Regioselectivity in Reactions of Bis-Hydrazonoyl Halides with Some Bifunctional Heterocycles

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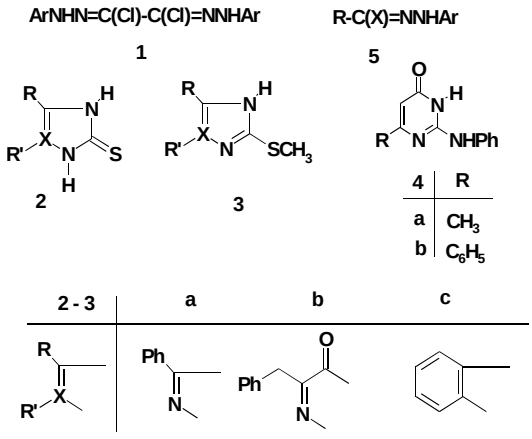
Bis-hydrazonoyl chloride **1** reacts regioselectively with 3-mercapto-1,2,4-triazole **2a**, 2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one **2b** and 2-mercaptobenzimidazole **2c** to give the hitherto unknown annelated 2,3-bis-(phenylhydrazono)thiazoles **6a-c**, respectively. Reactions of **1** with the methylthio derivatives of such heterocycles afforded the annelated 3,3′-bis-(1,2,4-triazoles) **11a-c**, respectively. Similar reaction of **1** with 2-phenylamino-4(3H)-pyrimidinones **4** gave 2,3-bis(phenylhydrazono)imidazo[1,2-a]pyrimidin-5(1H)-ones **16**. Oxidation of **6c** yielded the corresponding bis(phenylazo) derivative **15**. The regiochemistry of the studied reactions is discussed.

INTRODUCTION

In preceeding papers from our laboratory, it has been shown that bis-hydrazonoyl halides **1** can be used as precursors for synthesis of a variety of heterocyclic systems.[1-5] In continuation of this work, we wish to report herein the results of our study of the reactions of **1** (Ar = C_6H_5) with some heterocyclic thiones namely 1,2,4-triazole-3-thione **2a**, 1,2,4-triazine-3-thione **2b**, benzimidazole-2-thione **2c** together with their 2-methylthio derivatives **3a-c**, respectively (Chart 1). In addition, reactions of **1** with 2-phenylamino-6-substituted 4-pyrimidinones **4a,b** (Chart 1) were also investigated. Our objective of such a study was to cast light on the regioselectivity in the reactions of **1** with **2-4**. It is worth mentioning that in contrast to the extensive studies reported on the reactions of monohydrazonoyl halides **5** with numerous heterocycles,[6-9] reactions of bis-hydrazonoyl halides of type **1** have received much less attention.

Chart 1

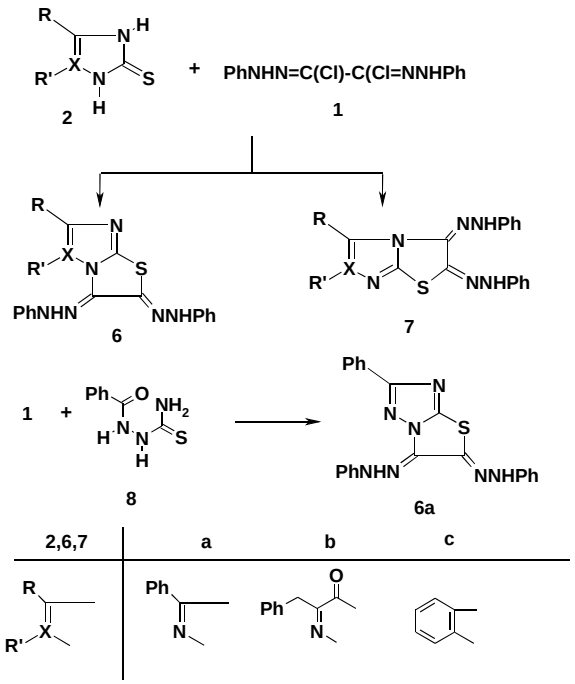


RESULTS AND DISCUSSION

The required bis-hydrazonoyl chloride **1**,[10] the thiones **2a-c**[11-13] and their methylthio derivatives **3a-c**[11,14,15] were prepared by known methods. Also, 6-methyl-2-phenylamino-4(3H)-pyrimidinone **4a** was prepared by a method from the literature.[16] As 6-phenyl-2-phenylamino-4(3H)-pyrimidinone **4b** has not been reported hitherto, it was thus prepared in this work by reaction of 2-methylthio-6-phenyl-4(3H)-pyrimidinone with aniline. Its structure was consistent with its spectral (IR, ^{1}H NMR and MS) and elemental analysis data (see Experimental).

When 5-phenyl-1,2,4-triazole-3-thione **2a** was allowed to react with **1**, either in ethanol in the presence of sodium ethoxide at room temperature (Method A) or in refluxing chloroform in the presence of triethylamine (Method B), it gave, in both cases, one and the same crystalline product whose mass spectrum [*m/z* 411 (M^+)] and microanalysis data were consistent with the molecular formula $C_{22}H_{17}N_7S$. Such a result indicated that the isolated product can be either one of the two regioisomers namely 5,6-bis-(phenylhydrazono)-2-phenylthiazolo[3,2-b][1,2,4]triazole and 5,6-bis-(phenylhydrazono)-3-phenylthiazolo[2,3-c][1,2,4]triazole, **6a** and **7a**, respectively (Scheme I). The isolated product was assigned the former structure **6a** on the basis of its independent and unambiguous synthesis by reaction of **1** with 1-benzoylthiosemicarbazide **8** (Scheme I). The product obtained from the latter reaction proved to be identical in all respects (mp., mixed mp., IR) with that isolated from the reaction of **2a** and **1** (see Experimental). The formation of **6a** rather than **7a** could be attributed to the greater nucleophilicity of N2 of 1,2,4-triazole as a result of being adjacent to a nitrogen atom, whereas the N4 which would afford the regioisomer **7a** is de-

Scheme I Synthesis of 2,3-bis(phenylhydrazono) derivatives of thiazolo[2,3-c][1,2,4]triazole, thiazolo[3,2-b][1,2,4]triazin-7-one and thiazolo[3,2-a]benzimidazole **6a-c**

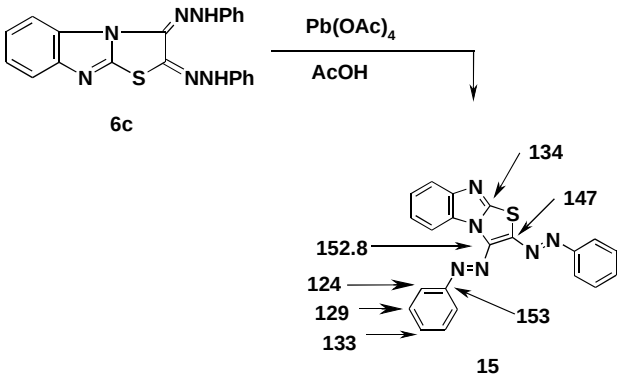


activated by the neighbouring electron deficient carbon atom. Formation of **6a** rather than **7a** is also in good agreement with literature reports which indicate that reaction of 3-mercapto-5-aryl-1,2,4-triazoles with haloketones afforded 2-aryl-1,2,4-triazolo[3,2-b]thiadiazole derivatives.[17-20]

Reaction of **1** with 6-benzyl-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one **2b** in ethanol in the presence of sodium ethoxide at room temperature gave a mixture of two products **A** and **B** in 72 and 10% yields, respectively. Both mass spectra and elemental analyses of these two products **A** and **B** indicated that their molecular formulas are $C_{24}H_{19}N_7OS$ and $C_{34}H_{24}N_{10}O_2$, respectively. Such data suggest that the former product **A** can be assigned either structure **6b** or **7b** (Scheme I) whereas the second product **B** can have either structure **11b** or **12b** (Scheme III). The IR spectra of the products **A** and **B** revealed their amide-I absorption bands at 1658 and 1660 cm^{-1}, respectively. Such stretching frequencies, while they are similar to those reported for azolo[b][1,2,4]triazin-7-ones (1660-1665 cm^{-1}),[21] differ from those reported for azolo[c][1,2,4]triazin-5-ones (1680-1690 cm^{-1}).[22] The difference in the amide carbonyl stretching frequencies is attributed to the difference in the type of conjugation exhibited by the acylguanidine residue in such structures. Such a residue exhibits through conjugation in structures of type **6b** and **11b** and cross conjugation in structures of type **7b** and **12b**.[23,24] On this basis, the two products **A** and **B** were identified as 2,3-bis(phenylhydrazono)thiazolo[3,2-b][1,2,4]triazin-7-one **6b** and 3,3′-bis-(1,2,4-triazolo[4,3-b][1,2,4]triazin-7(1H)-one) **11b**, respectively (Scheme III). The structure of the latter product **11b** was further confirmed unambiguously by its alternate synthesis as outlined below by reaction of **1** with 3-methylthio-5(4H)-1,2,4-triazinone **3b** (Scheme III).

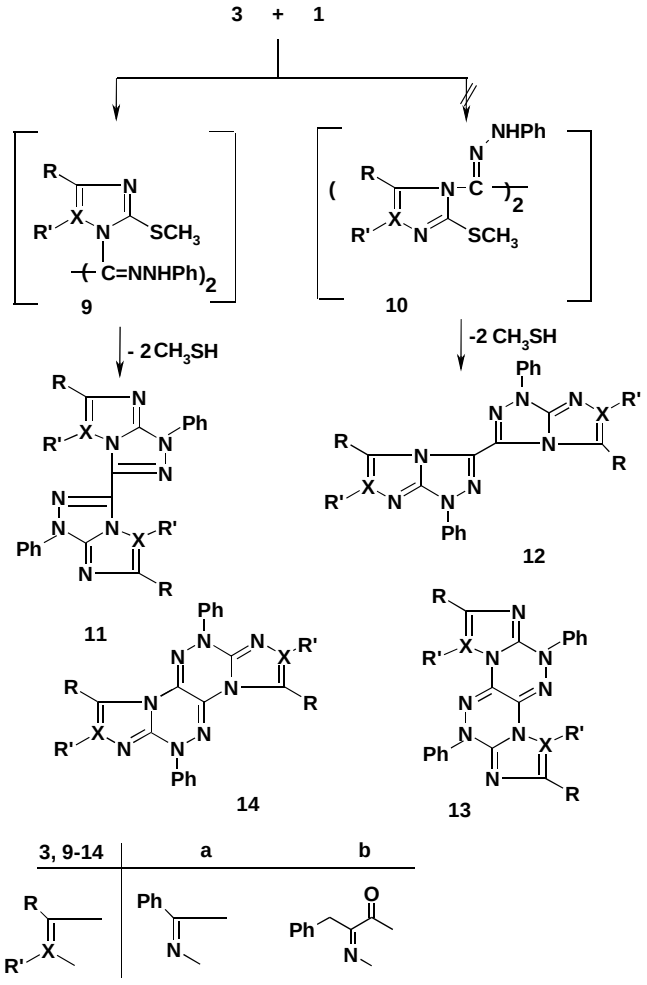
The reaction of **1** with 2-mercaptobenzimidazole **2c** is straightforward. Thus, treatment of **1** with **2c** in chloroform in the presence of triethylamine at room temperature afforded a single product. As compound **2c** is, in reality, symmetrical cyclic thiourea, there is no ambiguity as to the direction of annelation. Accordingly, the product isolated was identified as 2,3-bis(phenylhydrazono)thiazolo[3,2-a]benzimidazole **6c** (Scheme I). The structure of the latter was based on both its spectral (mass, NMR and IR) and elemental analyses (see Experimental). The assigned bis-hydrazone structure was further evidenced by the oxidation of **6c**. In our hands, treatment of **6c** with lead(IV) acetate in DMF-acetonitrile mixture afforded the corresponding bis-(phenylazo) derivative **15** (Scheme II). The elemental analyses and the spectral data (MS, IR, ^{1}H- and ^{13}C-NMR) are compatible with the assigned structure **15**. Thus, while its IR spectrum showed no absorption for the NH group, its mass spectrum revealed low intensity peaks for molecular ion. Its ^{13}C-NMR spectrum shows the characteristic signals of the phenylazo residue as indicated in Scheme II. Also the electronic absorption spectra revealed strong absorption bands assignable to the azo chromophores near λ 500 (log ε 4.17) and λ 337 (log ε 4.40) nm.

Scheme II Synthesis of 2,3-bis(phenylazo)thiazolo-[3,2-a]benzimidazole **15**



Next, reactions of **1** with each of **3a-c** were examined. In our hands, such reactions, when carried out in pyridine at reflux, afforded, in each case, one product as evidenced by tlc analysis of the crude product. Repetition of this reaction in refluxing ethanol in the presence of sodium ethoxide afforded the same products. The mass spectral and the elemental analysis data of the isolated products showed that the latter are free of sulfur and were consistent with either one of the four possible structures **11**-**14** (Scheme III). Since **3c** is symmetrical cyclic thiourea, it follows that the two structures **11c** and **12c** are equivalent and that the two structures **13c** and **14c** are also equivalent. In addition, the product isolated from reaction of **1** with **3b** proved identical with the product **11b** obtained above from reaction of **1** with **2b**.

Scheme III Synthesis of 3,3′-bis(annelated 1,2,4-triazoles **11a,b**



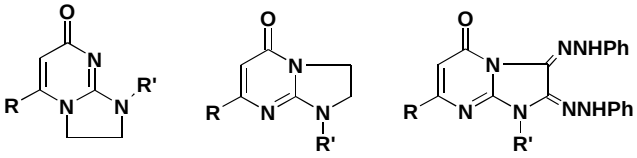
Attempts to elucidate the actual structures of the products isolated from the reactions of **1** with **3a-c** by the use of ^{13}C NMR spectra were unsuccessful. This was due to the poor solubility of the isolated products in most NMR solvents. Accordingly, distinction between structures **11**-**14** was made by comparison of their heat of formation (ΔH_f). The calculations of the ΔH_f's of **11-14** were made at the AM1 level using the Hyperchem program package (version 4.0). For each structure, full geometry optimization was performed, and the energy values reported are those for the equilibrium geometries. The results are summarized in Table 1. The data indicate that structures **11a-c** are the most stable ones. On the basis of this finding and mass spectra and elemental analyses, the products isolated from reactions of **1** with **3a-c** were assigned the structures **11a-c**, respectively. The regiochemistry in such reactions seems to be controlled by the basicity of the ring-nitrogens. The overall electronic distribution in **2b** or **3b** reveals that N2 is more nucleophilic than N4 because the latter is situated between two electron-deficient carbon atoms[25] and thus attack by N2 is more favourable and accordingly leads to the intermediates **9** which cyclize *in situ* to give the respective **11** as the end products (Scheme III).

Table 1. Heat of Formation (ΔH_f) of the Isomeric Structures **11-14**

Structure no.	$-\Delta H_f$, kJ. mol^{-1}		
	a	**b**	**c**
11	758.37	744.48	532.40
12	691.27	643.44	532.40
13	746.71	638.20	504.80
14	690.33	585.04	504.80

Finally, reactions of **1** with 2-phenylamino-6-substituted pyrimidin-4(3H)-ones **4a,b** were examined. As each of the latter pyrimidinones **4**, being unsymmetrical, reaction of each with **1** is expected to give either 2,3-dihydro-7-substituted-2,3-bis(phenylhydrazono)imidazo[1,2-a]pyrimidin-5(1H)-one **16** or its regioisomer 2,3- dihydro-5-substituted-2,3-bis(phenylhydrazono)imidazo[1,2-a]pyrimidin-7(1H)-one **17** or both depending on the direction of substitution (Scheme IV). In our hands, treatment of pyrimidinones **4a,b**, each with **1** furnished, in each case, a single product as evidenced by tlc analysis of the crude products. The IR spectra of the isolated products revealed the amide carbonyl band at 1670-1676 cm^{-1} and their ^{13}C NMR spectra showed the amide carbon signals at δ 161-162. Such spectral data are consistent with structure **16** and not with **17**. This is because comparison of these data with those reported for derivatives of imidazo-[1,2-a]pyrimidin-7(1H)-one and imidazo[1,2-a]pyrimidin-5(1H)-one ring systems **I** and **II**, respectively (Chart 2),[23,24] indicates that the spectral data of the isolated products from

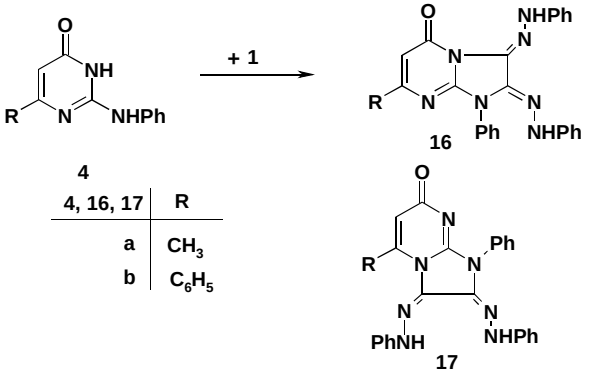
Chart 2



I	II	16
δCO 175-176	δCO 165-168	δCO 161-162
υCO 1656-1659 cm^{-1}	υCO 1690-1670 cm^{-1}	υCO 1670-1676 cm^{-1}

the studied reactions are similar to those of derivatives of **II**. On the basis of such similarity, the products isolated from reactions of **1** with **4a,b** were identified as **16a,b**, respectively. This regiochemical assignment is further evidenced by its analogy to that reported for the formation of imidazo[1,2-a]pyrimidin-5(1H)-ones from 1,2-dibromoethane with 2-arylamino-4(3H)-pyrimidinone derivatives.[26] Had the isolated products structure **17**, it would be expected to observe their amide carbonyl stretching bands at lower frequencies (1650-1660 cm^{-1}) and signal for the amide carbonyl carbon at δ 170-175 values.[23,24]

Scheme IV Synthesis of 2,3-bis(phenylhydrazono)-imidazo[1,2-a]pyrimidin-5(1H)-ones **16**



4, 16, 17	R
a	CH_3
b	C_6H_5

EXPERIMENTAL SECTION

Melting points were determined in open capillary tubes and are uncorrected. The IR spectra were recorded on a Pye-Unicam SP300 instrument. The ^{1}H- and ^{13}C-NMR spectra were recorded for solutions in deuterated chloroform or dimethylsulfoxide with a Varian Gemini spectrometer using TMS as an internal standard. Mass spectra were obtained in a GCMS-Q1000-EX spectrometer. Electronic absorption spectra were obtained using a Shimadzu UV and Visible 3101 PC spectrophotometer. Microanalyses were performed by the Microanalytical Center of Cairo University, Giza, Egypt.

The starting reagents namely bis-hydrazonoyl chloride **1**,[10] the thiones **2a-c**,[11-13] and their methylthio derivatives **3a-c**[11,14,15] and 2-phenylamino-6-methyl-4(3H)-pyrimidinone **4a**[16] were prepared as previously described.

Synthesis of 2-Phenylamino-6-phenyl-4(3H)-pyrimidinone 4b

A mixture of 2-methylthio-6-phenyl-4(3H)-pyrimidinone (2.17 g, 0.01 mol) and aniline (0.93 g, 0.01 mol) was heated at 180-190 °C in an oil bath for 4 h, then cooled. The reaction mixture was poured onto crushed ice with stirring. The precipitated solid was filtered off, dried and finally crystallized from dimethylformamide to give **4b**, yield 80%; m.p. 284 °C (DMF), IR, ν (cm^{-1}) 3100-3045, 1658, 1631; ^{1}H NMR (δ) 6.03 (s, 1H), 7.05-8.05 (m, 10H), 8.94 (s, 1H), 10.79 (s, 1H); Anal. for $C_{16}H_{13}N_3O$ (263.3) Found (Calcd.): C, 73.0 (72.99); H, 4.8 (4.98); N, 15.8 (15.96) %.

Synthesis of annelated thiazoles 6a-c

Method A

To an ethanolic sodium ethoxide solution, prepared from sodium metal (0.115 g, 5 mmol) and absolute ethanol (30 mL), was added the appropriate thione **2** (5 mmol) and the mixture was stirred. To the resulting mixture was added the bis-hydrazonoyl chloride **1** (5 mmol) and stirring was continued for 24 h at room temperature. The excess solvent was then distilled under reduced pressure and the mixture was cooled. The solid that was precipitated was filtered off, washed with water and dried. Crystallization from dimethylformamide-ethanol mixture gave the fused thiazole derivatives **6**. The physical constants of the products **6a-c** prepared are presented below.

Method B

To a mixture of equimolar quantities of **1** and the appropriate **2** (5 mmol each) in chloroform (30 mL) was added triethylamine (0.7 mL, 5 mmol) and the resulting mixture was refluxed 5 h. Workup of the reaction mixture as above gave the products **6** identical in all respects with those obtained by method-A.

Compound 6a: Yield 60%; m.p. 244 °C (EtOH/DMF), IR, ν (cm^{-1}) 3321-3161; ^{1}H NMR (δ) 6.73-8.22 (m, 15H), 9.56 (s, 1H), 12.83 (s, 1H); MS. *m/z* (%) 411 (M^+, 27), 236 (19), 206 (5), 177 (11), 132 (9), 118 (9), 104 (36), 91 (25), 77 (100), 65 (38), 51 (38). Anal. for $C_{22}H_{17}N_7S$ (411.5) Found (Calcd.): C, 63.90 (64.22); H, 4.10 (4.16); N, 23.70 (23.83) %.

Compound 6b:Yield 72%; m.p. 240 °C (DMF), IR, ν

(cm^{-1}) 3220, 3180, 1699; ^1H NMR (δ) 4.1 (s, 2H), 6.8-8.1 (m, 15H), 10.4 (s, 1H), 11.6 (s, 1H); MS. *m/z* (%) 454 (M^+, 12), 347 (8), 328 (7), 229 (10), 219 (13), 206 (7), 145 (6), 117 (18), 105 (14), 91 (65), 86 (15), 77 (100), 65 (31), 51 (46). Anal. for $C_{24}H_{19}N_7OS$ (453.5) Found (Calcd.): C, 63.30 (63.56); H, 4.10 (4.22); N, 21.40 (21.62) %.

Compound 6c: Yield 75%; m.p. 260 °C (EtOH/DMF), IR, ν (cm^{-1}) 3294-3180; ^1H NMR (δ) 6.91-8.3 (m, 14H), 10.57 (s, 1H), 11.1 (s, 1H); MS. *m/z* (%) 384 (M^+, 32), 292 (18), 206 (5), 186 (5), 150 (6), 134 (8), 105 (59), 92 (18), 77 (100), 65 (22), 51 (18). Anal. for $C_{21}H_{16}N_6S$ (384.4) Found (Calcd.): 65.50 (65.61); H, 4.10 (4.19); N, 21.70 (21.86).

Oxidation of 6c

To a stirred solution of **6c** (3.84 g, 0.01 mole) in dry dimethylformamide-acetonitrile (15 mL each) was added lead tetraacetate (0.012 mole) and the resulting mixture was further stirred for 24 h. The mixture was then poured onto cold water. The crude solid that precipitated was filtered off, dried and finally crystallized from DMF-water to give pure bis-azo derivative **15**.

Compound 15: Yield 40%; m.p. 200 °C (DMF/H_2O), ^1H NMR (δ) 7.28-8.27 (m); MS. *m/z* (%) 382 (M^+, 15), 292 (5), 259 (6), 134 (7), 121 (9), 105 (32), 90 (7), 77 (100), 65 (7), 51 (20). Anal. for $C_{21}H_{14}N_6S$ (382.4) Found (Calcd.): C, 65.70 (65.95); H, 3.50 (3.69); N, 21.70 (21.97) %.

Alternate Synthesis of thiazolo[3,2-b][1,2,4]triazole 6a

To a stirred solution of equimolar quantities of 1-benzoylthiosemicarbazide **8** and bishydrazonoyl chloride **1** (5 mmol each) in ethanol (30 mL) was added triethylamine (1.4 mL, 10 mmol). The mixture was stirred at room temperature for 24 h. The solid that precipitated during this period was filtered off, washed with water and dried. Crystallization from dimethylformamide-ethanol mixture gave **6a** in 60% yield (1.23 g), mp. 244 °C. The isolated product proved identical in all respects (mp., mixed mp. and IR) with **6a** that was isolated above from the reaction of **1** and **2a**.

Synthesis of 3,3′-Bis(annelated [1,2,4]triazoles) 11

To an ethanolic sodium ethoxide solution, prepared from sodium metal (0.115 g, 5 mmol) and absolute ethanol (30 mL), was added methylthio derivative **3** (5 mmol) while stirring the mixture. To the latter was added the bishydrazonoyl chloride **1** (5 mmol) and the reaction mixture was refluxed till methanethiol ceased to evolve (15 h). The excess solvent was distilled under reduced pressure and the reaction mixture was cooled. The solid that formed upon cooling was collected, washed with water, dried and finally crystallized from dimethylformamide-water to give the corresponding **11**. The physical constants of the products **11a-c** prepared are given below.

Compound 11a: Yield 48%; m.p. 232-233 °C (DMF/H_2O), ^1H NMR (δ) 7.15-8.3 (m); MS. *m/z* (%) 520 (M^+, 52), 285 (10), 261 (5), 103 (100), 91 (27), 77 (51), 64 (7), 51 (15). Anal. for $C_{30}H_{20}N_{10}$ (520.5) Found (Calcd.): C, 68.80 (69.22); H, 3.30 (3.87); N, 26.60 (26.91) %.

Compound 11b: Yield 60%; m.p. 284-286 °C (EtOH/DMF), IR, ν (cm^{-1}) 1660; ^1H NMR (δ) 4.1 (s, 4H), 7.0-8.2 (m, 20H); MS. *m/z* (%) 605 (M^+, 5), 487 (14), 371 (28), 345 (12), 302 (7), 116 (33), 91 (100), 77 (31), 64 (26), 51 (31). Anal. for $C_{34}H_{24}N_{10}O_2$ (604.6) Found (Calcd.): C, 67.20 (67.54); H, 3.90 (4.00); N, 23.00 (23.17) %.

Compound 11c: Yield 43%; m.p. > 300 °C (DMF/H_2O), MS. *m/z* (%) 467 (M^+, 49), 378 (89), 259 (59), 207 (70), 169 (19), 144 (17), 130 (19), 103 (100), 91 (60), 77 (97), 65 (66), 51 (53). Anal. for $C_{28}H_{18}N_8$ (466.5): Found (Calcd.): C, 72.00 (72.09); H, 3.90 (3.89); N, 23.90 (24.20) %.

Synthesis of 2,3-dihydro-1-phenyl-2,3-bis-(phenylhydrazono)-7-substituted-imidazo[1,2-a]pyrimidin-5(1H)-ones 16a,b

To an ethanolic sodium ethoxide solution, prepared from sodium metal (0.115 g, 5 mmol) and absolute ethanol (30 mL), was added the appropriate 2-phenylaminopyrimidinone **4** (5 mmol) and the mixture was stirred. To the resulting mixture was added bis-hydrazonoyl chloride **1** (5 mmol) and stirring was continued for 24 h at room temperature. The excess solvent was then distilled under reduced pressure and the mixture was cooled. The solid that was formed was filtered off, washed with water and dried. Crystallization from dimethylformamide-ethanol mixture gave the fused imidazole derivative **16**. The physical constants of the products **16a,b** prepared are presented below.

Compound 16a: Yield 76%; m.p. 178 °C; (EtOH/DMF), IR, ν (cm^{-1}) 3319, 3157, 1670, 1647; ^1H NMR (δ) 2.13 (s, 3H), 6.03 (s, 1H), 6.72-7.59 (m, 15H), 10.71 (s, 1H), 12.81 (s, 1H); MS. *m/z* (%) 436 (M^+ +1, 27), 435 (M^+, 25), 343 (14), 270 (18), 107 (43), 93 (100), 92 (31), 77 (80). Anal. for $C_{25}H_{21}N_7O$ (435.5) Found (Calcd.): C, 69.00 (68.95); H, 4.70 (4.86); N, 22.30 (22.51) %.

Compound 16b: Yield 90%; m.p. 280 °C (EtOH/DMF), IR, ν (cm^{-1}) 3200, 3150, 1676, 1650; ^1H NMR (δ) 6.53 (s, 1H), 6.84-7.92 (m, 20H), 11.05 (s, 1H), 12.76 (s, 1H); MS. *m/z* (%) 497 (M^+, 52), 405 (23), 129 (18), 105 (18), 77 (100). Anal. for $C_{30}H_{23}N_7O$ (497.5) Found (Calcd.): C, 72.40

(72.42); H, 4.50 (4.66); N, 19.60 (19.71) %.

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Key Words

Hydrazones; Synthetic methods; Thiazoles; Triazoles.

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