  Bull. Chem. Soc. Jpn., 61, 1339—1344 (1988)

Condensation and Cyclization Reactions of 2-Hydrazinobenzimidazole, -benzoxazole, and -benzothiazole

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(Received June 16, 1986)

2-Hydrazinobenzoxazole (**1**), -benzimidazole (**2**), and benzothiazole (**3**) were condensed with ethyl chloroformate and/or diethyl oxalate to produce, 1,2,4-triazolo- and 1,2,4-triazino-fused ketones of the title azoles respectively. Condensation of **1** and **2** with aromatic aldehydes and/or acetic anhydride produced, 3-aryl- and 3-methyl-substituted 1,2,4-triazolo-fused azoles respectively. The hydrazines **1** and **2** cyclized with acetylacetone to produce the corresponding 2-(1-pyrazolyl) derivatives. 2-Acetylthiazolobenzimidazole reacted with hydroxylamine and/or alkylamines, to produce the corresponding condensation products. Also it condensed with aromatic aldehydes to give the chalcones. When reacted with benzenediazonium salt, it gave the corresponding 2-arylazo-substituted compounds.

Thiazolo[3,2-*a*]benzimidazole derivatives have long been known for their antibacterial activity[1] and their quaternary salts as hypoglycaemicagents.[2] Fungicidal,[2,3,5] herbicidal,[4] insecticidal,[5] and plant-growth-regulating[6] properties of thiazolobenzimidazoles have also been reported. On the other hand, benzimidazoles have been reported to be used as anthelmintics,[7] for treatment of *Echinoccus granulosus* or *Tinea hydatigena*[8] and as antiabesity together with other variable applications.

In the present paper we report new procedures for synthesis of new benzimidazoles, benzoxazoles, and benzothiazoles and the thiazolo[3,2-*a*]benzimidazoles through variable condensation and cyclization reactions.

Results and Discussion

As a continuation for our studies[9] on synthesis of fused heterocyclic ring systems constituting triazolo, triazino, and tetrazolo moiety, through cyclization

Table 1. Physical and Analytical Data of 3-Aryltriazolobenzoxazoles (**4a—f**) and 3-Aryltriazolobenzimidazoles (**5a—f**)

Compd[a]	Mp(θ_m/°C) (Solvent)	Yield/%	Molecular Formula	Anal. (Calcd / Found)/%		
				C	H	N
4a	92 (EtOH)	60	$C_{14}H_9N_3O$	71.49 71.50	3.83 3.80	17.87 17.85
4b	315 (AcOH)	75	$C_{14}H_8N_4O_3$[b]	60.00 60.00	2.86 2.89	20.00 20.02
4c	219 (AcOH)	67	$C_{14}H_8N_3OCl$	62.22 62.25	2.96 3.00	15.56 15.54
4d	162 (AcOH)	54	$C_{15}H_{11}N_3O_2$	67.93 67.98	4.15 4.18	15.85 15.82
4e	249 (AcOH)	48	$C_{16}H_{14}N_4O$[b]	69.07 69.05	5.04 5.08	20.14 20.15
4f	233 (AcOH)	43	$C_{15}H_{11}N_3O$	72.29 72.30	4.42 4.41	16.87 16.83
5a	270 (aq. EtOH)	62	$C_{14}H_{10}N_4$	71.80 71.83	4.27 4.30	23.93 23.96
5b	318 (AcOH)	78	$C_{14}H_9N_5O_2$	60.22 60.26	3.23 3.26	25.09 25.08
5c	288 (EtOH)	70	$C_{14}H_9N_4Cl$	62.45 62.46	3.35 3.31	20.82 20.85
5d	245 (aq. EtOH)	58	$C_{15}H_{12}N_4O$	68.18 68.20	4.55 4.53	21.21 21.26
5e	255 (EtOH)	55	$C_{16}H_{15}N_5$	69.31 69.35	5.46 5.50	25.27 25.31
5f	257 (AcOH)	50	$C_{15}H_{12}N_4$	72.58 72.60	4.84 4.80	22.58 22.60

a) IR(KBr); **4a**, 1610 (C=N), 1150 (C-O-C), 1615, 1610, 1570 cm^{-1} (oxazole); **4b**, 1660 (C=N), 1100 (C-O-C), 1615, 1610, 1585 (oxazole), 1550, 1370 cm^{-1} (NO_2); **4c**, 1615 (C=N), 1080 (C-O-C), 1600, 1585, 1575 (oxazole), 690 cm^{-1} (Cl); **4d**, 1615 (C=N), 1110 (C-O-C), 1580, 1570 cm^{-1} (oxazole), **4e**, 1660 (C=N), 1105 (C-O-C), 1600, 1545, 1540 (oxazole), **4f**, 1680 (C=N), 1090 (C-O-C), 1630, 1610, 1590 (oxazole), 1450, 1310 cm^{-1} (CH_3); **5a**, 1650 (C=N), 3410 cm^{-1} (NH), **5b**, 1630 (C=N), 3400 (NH), 1560, 1330 cm^{-1} (NO_2); **5c**, 1650 (C=N), 3420 (NH), 370 cm^{-1} (Cl); **5d**, 1650 (C=N), 3390 (NH), 1125 cm^{-1} (OCH_3); **5e**, 1650 (C=N), 3510 (NH), 800 cm^{-1} ($N(CH_3)_2$); **5f**, 1700 (C=N), 3420 (NH), 1450 cm^{-1} ($-CH_3$). b) Molecular ions, **4b**, *m/z* 280; **4e**, *m/z* 296.

Table 2. Physical and Analytical Data of (2-Benzoxazolyl)hydrazones (**6a—f**) and (2-Benzimidazolyl)hydrazones (**7a—f**)

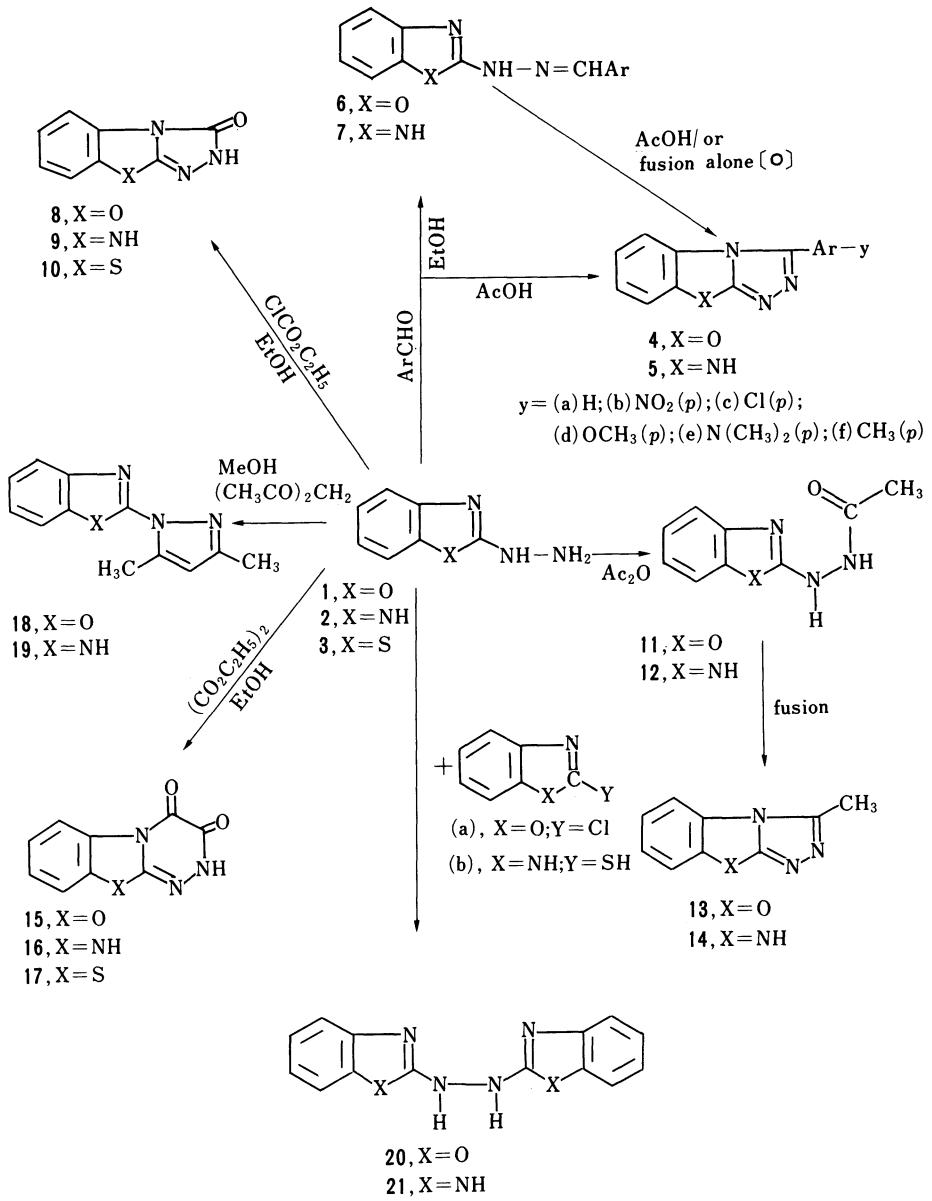
Compd[a]	Mp(θ_m/°C) (Solvent)	Yield/%	Molecular formula	Anal. (Calcd / Found)/%			Ref.
				C	H	N	
6a	204.5 (EtOH)	60	—	—	—	—	8
6b	245 (EtOH)	75	$C_{14}H_{10}N_4O_3$	59.58 59.50	3.55 3.65	19.86 19.99	—
6c	248 (DMF)	91	—	—	—	—	19
6d	207 (EtOH)	89	—	—	—	—	19
6e	224 (aq. DMF)	83	—	—	—	—	19
6f	215 (EtOH)	51	$C_{15}H_{13}N_3O$	71.71 71.75	5.18 5.23	16.73 16.66	—
7a	291 (EtOH)	63	$C_{14}H_{12}N_4$	71.19 71.15	5.09 5.00	23.71 23.75	—
7b	283 (EtOH)	68	—	—	—	—	20
7c	270 (EtOH)	70	$C_{14}H_{11}N_4Cl$	61.99 62.03	4.06 4.00	20.66 20.70	—
7d	212 (EtOH)	58	—	—	—	—	20
7e	245 (EtOH)	49	—	—	—	—	20
7f	277 (EtOH)	50	$C_{15}H_{14}N_4$	72.00 72.11	5.6 5.62	22.40 22.35	—

a) Compound **6a**, ^{1}H NMR ($CDCl_3$) δ=7.40—7.45 (m, 5H, Ar), 7.70—7.85 (m, 4H, Ar), 8.60 (s, 1H, -CH=N- and NH proton is downfield: **6b**, IR(KBr), 1700 (C=N), 3420 (NH), 3020 cm^{-1} (NH, imidazole); ^{1}H NMR (DMSO), δ=2.40 (s, 3H, CH_3), 7.1—7.55 (m, 8H, Ar), 7.65—7.80 (s, 2H, 2NH), 8.15 (s, 1H, -N=CH-).

Table 3. Physical and Analytical Data of Compound **8—12** and **15—19**

Compd[a]	Mp(θ_m/°C) (Solvent)	Yield/%	Molecular formula	Anal. (Calcd / Found)/%			
				C	H	N	S
8	218 (EtOH)	55	$C_8H_5N_3O_2$	54.86 54.98	2.86 2.96	24.00 24.13	—
9	173 (EtOH)	43	$C_8H_6N_4O$	55.17 55.23	3.45 3.54	32.18 32.13	—
10	176 (EtOH)	50	$C_8H_5N_3OS$	50.26 50.18	2.62 2.60	21.99 21.88	16.76 16.75
11	110 (Benzene)	89	$C_9H_9N_3O_2$	56.55 56.60	4.71 4.78	21.99 22.01	—
12	273 (AcOH)	85	$C_9H_{10}N_4O$	56.84 56.98	5.26 5.32	29.47 29.41	—
15	360 (EtOH)	85	$C_9H_5N_3O_3$	53.20 53.35	2.46 2.49	20.69 20.75	—
16	360 (abs EtOH)	80	$C_9H_6N_4O_2$	53.47 53.61	2.97 3.01	27.72 27.68	—
17	340 (EtOH)	82	$C_9H_5N_3O_2S$	49.32 49.38	2.28 2.25	19.19 19.23	14.61 14.53
18	120—121 (EtOH)	60	$C_{12}H_{11}N_3O$	67.59 67.61	5.20 5.30	19.71 19.72	—
19	175 (EtOH)	48	$C_{12}H_{12}N_4$	67.92 68.10	5.66 5.70	26.42 26.42	—

a) Compound **8**, IR(KBr) 3385 (NH), 1710 (C=O enolic), 1660 (C=N), 1100 (C-O-C), 1610, 1590, 1560 cm^{-1} (oxazole); **10**, IR(KBr) 3300 (NH), 1590 (C=O), 1640 (C=N), 1240 cm^{-1} (C-O-C); **11**, IR(KBr) 3310 (NH), 1725 cm^{-1} (C=O), **12**, IR(KBr) 3315 (NH), 1670 cm^{-1} (C=O), ^{1}H NMR ($CDCl_3$) δ=2.50 (s, 3H), 7.40 (m, 4H) δ of NH is downfield; **15**, IR(KBr) 1695, 1645 (COCONH), 1610 (C=N), 1605, 1585, 1555 (oxazole), 1090 cm^{-1} (C-O-C); **16**, IR(KBr) 1710, 1703 (COCONH), 1675 (C=N), 3220 (NH), 1185 cm^{-1} (C-N); **17**, IR (KBr) 1590 (COCONH), 1620 (C=N), 3300 (NH), 1200 cm^{-1} (C-S-C); **18**, ^{1}H NMR ($CDCl_3$) δ=2.60 (s, 3H), 3.20 (s, 3H), 7.3—8.0 (m, 5H, 4HAr+1H, C=CH); **19**, ^{1}H NMR ($CDCl_3$) δ=2.15 (s, 3H), 2.35 (s, 3H), 7.15—7.77 (m, 5H, 4HAr+1H, C=CH), 11.50 (1H, NH).



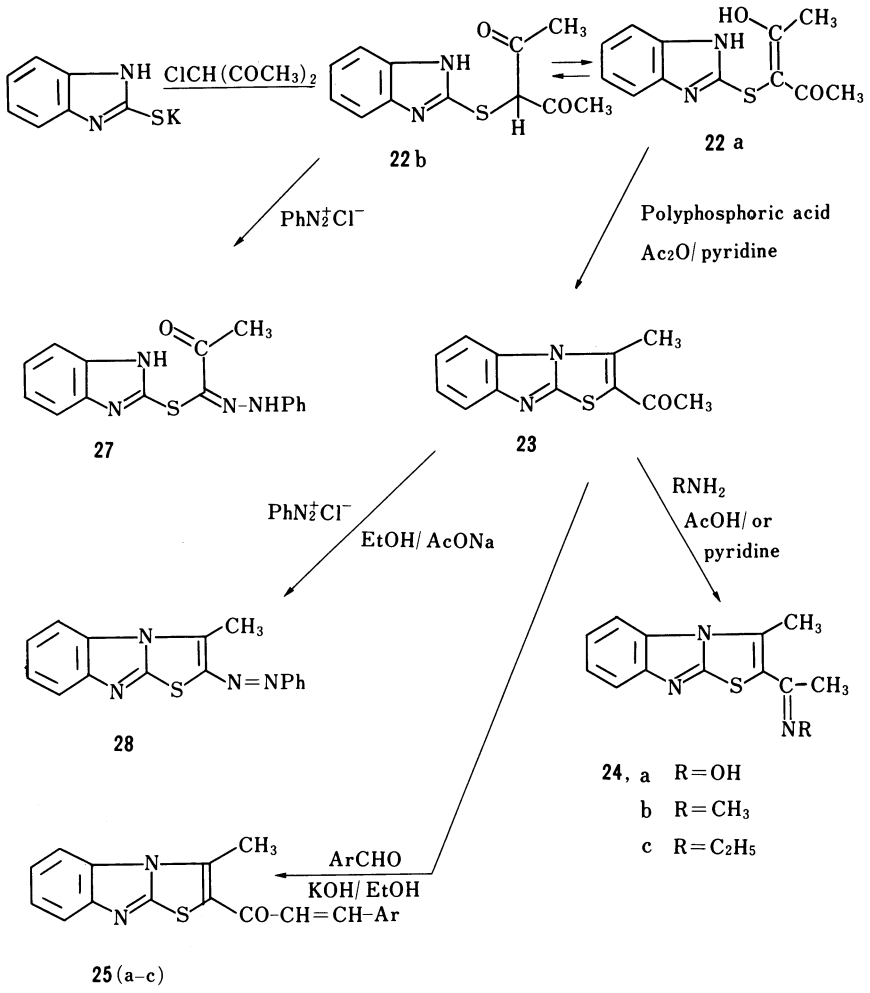
Scheme 1.

reactions, we had discussed the synthesis of comparable heterocycles constituting benzoxazoles, benzimidazoles, and benzothiazoles and thiazolobenzimidazole ring systems.

Reaction of 2-hydrazinobenzoxazole (**1**)[10] and/or 2-hydrazinobenzimidazole (**2**)[10] with benzaldehyde and its *p*-nitro, *p*-chloro, *p*-methoxy, *p*-dimethylamino, and *p*-methyl derivatives in glacial acetic acid gave the corresponding 3-aryl-1,2,4-triazolo[4,3-*b*]benzoxazoles (**4a—f**) and 3-aryl-1,2,4-triazolo[4,3-*a*]benzimidazoles (**5a—f**) respectively. The IR spectra (Table 1) of **4** and **5** showed no (NH_2) bands at 3300, 3200, and 3350, 3250 cm^{-1}, but exhibited (C=N) bands at 1610—1680 and 1650—1700 cm^{-1} together with other characteristic bands. The NMR spectrum of (**5a**) (in DMSO-d_6) showed multiplet at δ 7.1—7.45 (9H, aromatic protons) and broad singlet at δ 9.1—9.85 (1H, NH proton). Compounds **4** and **5** were further produced through ring closure reactions of the corresponding aldehyde (2-benzoxazolyl)hydrazones (**6a—f**) and/or aldehyde (2-benzimidazolyl)hydrazones (**7a—f**) by their refluxing with glacial acetic acid or by its fusion through air oxidation[9,11] (Table 2).

Refluxing **1**, **2**, and **3** with ethyl chloroformate in absolute ethanol produced 1,2,4-triazolo[4,3-*b*]benzoxazol-3(2*H*)-one (**8**); 9*H*-1,2,4-triazolo[4,3-*a*]benzimidazol-3(2*H*)-one (**9**) and/or 1,2,4-triazolo[4,3-*b*]benzothiazol-3(2*H*)-one (**10**) respectively (Table 3).

Refluxing **1** and/or **2** with acetic anhydride produced the corresponding monoacetyl derivatives (**11** and **12**) which cyclized on heating over its melting points into 3-methyl-1,2,4-triazolo[4,3-*b*]benzoxazole (**13**) and 3-methyl-9*H*-1,2,4-triazolo[4,3-*a*]benzimidazole (**14**) respectively in comparable cyclization mechanism as recorded before.[9,12] The IR spectra of both **11** and **12** showed disappearance of (NH_2) bands



Scheme 2.

and the presence of (NH) group which was also characterized by other spectral means (Table 3).

Similarly, refluxing **1**, **2**, and **3** with diethyl oxalate in absolue ethanol produced the cyclization products, 2*H*-1,2,4-triazino[4,3-*b*]benzoxazole-3,4-dione (**15**), 1,2,4-triazino[4,3-*a*]benzimidazole-3,4-dione (**16**) and 1,2,4-triazino[4,3-*b*]benzothiazole-3,4-dione (**17**) respectively. The IR spectra showed characteristic bands (Table 2). On the other hand, refluxing **1** and **2** with 2,4-pentanedione in methanol produced, 2-(3,5-dimethyl-1-pyrazolyl)benzoxazole (**18**) and 2-(3,5-dimethyl-1-pyrazolyl)benzimidazole (**19**) respectively in similar cyclization step as before,[13,14] which showed characteristic NMR spectra (Table 3). Moreover, refluxing **1** with 2-chlorobenzoxazole and refluxing **2** with benzimidazole-2-thiol in absolute ethanol produced 2,2′-hydrazobis(benzoxazole) dihydrochloride (**20**) and 2,2′-hydrazobis(benzimidazole) (**21**) respectively. Their IR spectra showed disappearance of (NH_2) bands at 3300, 3200 and 3350, 3250 cm^{-1}.

Heating of 3-(2-benzimidazolylthio)-2,4-pentanedione (**22b**) with polyphosphoric acid or refluxing in acetic anhydride-pyridine mixture produced 2-acetyl-3-methylthiazolo[3,2-*a*]benzimidazole (**23**).[15] Its IR spectrum showed the disappearance of the (enolic OH) and (NH) bands at 3370 and 3350 cm^{-1}. Its NMR (in $CDCl_3$) showed singlet at δ 2.48 (3H, CH_3), singlet at δ 3.03 (3H, $COCH_3$) and multiplet at δ 7.05—8.15 (4H, aromatic protons).

Coupling of compounds **22b** and **23** with benzenediazonium salt and sodium acetate in ethanol had resulted into a Japp-Klingemann type reaction[16] producing the corresponding products, 1-(2-benzimidazolylthio)-1-(arylhydrazono)-2-propanone (**27**) and 2-phenylazo-3-methylthiazolo[3,2-*a*]benzimidazole (**28**) respectively. The IR spectrum of **27** showed appearance of bands at 1650 (C=O) and 3150 cm^{-1} (NH), while that of **28** showed disappearance of (C=O) band at 1645, and appearance of (N=N) band at 1640 cm^{-1} together with other characteristic bands.

Refluxing **23** with hydroxylamine, methylamine, and/or ethylamine hydrochloride in acetic acid or in pyridine produced the corresponding oxime **24a** and/or Schiff's bases **24b** and **c**. Higher aliphatic alkyl and aromatic amines were unsuccessfully condensed under variaty of conditions which may be attributed to steric factors. The IR spectra of **24a—c** showed no (C=O) band at 1645, but (C=N) band at 1610 and a broad (OH) band at 3450 cm^{-1} in the oxime **24a** spectrum.

Table 4. Physical and Analytical Data of Compound **24** and **25**

Compd[a]	Mp(θ_m/°C) (Solvent)	Yield/%	Molecular formula	Anal. (Calcd / Found)/%			
				C	H	N	S
24a	285 (AcOH)	75	$C_{12}H_{11}N_3OS$	58.78 58.76	4.49 4.50	17.14 17.20	13.06 13.10
24b	160 (EtOH)	62	$C_{13}H_{13}N_3S$	64.20 64.25	5.35 5.38	17.28 17.30	13.17 13.15
24c	175 (EtOH)	50	$C_{14}H_{15}N_3S$	65.37 65.40	5.84 5.86	16.34 16.30	12.45 12.48
25a	188 ($AcOH/H_2O$)	90	$C_{19}H_{14}N_2OS$	71.70 71.68	4.41 4.39	8.81 8.84	10.06 10.10
25b	200 (EtOH)	52	$C_{19}H_{13}N_3O_3S$	62.81 62.85	3.58 3.53	11.57 11.55	8.82 8.86
25c	180 (AcOH)	50	$C_{12}H_{19}N_3OS$	69.81 69.85	5.26 5.22	11.63 11.63	8.86 8.88

a) Compound **25a**, ^{1}H NMR (DMSO) δ=2.5 (s, 3H), 6.9—7.8 (m, 11H, 9HAr+2H, HC=CH); **25b**, ^{1}H NMR (DMSO) δ=2.51 (s, 3H, CH_3), 7.2—8.5 (m, 10H, 8HAr+2H, CH=CH).

Condensation of **23** with benzaldehyde and its *p*-nitro and *p*-dimethylamino substituents in ethanolic KOH produced the corresponding 2-(3-aryl-1-oxo-2-propenyl)-3-methylthiazolo[3,2-*a*]benzimidazoles (**25a—c**) (Table 4).

Experimental

Melting points were uncorrected. Infrared spectra were recorded on Unicam SP 200 g. Perkin-Elmer 599B and Shimadzu infrared spectrophotometers using potassium bromide Wafer technique. Ultraviolet spectra in ethanol were measured on Shimadzu 200S spectrophotometer and NMR spectra were recorded on Varian A60 and EM-390 (90MHz). MS were recorded on AEI MSI2 spectrophotometer at 70 eV.

Reactions of 2-Hydrazinobenzoxazole and 2-Hydrazinobenzimidazole (1 and 2) with Aromatic Aldehydes: i) (2-Benzoxazolyl)hydrazones (6a—f) and (2-Benzimidazolyl)hydrazones (7a—f): The hydrazino compounds[10] **1** and/or **2** (0.1 mol) and aromatic aldehydes (0.01 mol), namely benzaldehyde (**a**) and *p*-nitro- (**b**), *p*-chloro- (**c**), *p*-methoxy- (**d**), *p*-dimethylamino- (**e**), and *p*-methylbenzaldehyde (**f**) were refluxed in ethanol. The solids were separated on cooling, filtered and recrystallized from the proper solvent to give the corresponding hydrazones **6** and **7** which show characteristic mps as listed in Table 2.

ii) 3-(*p*-Substituted phenyl)-1,2,4-triazolo[4,3-*b*]benzoxazoles (4) and 3-(*p*-Substituted phenyl)-1,2,4-triazolo[4,3-*a*]benzimidazole:[5] General Procedure: A mixture of the hydrazino compound **1** and/or **2** (0.01 mol) and the aromatic aldehydes (0.01 mol) was refluxed in glacial acetic acid. After cooling, the separated solid was recrystallized from proper solvent, which gave the characteristic mps as shown in Table 1. The same compounds were produced from the corresponding hydrazones **6** and **7** on refluxing in glacial acetic acid for 8 h or on heating over their mp for 10 min.

1,2,4-Triazolo[4,3-*b*]benzoxazol-3(2*H*)-one (8), 9*H*-1,2,4-Triazolo[4,3-*a*]benzimidazol-3(2*H*)-one (9), and 1,2,4-Triazolo-[4,3-*b*]benzothiazol-3(2*H*)-one (10): A mixture of corresponding hydrazino compounds **1—3** (0.01 mol) and ethyl chloroformate (0.1 mol) in absolute ethanol (10 ml) was refluxed for 4 h. The solid separated was filtered and recrystallized from proper solvent to separate the corresponding triazolo compounds in Table 3.

3-Methyl-1,2,4-triazolo[4,3-*b*]benzoxazole (13) and 3-Methyl-9*H*-1,2,4-triazolo[4,3-*a*]benzimidazole (14): i) A mixture of hydrazino compounds **1** and **2** (0.1 mol) and acetic anhydride was refluxed for 8 h. The solid separated on cooling, filtered, and recrystallized from proper solvent to give the corresponding monoacetyl compounds **11** and **12** respectively as in Table 3.

ii) The monoacetyl compounds **11** and **12** were heated over their melting points for 30 min, cooled and recrystallized from 1-butanol to produce the corresponding methyltriazoles **13** and mp 170 °C and **14** mp 231 °C[17] respectively. Found: C, 62.42; H, 4.10; N, 24.33%. Calcd for $C_9H_7N_3O$ (**13**): C, 62.43; H, 4.05; N, 24.3%.

2*H*-1,2,4-Triazino[4,3-*b*]benzoxazole-3,4-dione (15), 1,2,4-Triazino[4,3-*a*]benzimidazole-3,4-dione (16), and 1,2,4-Triazino[4,3-*b*]benzothiazole-3,4-dione (17): A mixture of the corresponding hydrazino compounds (0.1 mol) and diethyl oxalate (0.1 mol) in absolute ethanol (10 ml) refluxed for 3 h. The solid separated on cooling was filtered and recrystallized from proper solvent to give corresponding triazino compounds as in Table 3.

2-(3,5-Dimethyl-1-pyrazolyl)benzoxazole (18) and 2-(3,5-Dimethyl-1-pyrazolyl)benzimidazole (19): A mixture of the corresponding hydrazino compounds (0.1 mol) and 2,4-pentanedione (0.1 mol) in methanol (20 ml) was refluxed for 3 h. The solid separated on cooling, filtered and recrystallized from proper solvent into the corresponding pyrazolyl compounds **18**[18] and **19** respectively as in Table 3.

2,2′-Hydrazinobis(benzoxazole) (20): A mixture of **1** (0.1 mol) and 2-chlorobenzoxazole (0.1 mol) in absolute ethanol was refluxed for 2 h. The solid separated on cooling, filtered, and recrystallized from ethanol as white crystals of **20** as hydrochloride; yield 60%, mp 198 °C. Found: C, 49.50; H, 3.48; N, 16.40; Cl, 20.88%. Calcd for $C_{14}H_{10}N_4O_2 \cdot 2HCl$: C, 49.41; H, 3.59; N, 16.47; Cl, 21.17%.

2,2′-Hydrazinobis(benzimidazole) (21): A mixture of **2** (0.1 mol) and 2-mercaptobenzimidazole (0.1 mol) was heated at 290—300 °C for 5 h. After cooling, the solid separated filtered and recrystallized from ethanol as colorless crystals, yield 52%, mp 257 °C. Found: C, 63.60; H, 4.60; N, 31.91%. Calcd for $C_{14}H_{12}N_6$: C, 63.64; H, 4.55; N, 31.82%.

2-Acetyl-3-methylthiazolo[3,2-*a*]benzimidazole (23): i) A mixture of 2-mercaptobenzimidazole (1.5 g) and KOH 85%

(0.75 ml) in ethanol (12 ml) was heated at 80 °C for 10 min. To the cooled reaction mixture was added 3-chloro-2,4-pentanedione (1.4 ml) and stirred for 4 h. The separated solid from ice-water mixture was filtered and recrystallized from ethanol as pale brown crystals of 3-(2-benzimidazolylthio)-2,4-pentanedione (**22**), yield 52%, mp 218 °C. Spectral analysis confirm the tautomeric enol form **22a** where the IR spectrum showed (OH) strong band at 3370 cm^{-1}. The ^1H NMR spectrum (in DMSO) showed signals at δ=2.4 (s, 6H, $2CH_3$), 3.4 (br, 2H, NH-OH), and 7.1—7.6 (m, 4H, Ar). Found: C, 58.18; H, 4.90; N, 11.31; S, 12.88%. Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.07; H, 4.84; N, 11.29; S, 12.09%.

ii) A mixture of **22** (2 g) and polyphosphoric acid (10 g) was heated at 100 °C for 1 h, then at 125 °C for 15 min. The solid separated with ice-water, was filtered and recrystallized from ethanol into white crystals of **23**, yield 49%, mp 169—170 °C. The same compound was separated in 90% yield or refluxing **22** with acetic anhydride-pyridine (2:3) mixture for 2 h. Found: C, 62.65; H, 4.39; N, 12.20; S, 13.96%. Calcd for $C_{12}H_{10}N_2OS$: C, 62.61; H, 4.35; N, 12.17; S, 13.91%.

Reaction of Benzenediazonium Salt with Compounds 22 and 23: To ice-cooled mixture of **22** (1.3 g) and/or **23** (1.3 g) and sodium acetate (3 g) in ethanol (20 ml) was added benzenediazonium chloride (from 1.3 g aniline) while stirring, then left for 1 h and poured on cooled water. The separated solid was filtered and recrystallized from benzene into corresponding yellow compounds, 1-(2-benzimidazolylthio)-1-(arylhydrazone)-2-propanone (**27**), yield 50%, mp 99 °C and 2-phenylazo-3-methylthiazolo[3,2-*a*]benzimidazole (**28**), yield 68%, mp 183 °C respectively. **27**: Found: C, 61.98; H, 4.50; N, 18.01; S, 10.36%. Calcd for $C_{16}H_{14}N_4OS$: C, 61.94; H, 4.52; N, 18.07; S, 10.32%. **28**: Found: C, 65.80; H, 4.07; N, 19.20; S, 10.97%. Calcd for $C_{16}H_{12}N_4S$: C, 65.75; H, 4.11; N, 19.18; S, 10.96%.

Reactions of 23 with the Appropriate Amino Compounds: General Procedure: A mixture of **23** (1 mol) and the aliphatic amines (1.1 mol), namely, hydroxylamine, methylamine, and/or ethylamine hydrochloride, ether in glacial acetic acid or in pyridine, was refluxed, and cooled. The separated solid filtered and recrystallized from proper solvent into the corresponding oxime and/or Schiff's bases (**24a—c**) respectively as in Table 4.

2-(3-Aryl-1-oxo-2-propenyl)-3-methylthiazolo[3,2-*a*]benzimidazoles (25a—c): A mixture of **23** (0.1 mol) and aromatic aldehydes (0.01 mol), benzaldehyde and its *p*-nitro and *p*-dimethylamino derivatives together with KOH solution (10 ml, 4%) in ethanol (50 ml). The mixture was kept overnight, acidified with dilute acetic acid. The separated chalcones filtered and recrystallized from proper solvent as in Table 4.

M. Z. A. Badr is thankful to Dr. Kevin S. Peters of Harvard University, U.S.A., for his assistance with some NMR and mass spectral analyses.

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