RING CONTRACTION OF THIA(SELENO)DIAZINE RINGS INTO PYRAZOLES IN THE REACTION OF 3-ARYL-10-METHYL-2H-1,3,4-THIA(SELENO)DIAZINO[3,2-*a*]BENZIMIDAZOLIUM SALTS WITH BASES

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Reaction of 3-aryl-10-methyl-2H-1,3,4-thiadiazino[3,2-a]benzimidazolium salts with triethylamine led to ring contraction of the thiadiazine ring to a pyrazole ring with the formation of a mixture of derivatives of 3-mercaptopyrazolobenzimidazole and di(pyrazolo[1,5-a]benzimidazolyl-3) disulfide. The disulfides were formed exclusively when these salts react with ethanolic alkali. The reaction with potassium carbonate in acetic anhydridegave3-acetylthiopyrazolo[1,5-a]benzimidazoles. 2-Aryl-4-alkylpyrazolo[1,5-a]benzimidazoles were formed by heating thiadiazino[3,2-a]benzimidazolium salts in formamide and by treating selenodiazino[3,2-a]benzimidazolium salts with potassium carbonate in acetic anhydride.

It is known that salts of many condensed 1,3,4-thiadiazines undergo contraction of the thiadiazine ring to give pyrazole derivatives under the influence of triethylamine [1-4]. It appeared interesting to study the behavior under similar conditions of the 3-aryl-10-methyl-2H-1,3,4-thia(seleno)diazino[3,2-*a*]benzimidazolium bromides recently synthesized by us [5], particularly since the expected products are the 2-aryl-4-alkylpyrazolo[1,5-*a*]benzimidazoles for which a synthesis has not yet been developed.

When 1-amino-3-methylbenzimidazolin-2-thiones(selenones) Ia,b and IIa reacted with phenacyl bromides in ethanol a series of new bromides IIIb-i and IVb,f,g was obtained in addition to the known thia(seleno)diazinium salts IIIa and IVa. It was established using phenacyl bromide that salts of type V, formed as intermediates, could be isolated with a short reaction time. (See scheme on following page.)

Reaction of bromides IIa and g with triethylamine in ethanol gave a mixture of previously unknown di(pyrazolo[1,5-*a*]benzimidazolyl-3) disulfides IXa and g (~9%) and compounds Xa and g. Salts IIIe and i, which contain bulky sterically hindered phenol substituents, did not form disulfides but gave compounds Xe and i exclusively (~80%). Considering the considerable CH-acidity of the CH_2 group in the thiadiazine ring it may be suggested that the C-anion VI is formed in the presence of base and then transforms (possibly via the thiirane intermediate VII) into the S-anion VIII. The latter either dimerizes to give the disulfide IX or attacks position 2 of the nonionized salt III as a nucleophile. The benzimidazolin-2-thione unit acts as the leaving group. Formation of similar compounds under analogous conditions has been observed for 1,2,4-triazolothiadiazinium bromides [2].

The structure of the compounds synthesized was confirmed from spectroscopic results (IR, ^{1}H NMR, mass spectra). For example, in the ^{1}H NMR spectra of compounds X the CH_2 signal is shifted 0.9 ppm to strong field relative to the signal of the starting material and is observed as a multiplet at 3.9-4.1 ppm. When compound Xg was reduced with Raney nickel in ethanol 4-methyl-2-β-naphthylpyrazolo[1,5-*a*]benzimidazole (XIIg) and 1-amino-3-methylbenzimi-dazolin-2-thione (Ia) were isolated which confirms the presence of these units in Xg. Disulfide IXa was also obtained by the reverse synthesis, boiling 4-methyl-2-phenylpyrazolo[1,5-*a*]benzimidazole (XIIa) with sulfur in DMF.

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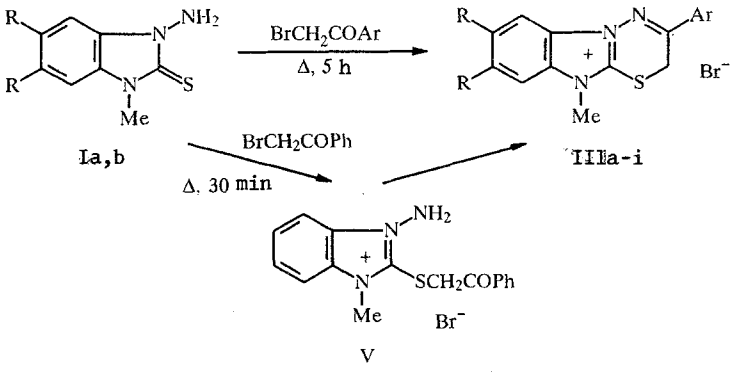
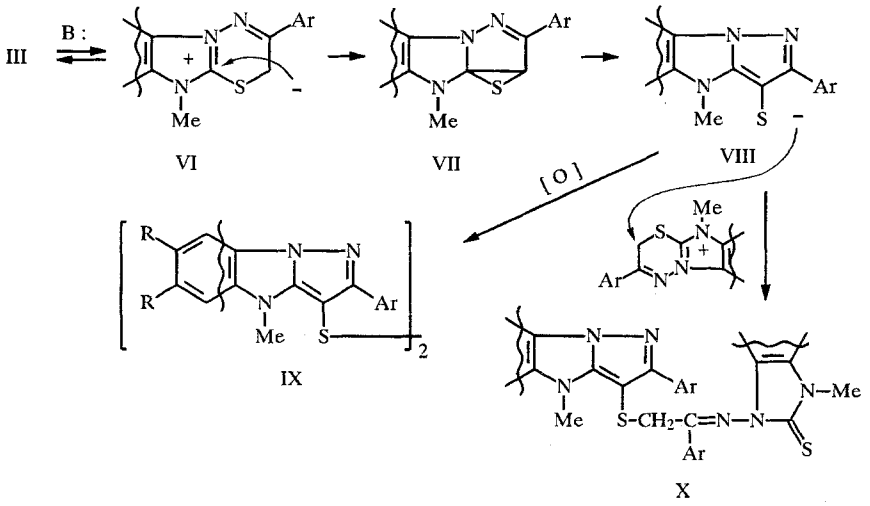
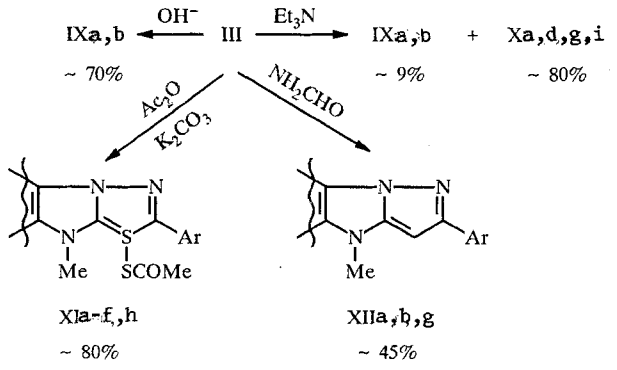






Ia,b R = H; Ib R = Me; III, IX, X, XI, XII a R = H, Ar = Ph; b R = H, Ar = C_6H_4OMe-*p*; c R = H, Ar = $C_6H_3(OMe)_2$-2,5; d* R = H, Ar = C_6H_4OH-*p*; e R = H, Ar = $C_6H_2(CMe_3)_2$-3,5-OH-4; f R = H, Ar = $C_6H_4NO_2$-*p*; g R = H, Ar = β-naphthyl, h R = Me, Ar = Ph; i R = Me, Ar = $C_6H_2(Me_3)_2$-3,5-OH-4

* XI d Ar = C_6H_4OCOMe-*p*

The reaction of salts IIIa and b with ethanolic alkali occurs more regioselectively to give the disulfides IXa and b (~70%). Apparently the alkali, a stronger base than triethylamine, shifts the salt III ⇄ C–anion VI equilibrium towards the anion so that the concentration of the initial salt in the mixture becomes minimal and very little of compound X is formed.

The formation of the S–anion VIII can be frozen in if an electrophile, e.g., acetic anhydride, is included in the reaction mixture along with potassium carbonate as base: in this case the 3–acetylthiopyrazolo[1,5–*a*]benzimidazoles XI are formed. Under these conditions 3–(*p*–hydroxyphenyl)thiadiazino[3,2–*a*]benzimidazolium bromide IIId is acetylated at the hydroxy

TABLE 1. Characteristics of the Compounds Synthesized.

Compound	Molecular formula	mp, °C	Yield, %
IIIa	$C_{16}H_{14}BrN_3S$	233...234	88
IIIb	$C_{17}H_{16}BrN_3OS$	240...241	79
IIIc	$C_{18}H_{18}BrN_3O_2S \cdot 2H_2O$	165...166	83
IIId	$C_{16}H_{14}BrN_3OS$	277...278	82
IIIe	$C_{24}H_{30}BrN_3OS \cdot H_2O$	229...230	76
IIIf	$C_{16}H_{13}BrN_4O_2S$	259...260	86
IIIg	$C_{20}H_{16}BrN_3S \cdot 2H_2O$	237...238	92
IIIh	$C_{18}H_{18}BrN_3S$	274...275	80
IIIi	$C_{26}H_{34}BrN_3OS \cdot 2H_2O$	258...260	82
IIIj	$C_{17}H_{16}BrN_3S$	221...222	96
IVa	$C_{16}H_{14}BrN_3Se$	252...253	98
IVb	$C_{17}H_{16}BrN_3OSe$	246...247	93
IVf	$C_{16}H_{13}BrN_4O_2Se$	261...262	98
IVg	$C_{20}H_{16}BrN_3Se$	247...248	92
XIa**	$C_{18}H_{15}N_3OS$	107...108	72
XIb	$C_{19}H_{17}N_3O_2S$	137...138	79
XIc	$C_{20}H_{19}N_3O_3S$	145...146	90
XId	$C_{20}H_{17}N_3O_3S$	147...148	83
XIe	$C_{26}H_{31}N_3O_2S$	257...258	81
XIf	$C_{18}H_{14}N_4O_3S$	211...212	82
XIh	$C_{20}H_{19}N_3OS$	152...153	70
XIIa	$C_{16}H_{13}N_3S$	109...110	A 45, B 84, C 79, D 65
XIIb	$C_{17}H_{15}N_3O$	115...116	A 48, D 60
XIIc	$C_{18}H_{17}N_3O_2$	113...114	C 72
XIIe	$C_{24}H_{29}N_3O$	201...202	C 75
XIIf	$C_{16}H_{12}N_4O_2$	205...206	D 65
XIIg	$C_{20}H_{15}N_3$	170...171	A 50, B 76, D 67
XIIj	$C_{17}H_{15}N_3$	151...152	A 57, B 69, C 58

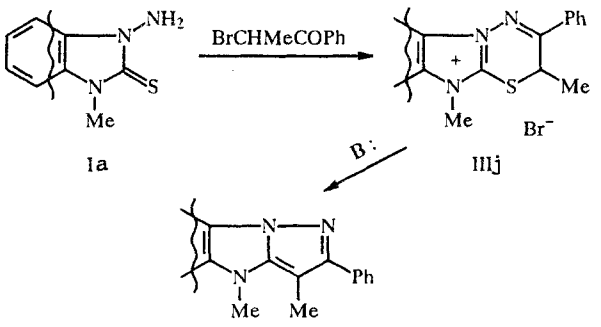
*Compound IVa was recrystalized from water, IVf, XIf, and XIIf from DMF, IVg and XId from butanol, XIa, XIIa and b from heptane, and the remaining compounds from ethanol.

**The $\nu_{C=O}$ band in the IR spectra of compounds XII: a) 1704, b) 1707, c) 1683, d) 1705 and 1770, e) 1704, f) 1704, and g) 1697 cm^{-1}.

group to give compound XId. Alkaline hydrolysis of the 3-acetylthiopyrazolobenzimidazoles XI leads rapidly to the formation of the disulfides IX, while reduction with Raney nickel gives 4-alkyl-2-arylpyrazolo[1,5-*a*]benzimidazole XII without a 3-substituent. Compound XII was also obtained by reduction of the disulfides IX with Raney nickel.

We have established that sulfur atom extrusion occurs to give 4-arylpyrazolobenzimidazoles XII when salts III are boiled in formamide. Evidently formamide acts as both a base and a reducing agent in this case. Similarly the pyrazolobenzimidazoles XIIa and g are readily formed when the disulfides IXa and g are boiled in formamide. The disulfide IXf was isolated when the 3-(*p*-nitrophenyl)thiadiazinium salt IIIf reacted in formamide. The reason for the stability of this disulfide is not at all clear.

The 2-methyl substituted thiadiazinium bromide IIIj, obtained from the reaction of thione Ia with α-bromopropiophenone, was converted into 3,4-dimethyl-2-phenylpyrazolo[1,5-*a*]benzimidazole (XIIj) by triethylamine, alcoholic alkali, or potassium carbonate in acetic anhydride, analogously to the other 2-substituted compounds 1,2,4-triazolo[3,4-*b*]- and pyrido[2,1-*b*]thiadiazines [2,3]. The methyl leaving group facilitates the conversion of the S-anion into the pyrazolobenzimidazole XIIj and prevents the formation of a disulfide.

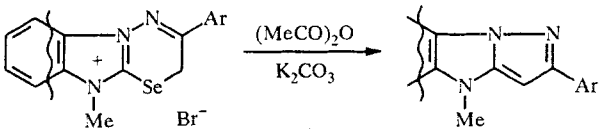


Ia IIIj

XIIj

57-69%

In distinction from the bromides III, the selenodiazobenzimidazolium salt IV gave the unsubstituted pyrazolo[1,5−*a*]benzimidazoles XIIa, b, f, and g, and not selenoacetyl derivatives of type XI, and when treated with potassium carbonate in acetic anhydride. It is possible that the acetylseleno derivatives are formed but are unstable and decompose into compounds XII, acetic acid, and selenium which is retained in the reaction mixture.



IV a, b, f, g XII a, b, f, g

IV, XII a Ar = Ph; b Ar = C_6H_4OMe-4; f Ar = $C_6H_4NO_2$-4; g Ar = β-naphthyl

A complex and inseparable mixture of products was obtained when the selenodiazines IV were heated with triethylamine of ethanolic alkali.

EXPERIMENTAL

IR spectra were recorded as Nujol mulls with Specord−75 machine. ^{1}H NMR spectra of compounds Ib, IVa, IXa, Xa and Xe were recorded with a Tesla BS−587 (100 MHz), of compound Xi with a Bruker WH−90, and the remainder on a Tesla BS−487 (80 MHz) with HMDS as internal standard. Mass spectra were obtained by direct insertion with a Varian MAT−311 instrument with an ionizing voltage of 70 eV. The progress of reactions and the purity of products were monitored by TLC on Al_2O_3 (activity III) strips with chloroform as eluent and iodine vapour development.

Characteristics of the compounds prepared are given in Table 1. Elemental analysis results for C, H, and N agreed with calculated figures.

1−Amino−3,5,6−trimethylbenzimidazolin−2−thione (Ib, $C_{10}H_{13}N_3S$). A solution of 1−amino−3,5,6−trimethylbenzimadozolium iodide [6] (7.57 g, 0.025 mol) , elemental sulfur (0.96 g, 0.03 mol), and triethylamine (3.6 ml, 0.025 mol) in DMF (30 ml) was boiled for 1 h, cooled, diluted with water (60 ml), the dark precipitate filtered off and washed with water, a small amount of ethanol, and ether to give white crystals of Ib (4 g, 77%), m.p. 219−220°C (from butanol). IR spectrum : 1590, 1630; 3168, 3268 cm^{-1} (NH_2). ^{1}H NMR spectrum ($CDCl_3$): 2.30 (6H, s 5,6−CH_3), 3.69 (3H, s, NCH_3), 4.47 (2H, br m, NH_2, disappeared on deuteration), 6.90 (1H, s, 4−H), and 7.16 ppm (1H, s, 7−H).

1−Amino−3,5,6−trimethylbenzimidazolin−2−selenone (IIb, $C_{10}H_{13}N_3Se$) was synthesized analogously to thione Ib as grayish crystals (75% yield), m.p. 217−218°C (from aqueous DMF). IR spectrum: 1617, 1640; 3174, 3290 cm^{-1} (NH_2).

3−Aryl−10−methyl−2H−1,3,4−thiadiazino[3,2−*a*]benzimidazolium Bromides (IIIa−i). Solutions of equimolar quantities of the thiones Ia and b and the corresponding phenacyl bromides in ethanol were boiled for 5 h. The mixtures were cooled, the precipitates filtered off and recrystallized from aqueous ethanol. ^{1}H NMR spectrum (DMSO−D_6) of

10-methyl-3-phenyl-2H-1,3,4-triazino[3,2-*a*]benzimidazolium bromide (IIIa): 4.05 (3H, s, NCH_3), 4.9 (2H, s, CH_2), 7.66 (5H, m, H_{arom}), and 8.1 ppm (4H, m, H_{arom}).

2,10-Dimethyl-3-phenyl-2H-1,3,4-triazino[3,2-*a*]benzimidazolium bromide (IIIj) was synthesized from Ia and α-bromopropiophenone analogously to salts IIIa-i.

1-Amino-3-methyl-2-phenacylthiobenzimidazolium Bromide (V, $C_{16}H_{16}BrN_3OS$). A solution of thione Ia (0.54 g, 3 mmol) and phenacyl bromide (0.6 g, 3 mmol) in ethanol (15 ml) was boiled for 30 min, cooled, and the precipitate filtered off to give colorless crystals (0.97 g, 85%) which premelted at 120-125°C, then solidified and finally melted at 233-234°C. IR spectrum: 1705 (C=O), 3425, 3515 cm^{-1} (NH_2).

3-Aryl-10-methyl-2H-1,3,4-selenodiazino[3,2-*a*]benzimidazolium Bromides (IVa, b, f, g) were obtained analogously to salts III from 1-amino-3-methylbenzimidazolin-2-selenone (IIa) [5]. ^1H NMR spectrum (DMSO-d_6) of 10-methyl-3-phenyl-2H-selenodiazino[3,2-*a*]benzimidazolium bromide (IVa): 4.08 (3H, s, NCH_3), 4.6 (2H, s, CH_2), 7.6 (5H, m, H_{arom}) and 8.1 ppm (4H, m, H_{arom}).

Reaction of Salts III with Triethylamine. Salt IIIa. Triethylamine (0.45 ml, 3 mmol) was added to a suspension of bromide IIIa (1.04 g, 3 mmol) in ethanol (10 ml) and the mixture was boiled for 2 h. The original red color of the reaction mixture disappeared rapidly on heating. The glistening yellow flocculent material which slowly precipitated was filtered off (0.6 g). The solid was dissolved in chloroform (10 ml) and chromatographed on an Al_2O_3 column (15 x 300 mm) with chloroform as eluent. The first fraction isolated (R_f) was **3-methyl-2-thio-N-[1-phenyl-2-(2-phenyl-4-methylpyrazolo[1,5-*a*]benzimidazolyl-3-thio)ethyliden-1]benzimidazolinyl-1-amine (Xa, $C_{32}H_{26}N_6S_2$)** (0.45 g, 54%), as glistening yellow needles, m.p. 166-167°C (from butanol). 1H NMR spectrum ($CDCl_3$): 3.39 (3H, s, NCH_3), 3.58 (3H, s, NCH_3), 3.99 (2H, br s, CH_2). 6.24 (1H, d, J = 7.5 Hz, H_{arom}), 6.68 (2H, t, J = 7.5 Hz, H_{arom}), 6.96 (2H, m. H_{arom}), 7.26 (8H, m, H_{arom}), 7.60 (3H, m, H_{arom}) and 7.95 ppm (2H, m, H_{arom}). Mass spectrum, *m/z*, (%): 280 (5.6), 278 (100), 175 (60.5), 160 (11.5), 131 (15.7).

Yellow crystals of **di(4-methyl-2-phenylpyrazolo[1,5-a]benzimidazolyl-3) Disulfide (IXa, $C_{32}H_{24}N_6S_2$)** (m.p. 240-241°C (butanol)) (0.08 g, 9%) were isolated from the second fraction (R_f 0.4). ^1H NMR spectrum ($CDCl_3$): 3.53 (6H, s, NCH_3). 6.98 (8H, m, H_{arom}), 7.22 (4H, m, H_{arom}), and 7.69 ppm (6H, m, H_{arom}). Mass spectrum, *m/z* (%): 278 (100), 250 (3.0), 246 (3.7), 175 (60.2), 160 (11.5), 131 (15.8), 102 (4.8).

Salt IIIg. Bromide IIIg reacted with triethylamine in the same way as compound IIIa to give **3-methyl-2-thio-N-[1-β-naphthyl-2-(2-β-naphthyl-4-methylpyrazolo[1,5-*a*]benzimidazolyl-3-thio]ethyliden-1]benzimidazolinyl-1-amine (Xg, $C_{38}H_{30}N_6S_2$)** (60%) as glistening yellow needles, m.p.171-172°C (butanol). ^1H NMR spectrum ($CDCl_3$): 3.18 (3H, s, NCH_3), 3.30 (3H, s, NCH^D3
), 4.0 (2H, m, CH_2), 6.25 (1H, d, J = 7.5 Hz, H_{arom}), 6.6-8.2 ppm (21H, m, H_{arom}).

Di(4-methyl-2-(β-naphthyl)pyrazolo[1,5-*a*]benzimidazolyl-3) disulfide (IXg, $C_{38}H_{28}N_6S_2$) was obtained as yellow crystals (8% yield), m.p.225-226°C (DMF).

Salt IIIe. The clear red solution formed after mixing bromide IIIe (0.5 g, 1 mmol) and triethylamine (0.15 ml, 1 mmol) in ethanol (10 ml) was boiled for 2 h. The solution decolorized over 1 h and a precipitate started to appear. It was filtered off after cooling, and washed with ethanol and ether to give colorless prisms of **3-methyl-2- thio-N-(1-(3,5-di *tert*butyl-4-hydroxyphenyl)-2-[2-(3,5-di-*tert*butyl-4-hydroxyphenyl)-4-methyl-pyrazolo[1,5-*a*]benzimidazolyl-3-thio]ethyliden-1-)benzimidazolinyl-1-amine (Xe, $C_{18}H_{58}N_6O_2S_2$)** (0.35 g, 86%), m.p. 227-228°C (dec., aqueous DMF). IR spectrum: 1568, 1616, 3568 cm^{-1}. ^1H NMR spectrum ($CDCl_3$): 1.25 (18H, s, 2 $C(CH_3)_3$)), 1.35 (18H, s, 2 $C(CH_3)_3$)), 3.38 (3H, s NCH_3), 3.48 (3H, s, NCH_3), 3.88 (2H, m, CH_2), 5.13 (1H, s, OH, disappears on deuteration), 5.38 (1H, s, OH, disappears on deuteration), 6.32 (1H, d, J = 7.5 Hz, H_{arom}), 6.60-7.15 (7H, m, H_{arom}), 7.64 (2H, m, H_{arom}), and 7.73 ppm (2H, m. H_{arom}). Mass spectrum, *m/z* (%): 1703

Salt IIIi. Bromide IIIi reacted with triethylamine in the same was as IIIa to give glistening yellow crystals of **3-methyl-2-thio-5,6-dimethyl-N-(1-(3,5-di-*tert*butyl-4-hydroxyphenyl)-2-[2-(3,5-di-*tert*butyl-4-hydroxyphenyl)-4,6,7-trimethylpyrazolo[1,5-*a*]benzimidazolyl-3-thio]ethyliden-1-}benzimidazolinyl-1-amine (Xi, $C_{52}H_{66}N_6O_2S_2 \cdot (CH_3)_2NCHO$)**, (0.3 g, 70%), m.p. 248-249°C (dec., DMF). IR spectrum: 1594, 1673 (C=O), 3317. 3672 cm^{-1}. ^1H NMR spectrum (DMSO-d_6): 1.35 (18H, s, 2 $C(CH_3)_3$), 1.37 (18H, s, 2 $C(CH_3)_3$), 2.01 (3H, C-CH_3), 2.18 (3H, s, C-CH_3), 2.36 (6H, s, C-CH_3), 2.66 (3H, s, DMF), 2.81 (3H, s, DMF), 3.38 (3H, s, NCH_3). 3.48 (3H, s, NCH_3), 4.09 (2H, m, CH_2), 6.09 (1H, s, 2-H'), 6.78 (1H, s, 2-H'), 6.91 (1H, s, OH, disappears on deuteration), 7.2 (1H, s, 6-H'), 7.43 (1H, s, 6-H'), 7.52 (1H, s, OH, disappears on deuteration), 7.72 (2H, s, H_{arom}), 7.76 (2H, s, H_{arom}) and 7.95 ppm (1H, s, DMF).

Reduction of Compound Xg with Raney Nickel. A suspension of compound Xg (0.66 g, 1 mmol and Raney nickel (from 1.5 g of alloy) in ethanol (20 ml) was heated for 2h during which time Xg slowly dissolved. The solution was filtered and the mother liquor evaporated to dryness. The residue was dissolved in acetone (10 ml) and acidified to pH 1 with conc. HCl. The colorless precipitate was separated and treated with conc aqueous NH_4OH to give 4-methyl-2-β-naphthylpyrazolo[1,5-*a*]benzimidazole (XIIg) (0.22 g, 73%). ^1H NMR spectrum ($CDCl_3$): 3.52 (3H, s, NCH_3), 6.05 (1H, s, 3-H), 7.1 (3H, m, 5,6,7-H), 7.38 (2H, m, H_{arom}), 7.83 (5H, m, H_{arom}), 8.28 ppm (1H, m, H_{arom}).

The acetone mother liquor was evaporated to dryness and 1-amino-3-methylbenzimidazlin-2-thione (Ia) (0.12 g, 66%) was obtained after chromatography on an Al_2O_3 column (15 x 150 mm, chloroform as eluent). The compound was identical to an authentic sample of thiones Ia [5].

Thiolation of 4-methyl-2-phenylpyrazolo[1,5-*a*]benzimidazole (XIIa). A solution of compound XIIa (0.36 g, 1.5 mmol) and sulfur (0.06 g, 2 mmol) in DMF (3 ml) was heated for 2 h. The yellow precipitate was filtered off and washed with ethanol to give compound IXa (0.34 g, 80%), m.p. 240-241°C (butanol), identical to an authentic sample of the disulfide IXa.

Effect of Ethanolic Alkali on Bromides IIIa and b. Salt IIIa or b (1 mmol) was added to a solution of potassium hydroxide (0.12 g, 2 mmol). The initial red color rapidly disappeared and the solution became yellow. It was boiled for 3-5 min, kept at room temperature for 1 h, and the yellow precipitate was filtered off and washed with water to give **di(4-methyl-2-phenylpyrazolo[1,5-*a*]benzimidazolyl-3) disulfide (IXa)** (yield 75%, no depression of the melting point of samples of IXa prepared in the preceding experiments and **di(4-methyl-2-(*p*-methoxyphenyl---pyrazolo[1,5-*a*]benzimidazolyl-3) disulfide (IXb, $C_{34}H_{28}N_6O_2S_2$)**(yield 70%, m.p. 219-220°C (butanol)).

2-Aryl-3-acetylthio-4-methylpyrazolo[1.5-*a*]benzimidazoles (XIa-f, h). Solutions of compounds III (2 mmol) in acetic anhydride (10 ml) were boiled with potassium carbonate (2 mmol) for 1.5-2 h. The mixture was cooled, water (30 ml) added, and the precipitate was filtered off after decomposition of the acetic anhydride and washed with water. It was purified by chromatography on Al_2O_3 with elution by chloroform. ^1H NMR spectrum of 3-acetylthio-4-methyl-2-phenylpyrazolo[1,5-*a*]benzimidazole (XIa): 2.38 (3H, s $COCH_3$), 3.80 (3H, s, NCH_3), 7.34 (6H, m, H_{arom}), 7.80 ppm (3H, m, H_{arom}).

^1H NMR spectrum of 3-acetylthio-4-methyl-2-phenylpyrazolo[1,5-*a*]benzimidazole (XId): 2.20 (3H, s, $SCOCH_3$), 2.29 (3H, s $OCOCH_3$), 3.70 (3H, s, NCH_3), 7.15 (2H, d, J = 8.4 Hz, 3,5-H′), 7.25 (3H, m, 5,6,7-H), 7.83 (1H, m, 8-H) and 7.83* ppm (2H, d, J = 8.4 Hz, 2,6-H′).

Reaction of 2-aryl-3-acetylthio-4-methylpyrazolo[1,5-*a*]benzimidazoles XIa and f with Alkali. A solution of compound XIa or f (1 mmol) and sodium hydroxide (0.08 g, 2 mmol) in ethanol (5 ml) was heated for 3-5 min. The solution was cooled, the yellow precipitate of the disulfides IXa or f was filtered of and washed with water to give di(4-methyl-2-phenylpyrazolo[1,5-*a*]benzimidazolyl-3) disulfide (IXa) (yield 85%, m.p. 240-241°C, identical with samples of compound IXa obtained in previous experiments) and **di(4-methyl-2-phenylpyrazolo[1,5-*a*]benzimidazolyl-3) disulfide (IXf, $C_{32}H_{22}N_8O_4S_2$)** (yield 87%, m.p. 279-280°C (DMF)).

2-aryl-4-methylpyrazolo[1,5-*a*]benzimidazoles (XIIa-c, e-g). A. Salts IIIa,b, or g (2 mmol) were boiled in formamide (5 ml) for 0.5 h. The solution was strongly colored and a thich dark oil formed at the surface. The cooled solution was diluted with water (10 ml) and extracted with chloroform (20 ml). 2-Arylpyrazolo benzimidazoles XIIa,b and g were obtained in 45-50% yield after chromatographic purification of the chloroform solution extract on an Al_2O_3 column with benzene as eluent. ^1H NMR spectrum ($CDCl_3$) of 4-methyl-2-(*p*-methoxyphenyl)pyrazolo[1,5-*a*]benzimidazole (XIIb): 3.58 (3H, s, OCH_3), 3.73 (3H, s, NCH_3), 6.0 (1H, s 3-H), 6.93 (2H, d, J = 9.0 Hz, 3,5-H′), 7.15 (3H, m, 5,6,7-H), 7.80 ppm (2H, d, J = 9.0 Hz, 2,6-H′).

B. A suspension of disulfide IXa (0.56 g, 1 mmol) in formamide (10 ml) was boiled for 20 min. The initially yellow reaction mixture became green and then colorless. The solution was cooled, water (20 ml) added, and the mixture extracted with chloroform (30 ml). The chloroform extract was evaporated to give the pyrazolobezimidazole XIIa (0.42 g, 84%). Compound XIIg was made analogously.

C. A suspension of a 3-acetylthio derivative XIa, c, or e (2 mmol) and Raney nickel (from 3 g of alloy) in ethanol (20 ml) was boiled for 1h, filtered, and the mother liquor evaporated to dryness. The residue was dissolved in chloroform (5

*As in Russian original — Translator.

ml) and chromatographed on an Al_2O_3 column with chloroform as eluent to give the pyrazolobenzimidazoles XIIa, c, and e in 72–79% yield. ^1H NMR spectrum ($CDCl_3$) of 2–(2,5–dimethoxyphenyl)–4–methylpyrazolo[1,5–*a*]benzimidazole (XIIc) : 3.53 (3H, s, NCH_3), 3.75 (6H, s 2 OCH_3), 6.25 (1H, s, 3–H), 6.8 (2H, s, 3,4–H′), 7.13 (3H, m, 5,6,7–H), 7.68 (1H, s, 6–H′), 7.8 ppm (1H, m, 8–H). ^1H NMR spectrum ($CDCl_3$) of 2–(3,5–di-*tert*-butyl–4–hydroxyphenyl)–4–methylpyrazolo[1,5–*a*]benzimidazole (XIIe): 1.38 (18H, s 2 $C(CH_3)_3$), 3.60 (3H, s, NCH_3), 5.22 (1H, s, OH, disappeared on deuteration), 5.9 (1H, s, 3–H), 7.15 (2H, s, 2,6–H′), 7.68 (3H, m, 5,6,7–H), 7.83 ppm (1H, m, 8–H).

D. A suspension of a 3–arylselenodiazino[3,2–*a*]benzimidazolium bromide IV (2 mmol) and potassium carbonate (2 mmol) in acetic anhydride (15 ml) was boiled for 1 h, the precipitated selenium and inorganic salts were removed, the mother liquor was diluted with water (10 ml) and carefully neutralized with conc. aqueous NH_3. The thick oils of XIIa and b which separated were extracted with chloroform (20 ml), while the solid compounds XIIf and g were filtered off. All were purified by column chromatography on Al_2O_3 with benzene as eluent. Yields 60–67%.

3,4–Dimethyl–2–phenylpyrazolo[1,5–*a*]benzimidazole (XIIj). A. A solution of bromide IIIj (2.62 g, 7 mmol) and triethylamine (1.1 ml, 7 mmol) in ethanol (30 ml) was boiled for 2 h, the solution evaporated to dryness, and the residue chromatographed on an Al_2O_3 column (25 x 300 mm) with benzene as eluent, and the fraction with R_f 0.9 selected to give XIIj (1.05 g, 57%). ^1H NMR spectrum ($CDCl_3$): 2.20 (3H, s, C–CH_3), 3.50 (3H, s, NCH_3), 7.0 (3H, m, H_{arom}), 7.3 (3H, m, 5,6,7–H), 7.63 (2H, m, H_{arom}), and 7.73 ppm (1H, m, 8–H).

B. Bromide IIIj (0.38 g, 1 mmol) was added to a solution of NaOH (0.08 g, 2 mmol) in ethanol (10 ml) and the solution was boiled for 1.5 h. The solution was evaporated to dryness and the product purified as in the preceding experiment. Yield 0.18 g (69%). The compound was identical to that described in experiment A.

C. A suspension of bromide IIIj (0.76 g, 2 mmol) and potassium carbonate (0.28 g, 2 mmol) in acetic anhydride (5 ml) was boiled for 1 h, cooled, diluted with water, and neutralized with $NaHCO_3$. The precipitate was filtered off. Yield 0.3 g (58%). The compound was identical in physico–chemical properties to samples obtained in the previous experiments.

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