*Arylazo Derivatives of Pyrazolo[3,4-*d*]pyrimido-[1,6-*b*][1,2,4]triazine*

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*Síntesis selectiva y tautomería de derivados arilazo de pirazolo[3,4-*d*]pirimido[1,6-*b*][1,2,4]triazina*

*Síntesi selectiva i tautomeria de derivats arilazo de pirazole[3,4-*d*]pirimido[1,6-*b*][1,2,4]triazina*

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RESUMEN

Se describe una estrategia sintética sencilla para la síntesis de las hasta ahora no descritas 5-arilazo-1,3-difenil-6-substituido-*1H*-pirazole[3,4-*d*]pirimido[1,6-*b*][1,2,4]triazinas 5a-n. Los datos de los espectros indican que los compuestos estudiados existen predominantemente en la forma tautomérica hidrazona 5A. Se discute la selectividad y el mecanismo de las reacciones estudiadas.

Palabras clave: **Haluros de hidrazonoílo. Tautomería azo-hidrazona. Heterociclos.**

SUMMARY

A simple synthetic strategy is described for synthesis of the hitherto unreported 5-arylazo-1,3-diphenyl-6-substituted-*1H*-pyrazolo[3,4-*d*]pyrimido[1,6-*b*][1,2,4]triazines 5a-n. The spectral data indicated that the studied compounds exist predominantly in the hydrazone tautomeric form 5A. The site-selectivity and mechanism of the studied reactions are discussed.

Key words: **Hydrazonoyl halides. Azo-hydrazone tautomerism. Heterocycles.**

RESUM

Es descriu una estratègia sintètica senzilla per a la síntesi de les fins ara no descrites 5-arilazo-1,3-difenil-6-substituït-*1H*-pirazole[3,4-*d*]pirimido[1,6-*b*][1,2,4]triazines 5a-n. Les dades dels espectres indiquen que els compostos estudiats existeixen predominantment en la forma tautomèrica hidrazona 5A. Es discuteix la selectivitat i el mecanisme de les reaccions estudiades.

***Mots clau*: Halurs d'hidrazonoïl. Tautomeria azo-hidrazona. Heterocicles.**

INTRODUCTION

Arylazo heterocycles are known to be useful in the field of material sciences and theoretical chemistry[1-7]. In addition to these applications, azo compounds are used as photosensitive species in photographic or electrophotographic systems and are the dominant organic photoconductive materials in commercial copiers[8]. To the best of our knowledge reactions of 5-amino-4,5-dihydro-1,3-diphenyl-4-imino-*1H*-pyrazolo[3,4-*d*]pyrimidine **1** with hydrazonoyl halides have not been reported hitherto since we have reported its preparation in 1994[9]. In continuation of our previous studies in chemistry of hydrazonoyl halides[10-17] and azo-hydrazone tautomerism of arylazo heterocycles[1-7], we wish to report here in a convenient synthesis of the title compounds via reactions of **1** with various hydrazonoyl halides **2** and elucidation of their tautomeric form.

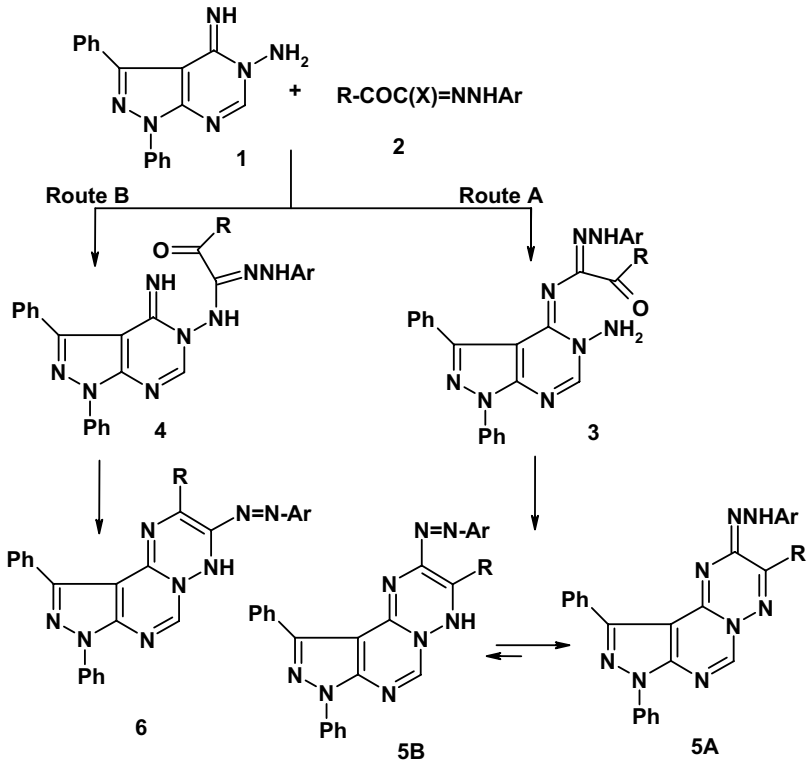
RESULTS AND DISCUSSION

5-Amino-4,5-dihydro-1,3-diphenyl-4-imino-*1H*-pyrazolo[3,4-d]pyrimidine **1**[9] and the hydrazonoyl halides **2**[18] were prepared by literature methods. Reaction of 1 with each of the hydrazonoyl halides **2** in refluxing ethanol in the presence of triethylamine gave in each case one isolable product as evidenced by tlc analysis of the crude product. This finding indicates that the studied reaction is site- and regioselective. This is because the studied reaction can theoretically proceed through either one of the two routes **A** or **B** depicted in Scheme 1, leading thus to the formation of either **5** and/ or **6**. On the basis of elemental analyses and IR, ^{1}H NMR and UV spectra (see Experimental), the isolated products were assigned structure **5** rather than the isomeric structure **6**. For example, their IR spectra revealed in each case a hydrazone NH absorption band in the region 3309 – 3474 cm^{-1}. In addition their ^{1}H NMR spectra are charaterized by a singlet signal assignable to the hydrazone NH proton at δ 10.16 – 10.80.

The assigned structure **5** was further confirmed by an alternate synthesis of the product **5a** as a typical example of the series prepared. Thus, treatment of **1** with phenacyl bromide in refluxing pyridine gave **9** (Scheme 2). Coupling of the latter with benzenediazonium chloride in ethanol in the presence of sodium hydroxide yielded the product **5a** that proved identical in all respects (m.p., mixed m.p., IR, ^{1}H NMR and UV) with that one obtained above from the reaction of **1** with **2a** (Scheme 1).

On the basis of the foregoing evidence, it is not unreasonable to suggest that the studied reaction of **1** with **2** is regio- and site-selective. This selectivity seems to be due to the fact that the imino nitrogen is more nucleophilic than the amino group. Thus, it is not unreasonable to suggest that the studied reaction starts with the initial nucleophilic attack of the imino nitrogen at the hydrazonoyl halide to give the amidrazone **3** rather than its isomer **4** (Scheme 1). The intermediate **3** underwent *in situ* dehydrative cyclization under the employed reaction conditions to give **5** as end product. This rationalization is also consistent with literature data. For example, literature reports indicate that reactions of heterocycles having N-amino-C-imino group with halo ketones, acyl halides and halo esters proceed *via* nucleophilic displacement of the halogen by the imino group followed by condesation of the amino group with the carbonyl group leading thus to the formation of fused 3-substituted-1,2,4-triazole derivative[19].

Finally, as shown in Scheme 1, the products **5** can have two tautomeric forms namely the hydrazone form **5A** and the azo tautomeric form **5B**. Of these two forms, the tautomeric form **5A** seems to be the form of choice for the studied compounds as it is consistent with their electronic absorption spectra and ^{1}H NMR spectra. For example, like typical hydrazones[20, 21] the electronic absorption spectra of **5** in dioxane revealed, in each case two characteristic absorption bands in the regions 378–350 and 295–249 nm (Table 1) and the spectra of compound **5h**, taken as a typical example of the series prepared, in different solvents exhibit little, if there is any, solvent dependence (Table 1). On the basis of such absorption pattern, it can be concluded that the



X = Cl or Br
Ar = C_6H_4Y

R/Y: a, Ph / H; b, Ph / 4-Cl; c, 2-thienyl / H; d, 2-thienyl / 4-Cl; e, Me / 4-MeO; f, Me / 4-Me; g, Me / 4-Cl; h, Me / H; i, Me / 4-Cl; j, Me / 3-Cl; k, Me / 3-NO_2; l, Me / 4-NO_2; m, Me / 4-Ac; n, Me / 4-EtOCO

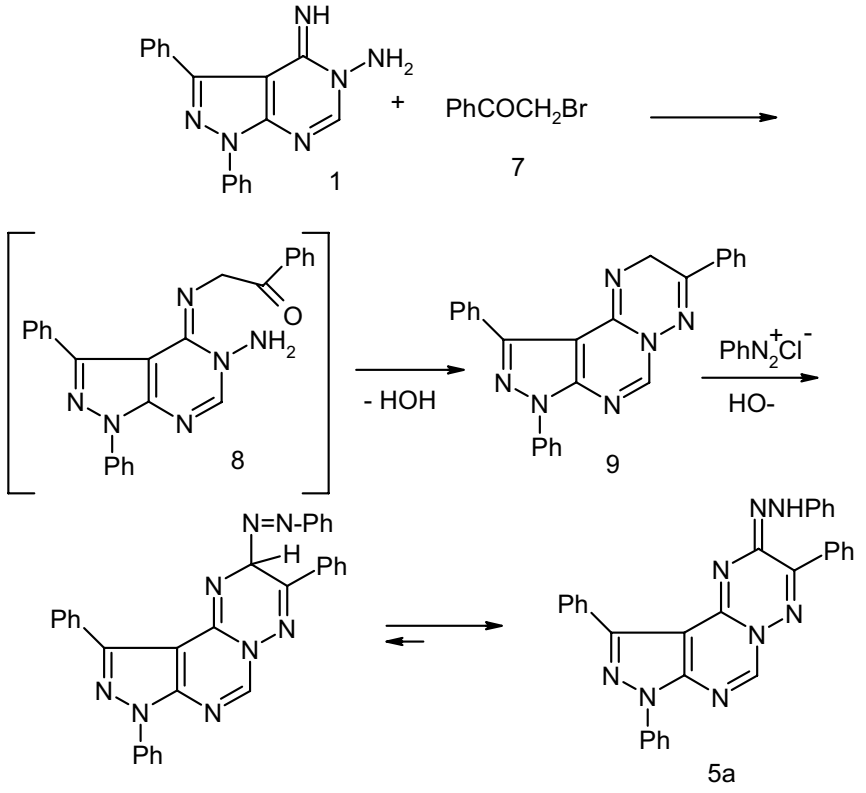
Scheme 1.

studied compounds **5** exist in solution in one tautomeric form namely **5A**. This conclusion was also confirmed by their ^{1}H NMR spectra. Thus whereas the latter spectra showed a hydrazone NH proton signal in the region δ 10.16–10.60 (see Experimental), they revealed the absence of signal near δ 11.69 characteristic for the NH of the azo-enamine form **5B**[22].

EXPERIMENTAL

Melting points are uncorrected. IR spectra were recorded (KBr) on Pye Unicam SP-1000 Spectrophotometer. ^{1}H NMR spectra were obtained on Varian Gemini 200 MHz spectrometer using TMS as internal reference. Chemical shifts are expressed as δ. Mass spectra were recorded on a GCMS-QP 1000 EX mass spectrometer operating at 70 eV.

The elemental analyses were performed at the Microanalytical Center at Cairo University. The starting compound 5-Amino-1,3-diphenyl-4-imino-4,5-dihydro-*1H*-pyrazolo[3,4-*d*]pyrimidine **1** was prepared according to literature procedure[9].



Scheme 2.

Reaction of 5-amino-1,3-diphenyl-4-imino-4,5-dihydro-*1H*-pyrazolo-[3,4-*d*]pyrimidine 1 with hydrazonoyl halides.

General method - To a mixture of 5-amino-1,3-diphenyl-4-imino-4,5-dihydro-*1H*-pyrazolo[3,4-*d*]pyrimidine **1** (1.56 g, 5 mmole) and the appropriate hydrazonoyl halide **2** (5 mmole) in ethanol (40 ml), triethyl amine was added (0.7 ml, 5 mmole). The mixture was refluxed for 5 h, then left to cool to room temperature. The solid product that precipitated, was filtred off, dried and crystallized from ethanol/DMF to give the respective product **5**. The physical constants of the compounds prepared **5a-n** are listed below.

5-Phenylazo-1,3,6-triphenyl-1H-pyrazolo[3,4-d]pyrimido[1,6-b][1,2,4]triazine (**5a**) Orange solid (2.28 g, 90 %), mp 210ºC. IR (cm^{-1}): 3316, ^{1}HNMR (DMSO-d_6) 7.02-8.20 (m, 20H, ArH), 8.22 (s, 1H, ArH), 9.96 (s, 1H, NH). Ms m/*z* (%) 508 (M$^+$ +2, 4), 507 (M$^+$ +1, 3), 506 (M$^+$, 6), 416 (17), 389 (14), 387 (18), 286 (13), 105 (79), 104 (17), 77 (100). Anal. calcd. for $C_{31}H_{22}N_8$ (506.57) C, 73.52, H 4.35, N 22.13. Found: C 73.45, H 4.34, N 22.46 %.

5-(4-Chlorophenylazo)-1,3,6-triphenyl-1H-pyrazolo[3,4-d]pyrimido-[1,6-b][1,2,4]triazine (**5b**) Orange solid (2.40 g, 89 %), mp 220ºC. IR (cm^{-1}): 3309,^{1}HNMR (DMSO-d_6) 6.99-8.09 (m, 15H, ArH), 8.17 (s, 1H, ArH), 8.46 (d, J = 9Hz, 2H, ArH), 8.82 (d, J = 9Hz, 2H, ArH), 9.96 (s, 1H, NH). Ms m/*z* (%) 542 (M$^+$ +2, 6), 541 (M$^+$ +1, 5), 540 (M$^+$, 7), 416 (36), 387 (18), 287 (18), 286 (11), 111 (5), 105 (78), 77 (100). Anal. calcd. for $C_{31}H_{21}ClN_8$ (541.01) C, 68.83, H 3.89, N 20.72. Found: C 68.67, H 3.80, N 20.82%

5-Phenylazo-1,3-diphenyl-6-thienyl-1H-pyrazolo[3,4-d]pyrimido[1,6-b][1,2,4]triazine (**5c**) Orange solid (2.3 g, 90 %), mp 200ºC. IR (cm^{-1}): 3472, ^{1}H NMR ($CDCl_3$) 7.01-8.29 and 8.35-8.85 (m, 18H, ArH), 8.31 (s, 1H, ArH), 10.08 (s, 1H, NH). Ms m/*z* (%) 513 (M$^+$ +1, 1), 512 (M$^+$, 1), 422 (47), 362 (11), 287 (29), 127 (8), 111 (100), 91(4), 77(41). Anal. calcd.

TABLE I

The characteristic electronic absorption spectra of Compounds 5a-n in dioxane.

Compd. No.	λ (log ε)	Compd. No.	λ (log ε)
5a	381.3(3.76), 284.7 (3.72)	**5h***	365.6(3.37),256.2 (3.54)
5b	379.4(4.27), 291.4 (4.17)	**5i**	368.8(3.24),253.2 (3.36)
5c	339.8(4.16), 257.6 (4.45)	**5j**	364.8 (3.19), 252.0 (3.36)
5d	364.4(3.59), 268.6 (3.70)	**5k**	374.0 (3.35), 250.0 (3.23)
5e	373.0 (3.21),253.0 (3.33)	**5l**	374.8 (3.21), 251.8 (3.55)
5f	365.0 (3.19),248.6 (3.38)	**5m**	378.0 (3.37), 295.2 (3.28)
5g	365.8 (3.19),253.0 (3.47)	**5n**	349.8 (3.25), 263.8 (3.40)

*Compound **5h** in different solvents: Solvent, λ (log ε): Ethanol, 326.0 (3.33), 260.2 (3.63); Acetone, 342.8 (3.38), 259.6 (3.69)
DMF, 338.2 (3.45), 276.8 (3.74); Acetic acid, 348.4 (3.38), 279.2 (3.63)

for $C_{29}H_{20}N_8S$ (512.59) C, 67.96, H 3.91, N 21.88. Found: C 67.72, H 3.71, N 21.86 %.

5-(4-Chlorophenylazo)-1,3-diphenyl-6-thienyl-1H-pyrazolo[3,4-d]pyrimido[1,6-b][1,2,4]triazine (**5d**) Orange solid (2.50 g, 92 %), mp 235ºC. IR (cm^{-1}): 3474, ^{1}H NMR ($CDCl_3$) 7.16-7.83 (m, 13H, ArH), 8.01 (d, J = 8Hz, 2H, ArH), 8.12 (d, J = 8 Hz, 2H, ArH), 8.31 (s, 1H, ArH), 10.06 (s, 1H, NH). Ms m/*z* (%) 549 (M^+ +2, 2), 548 (M^+ +1), 422 (25), 279 (3), 140 (2), 111 (100), 78 (7). Anal. calcd. for $C_{29}H_{19}ClN_8S$ (547.03) C, 63.68, H 3.48, N 20.49. Found: C 63.90, H 3.32, N 20.49 %.

6-Methyl-5-(4-methoxyphenylazo)-1,3-diphenyl-1H-pyrazolo[3,4-d]pyrimido[1,6-b][1,2,4]triazine (**5e**) Dark orange solid (1.8 g, 78 %), mp > 340ºC. IR (cm^{-1}): 3349, ^{1}HNMR (DMSO-d_6) 2.39 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 7.37-7.72 and 8.03-8.27 (m, 10H, ArH), 7.94 (s,1H, ArH), 8.37 (d, J = 8 Hz, 2H, ArH), 8.80 (d, J = 8 Hz, 2H, ArH), 10.20 (s, 1H, NH). Ms m/*z* (%) 476 (M^+ +2, 5), 475 (M^+ +1, 33), 474 (M^+, 100), 459 (52), 141 (11), 121 (22), 95 (21), 92 (10), 77 (52). Anal. calcd. for $C_{27}H_{22}N_8O$ (474.52) C, 68.35, H 4.64, N 23.62. Found: C 68.17, H 4.82, N 23.93 %.

6-Methyl-5-(4-methylphenylazo)-1,3-diphenyl-1H-pyrazolo[3,4-d] pyrimido[1,6-b][1,2,4]triazine (**5f**): Orange solid (1.83 g, 80 %), m.p 265ºC. IR (cm^{-1}): 3446. ^{1}H NMR ($CDCl_3$) 2.18 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 6.84-7.52 (m, 10H, ArH), 7.73 (d, J = 9 Hz, 2H, ArH, 8.30 (d, J = 9 Hz, 2H, ArH), 8.42 (s, 1H, ArH), 10.30 (s, 1H, NH). Ms m/*z* (%) 460 (M^+ +2, 6), 459 (M^+ +1, 33), 458 (M^+, 100), 354 (21), 287 (47), 129 (15), 111 (21), 104 (15), 91 (34), 77 (74). Anal. calcd. for $C_{27}H_{22}N_8$ (458.52) C, 70.74, H 4.80, N 24.45. Found: C 70.59, H 4.94, N 24.22 %.

6-Methyl-5-(3-methylphenylazo)-1,3-diphenyl-1H-pyrazolo[3,4-d]pyrimido[1,6-b][1,2,4]triazine (**5g**) Dark yellow solid (1.9 g, 83 %), mp > 340ºC. IR (cm^{-1}): 3350, ^{1}H NMR (DMSO-d_6) 2.50 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 7.43-8.84 (m, 14H, ArH), 8.0 (s, 1H, ArH), 10.16 (s, 1H, NH). Ms m/*z* (%) 459 (M^+ +1, 8), 458 (M^+, 24), 354 (45), 326 (30), 286 (38), 153 (11), 106 (20), 91 (47), 83 (32), 77 (100). Anal. calcd. for $C_{27}H_{22}N_8$ (458.52) C, 70.74, H 4.80, N 24.45. Found: C 70.57, H 4.54, N 24.8 %.

6-Methyl-5-phenylazo-1,3-diphenyl-1H-pyrazolo[3,4-d]pyrimido[1,6-b][1,2,4]triazine (**5h**) Yellow solid (1.8 g, 81 %), mp > 340ºC. IR (cm^{-1}): 3423, ^{1}H NMR (DMSO-d_6) 2.71 (s, 3H, CH_3), 7.43-8.84 (m, 15H, ArH) 10.18 (s, 1H, NH). Ms m/*z* (%) 446 (M^+ +2, 4), 445 (M^+ +1, 10), 444 (M^+, 22), 443 (12), 298 (6), 286 (7), 103 (6), 91 (14), 77 (96). Anal. calcd. for $C_{26}H_{20}N_8$ (444.49) C, 70.27, H 4.50, N 25.22. Found: C 70.17, H 4.28, N 25.45 %.

6-Methyl-5-(4-chlorophenylazo)-1,3-diphenyl-1H-pyrazolo[3,4-d]pyrimido[1,6-b][1,2,4]triazine (**5i**) Yellow solid (1.87 g, 78 %), mp 280ºC. IR (cm^{-1}): 3314, ^{1}H NMR (DMSO-d_6) 2.40 (s, 3H, CH_3), 7.34 (s, 1H, ArH), 7.37-7.70 (m, 10H, ArH), 8.08 (d, J = 8 Hz, ArH), 8.80 (d, J = 8 Hz, 2H, ArH), 10.26 (s, 1H, NH). Ms m/*z* (%) 481 (M^+ +2, 10), 480 (M^+ +1, 14), 479 (M^+, 27), 478 (27), 297 (12), 126 (12), 111 (40), 110 (42), 77 (95), 76 (100). Anal. calcd. for $C_{26}H_{19}ClN_8$ (478.94) C, 65.20, H 3.97, N 23.40. Found: C 65.27, H 4.09, N 23.38 %.

5-(3-Chlorophenylazo)-1,3-diphenyl-6-Methyl-1H-pyrazolo[3,4-d]pyrimido[1,6-b][1,2,4]triazine (**5j**): Yellow solid (2.0 g, 85 %), mp > 340ºC. IR (cm^{-1}): 3350, ^{1}H NMR (DMSO-d_6) 2.73 (s, 3H, CH_3), 7.51-8.52 (m, 14H, ArH), 8.82 (s, 1H, ArH), 10.16 (s, 1H, NH). Ms m/*z* (%) 480 (M^+ +1, 4), 479 (M^+, 3), 478 (9), 327 (26), 326 (68), 287 (23), 286 (19), 153 (14), 127 (25), 111 (22), 103 (21), 91 (12), 77 (100). Anal. calcd. for $C_{26}H_{19}ClN_8$ (478.94) C, 65.20, H 3.97, N 23.40. Found: C 65.32, H 4.12, N 23.70 %.

6-Methyl-5-(3-nitrophenylazo)-1,3-diphenyl-1H-pyrazolo[3,4-d] pyrimido[1,6-b][1,2,4]triazine (**5k**) Orange solid (2.2 g, 90 %), mp 290ºC. IR (cm^{-1}): 3319, ^{1}H NMR (DMSO-d_6) 2.18 (s, 3H, CH_3), 7.44-8.12 (m, 14H, ArH), 8.39 (s, 1H, ArH), 10.60 (s, 1H, NH). Ms m/*z* (%) 490 (M^+ +1, 3), 489 (M^+, 8), 488 (1), 326 (100), 312 (18), 163 (14), 129 (19), 103 (23), 91 (17), 77 (75). Anal. calcd. for $C_{26}H_{19}N_9O_2$ (489.49) C, 63.80, H 3.89, N 25.77. Found: C 63.70, H 4.29, N 25.47 %.

6-Methyl-5-(4-nitrophenylazo)-1,3-diphenyl-1H-pyrazolo[3,4-d]pyrimido[1,6-b][1,2,4]triazine (**5l**) Yellow solid (1.98 g, 81 %), mp > 340ºC. IR (cm^{-1}): 3422, ^{1}H NMR (DMSO-d_6) 2.49 (s, 3H, CH_3), 7.01 (d, J = 9 Hz, 2H, ArH), 7.41-8.39 (m, 10H, ArH), 8.05 (s, 1H, ArH), 8.81 (d, J = 9 Hz, 2H, ArH), 10.20 (s, 1H, NH). Ms m/*z* (%) 490 (M^+ +1, 10), 489 (M^+, 30), 422(36), 287(24), 236(15), 129(31), 123(25), 105(29), 91(25), 81(54), 77(54). Anal. calcd. for $C_{26}H_{19}N_9O_2$ (489.49) C, 63.80, H 3.89, N 25.77. Found: C 63.67, H 3.77, N 25.52 %.

6-Methyl-5-(4-acetylphenylazo)-1,3-diphenyl-1H-pyrazolo[3,4-d] pyrimido[1,6-b][1,2,4]triazine (**5m**) Yellow solid (2.07 g, 85 %), mp 235ºC. IR (cm^{-1}): 3338, 1688. ^{1}H NMR (DMSO-d_6) 2.44 (s, 3H, CH_3), 2.49 (s, 3H, $COCH_3$) 7.39-7.60 (m, 10H, ArH), 8.02 (s, 1H, ArH), 8.09 (d, J = 8 Hz, 2H, ArH), 8.43 (d, J = 8 Hz, 2H, ArH), 10.82 (s, 1H, NH). Ms m/*z* (%) 487 (M^+ +1, 4), 458 (10), 223 (10), 208 (15), 145 (24), 123 (20), 111 (49), 97 (71), 73 (31). Anal. calcd. for $C_{28}H_{22}N_8O$ (486.53) C, 69.14, H 4.53, N 23.05. Found: C 69.37, H 4.82, N 23.00 %.

5-(4-Ethoxycarbonylphenylazo)-1,3-diphenyl-6-Methyl-1H-pyrazolo[3,4-d]pyrimido[1,6-b][1,2,4]triazine (**5n**): Yellow solid (2.2 g, 86 %), mp > 340ºC. IR (cm^{-1}): 3349, 1685. ^{1}H NMR (DMSO-d_6) 1.06 (t, J = 7 Hz, 3H, CH_3), 2.49 (s, 3H, CH_3), 4.28 (q, J = 7 Hz, 2H, CH_2) 7.40-8.03 (m, 10H, ArH), 8.10 (d, J = 9 Hz, 2H, ArH), 8.57 (s,1H, ArH), 8.82 (d, J = 9 Hz, 2H, ArH), 10.20 (s, 1H, NH). Ms m/*z* (%) 517 (M^+ +1, 10), 516 (M^+, 25), 515 (5), 488 (27), 368 (36), 326 (59), 325 (40), 264 (21), 247 (24), 165 (29), 133 (35), 110 (62), 84 (100). Anal. calcd. for $C_{29}H_{24}N_8O_2$ (516.55) C, 67.44, H 4.65, N 21.71. Found: C 67.67, H 4.46, N 21.48 %.

Alternate synthesis of 5a:

To solution of 1 (1.56 g, 5 mmole) in pyridine (10 ml) phenacyl bromide (1.00 g, 5mmole) was added. The mixture was reflexed for 4hrs, cooled and poured onto ice-cold hydrochloric acid with stirring. The solid precipitate, so formed, was filtered off, washed with water and finally crystallized from dioxane to give 9 as dark orange crystals (1.65 g, 82%).

mp 195ºC. IR (cm^{-1}): 3475, ^{1}H NMR (DMSO-d_6) 6.09 (s, 1H, ArH), 7.33-8.20 (m, 15H, ArH), 8.40 (s, 1H, ArH), 12.40 (s, 1H, NH). Ms m/*z* (%) 403 (M^+ +1, 10), 402 (M^+, 20), 401 (18), 387 (18), 327(4), 298(20), 287 (17), 142 (10), 127 (15), 103(23), 77 (100). Anal. calcd. for $C_{25}H_{18}N_6$ (402.46) C, 74.62, H 4.48, N 20.90. Found: C, 74.33, H, 4.45, N, 20.99 %.

To a solution of 9 (2.01 g, 5 mmole) in ethanol (40 ml) was added sodium hydroxide (0.5 g) and the mixture was cooled in an ice bath at 0-5ºC while being stirred. To the resulting cold solution was added portionwise a cold solution of the benzene diazonium chloride, prepared as usual by diazotized aniline (0.5 g, 5 mmole) in hydrochloric acid (6M, 3 ml) with sodium nitrite (0.35 g, 5 mmole) in water (5 ml), after all the diazonium salt was added, the mixture was stirred for further 30 min. while cooling in ice-bath. The solid that precipitated was filtered off, washed with water, dried and finally crystallized from ethanol/DMF to give compound 5a which proved to be identical in all respects (mp., mixed mp., IR, Ms. and ^{1}HNMR spectra) with the product isolated above from the reaction of N-phenyl-2-oxo-2-phenyl-ethanehydrazonoyl chloride **2a** with **1**.

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