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CONDENSED IMIDAZO-1,2,4-AZINES. 31*. SYNTHESIS AND CHEMICAL TRANSFORMATIONS OF SUBSTITUTED 1,2,4-TRIAZEPINO[2,3-*a*]BENZIMIDAZOLES

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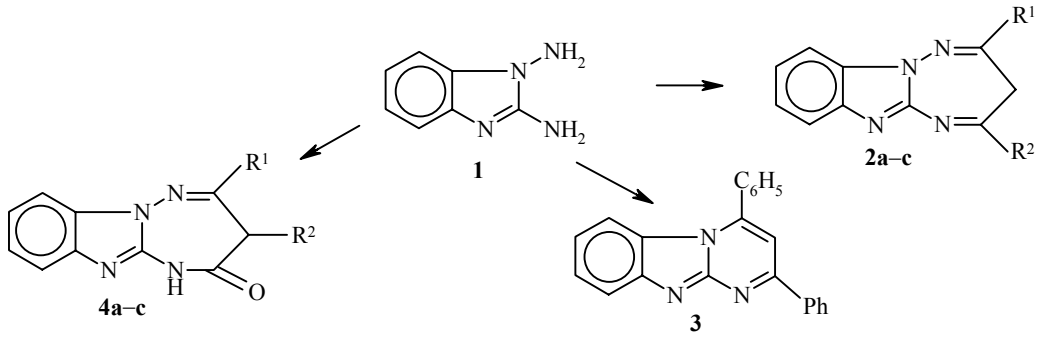
By reaction of 1,2-diaminobenzimidazole with 1,3-diketones, acetoacetic ester and its derivatives, we have synthesized substituted 1,2,4-triazepino[2,3-a]benzimidazole and 5H-1,2,4-triazepino[2,3-a]-benzimidazol-4-one. By reaction of 5H-2-methyl-1,2,4-triazepino[2,3-a]benzimidazol-4-one with aromatic aldehydes or phenyldiazonium chloride, we have obtained 3-arylidene(phenylazo) derivatives of this compound, and by reaction with P_2S_5 we have obtained 5H-2-methyl-1,2,4-triazepino[2,3-a]-benzimidazole-4-thione. We have shown that when reacted with ammonia, primary or secondary amines, the latter forms 4-amino-substituted 2-methyl-1,2,4-triazepino[2,3-a]benzimidazole.

Keywords: 1,2-diaminobenzimidazole, dinucleophilic reagents, 1,2,4-triazepino[2,3-*a*]benzimidazole, tautomerism.

Reaction of 1,2-diaminobenzimidazole (**1**) with chalcones in refluxing DMF occurs with elimination of the amino group of the heterocycle, leading to formation of pyrimido[2,3-*a*]benzimidazoles [2]. Continuing a study of reactions of **1** with dinucleophilic reagents [2-4], in this paper we present data on its condensation with 1,3-diketones, acetoacetic ester and its derivatives, and also on the behavior of the synthesized 5H-2-methyl-1,2,4-triazepino[2,3-*a*]benzimidazol-4-one (**4a**) when treated with electrophilic and nucleophilic reagents.



2a,b, **4a,b** R^1 = Me, **2c** R^1 = Ph, **4c** R^1 = CH_2CO_2Et;
2a R^2 = Me, **2b,c** R^2 = Ph, **4a,c** R^2 = H, **4b** R^2 = Et

* For the previous communication, see [1].

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In studying the conditions for condensation of **1** with pentane-2,4-dione, we found that of all the studied solvents (refluxing in lower alcohols, dioxane, acetic acid, *m*-xylene, polyphosphoric acid (PPA)), the most effective is 1-hexanol with additions of mineral acids. For example, the yield of 2,4-dimethyl-1,2,4-triazepino[2,3-*a*]benzimidazole (**2a**) is 7% in boiling *m*-xylene, 20% in PPA, and 69% in 1-hexanol with hydrochloric acid. In the absence of an acid catalyst, formation of a tricyclic heterosystem in trace amounts (<1%) was observed only by chromatography, while when the reactions were carried out in lower alcohols or dioxane, independent of the presence of mineral acid we recovered the starting compounds from the reaction mixture.

Condensation of diaminobenzimidazole **1** with 4-phenylbutane-2,4-dione or dibenzoylmethane requires more rigid conditions than for pentane-2,4-dione. Synthesis of triazepinobenzimidazoles **2b,c** could be accomplished only on heating the starting compounds in PPA at 110°C-115°C.

The spectral characteristics of the synthesized tricycles **2a-c** are presented in Table 1.

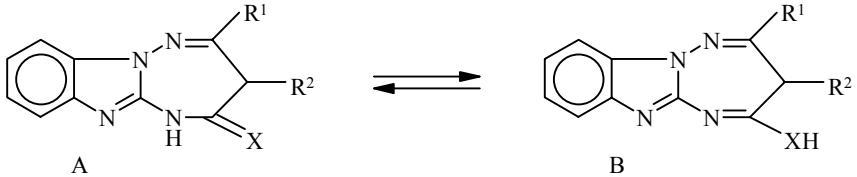
In the mass spectra of triazepinobenzimidazoles **2b,c**, we observe peaks for molecular $[M^+]$ ions of intensity 100% (Table 2) and doubly charged ions $[M^{2+}]$, which suggests a condensed structure for compounds **1b,c** [5]. Decomposition of M^+ under electron impact conditions begins with cleavage of the bonds in the triazepine ring, and proceeds in two main directions. The first direction is associated with successive elimination of two nitrile molecules and formation of the ions $[M\text{-}R^1CN]^+$ (Φ) and $[\Phi\text{-}R^2CN]^+$ (Φ_1). The second direction for decomposition of M^+ is due to cleavage of the species NCR^1CH^2 (the Φ_2 ion). Formation of $\Phi\text{-}\Phi_2$ ions confirms the structure of the triazepine ring, and the fragmentary ions observed in the spectrum with *m*/*z* 118, 117, 103, 90, 77 confirm the structure of the benzimidazole moiety of compounds **2b,c**.

The electronic spectra of compounds **2a-c**, in contrast to the two-band spectrum of compound **1** (λ_{max} 250 nm and 280 nm), are characterized by three absorption maxima (Table 1). The sensitivity of the position of the long-wavelength band to substitution of the methyl radical at the $C_{(4)}$ atom by a phenyl group suggests interaction of π-electrons of the aromatic ring and the multiple bonds of the tricycles **1b,c**, leading to lengthening of the main chromophore.

The reaction of compound **1** with β-diketones under high-temperature condensation conditions leads to different results. Thus when compound **1** is refluxed with dibenzoylmethane in nitrobenzene or when it is heated without a solvent (240°C-250°C) in the presence of $ZnCl_2$, the compound 2,4-diphenylpyrimido[1,2-*a*]-benzimidazole (**3**) is isolated [2, 6]. In this case, as for condensation of compound **1** with chalcones [2], the reaction occurs with elimination of an amine group from the hydrazine moiety of the heterocycle.

When compound **1** is reacted with acetoacetic ester, its ethyl-substituted derivative, or 1,3-diethoxycarbonylacetone, then the corresponding 2-substituted 5H-1,2,4-triazepino[2,3-*a*]benzimidazol-4-ones (**4a-c**) are formed. The reaction proceeds smoothly in boiling acetic acid and, in contrast to synthesis of analogous compounds from 1,2-diaminoimidazoles [7], does not require addition of sodium acetate.

Considering the possibility that lactam–lactim tautomerism exists for compounds **4a-c** (forms A, B), we used physical and chemical investigation methods to estimate the position of the tautomeric equilibrium A⇄B in different aggregate states

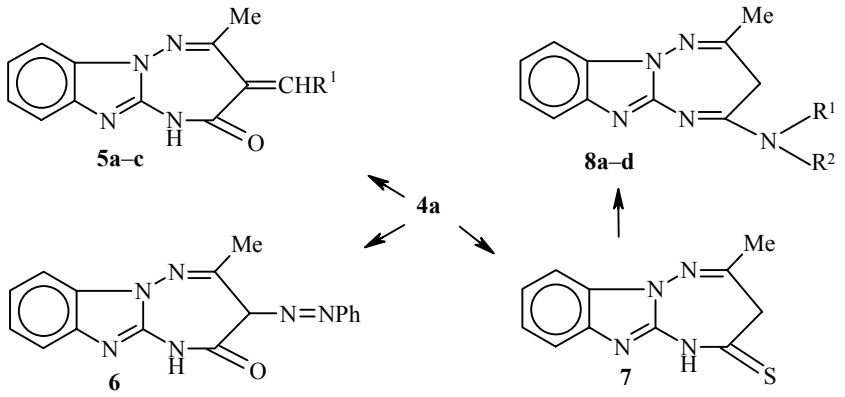


X = O, S, N

We showed earlier [8] that in the IR spectra (in KBr tablets) of tricycles **4a,c**, we observe absorption bands from carbonyl and imine groups of the triazepine ring, which are evidence that compounds **4a,c** in crystalline form exist predominantly in the lactam form A.

In the ^{1}H NMR spectra of solutions of heterocycles **4a,b** in DMSO-d_6 (Table 1), in addition to signals characterizing the structure of the substituents, we observe resonance from the proton of the imine group. The absence of signals from the proton of the hydroxyl group in the spectra provides a basis for saying that in solution, as in the crystalline state, form A is characteristic for compounds **4a,c**.

Analysis of the mass spectra of lactams **4a,c** showed that the fragmentation pattern under electron impact conditions is somewhat different from that described above.



5 a R^1 = Ph , **b** R^1 = 4-$MeOC_6H_4$, **c** R^1 = 4-$O_2NC_6H_4$; **8 a** $R^1 = R^2$ = H;
b R^1 = H, R^2 = CH_2Ph; **c** R^1+R^2 = $CH_2(CH_2)_3CH_2$; **d** R^1+R^2 = $(CH_2)_2O(CH_2)_2$

Only in compound **4a**, analogously to tricycles **2b,c** and 5H-imidazo[1,2-*c*]-1,2,4-triazepin-4-ones [7], do we observe cleavage of acetonitrile in the initial stages of decomposition of M^+, leading to the Φ ion. The lactams **4b,c** initially lose a CO (the Φ ion), and only then the formation of the $[\Phi\text{-}R^1CN]^+$ ion occurs. Moreover, along with the fragmentation scheme for M^+ of triazepinobenzimidazolones **4a,b** on the whole is general and is characterized by (in addition to the indicated ions) Φ_1-$[M\text{-}COH]^+$, Φ_2-$[M\text{-}HNCO]^+$, Φ_3-$[M\text{-}CHR^2CO]^+$, and Φ_4-$[M\text{-}NCR^1CR^2CO]^+$, which confirm the structure of the 1,2,4-triazepine ring. The formation of the Φ-Φ_4 ions directly from M^+ is demonstrated by the mass spectra of the metastable ions (DADI technique, "direct analysis of daughter ions") [9]. Additional confirmation of the nature and position of the substituent R^2 in the molecule of tricycle **4b** comes from the ion peaks for Φ_5-$[\Phi\text{-}C_2H_5]^+$, Φ_6-$[M\text{-}C_2H_5CHCO]^+$, and Φ_7-$[(\Phi\text{-}CH_3CN)\text{-}C_2H_4]^+$ observed in the spectrum.

The presence of a labile ester group in the 2-ethoxycarbonylmethyl-substituted tricycle **4c** results in changes in the fragmentation scheme for its M^+, where along with formation of Φ and Φ_4 ions, there are charged fragments illustrating the structure of the substituent at the $C_{(2)}$ atom: Φ_5-$[M\text{-}COOC_2H_4]^+$, Φ_6-$[M\text{-}COOC_2H_5]^+$, and Φ_7-$[(M\text{-}COOC_2H_5)\text{-}H]^+$. Detection of ions with *m*/*z* 118, 117, 105, 104, 91, 90, and 77 confirms the structure of the benzimidazole moiety of the molecule for lactams **4a-c**.

A typical feature of the mass spectra of compounds **4a,b** is elimination of a COH from M^+. Formation of $[M\text{-}OH]^+$ ions indicates predominance of the lactim form B of tricycles **4a-c** in the gas phase. Comparison of the intensities of individual $[M\text{-}CO]^+$ and $[M\text{-}COH]^+$ ions of compounds **4a,b** makes it possible to make a quantitative estimate of the tautomeric forms A and B [9, 10]. According to these calculations, the fraction of tautomeric form B in tricycles **4a,b** is ~36% and 50% respectively.

Triazepinobenzimidazol-4-one **4a** proved to be quite reactive. When lactam **4a** and aromatic aldehydes are reacted in boiling 1-butanol with addition of piperidine, then 5H-3-arylidene-2-methyl-1,2,4-triazepino-[2,3-*a*]benzimidazol-4-ones **5a-c** are synthesized; and upon azo coupling of lactam **4a** with phenyldiazonium chloride in dioxane, 3-phenylazo-substituted tricycle **6** is formed.

In the ^{1}H NMR spectra of compounds **5a-c, 6**, the signals for methylene protons are missing, which together with the resonance for protons of the methyl group (Table 1) confirms that the methylene moiety of tricycle **4a** participates in the condensation and azo coupling.

TABLE 1. Characteristics of the Syntesized Compounds

Compound	Empirical formula	Found, % / Calculated, %			mp, °C*	^{1}H NMR spectrum (CF_3COOH), δ, ppm*[2]			UV spectrum, λ_{max}, nm (log ε)	Yield, %
		C	H	N		H_{arom}, m	CH_2, s	CH_3, s		
1	2	3	4	5	6	7	8	9	10	11
2a	$C_{12}H_{12}N_4$	68.11 67.90	5.89 5.70	26.22 26.40	204-205	7.15	3.30	2.13	280 (4.45), 305 (3.95), 390 (2.84)	69
2b	$C_{17}H_{14}N_4$	74.62 74.43	5.12 5.14	20.51 20.43	200-201	6.94	3.39	2.15	285 (4.40), 325 (3.85), 410 (2.92)	61
2c	$C_{22}H_{16}N_4$	78.36 78.55	4.72 4.79	16.48 16.66	268-269	6.89	4.00	—	285 (4.40), 335 (3.90), 410 (2.98)	71
4a	$C_{11}H_{10}N_4O$	61.80 61.67	4.81 4.71	25.97 26.0	281-282	7.16*[2]	3.50	2.17	250 (4.32), 285 (4.05)	72
4b	$C_{13}H_{14}N_4O$	64.62 64.45	5.66 5.82	23.22 23.20	254-255	6.97*[2]	3.55, t	2.17 2.32, t	250 (4.17), 282 (3.92)	68
4c	$C_{14}H_{14}N_4O_3$	58.84 58.74	4.83 4.93	19.42 19.57	227-228				260 (4.36), 290 (4.05)	64
5a	$C_{18}H_{14}N_4O$	71.51 71.81	4.67 4.77	18.53 18.29	258-259	7.19	—	2.02	278 (4.09), 320 (3.70)	67

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11
5b	$C_{19}H_{16}N_4O$	68.80 68.54	5.18 5.02	16.52 16.83	275-276	6.98	—	2.08 3.48	260 (4.08), 320 (4.20)	65
5c	$C_{18}H_{13}N_5O_3$	62.51 62.25	3.64 3.77	20.04 20.16	270-271	7.24	—	2.17	250 (4.13), 320 (4.11)	59
6	$C_{17}H_{13}N_6O$	64.42 64.36	4.34 4.13	26.37 26.49	273-274	6.90	—	2.22	240 (3.96), 275 (3.89), 387 (4.09)	64
7	$C_{11}H_{10}N_4S$	57.48 57.37	4.63 4.38	24.02 24.33	247-248	7.16	3.77	2.08	274 (4.22), 325 (4.33)	69
8a	$C_{11}H_{11}N_5$	62.04 61.96	5.43 5.20	33.04 32.84	269-271				250 (4.31), 310 (4.53)	61
8b	$C_{18}H_{17}N_5$	71.53 71.29	5.51 5.61	23.00 23.10	264-265	7.10 6.84	3.27 4.27	2.05	260 (4.64), 310 (4.55)	68
8c	$C_{16}H_{19}N_5$	68.20 68.30	7.01 6.81	25.21 24.89	204-205	7.04*[3]	3.38	2.07	260 (4.54), 315 (4.51)	53
8d	$C_{15}H_{17}N_5O$	63.38 63.59	6.21 6.05	24.80 24.72	234-235	7.11*[4]	3.30	2.08	255 (4.27), 310 (4.42)	57

* The compounds were recrystallized as follows: **2a, 8b,d** – from toluene; **2b,c, 4a,b, 5b, 6, 7** – from DMF; **4c, 8a** – from ethanol; **4a,b** – from aqueous DMF; **7b** – from 1-butanol.

*[2] ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: **4a** 8.84 (1H, br. s, NH); 7.39 (4H, m, H_{arom}); 3.55 (2H, s, CH_2); 2.41 (3H, s, CH_3); **4b** – 8.92 (1H, br. s, NH); 7.42 (4H, m, H_{arom}); 5.62 (1H, s, 4-CH); **8b** – 8.68 (1H, br. s, NH); 7.19 (9H, m, H_{arom}); 4.45 (2H, d, CH_2–N); 2.18 (3H, s, CH_3).

*[3] Signals from the piperidine moiety, δ, ppm: 3.56 (4H, m, $(CH_2)_2N$); 1.40 (6H, m, $(CH_2)_3$).

*[4] Signals from the morpholine moiety, δ, ppm: 3.94 (4H, br. m, $(CH_2)_2O$); 3.52 (4H, br. m, $(CH_2)_2N$).

TABLE 2. Mass Spectra of Compounds **2b,c**, **4a-c** (Ion Peaks with Intensity ≥10% Relative to I_{max} are Given)

Com-pound	*m/z* (I_{rel}, %)							
	$[M+1]^+$	M^+	Φ	$Φ_1$	$Φ_2$	$Φ_3$	$Φ_4$	other ions
2b	275 (12)	274 (100)	233 (34)	130 (17)	219 (37)	—	—	M^{2+} – 137 (11), 129 (41), 118 (17), 117 (12), 103 (20), 90 (11), 77 (24)
2c	337 (13)	336 (100)	233 (31)	130 (12)	219 (13)	—	—	M^{2+} – 168 (14), 234 (62), 129 (35), 118 (11), 117 (28), 103 (31), 90 (10), 77 (51)
4a	215 (14)	214 (100)	173 (12)	185 (19)	171 (13)	172 (21)	132 (25)	$[M - CO]^+$ – 186 (34), $[M-COH]^+$ – 185 (19), $[Φ - CO]^+$ – 145 (26), 131 (27), 118 (82), 117 (28), 105 (39), 104 (38), 91 (14), 90 (59), 77 (41)
4b	243 (15)	242 (100)	214 (13)	213 (13)	199 (16)	172 (23)	132 (24)	$Φ_5$ – 185 (20), $[Φ - CH_3CN]^+$ – 173 (15), $Φ_6$ – 172 (23), $Φ_7$ – 145 (10), 118 (52), 117 (23), 105 (14), 104 (20), 90 (43), 77 (21)
4c	287 (11)	286 (68)	258 (10)	—	—	—	132 (25)	$Φ_5$ – 214 (14), $Φ_6$ – 213 (17), $Φ_7$ – 212 (16), $[Φ_5 - HCO]^+$ – 185 (28), $[Φ - NCR^1]^+$ –145 (12), $[Φ - HNCR^1]^+$ – 144 (12), 118 (89), 117 (29), 105 (28), 104 (29), 91 (24), 90 (100), 77 (38), 67 (47)

A characteristic feature of the UV spectra of triazepinobenzimidazolones **4a-c, 6** is a bathochromic shift of the long-wavelength maximum compared with the spectrum of lactam **4a**; and in the case of azo compound **6**, we observe an additional band associated with absorption of the azo group. In subsequent experiments, we observed that triazepinobenzimidazolone **4a** enters into a thionylation reaction. When compound **4a** is treated with phosphorus pentasulfide in boiling dioxane or pyridine, its thio analog **7** is obtained. The reaction proceeded most efficiently when lactam **4a** was refluxed with a two-fold excess of P_2S_5 in dry dioxane.

The ^{1}H NMR spectral data (Table 1) confirm the structure of the synthesized compound **6**, and the absorption bands observed in the IR spectrum for the C=S bond and the ring imine group (see the experimental section) suggest predominance of the thione form A.

Thione **5** enters into a nucleophilic substitution reaction with ammonia and amines. When compound **7** is refluxed with ammonia, benzylamine, piperidine, or morpholine, we obtain 4-amino-substituted tricycles **8a-d**.

Missing in the IR spectra of the substitution products of **8a-d** is the absorption band for the C=S bond, which is specific for the spectrum of the starting thione **7.** The ν_{NH} absorption in the 3370-3390 cm^{-1} region is characteristic for the IR spectra of compounds **8a,b** and is observed in the spectrum of lactam **4a** [8] and its thio analog **7**. Such a similarity shows that the considered compounds **8a,c** are found in the imine A form.

The ^{1}H NMR spectra of compounds **8b-d** (Table 1) are consistent with the proposed structure.

An attempt to carry out the reaction of hydrazine hydrate with thione **6** led to decomposition of the heterocycle, the major product of which was the diamine **1**. The reason for such decomposition is not the reducing properties of the hydrazine hydrate, but rather the alkaline medium created when it is present. Confirmation of this comes from decomposition of thione **7** on refluxing in a 5% sodium hydroxide solution. In this case, compound **1** is isolated in practically quantitative yield.

Thus when reactions of compound **7** are carried out using basic reagents, a preliminary estimate of their destructive effect on the heterocycle is required. Investigations of biological activity showed that compounds **4a,b** have slight muscle relaxant action, **4c** has moderate anticonvulsive activity, **5c** has antimicrobial properties, while tricycles **7, 8a** exhibit slight antiviral activity.

EXPERIMENTAL

The IR spectra were recorded on an IKS-22 in KBr tablets; the NMR spectra were recorded on Bruker WH-90 (90 MHz) and Tesla BS-487C spectrometers in DMSO-d_6 (TMS) and CF_3COOH (HMDS). The electron absorption spectra were taken on an SF-46 spectrophotometer in dioxane for a concentration of the compounds equal to $0.2\text{-}0.4\cdot10^{-4}$ mol/l. The mass spectra were obtained on a Finnigan HSQ-30 spectrometer with direct injection of samples into the ion source.

2,4-Dimethyl-1,2,4-triazepino[2,3-*a*]benzimidazole (2a). A solution of 1,2-diaminobenzimidazole [11] (0.45 g, 3 mmol), pentane-2,4-dione (0.4 g, 4 mmol), and conc. HCl (3 drops) in 1-hexanol (40 ml) was refluxed for 4 h. The solution was evaporated down under vacuum to 1/2 volume; the residue formed was filtered out, washed with cold toluene, and dried.

2-Methyl(phenyl)-4-phenyl-1,2,4-triazepino[2,3-*a*]benzimidazoles (2b,c). A mixture of compound **1** (0.6 g, 4 mmol), the corresponding β-diketone (4 mmol), and PPA (7 ml) was stirred for 1.5 h at 110-115°C. The reaction mixture was cooled down and poured over ice (70 g); the precipitate was filtered out and suspended in water (50 ml) and then a 10% $NaHCO_3$ solution was added until pH ~8 was reached, and then it was allowed to stand for 2 h. The suspension was filtered and the residue was washed with water and dried.

2,4-Diphenylpyrimido[1,2-*a*]benzimidazole (3). A. A mixture of compound **1** (0.9 g, 6 mmol), dibenzoylmethane (1.46 g, 6.5 mmol), and anhydrous $ZnCl_2$ (1.1 g) was heated for 1.5 h at 240-250°C. After cooling the fusion cake was triturated, a 40% NaOH solution (20 ml) was added, and it was extracted with

benzene (6×50 ml). The benzene extracts were combined, evaporated down under vacuum until a precipitate was obtained, then they were cooled down and the precipitate was filtered out and crystallized from DMF. Yield 1.0 g (48%); mp 312-315°C.

B. A solution of dibenzoylmethane (0.6 g, 4 mmol) in nitrobenzene (5 ml) was refluxed for 5 h, and after cooling the precipitate was filtered out. Yield 0.4 g (31%); mp 312-315°C (DMF), matches the data in [6].

Substituted 5H-1,2,4-triazepino[2,3-*a*]benzimidazol-4-one (4a-c). The corresponding acetoacetic ester or 1,3-diethoxycarbonylacetone (6 mmol) were added to a solution of compound **1** (0.6 g, 4 mmol) in acetic acid (30 ml), and then refluxed for 3 h. The reaction mixture was cooled; then the residue was filtered out, washed with ethanol, and dried.

5H-3-Arylidene-2-methyl-1,2,4-triazepino[2,3-*a*]benzimidazol-4-one (5a-c). A solution of compound **4a** (0.43 g, 2 mmol) and the corresponding aldehyde (2.1 mmol) in 1-butanol (40 ml) with 3 drops of piperidine was refluxed for 30 min. The reaction mixture was evaporated down under vacuum until a precipitate appeared; then it was cooled down and the precipitate was filtered out, washed with ethanol, and dried.

5H-2-Methyl-3-phenylazo-1,2,4-triazepino[2,3-*a*]benzimidazol-4-one (6). A solution of phenyldiazonium salt (2.3 mmol) was added with stirring to a solution of triazepinobenzimidazolone **4a** (0.43 g, 2 mmol) in DMF (75 ml) and then held for 3 h at a temperature of 18-20°C. The solution was diluted with water (5 ml) and the precipitated orange crystals were filtered out and dried. IR spectrum, ν, cm^{-1}: 3390-3415 (NH), 1710 (C=O), 1430 (N=N).

5H-2-Methyl-1,2,4-triazepino[2,3-*a*]benzimidazole-4-thione (7). A mixture of tricycle **4a** (0.64 g, 3 mmol), P_2S_5 (0.67 g, 3 mmol) in dry pyridine (40 ml) was refluxed for 4 h. The solution was cooled down; then the precipitate was filtered out, washed successively with water, dioxane, and water, and then dried. IR spectrum, ν, cm^{-1}: 3375-3400 (NH), 1155 (C=S).

4-Amino-substituted 2-Methyl-1,2,4-triazepino[2,3-*a*]benzimidazole (8a-d). Conc. ammonia (0.7 ml) or the corresponding amine (0.3 mmol) was added to a solution of thione **7** (0.58 g, 2.5 mmol) in 2-propanol (30 ml) and then was refluxed for 6 h. The solution was concentrated down at reduced pressure until a precipitate appeared, and then was filtered.

Degradation of 5H-2-methyl-1,2,4-triazepino[2,3-*a*]benzimidazole-4-thione (7). A solution of thione **6** (0.64 g, 3 mmol) in a 5% solution of potassium hydroxide (15 ml) was refluxed for 1 h and cooled down; the precipitate was filtered out and washed with water. Obtained 0.45 g (99%) of compound **1**; mp 255-257°C (water), which matches data in [11].

When compound **6** (3 mmol) was refluxed with 70% hydrazine hydrate (4 mmol) in 2-propanol (30 ml), the yield of compound **1** was 0.37 g (81%).

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