_{(3)}–C_{(3)}$	1.293(4)	$C_{(15)}–C_{(16)}$	1.371(5)
$N_{(4)}–C_{(2)}$	1.368(4)	$C_{(16)}–C_{(17)}$	1.382(5)
$C_{(1)}–C_{(6)}$	1.376(4)	$C_{(17)}–O_{(1)}$	1.364(4)
$C_{(1)}–C_{(7)}$	1.470(4)	$C_{(17)}–C_{(18)}$	1.373(5)
$C_{(3)}–C_{(14)}$	1.474(4)	$C_{(18)}–C_{(19)}$	1.394(4)
$C_{(3)}–C_{(4)}$	1.512(4)	$C_{(20)}–O_{(1)}$	1.413(5)
$C_{(4)}–C_{(5)}$	1.524(4)	$C_{(21)}–C_{(26)}$	1.380(5)
$C_{(5)}–C_{(6)}$	1.507(4)	$C_{(21)}–C_{(22)}$	1.383(5)
$C_{(5)}–C_{(21)}$	1.533(4)	$C_{(22)}–C_{(23)}$	1.386(5)
$C_{(7)}–C_{(8)}$	1.382(5)	$C_{(23)}–C_{(24)}$	1.362(6)
$C_{(7)}–C_{(12)}$	1.390(5)	$C_{(24)}–C_{(25)}$	1.369(6)
$C_{(8)}–C_{(9)}$	1.386(5)	$C_{(25)}–C_{(26)}$	1.373(5)
$C_{(9)}–C_{(10)}$	1.376(5)		

The pyridazine ring has the conformation of a distorted sofa. The deviations of the $C_{(5)}$ and $C_{(6)}$ atoms from the mean-square plane of $C_{(4)}$, $C_{(3)}$, $N_{(3)}$, and $N_{(2)}$ atoms are 0.74 and 0.21 Å respectively. The substituent at the saturated carbon atom has a pseudoaxial orientation [torsion angle $C_{(1)}–C_{(6)}–C_{(5)}–C_{(21)}$ is -84.3(3)°].

The orientation of the aryl substituents at atoms $C_{(1)}$ and $C_{(3)}$ and also the bond lengths of $C_{(1)}–C_{(7)}$ 1.470(4) and $C_{(3)}–C_{(14)}$ 1.474(4) Å indicate the presence of conjugation between the π-systems of the benzene rings and the imidazopyridazine fragment [torsion angles $C_{(6)}–C_{(1)}–C_{(7)}–C_{(8)}$ 5.5(5)° and $N_{(3)}–C_{(3)}–C_{(14)}–C_{(15)}$ 10.1(4)°]. Such a disposition of aryl substituents apart from the effects of conjugation is favored also by the attraction interactions $N_{(1)}\cdots H_{(12)}$ (distance 2.49 Å, sum of the van der Waals radii 2.66 Å [7]) and $N_{(3)}\cdots H_{(15)}$ (2.46 Å).

The amino group has a trigonal-pyramidal structure (sum of the valence angles at $N_{(4)}$ atom is 343°) and is conjugated with the π-system of the imidazole ring [$N_{(4)}–C_{(2)}$ bond length is 1.368(4) Å].

The molecules of the compound IIIb form centrosymmetrical dimers in the crystal due to hydrogen bonds ($N_{(4)}–H_{(4NA)}\cdots N_{(1')}$ (1-x, 1-y, -z) (N···H 2.12 Å, N–H...N' 170°).

Together with the chalcones IIa-e benzylideneacetone (VIII) was reacted with diamine Ic and led to the formation of dihydropyridazine IX, the structure of which was confirmed by IR and ^{1}H NMR spectrometry (Tables 1, 2). The best results were obtained on carrying out the reaction in acetic acid.

The structure of imidazo[1,2-b]1,2,4-triazepine was assigned in [8] to the products of interaction of diamine Ia with 1,3-diarylpropenones. Analogous structures were proposed in [9, 10] devoted to the study of the interaction of diamine Ia with β-diketones. The formation of imidazo[1,5-b]pyridazine systems by the reaction of diamine Ia with β-diketones and β-keto esters was described in [11].

We reproduced the conditions described previously in [9-11] for the interaction of ketone X and diamine Ic. Products XI and XII were isolated from the reaction mixture. Compound XI was identified as imidazo[1,5-b]-pyridazine and compound XII – as the product of its condensation with second molecule of acetylacetone (peaks of the molecular ions M$^+$ 400/398 were observed in the mass spectrum).

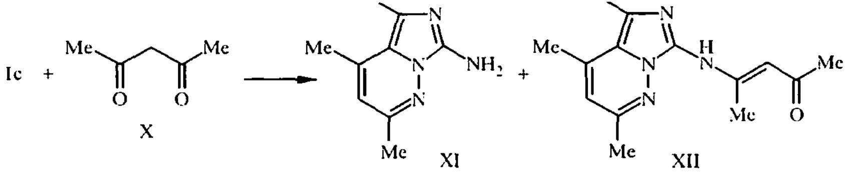

TABLE 4. Valence Angles (ω) in the Compound IIIb Molecule

Angle	ω, deg	Angle	ω, deg
$C_{(2)}$–$N_{(1)}$–$C_{(1)}$	105.5(2)	$C_{(8)}$–$C_{(9)}$–$C_{(10)}$	122.1(3)
$C_{(2)}$–$N_{(2)}$–$C_{(6)}$	108.5(2)	$C_{(11)}$–$C_{(10)}$–$C_{(9)}$	116.2(3)
$C_{(2)}$–$N_{(2)}$–$N_{(3)}$	122.9(2)	$C_{(11)}$–$C_{(10)}$–$C_{(13)}$	121.9(3)
$C_{(6)}$–$N_{(2)}$–$N_{(3)}$	128.5(2)	$C_{(9)}$–$C_{(10)}$–$C_{(13)}$	121.9(3)
$C_{(3)}$–$N_{(3)}$–$N_{(2)}$	115.7(2)	$C_{(10)}$–$C_{(11)}$–$C_{(12)}$	122.3(3)
$C_{(6)}$–$C_{(1)}$–$N_{(1)}$	110.1(3)	$C_{(11)}$–$C_{(12)}$–$C_{(7)}$	121.7(3)
$C_{(6)}$–$C_{(1)}$–$C_{(7)}$	130.8(3)	$C_{(19)}$–$C_{(14)}$–$C_{(15)}$	117.2(3)
$N_{(1)}$–$C_{(1)}$–$C_{(7)}$	119.1(3)	$C_{(19)}$–$C_{(14)}$–$C_{(3)}$	122.5(3)
$N_{(1)}$–$C_{(2)}$–$N_{(2)}$	111.4(2)	$C_{(15)}$–$C_{(14)}$–$C_{(3)}$	120.3(3)
$N_{(1)}$–$C_{(2)}$–$N_{(4)}$	127.3(3)	$C_{(16)}$–$C_{(15)}$–$C_{(14)}$	121.0(3)
$N_{(2)}$–$C_{(2)}$–$N_{(4)}$	121.2(3)	$C_{(15)}$–$C_{(16)}$–$C_{(17)}$	120.8(3)
$N_{(3)}$–$C_{(3)}$–$C_{(14)}$	116.3(3)	$O_{(1)}$–$C_{(17)}$–$C_{(18)}$	124.7(3)
$N_{(3)}$–$C_{(3)}$–$C_{(4)}$	121.9(3)	$O_{(1)}$–$C_{(17)}$–$C_{(16)}$	115.7(3)
$C_{(14)}$–$C_{(3)}$–$C_{(4)}$	121.7(3)	$C_{(18)}$–$C_{(17)}$–$C_{(16)}$	119.5(3)
$C_{(3)}$–$C_{(4)}$–$C_{(5)}$	113.0(2)	$C_{(17)}$–$C_{(18)}$–$C_{(19)}$	119.4(3)
$C_{(6)}$–$C_{(5)}$–$C_{(4)}$	106.6(2)	$C_{(14)}$–$C_{(19)}$–$C_{(18)}$	122.0(3)
$C_{(6)}$–$C_{(5)}$–$C_{(21)}$	110.8(2)	$C_{(26)}$–$C_{(21)}$–$C_{(22)}$	117.2(3)
$C_{(4)}$–$C_{(5)}$–$C_{(21)}$	114.0(3)	$C_{(26)}$–$C_{(21)}$–$C_{(5)}$	119.6(3)
$C_{(1)}$–$C_{(6)}$–$N_{(2)}$	104.5(3)	$C_{(22)}$–$C_{(21)}$–$C_{(5)}$	123.2(3)
$C_{(1)}$–$C_{(6)}$–$C_{(5)}$	140.6(3)	$C_{(21)}$–$C_{(22)}$–$C_{(23)}$	120.8(4)
$N_{(2)}$–$C_{(6)}$–$C_{(5)}$	114.4(3)	$C_{(24)}$–$C_{(23)}$–$C_{(22)}$	121.0(4)
$C_{(8)}$–$C_{(7)}$–$C_{(12)}$	115.9(3)	$C_{(25)}$–$C_{(24)}$–$C_{(23)}$	118.6(4)
$C_{(8)}$–$C_{(7)}$–$C_{(1)}$	124.3(3)	$C_{(24)}$–$C_{(25)}$–$C_{(26)}$	120.8(4)
$C_{(12)}$–$C_{(7)}$–$C_{(1)}$	119.8(3)	$C_{(21)}$–$C_{(26)}$–$C_{(25)}$	121.5(4)
$C_{(7)}$–$C_{(8)}$–$C_{(9)}$	121.8(3)	$C_{(17)}$–$O_{(1)}$–$C_{(20)}$	118.2(3)

The structure of ketone XII was confirmed by independent synthesis. Boiling imidazopyridazine XI in acetylacetone leads to the formation of the product XII.

The data of IR and ^{1}H NMR spectra indicate the existence of compound XII in the form of enamino ketone (see Experimental) which is not at variance with the results of [12].

The obtained data are therefore in agreement with the results of [11] and indicate that on reacting diamines Ia-c with β-diketones and chalcones they behave as typical 1,3-dinucleophiles.

A partial aromatization of the products III takes place on reacting amines Ia-c with chalcones IIa-e in dimethylformamide. The same process was observed on continuous heating of compounds III in high-boiling solvents (DMSO, pyridine). Efficient aromatization of compounds IIIa-e also occurs in sulfur–pyridine system. Aromatization was not observed on using bromine–acetic acid system. The acyl derivative XIII was obtained in high yield on boiling compound III in acetic anhydride (see Tables 1,2).

EXPERIMENTAL

The IR spectra were recorded on a Specord IR 75 spectrometer in KBr disks. The ^{1}H NMR spectra were taken on a Bruker AM-300 spectrometer, internal standard was TMS, and solvent DMSO-d_6. Mass spectra were obtained with a Finnigan MAT 4651P instrument under standard conditions. The homogeneity of compounds was checked by TLC on Silufol UV 254 plates, eluent was ethyl acetate.

X-Ray Structural Investigation of Compound IIIb. Crystals of dihydroimidazopyridazine IIIb ($C_{26}H_{24}N_4O$) are monoclinic. Unit cell parameters at 20°C: a = 14.016(3), b = 6.604(1), c = 22.841(4) Å; β = 91.86(2)°; V = 2113.1(6) Å^3; d_{calc} = 1.284 g/cm^3; space group $P2_{1/n}$; Z = 4. The parameters of the unit cell and the intensities of 2929 independent reflections (R_{int} = 0.038) were measured on a Siemens P3/PC automatic four-circle diffractometer (λMoKα, graphite monochromator, θ/2θ scanning, $2\theta_{max}$ = 50°). The structure was solved by the direct method using the SHELXTL PLUS complex of programs [13]. The positions of the hydrogen atoms were calculated geometrically and refined according to a rider model with fixed $U_{iso} = nU_{eq}$ for the non-hydrogen atom bound to the given hydrogen atom (n = 1.5 for methyl groups and 1.2 for the other hydrogen atoms). Refinement according to F^2 by a full-matrix least-squares method in anisotropic approach for 2514 reflections for non-hydrogen atoms was carried out to $wR_2 = 0.163$ [$R_1 = 0.063$ for 2216 reflections with $F > 4\sigma(F)$, $S = 0.99$]. The final coordinates of nonhydrogen atoms are given in Table 3.

7-Amino-2,4-diphenyl-5-(*p*-tolyl)-3,4-dihydroimidazo[1,5-*b*]pyridazine (IIIa). A. Mixture of diamine Ib (0.4 g, 2.1 mmol) and 1,3-diphenylpropenone IIa (0.44 g, 2.1 mmol) in methanol (25 ml) containing methylmorpholine (0.3 ml) was boiled for 14 h. The precipitated solid was crystallized from methanol. Yellow crystals of product IIIa (0.76 g) were obtained.

B. A mixture of diamine Ib (0.4 g, 2.1 mmol) and 1,3-diphenylpropenone IIa (0.44 g, 2.1 mmol) in dimethylformamide (0.4 ml) was boiled under reflux for 1 h. The precipitated solid was crystallized from methanol. Yellow crystals of product IIIa (0.65 g, 73%) were obtained.

Compounds IIIb-e were obtained by analogous methods from diamines Ia-c and appropriate diarylpropenones.

7-Amino-4-(*p*-nitrophenyl)-2,5-diphenylimidazo[1,5-*b*]pyridazine (IVd). Solution of dihydroimidazopyridazine IIId (0.4 g, 1 mmol) in dimethylformamide (2 ml) was boiled under reflux for 2 h. After cooling, acetone (30 ml) was poured into the reaction mixture, which was then kept at room temperature for 16 h, and product IVd (0.3 g) filtered off.

Products IVa,c were obtained by an analogous procedure by boiling compounds IIIa,c in pyridine.

2-Amino-1-benzylideneamino-4-phenylimidazole (VIIa). Mixture of diamine Ia (0.4 g, 0.23 mmol), benzaldehyde Va (0.25 ml, 0.23 mmol), acetophenone (0.3 ml, 0.23 mmol), and DMF (0.4 ml) was boiled for 1 h. After cooling, acetone (20 ml) was poured into the reaction mixture, and product VIIa (0.5 g) was filtered off.

Products VIIb,c were obtained by an analogous procedure from diamine Ia,c and the appropriate benzaldehyde Va,b.

Mixed test samples of products VIIa-c synthesized by the procedure described above and by the procedure of [6] gave no depression of melting point.

7-Acetylamino-4-(*p*-bromophenyl)-2-phenyl-5-(p-tolyl)-3,4-dihydroimidazo[1,5-*b*]pyridazine (XIII). Solution of compound IIIc (0.2 g, 1 mmol) in acetic anhydride (5 ml) was boiled for 2 h. The solid which precipitated on cooling was filtered off and product XIII (0.23 g, 91%) was obtained.

7-Amino-5-(*p*-bromophenyl)-2-methyl-4-phenyl-3,4-dihydroimidazo[1,5-*b*]pyridazine (IX). Solution of diamine Ic (0.4 g, 1.5 mmol) and ketone VIII (0.22 g, 1.5 mmol) in glacial acetic acid (3 ml) was heated for 2 h on a boiling water bath, cooled, and water (2 ml) poured in. The precipitated solid was crystallized from ethanol (15 ml). Compound IX (0.45 g) was obtained.

7-Amino-5-(*p*-bromophenyl)-2,4-dimethylimidazo[1,5-*b*]pyridazine (XI) and 5-(*p*-Bromophenyl)-2,4-dimethyl-7-[(4-oxo-2-pent-2-enyl)amino]imidazo[1,5-*b*]pyridazine (XII). A. Solution of diamine I (0.4 g, 1.5 mmol) in acetylacetone X (0.8 ml, 8 mmol) was heated on a boiling water bath for 40 min, then diluted with ethanol (10 ml). The mixture of compounds XI and XII which precipitated on cooling was separated by crystallization. Product XI (0.2 g) and product XII (0.5 g) were obtained. Mass spectrum of compound XII (m/z, I_{rel}, %): 400 (M^+, 14), 398 (M^+, 18), 357 (9), 318 (76), 316 (80), 196 (9), 165 (21), 152 (12), 135 (26), 134 (100), 126 (15), 118 (24), 108 (29).

B. The compound XII was also obtained by heating solution of pyridazine XI (0.2 g, 0.7 mmol) in acetylacetone (0.5 ml) on a boiling water bath for 3 h. After cooling, methanol (10 ml) was added to the reaction mixture, and product XII (0.2 g, 73%) was filtered off.

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