A convenient one-pot synthesis of 3-arylazo derivatives of azino[b][1,2,4,5]tetrazines

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The reactions of 3-chloro-1,5-diarylformazans **1** with 3-amino-2-thiouracils **2(4)** and 3-amino-2-thioxo-6-methyl-1,2,4-triazin-5(4H)-ones **6** and their methylthio derivatives **3**(**5**) and **7**, respectively provide easy access to synthesis of 3-arylazo derivatives of 1,4-dihydro-1,8-disubstituted pyrimido[1,2-b][1,2,4,5]tetrazin-6-ones **8**(**9**) and 1,4-dihydro-1-aryl-7-methyl[1,2,4]triazino[4,3-b][1,2,4,5]-tetrazin-6-ones (**10**), respectively.

Keywords: 3-arylazo derivatives of azino[b][1,2,4,5]tetrazines

Recently, we have reported that reactions of 3-chloro-1,5-diarylformazans **1** with heterocyclic thiones, having a thiourea residue in their structure, provide direct, efficient and regioselective routes for synthesis of 3-arylazo-[1,2,4]triazolo[4,3-a]pyrimidin-5(1H)-ones.[1] In continuation of such studies, we have studied the reactions of **1** with heterocyclic systems having a thiosemicarbazide and thiocarbohydrazide residues in their structures such as 3-amino-2,3-dihydro-6-substituted-2-thioxo-4(1H)-pyrimidinones **2(4)** and 4-amino-2,3-dihydro-3-thioxo[1,2,4]triazin-5(4H)-one **6** as well as their methylthio derivatives **3**(**5**) and **7**, respectively. Our objectives were, on the one hand to develop a new simple one-step strategy for synthesis of 3-arylazo derivatives of pyrimido[1,2-b][1,2,4,5]tetrazines **8(9)** and 1,2,4-triazino[4,3-b][1,2,4,5]tetrazines **10** which cannot be prepared by direct methods and on the other hand to shed some light on the site- and regio-selectivities in the reactions to be studied. As far as we know, although numerous derivatives of azinotetrazines were reported, their 3-arylazo derivatives have not been reported hitherto.[2] In addition, the synthesis of each of pyrimido[1,2-b][1,2,4,5]tetrazines and 1,2,4-triazino[4,3-b][1,2,4,5]tetrazine ring systems from the respective thiones **2(4)** and **6** comprises at least three steps in each case.[2] Furthermore, the interest in developing a new convenient access to the target arylazoazinotetrazines **8–10** is due to the recent finding that derivatives of pyrimido[1,2-b][1,2,4,5]tetrazines ring system were reported to be the most active inhibitors of human cytomegalovirus protease.[3]

Results and discussion

The required starting heterocyclic thiones namely **2**(**3**), **4**(**5**) and **6**(**7**) were prepared as previously described.[4-6] The reactions of **1** with each of the thiones **2, 4** and **6** were carried out in ethanol in the presence of triethylamine at reflux. In all cases, it was noticed that hydrogen sulfide evolved during the course of the reaction. Accordingly the reaction mixture was refluxed until such gas ceased to evolve. Work up of the reaction mixture afforded, in each case, one product as evidenced by TLC analysis and which was found to be free of sulfur. The isolated products were identified as 3-arylazo derivatives of 1,4-dihydro-1,8-disubstituted-pyrimido[1,2-b][1,2,4,5]tetrazin-6-ones **8**, **9** and 1,4-dihydro-1,7-disubstituted-[1,2,4]triazino[4,3-b][1,2,4,5]tetrazin-6-ones **10**, respectively. The structures of the latter products **8–10** were elucidated on the basis of their spectra (MS, IR, UV and ^{1}H NMR) and microanalyses.

For example, the mass spectra of **8** and **9** revealed their molecular ion peaks at the expected *m/z* values and their relative intensities ranged from 12 to 36%. In addition, they revealed the presence of peaks at *m/z* values asignable to $[M^+ - ArN_2]$, $[M^+ - ArN_2C(:NH)N]$, $[M^+ - ArN_2C(:NH)NNHAr]$, $[ArN_2]$, [ArN], and [Ar] ionic species. Their IR spectra were characterised by the presence of NH and CO absorption bands in the regions 3301-3320 and 1660–1680 cm^{-1}, respectively. Furthermore, their ^{1}H NMR spectra exhibited a characteristic singlet NH signal in the region δ 9.5–10.6. The ^{13}C NMR spectra of the products **8b** and **9b**, taken as typical examples of the series prepared showed the carbonyl carbon signal near δ 156.8 and 159.5, respectively. Also, the products **10** display in their IR spectra absorption bands in the regions 3200–3260 and 1680–1690 cm^{-1} due to the NH and CO groups, respectively. Their ^{1}H NMR spectra, while they reveal the absence of the N-NH_2 proton signal present in the spectrum of **6** at δ 6.1, they showed a common characteristic singlet signal at δ 9.2– 9.4 assignable to NH proton. The latter signal disappeared upon exchange with D_2O. The mass spectra of **10** revealed peaks at *m/z* corresponding to $[M^+ - 28]$, $[M^+ - ArN_2]$, $[ArN_2]$, and [Ar] ionic species in addition to the respective molecular ion peaks which were not the parent peaks, however. Furthermore, the electronic absorption spectra of **8–10** in dioxane showed in each case two aborption bands in the regions 472–415 and 355– 300 nm (Table 1). Such absorption pattern is similar to that reported

Table 1 Electronic absorption spectra of the products **8–10**

Compd no.	λ_{max} (log ε) in dioxane	Compd no.	λ_{max} (log ε) in dioxane
8a	463 (4.21), 350 (4.29)	**9d**	415 (4.25), 303 (4.23)
8b[a]	445 (4.23), 323 (4.59)	**9e**	437 (4.19), 305 (4.13)
8d	450 (4.29), 306 (4.21)	**9f**	425 (4.23), 300 (4.92)
8e	455 (4.27), 305 (4.27)	**9g**	471 (4.26), 350 (4.26)
8g	466 (4.27), 350 (4.29)	**10a**	457 (4.21), 353 (4.29)
9a	461 (4.42), 355 (4.12)	**10b**[c]	445 (5.10), 312 (4.41)
9b[b]	450 (4.31), 330 (4.26)	**10d**	445 (4.11), 313 (4.42)
9c	446(4.29), 305(5.01)	**10g**	466 (4.27), 305 (411)

[a]UV spectra of **8b**: Solvent : λ_{max} (log ε) : Petroleum ether 450 (4.29), 320 (4.25); Ethanol 426 (4.27), 315 (4.29); Chloroform 435 (4.26), 320 (4.12). [b]UV spectra of **9b**: Solvent : λ_{max} (log ε) : Petroleum ether 472 (4.31), 305 (4.51); cyclohexane 468 (4.26), 300 (4.27); chloroform 461 (4.29), 310 (4.29). [c]UV spectra of **10b**: Solvent : λ_{max} (log ε) : Petroleum ether 446 (4.21), 310 (4.32); Chloroform 441 (4.42), 319 (5.01); Cyclohexane 445 (4.05), 300 (4.42); Ethanol 433 (4.01); 314 (4.82); DMF 431 (4.22), 303 (4.46); Acetic acid 426 (4.52), 320 (4.61).

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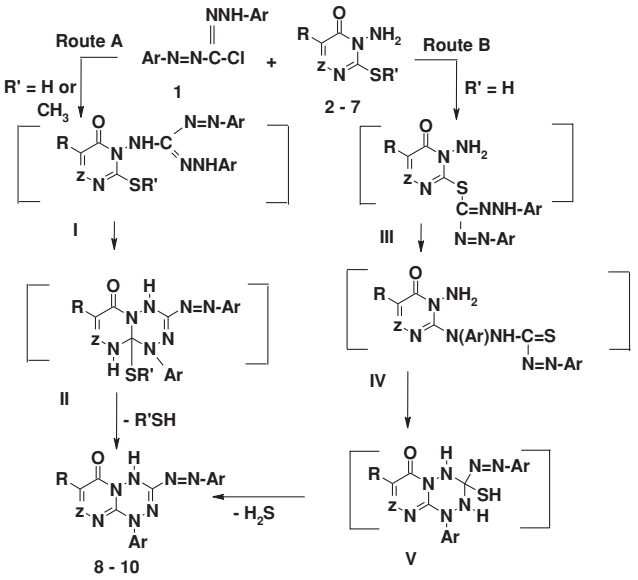

R / Z / R'	
2, 8	H / Me-C / H
3	H / Me-C / Me
4, 9	H / Ph-C / H
5,	H / Ph-C / Me
6, 10	Me / N / H
7	Me / N / Me

Ar = XC_6H_4

X : a, 4-MeO, b, 4-Me; c, 3-Me; d, H; e, 4-Cl; f, 3-Cl; g, 4-NO_2

Scheme 1

for typical arylazo compounds.[7] The spectra of **8b**, **9b** and **10b**, taken as typical examples of the three series prepared, each in solvents of different polarity showed little variation, if there is any (Table 1). This indicates that each of the studied compounds exists only in one tautomeric form.

To account for the formation of **8–10**, the two possible pathways A and B depicted in Scheme 1 were considered. Thus, it is suggested that reactions of **1** with each of **2, 4** or **6** presumably proceed through initial formation of the respective hydrazidine derivatives **I** which subsequently undergo *in situ* cyclisation with concurrent elimination of hydrogen sulfide to give the respective annelated tetrazines **8–10** as end products, respectively (Route-A). The formation of **I** is analogous to the reactions of hydrazonoyl halides with hydrazines which were reported to give the corresponding hydrazidines.[8] Alternatively, reaction of **1** with each of **2, 4** and **6** may start with the formation of the thiohydrazonic esters **III** which undergo *in situ* Smiles rearrangement[9,10] under the reaction conditions employed to afford the corresponding thiohydrazides **IV**. Then the latter thiohydrazides **IV** undergo cyclization as soon as they are formed with concurrent elimination of hydrogen sulfide to give the respective annelated tetrazine as the end products **8–10** (Route B, Scheme 1). All attempts to isolate any of the aforementioned intermediates **I, III** and **IV** were unsuccessful, however. Presumably, such intermediates are converted under the employed reaction conditions to the final products **8– 10** as soon as they are formed.

To distinguish between these two alternative pathways, the reactions of **1** with each of the methylthio derivatives **3, 5** and **7** were investigated. Thus, refluxing a mixture of **1** with each of **3**, **5** and **7** in refluxing pyridine afforded, in each case, one product whose ^{1}H NMR spectrum showed the absence of both the methylthio and amino proton signals present at δ 3.13 and 5.72, respectively in the spectra of the respective 3-amino-2-methylthio derivatives **3, 5** and **7**. Instead, the spectra of the isolated products revealed in each case, a characteristic one NH proton singlet in the region δ 9.0–9.4. Furthermore, such products proved identical in all respects (m.p., mixed m.p., IR) with those obtained above from reactions of **1** with **2, 4** and **6**, respectively. As compounds **3, 5** and **7** cannot form thiohydrazonates with **1**, it is not unreasonable to conclude that route-A in Scheme 1 seems to be the most plausible mechanism for the studied reactions of **1** with **2, 4** and **6** leading to **8– 10**, respectively.

In conclusion, the foregoing results indicate collectively that the studied reactions of 3-chloro-1,5-diarylformazans **1** with 3-amino-2-thiouracils **2(4)** and 3-amino-2-thioxo-6-methyl-1,2,4-triazin-5(4H)-ones **6** and their methylthio derivatives **3**(**5**) and **7**, respectively provide easy access to synthesis of 3-arylazo derivatives of 1,4-dihydro-1,8-disubstituted pyrimido[1,2-b][1,2,4,5]tetrazin-6-ones **8**(**9**) and 1,4-dihydro-1-aryl-7-methyl[1,2,4]triazino[4,3-b][1,2,4,5]-tetrazin-6-ones (**10**), respectively. The latter compounds **8–10** represent important extensions in the chemistry of ring-fused 4H-1,2,4,5-tetrazines. The availability of the 4-nitrogen atom for further substitution offers the potential for novel biologically active materials or dyestuffs.

Experimental

Melting points were measured on an electrothermal Gallenkamp melting point apparatus and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded in deuterated chloroform with tetramethylsilane (TMS) as an internal standard using a 300 MHz Varian Gemini spectrometer. The IR spectra were measured on a Fourier Transform and Pye Unicam Infrared spectrophotometers using potassium bromide wafer. Mass spectra were recorded on a GCMS-QP 1000 EX spectrometer at an ionising potential of 70 eV. The electronic absorption spectra were recorded on Perkin-Elmer Lambada spectrophotometer. Elemental microanalyses were carried out at the Microanalytical Laboratory of Cairo University, Giza, Egypt.

3-Chloro-1,5-diarylformazans **1** were prepared by coupling of the corresponding diazotized anilines with potassium chloromalonate as previously described.[11] 3-Amino-2,3-dihydro-6-methyl-2-thioxo-4(1H)pyrimidinone **2**, 3-amino-6-methyl-2-methylthio-4(3H)-pyrimidinone **3**, 3-amino-2,3-dihydro-6-phenyl-2-thioxo-4(1H) pyrimidinone **4** and 3-amino-6-phenyl-2-methylthio-4(3H)-pyrimidinone **5**, 4-Amino-6-methyl-3-thioxo-1,2-dihydro[1,2,4] triazin-5(4H)-one **6** and 4-amino-6-methyl-3-metylthio[1,2,4]triazin-5(4H)-one **7** were also prepared by literature methods.[4-6]

3-Arylazo-1,4-dihydro-1,8-disubstituted-6H-pyrimido[1,2-b] [1,2,4,5]-tetrazin-6-ones (8 and 9)

Method A: To a mixture of equimolecular quantities of the appropriate 3-chloro-1,5-diarylformazan **1** and 2-thiouracil derivative **2** (or **4**) (0.005 mole each) in absolute ethanol (40 ml) was added triethylamine (0.7 ml, 0.005 mole). The resulting mixture was refluxed until hydrogen sulfide ceased to evolve (4–6 h) and then cooled. The solid that precipitated upon cooling was filtered off, washed with water, dried and finally crystalliseed from ethanol to give the respective pure pyrimidotetrazine derivative **8** (or **9**) in 45 - 67% yield.

Method B: A mixture of equimolar quantities of the 2-methylthio derivative **3** (or **5**) and the appropriate 3-chloro-1,5-diarylformazan **1** (5 mmol each) were refluxed in pyridine for 10 h and cooled. The cold reaction mixture was then poured onto ice-cold hydrochloric acid with stirring. The solid that precipitated was collected, washed with water and finally crystallised from ethanol to give the corresponding pyrimidotetrazines **8** and **9,** respectively which were found identical in all respects with that obtained above from reactions of **1** with **2** and **4**.

The various pyrimido[1,2-b][1,2,4,5]tetrazines **8a–g** and **9a–g** that were prepared, together with their physical constants, are listed subsequently.

3-(4-Methoxyphenylazo)-1-(4-methoxyphenyl)-8-methyl-4H-pyrimido[1,2-b][1,2,4,5]tetrazin-6-one (**8a**)**:** Dark brown solid**,** Yield 55 %; m.p. 234ºC (EtOH); ν (cm^{-1}) 3304, 3194, 1643; ^{1}H NMR δ 2.12 (s, 3H), 3.85 (s, 3H), 3.92 (s, 3H), 6.01 (s, 1H), 6.97 (d, *J* = 7, 2H), 7.02 (d, *J* = 7, 2H), 7.55 (d, *J* = 7, 2H), 8.01 (d, *J* = 7, 2H), 9.54 (s, 1H); MS *m/z* (%) 406 (M^++1, 6.2), 405 (M^+, 23.8), 272(1.3), 230 (1.0), 135(16.3), 108 (8.4), 107 (100), 93 (2.8). Anal Calcd. for $C_{20}H_{19}N_7O_3$: (405.4) : C, 59.25; H, 4.72; N, 24.18. Found: C, 59.19; H, 4.51; N, 24.12 %.

3-(4-Methylphenylazo)-1-(4-methylphenyl)-8-methyl-4H-pyrimido[1,2-b][1,2,4,5]tetrazin-6-one (**8b**): Brown red solid, Yield 45 %; m.p. 258ºC (EtOH); ν (cm^{-1}) 3302, 3193, 1643; ^{1}H NMR δ 2.12 (s, 3H), 2.41(s, 3H), 2.40 (s, 3H), 6.03 (s, 1H), 7.20 (d, *J* = 6, 2H), 7.32 (d, *J* = 6, 2H), 7.55 (d, *J* = 6, 2H), 7.92

(d, *J* = 6, 2H), 9.54 (s, 1H); MS *m/z* (%) 374 (M^++1, 2.2), 373 (M^+, 2.4), 255(2.5), 214 (1.1), 157(100), 119 (1.5), 109 (2.7), 106 (1.9), 91 (14.4), 77(2.5). Anal Calcd. for $C_{20}H_{19}N_7O$: (373.4) : C, 64.33; H, 5.13; N, 26.26. Found: C, 64.21; H, 5.02; N, 26.11 %.

3-(Phenylazo)-1-phenyl-8-methyl-4H-pyrimido[1,2-b][1,2,4,5]tetrazin-6-one (**8d**): Brown red solid, Yield 30 %; m.p. 265°C (EtOH); ν (cm^{-1}) 3309, 3194, 1643; ^{1}H NMR δ 2.19 (s, 3H), 6.25 (s, 1H), 7.75-8.00 (m, 10H); 10.48 (s, 1H); MS *m/z* (%) 346 (M^++1, 17.7), 241 (1.3), 200 (1.6), 105 (13.6), 91 (2.8), 77(100). Anal Calcd. for $C_{18}H_{15}N_7O$ (345.3): C, 62.60; H, 4.38; N, 28.39. Found: C, 62.23; H, 4.29; N, 28.40 %.

3-(4-Chlorophenylazo)-1-(4-chlorophenyl)-8-methyl-4H-pyrimido[1,2-b][1,2,4,5]tetrazin-6-one (**8e**): Brown red solid, Yield 40 %; m.p. 258°C (EtOH); ν (cm^{-1}) 3302, 3194, 1640; ^{1}H NMR δ 2.21 (s, 3H), 6.09 (s, 1H), 7.53 (d, *J* = 6, 2H), 7.63 (d, *J* = 6, 2H), 7.82 (d, *J* = 6, 2H), 7.97 (d, *J* = 6, 2H), 9.52 (s, 1H); MS *m/z* (%) 414 (M^++1, 4.3), 413 (M^+, 8.0), 275(4.4), 235 (2.7), 157(100), 139 (7.7), 126 (27.1), 109 (9.4), 111 (47.9), 99 (4.8). Anal Calcd. for $C_{18}H_{13}Cl_2N_7O$ (414.2): C, 52.19; H, 3.16; N, 23.67. Found: C, 52.14; H, 3.11; N, 23.45**.**

3-(4-Nitrophenylazo)-1-(4-nitrophenyl)-8-methyl-4H-pyrimido[1,2-b][1,2,4,5]tetrazin-6-one (**8g**): Deep brown solid, Yield 45 %; m.p. 248°C (EtOH); ν (cm^{-1}) 3302, 3194, 1640; ^{1}H NMR δ 2.12 (s, 3H), 6.03 (s, 1H), 7.27 (d, *J* = 6, 2H), 7.34 (d, *J* = 6, 2H), 7.54 (d, *J* = 6, 2H), 7.92 (d, *J* = 6, 2H), 9.54 (s, 1H); MS *m/z* (%) 436 (M^++1, 16.6), 435 (12), 287(32), 245 (11.1), 150 (38.4), 153 (11.4), 136 (6.6), 122 (100), 109 (25.8), 108 (12.4). Anal Calcd. for $C_{18}H_{13}N_9O_5$ (435.3): C, 49.66; H, 3.01; N, 28.96. Found: C, 49.62; H, 3.00; N, 28.91 %.

3-(4-Methoxyphenylazo)-1-(4-methoxyphenyl)-8-phenyl-4H-pyrimido[1,2-b][1,2,4,5]tetrazin-6-one (**9a**): Brown red solid, Yield 50 %; m.p. 272°C (EtOH); ν (cm^{-1}) 3317, 1674 cm^{-1}; ^{1}H NMR δ 3.89 (s, 3H), 3.92 (s, 3H), 6.62 (s, 1H), 7.36 (d, *J* = 7, 2H), 7.39 (d, *J* = 7, 2H), 7.64 (d, *J* = 7, 2H), 8.03 (d, *J* = 7, 2H), 9.58 (s, 1H); MS *m/z* (%) 468 (M^+ + 1, 17.5), 467 (M^+, 19.7), 333 (1.2), 292 (1.6), 171 (4.4), 135 (18.2), 129 (7.0), 107 (100), 92 (28), 77 (56.9). Anal Calcd. for $C_{25}H_{21}N_7O_3$ (467.5): C, 64.23; H, 4.53; N, 20.97. Found: C, 64.21; H, 4.02; N, 20.92 %.

3-(4-Methylphenylazo)-1-(4-methylphenyl)-8-phenyl-4H-pyrimido[1,2-b][1,2,4,5]tetrazin-6-one (**9b**): Brown red solid, Yield 49 %; m.p. 256°C (EtOH); ν (cm^{-1}) 3170, 1658; ^{1}H NMR δ 2.44 (s, 3H), 2.46 (s, 3H), 6.64 (s, 1H), 7.25-7.37 (m, 5H),), 7.38 (d, *J* = 6, 2H), 7.63 (d, *J* = 6, 2H), 7.75 (d, *J* = 6, 2H), 7.94 (d, *J* = 6, 2H), 9.58 (s, 1H); ^{13}C NMR δ 21.3, 21.9, 103.2, 124.3, 125.0, 127.3, 129.3, 129.7, 131.1, 131.3, 133.3, 136.3, 136.9, 138.4, 144.2, 145.6, 149.9, 152.5, 159.5; MS *m/z* (%) 436 (M^+ + 1, 18), 435 (M^+, 0.1), 317 (2.5), 172 (5.6), 129 (6.6), 118 (8.8), 91 (100), 77 (6). Anal Calcd. for $C_{25}H_{21}N_7O$ (435.5): C, 68.95; H, 4.86; N, 22.51. Found: C, 68.81; H, 4.81; N, 22.44%.

3-(3-Methylphenylazo)-1-(3-methylphenyl)-8-phenyl-4H-pyrimido[1,2-b][1,2,4,5]tetrazin-6-one (**9c**): Brown red solid, Yield 60 %; m.p. 240°C (EtOH); ν (cm^{-1}) 3163, 1658; ^{1}H NMR δ 2.42 (s, 3H), 2.46 (s, 3H), 6.3 (s, 1H), 7.26-7.93 (m, 8H), 9.65(s, 1H); MS *m/z* (%) 436 (M^+ + 1, 18), 435 (M^+, 28), 317 (3), 219 (100), 171 (2), 129 (15), 119 (4), 91 (22), 77 (39). Anal Calcd. for $C_{25}H_{21}N_7O$ (435.5): C, 68.95; H, 4.86; N, 22.51. Found: C, 68.91; H, 4.17; N, 22.39 %.

3-(Phenylazo)-1,8-(diphenyl)-4H-pyrimido[1,2-b][1,2,4,5]tetrazin-6-one (**9d**): Brown red solid, Yield 50 %; m.p. 246°C (EtOH); ν (cm^{-1}) 3240, 1689; ^{1}H NMR δ 6.67 (s, 1H), 7.75-8.06 (m, 15H); 9.59 (s, 1H); MS *m/z* (%) 408 (M^+ + 1, 34.2), 407 (M^+, 30.7), 302 (2.1), 262 (1.9), 169 (0.2), 105 (14.1), 91 (1.9), 77 (100). Anal. Calcd. for $C_{23}H_{17}N_7O$ (407.4): C, 67.80; H, 4.21; N, 24.06. Found: C, 67.77; H, 4.11; N, 24.00 %.

3-(4-Chlorophenylazo)-1-(4-chlorophenyl)-8-phenyl-4H-pyrimido[1,2-b][1,2,4,5]tetrazin-6-one (**9e**): Brown red solid, Yield 54 %; m.p. 268°C (EtOH); ν (cm^{-1}) 3300, 1658; ^{1}H NMR δ 6.68 (s, 1H), 7.26 – 7.34 (m, 5H), 7.41 (d, *J* = 7, 2H), 7.48 (d, *J* = 7, 2H), 7.72 (d, *J* = 7, 2H), 8.00 (d, *J* = 7, 2H), 9.55 (s, 1H); MS *m/z* (%) 478 (M^+ + 2, 13.4), 477 (M^+ + 1, 8.8), 476 (M^+, 24.3), 337 (9.5), 296 (4.0), 139 (24.6), 125 (2.4), 111 (100), 77 (15.1), 65 (2.5). Anal. Calcd. for $C_{23}H_{15}Cl_2N_7O$ (476.3): C, 58.00; H, 3.17; N, 20.58. Found: C, 57.98; H, 3.14; N, 20.42 %.

3-(3-Chlorophenylazo)-1-(3-chlorophenyl)-8-phenyl-4H-pyrimido[1,2-b][1,2,4,5]tetrazin-6-one (**9f**): Brown red solid, Yield 45 %; m.p. 247°C (EtOH); ν (cm^{-1}) 3232, 1689; ^{1}H NMR δ 6.70 (s, 1H), 7.26-8.04 (m, 13H), 9.50 (s, 1H); MS *m/z* (%) 478 (M^+ + 2, 15.8), 477 (M^+ + 1, 9.2), 476 (M^+, 25.3), 337 (7.8), 296 (2.6), 139 (12.6), 125 (1.1), 111 (100), 77 (11.9); Anal. Calcd. for $C_{23}H_{15}Cl_2N_7O$ (476.3): C, 58.00; H, 3.17; N, 20.58. Found: C, 57.88; H, 3.22; N, 20.42 %.

3-(4-Nitrophenylazo)-1-(4-nitrophenyl)-8-phenyl-4H-pyrimido[1,2-b][1,2,4,5]tetrazin-6-one (**9g**): Brown red solid, Yield 40 %; m.p. 258°C (EtOH); ν (cm^{-1}) 3308, 1681; ^{1}H NMR δ 6.67 (s, 1H),), 7.37 (d, *J* = 6, 2H), 7.49 (d, *J* = 6, 2H), 7.52 – 7.60 (m, 5H), 7.77 (d, *J* = 6, 2H), 8.04 (d, *J* = 6, 2H), 9.59 (s, 1H); MS *m/z* (%) 498 (M^+ + 1, 36), 348 (100), 347 (71), 308 (43), 262 (40), 230 (17), 171 (32), 150 (24), 122 (65), 113 (17), 103 (50), 91 (16), 77 (79). Anal. Calcd. for $C_{23}H_{15}N_9O_5$ (497.4): C, 55.54; H, 3.04; N, 25.34. Found: C, 55.44; H, 2.94; N, 25.31 %.

Preparation of 3-Arylazo-1,4-dihydro-1-aryl-7-methyl-[1,2,4]triazino-[4,3-b][1,2,4,5]-tetrazin-6-ones (10)

These were prepared by the methods A and B outlined above using **6** and **7** *in lieu* of **2** (or **4**) and **3**(or **5**), respectively. The various [1,2,4]triazino[4,3-b][1,2,4,5]tetrazine-6-ones **10a–g** that were prepared, together with their physical constants, are listed below.

3-(4-Methoxyphenylazo)-1,4-dihydro-1-(4-methoxyphenyl)-7-methyl-[1,2,4]triazino[4,3-b][1,2,4,5]tetrazin-6-ones (**10a**): Deep brown solid, Yield 20 %; m.p. 230°C (EtOH); ν (cm^{-1}) 3263, 1682; ^{1}H NMR δ 2.45 (s, 3H), 3.85 (s, 3H), 3.92 (s, 3H), 6.99 (d, *J* = 6, 2H), 7.02 (d, *J* = 6, 2H), 8.58 (d, *J* = 6, 2H), 8.01 (d, *J* = 6, 2H), 9.4 (s, 1H); MS *m/z* (%) 407 (M^+ + 1, 23.1), 406 (M^+, 5.9), 272 (1.2), 135 (18.7), 121 (1.3), 107 (100), 92 (25.8). Anal Calcd. for $C_{19}H_{18}N_8O_3$ (406.4): C, 56.15; H, 4.46; N, 27.57. Found: C, 56.00; H, 4.32; N, 27.21%.

3-(4-Tolylazo)-1,4-dihydro-1-(4-tolyl)-7-methyl[1,2,4]triazino[4,3-b]-[1,2,4,5] tetrazin-6-one (**10b**): Reddish brown solid, Yield 18 %; m.p. 240°C (EtOH); ν (cm^{-1}) 3240, 1689; ^{1}H NMR δ 2.4 (s, 3H), 2.45 (s, 3H), 2.46 (s, 3H), 7.27 (d, *J* = 6, 2H), 7.34 (d, *J* = 6, 2H), 7.55 (d, *J* = 6, 2H), 7.91 (d, *J* = 6, 2H), 9.38 (s, 1H); ^{13}C NMR δ 159.1, 154.2, 151.6, 149.6, 145.8, 138.2, 137.3, 131.9, 131.2, 129.9, 125.2, 124.4, 21.9, 21.3, 17.7. MS *m/z* (%) 375 (M^+ + 1, 15.1), 374 (M^+, 12.3), 318 (0.9), 255 (0.3), 119 (10.1), 105 (1.6), 91 (100). Anal Calcd. for $C_{19}H_{18}N_8O$ (374.4): C, 60.95; H, 4.85; N, 29.93. Found: C, 60.80; H, 4.78; N, 29.85%.

3-(4-Phenylazo)-1,4-dihydro-1-phenyl-7-methyl[1,2,4]triazino[4,3-b]-[1,2,4,5]tetrazin-6-one (**10d**): Red solid, Yield 25 %; m.p. 225°C (EtOH); ν (cm^{-1}) 3209, 1682; ^{1}H NMR δ 2.47 (s, 3H), 7.26–8.03 (m, 10H), 9.40 (s, 1H); MS *m/z* (%) 247(M^+ + 1, 16.6), 346 (M^+, 13), 318 (0.9), 242 (0.7), 105 (16.3), 91(3.7), 77 (100). Anal Calcd. for $C_{17}H_{14}N_8O$ (346.3): C, 58.95; H, 4.07; N, 32.35. Found: C, 58.12; H, 4.01; N, 32.21%.

3-(4-Nitrophenylazo-1,4-dihydro-1-(4-nitrophenyl)-7-methyl-[1,2,4]triazino[4,3-b][1,2,4,5]tetrazin-6-one (**10g**): Red solid, Yield 49 %; m.p. 228°C (EtOH); ν (cm^{-1}) 3260, 1680; ^{1}H NMR δ 3.25 (s, 3H), 7.31 (d, *J* = 6, 2H), 7.46 (d, *J* = 7, 2H), 7.51 (d, *J* = 7, 2H), 7.92 (d, *J* = , 2H), 9.18 (s, 1H). MS *m/z* (%) 436 (M^+, 12), 427 (13), 410 (6), 320 (16), 296 (12), 228 (25), 135 (12), 91 (41), 77 (100). Anal Calcd. for $C_{17}H_{12}N_{10}O_5$ (436.3): C, 46.79; H, 2.77; N, 32.10. Found: C, 46.71; H, 2.72; N, 32.09%.

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