A new synthesis of the tricyclic system bis-pyrazolo[1,5-*a*][4',3'-*e*]pyrimidine

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Abstract

Starting from 2,7-dimethyl-8-phenylazo-4(6*H*)-pyrazolo[1,5-*a*]-pyrimidinone **1**, a series of functionalized derivatives of the title tricyclic system **4** have been synthesized *via* its reaction with various hydrazonoyl halides **2** and cyclization of the resulting substitution products **3**. The mechanism and the site selectivity of the reactions studied are discussed. The structures of the compounds **3** and **4** isolated were elucidated on the basis of their spectra, elemental analyses and alternate synthesis.

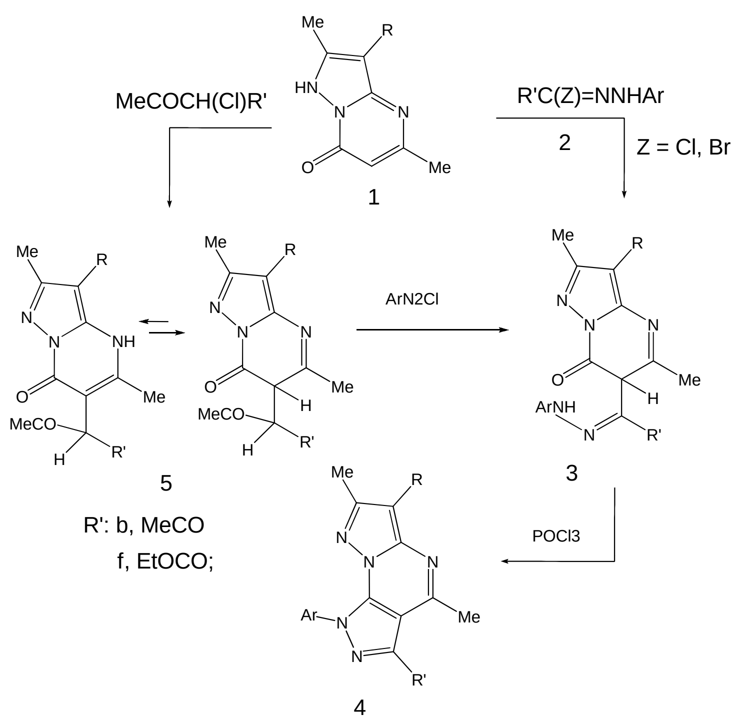
Keywords: Heterocycles, hydrazonoyl halides, enaminones, nitrilimines

Introduction

In continuation of our studies dealing with the utility of hydrazonoyl halides for synthesis of various heterocyclic ring systems,[1-11] we wish to report herein a new facile synthesis of bis-pyrazolo[1,5-*a*][4',3'-*e*]pyrimidine ring system and its various functionalized derivatives that have not been reported hitherto. The earlier methods reported for synthesis of such ring system are multisteps.[12-15] Our interest in exploring a new simple synthetic strategy for the latter ring system is due to the fact that literature search reveals that various derivatives of the two ring systems namely pyrazolo[1,5-*a*]pyrimidine and 1*H*-pyrazolo[3,4-*d*]pyrimidine were reported to exhibit various biological activities. For example, some derivatives of the former ring system exhibit anticonvulsant, sedative, anti-inflammatory, gastric antisecretory and central nervous system activities.[16-19] Also, some derivatives of 1*H*-pyrazolo[3,4-*d*]pyrimidine showed *in vitro* antiviral and antitumor activities.[20-23] Some other derivatives of this ring system were found toxic to embryonic chick liver cells, mouse cells and human cells.[24-27] In view of these findings, it was interesting to explore the synthesis of the title ring system which contains the ring residues of both pyrazolo[1,5-*a*]pyrimidine and 1*H*-pyrazolo[3,4-*d*]pyrimidine and explore the biological activities of some of its derivatives.

Results and Discussion

The synthetic strategy designed for the synthesis of the title ring system is outlined in Scheme **1**. The required 2,7-dimethyl-8-phenylazo-4(6*H*)-pyrazolo[1,5-*a*]pyrimidinone **1** was prepared by reaction of ethyl acetoacetate with 5-amino-4-arylazo-3-methyl-1H-pyrazole as previously described.[28] As no spectral data were reported for compound **1**, we wish to report herein its IR, ^{1}H- and ^{13}C-NMR as well as the UV and mass spectral data (see Experimental). For example, the IR spectrum of compound **1** revealed one carbonyl band and one NH band at υ 1674 and 3228 cm^{-1}, respectively. Its ^{1}H NMR spectrum of the isolated product showed four characteristic signals at δ 2.41, 2.43, 5.85, 7.40-8.03 and 11.89 for two methyl groups, the ring 3-CH, the aromatic-H and NH, respectively. In addition, its electronic absorption spectrum (Table 1) in dioxan exhibits two characteristic absorption bands at 492 and 321 nm. Such an absorption pattern is similar to that of typical azo chromophore.[1] Furthermore, the electronic absorption spectra of compound **1** in solvents of different polarities showed little, if any, shift (Table 1). On the basis of the foregoing data, compound **1** was assigned the indicated azo tautomeric structure **1** (Scheme 1) in both solid and solution phases.



1-5 : R = PhN=N-

2a-i, Z = Cl ; 2j-n, Z = Br

2-4 : Ar = 4-XC6H4 ; R' / X : a, Ph / H; b, MeCO / H; c, MeCO / Me; d, MeCO / Cl; e, MeCO / NO2; f, EtOCO / H; g, EtOCO / Me; h, EtOCO / Cl; i, EtOCO / NO2; j, PhCO / H; k, PhCO / Me; l, PhCO / Cl; m, PhCO / NO2; n, 2-thienoyl / H

Scheme 1

Reaction of compound **1** with each of the hydrazonoyl halides **2a-n** in dioxan in the presence of triethylamine at room temperature afforded, in each case, one isolable product that was identified, on the basis of its spectra (MS, IR, ^{1}H NMR) and its elemental analysis data (see experimental), as the substitution product **3** (Scheme 1). For example, whereas the IR spectrum of **3a** shows only one CO band at υ 1712 cm^{-1}, the IR spectra of **3b-n** showed, in each case, two CO bands in the regions ν 1678 -1743 and ν 1655 - 1703 cm^{-1}. In addition, the IR spectra of **3a-n** showed one NH band in the region ν 3074 – 3498 cm^{-1}. Their ^{1}H NMR spectra showed, in each case, two characteristic singlet signals at δ 5.30 – 6.28 and 11.21 – 12.63 assignable to the ring 3-CH and hydrazone NH protons, respectively. The formation of **3** from **1** and **2** provides an evidence that **1** behaves as cyclic enaminone. This is because many literature reports indicate that reactions of enaminones with halogen compounds lead to the corresponding substitution products.[29]

The assigned structure **3** for the new isolated compounds was further evidenced by the alternate synthesis of **3b** and **3f** as representative examples of the series prepared (Scheme 1). As depicted in the latter scheme, reaction of **1** with each of 3-chloro-2,4-pentanedione and ethyl 2-chloro-3-oxobutanoate in dioxan in the presence of triethylamine at room temperature yielded the respective substitution products **5b** and **5f**, respectively. Coupling of each of the latter products with benzenediazonium chloride in ethanol in the presence of sodium acetate afforded, *via* Japp-Klingmann reaction,[30] products proved identical in all respects (mp., mixed mp., MS and IR spectra) with **3b** and **3f**, respectively (Scheme 1).

When each of the products **3** was heated with phosphorus oxychloride, it cyclized to yield the respective 1-aryl-3-substituted-4,7-dimethyl-6-phenylazo-*bis*-pyrazolo[1,5-*a*][4',3'-*e*]pyrimidine **4** (Scheme 1). The structures of the isolated products **4a-n** were elucidated on the basis of their spectra (MS, IR, ^{1}H NMR, UV) and elemental analyses (see Experimental). For example, their IR spectra showed the absence of the hydrazone NH band present in the spectra of their precursors **3**. Also, while the IR spectrum of **4a** showed no CO band, the spectra of the products **4b-n** revealed, in each case, one CO band in the region ν 1686 – 1716 cm^{-1}. Their ^{1}H NMR spectra revealed also the absence of both signals corresponding to the ring 3-CH and the hydrazone NH proton signals that appeared in the spectra of their precursors **3a-n**. The electronic absorption spectral data of the studied compounds **4** are summarized in Table 1. As shown, each of the compounds **4** in dioxan exhibits two characteristic absorption bands in the regions 439-409 and 385-322 nm (Table 1). Such an absorption pattern is similar to that of typical azo chromophore.[1]

Conclusions

In conclusion we have achieved an efficient two-step synthetic strategy for synthesis of the title compounds **4** by reaction of **1** with **2** and cyclization of the intermediate substitution products **3**. This method is currently being extended for preparation of other new derivatives of this tricyclic ring system with the goal of generating a small library of compounds of biological interest and the results will be reported in due course.

Table 1. Electronic absorption spectra of compounds 1, 4 in dioxan

Compd. no.	λ_{max} (dioxan) (Log ε)	Compd. no.	λ_{max} (dioxan) (Log ε)
1[i]	492 (4.78), 321 (4.31)	**4h**	425 (4.73), 332 (4.37)
4a	438 (4.94), 365 (4.64)	**4i**	425 (4.65), 343 (4.73)
4b[ii]	409 (4.71), 329 (4.44)	**4j**	419 (4.76), 328 (4.56)
4c[iii]	434 (4.91), 338 (4.56)	**4k**	413 (4.75), 322 (4.54)
4d	411 (5.02), 385 (5.01)	**4l**	408 (4.67), 335 (4.50)
4e[iv]	443 (4.65), 334 (4.53)	**4m**	414 (4.89), 327 (4.74)
4f	434 (4.90), 322 (4.50)	**4n**	425 (4.71), 337 (4.52)
4g	439 (4.85), 330 (4.39)		

Solvent: λ_{max} nm (Log ε) **(i)** Ethanol: 493 (4.99); Chloroform: 406 (4.64); Benzene: 419 (4.69); 1-Propanol: 487 (4.72); Ether: 489 (4.83); 2-Propanol: 487 (4.82); Tetrahydrofuran: 422 (4.89); Methanol: 479 (4.94); DMF: 501 (4.61).
(ii) Ethanol: 491 (4.99); Chloroform: 490 (4.78); Benzene: 492 (4.83); 1-Propanol: 485 (4.83); Ether: 488 (4.76); 2-Propanol: 486 (4.83); Tetrahydrofuran: 491 (4.83); Methanol: 492 (4.99); DMF: 488 (4.93).
(iii) Ethanol: 488 (4.93); Chloroform: 399 (4.89); 1-Propanol: 484 (4.73); Ether: 487 (4.98); 2-Propanol: 478 (4.99); Tetrahydrofuran: 493 (4.83); Benzene: 490 (4.76).
(iv) Ethanol: 491 (4.63); Chloroform: 483 (4.72); Benzene: 484 (4.67); 1-Propanol: 484 (4.73); Ether: 488 (4.57); 2-Propanol: 485 (4.55); Tetrahydrofuran: 483 (4.70); Methanol: 485 (4.77); DMF: 483 (4.72).

Experimental Section

General Procedures. All melting points were determined on an electrothermal Gallenkamp apparatus and are uncorrected. Solvents were generally distilled and dried by standard literature procedure prior to their use. The IR spectra were measured on a Pye-Unicam SP300 instrument in potassium bromide discs. The P ^{1}H NMR spectra were recorded on a Varian Mercury VXR-300 spectrometer (300 MHz). The mass spectra were recorded on a GCMS-Q1000-EX Shimadzu and GCMS 5988-A HP spectrometers, the ionizing voltage was 70 eV. Electronic absorption spectra were recorded on Perkin-Elmer Lambada 40 spectrophotometer. Elemental analyses were carried out by the Microanalytical Center of Cairo University, Giza, Egypt. 2,7-Dimethyl-8-phenylazo-4(6H)-pyrazolo[1,5-*a*]pyrimidinone **1**[28] and hydrazonoyl halides **2a-n** were prepared by literature methods.[13,31]

2,5-Dimethyl-8-phenylazo-4(6*H*)-pyrazolo[1,5-*a*]pyrimidinone (1). This compound was prepared as previously described in literature[28] and was obtained as orange solid (11.35 g, 85 %), m.p. 218-220 °C [Lit. m.p. 250 °C][28] (dioxane/ MeOH); IR (KBr) ν 3228, 1674 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 2.41 (s, 3H, CH$_3$), 2.43 (s, 3H, CH$_3$), 5.85 (s, 1H, CH), 7.40-8.03 (m, 5H, ArH), 11.89 (s, 1H, NH); ^{13}C NMR (DMSO-d$_6$) δ 12.75, 20.11, 94.94, 120.99, 125.86, 130.31, 135.83, 142.87, 149.70, 150.75, 156.25, 161.69. MS m/z (%) 268 (M$^+$+1, 24), 267 (M$^+$, 100), 266 (12), 238 (9), 190 (42), 162 (33), 124 (7), 106 (7), 105 (5), 91 (6), 77 (19); Anal. Found (Calcd.) for $C_{14}H_{13}N_5O$ (267.29): C, 62.91 (62.74); H, 4.90 (4.81); N, 26.20 (26.06).

General procedure for synthesis of 2,7-dimethyl-8-phenylazo-3-[*N*-aryl-2-oxoalkanehydrazonoyl]pyrazolo[1,5-*a*]pyrimidin-4(3*H*)-ones (3a-n)

To a mixture of **1** (0.67 g, 2.5 mmole) and the hydrazonoyl halide **2** (2.5 mmole) in dioxane (30 ml), triethylamine (0.35 ml, 2.5 mmole) was added. The mixture was stirred at room temperature for 24 hr. The solid product that precipitated was filtered, washed with water and finally crystallized from the appropriate solvent to give the respective **3.** The physical constants of the isolated products **3a-n** are listed below.

2,7-Dimethyl-8-phenylazo-3-[(*N*-phenyl-1-phenylmethane-hydrazonoyl)]pyrazolo-[1,5-*a*]pyrimidin-4(3H)-one (3a). Yellow solid (0.97 g, 84 %), m.p. 248-250°C (dioxane); IR (KBr) ν 3193, 1712 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 2.27 (s, 3H, CH$_3$), 2.50 (s, 3H, CH$_3$), 5.74 (s,1H, CH), 6.76-8.23 (m, 15H, ArH), 10.82 (s, 1H, NH); MS m/z (%) 462 (M$^+$+1, 9), 461 (M$^+$, 43), 356 (9), 286 (15), 267 (18), 194 (55), 190 (31), 180 (42), 169 (26), 162 (12), 128 (3), 105 (7), 92 (100), 77 (71); Anal. Found (Calcd.) for $C_{27}H_{23}N_7O$ (461.52): C, 70.20 (70.27); H, 4.98 (5.02); N, 21.00 (21.24).

2,7-Dimethyl-8-phenylazo-3-[(*N*-phenyl-2-oxopropanehydrazonoyl)]pyrazolo[1,5-*a*]-pyrimidin-4(3H)-one (3b). Yellow solid (0.89 g, 83 %), m.p. 284-286°C (DMF/ MeOH); IR (KBr) ν 3247, 1700, 1685 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.91 (s, 3H, CH$_3$), 2.32 (s, 3H, CH$_3$), 2.50 (s, 3H, CH$_3$), 5.62 (s,1H, CH), 7.22-7.50 (m, 10H, ArH), 11.32 (s, 1H, NH); MS m/z (%) 429 (M$^+$+2, 4), 427 (M$^+$, 5), 382 (100), 268 (7), 235 (7), 202 (1), 180 (25), 106 (1), 95 (11), 82 (31), 76 (3); Anal. Found (Calcd.) for $C_{23}H_{21}N_7O_2$ (427.46): C, 64.54 (64.63); H, 4.82 (4.95); N, 22.84 (22.94)%.

2,7-Dimethyl-8-phenylazo-3-[(*N*-(4-methylphenyl)-2-oxo-propane-hydrazonoyl)]-pyrazolo-[1,5-*a*]pyrimidin-4(3*H*)-one (3c). Dark yellow solid (0.89 g, 81 %), m.p. 270-272°C (dioxane/ EtOH); IR (KBr) ν 3417, 1700, 1678 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 2.36 (s, 3H, CH$_3$), 2.39 (s, 3H, CH$_3$), 2.48 (s, 3H, CH$_3$), 2.49 (s, 3H, CH$_3$), 5.30 (s,1H, CH), 7.54 (d, J = 8 Hz, 2H, ArH), 7.30-7.37 (m, 5H, ArH), 7.79 (d, J = 8 Hz, 2H, ArH), 10.57 (s, 1H, NH); MS m/z (%) 442 (M$^+$+1, 3), 441 (M$^+$, 4), 356 (9), 281 (16), 268 (59), 267 (84), 251 (85), 190 (93), 183 (18), 162 (51), 132 (51), 105 (46), 91 (55), 77 (100); Anal. Found (Calcd.) for $C_{24}H_{23}N_7O_2$ (441.49): C, 65.00 (65.29); H, 5.36 (5.25); N, 22.00 (22.21)%.

2,7-Dimethyl-8-phenylazo-3-[(*N*-(4-chlorophenyl)-2-oxopropane-hydrazonoyl)]-pyrazolo-[1,5-*a*]pyrimidin-4(3*H*)-one (3d). Yellow solid (0.95 g, 82 %), m.p. 254-256°C (dioxane/

EtOH); IR (KBr) ν 3386, 1705, 1674 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.14 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 6.21 (s,1H, CH), 6.92 (d, J = 9 Hz, 2H, ArH), 7.43-7.53 (m, 5H, ArH), 8.23 (d, J = 9 Hz, 2H, ArH), 11.44 (s, 1H, NH); MS m/z (%) 462 (M^++1, 4), 461 (M^+, 9), 418 (10), 379 (2), 301 (13), 273 (20), 271 (33), 268 (49), 267 (86), 190 (100), 162 (43), 152 (24), 125 (22), 111 (10), 105 (10), 91 (18), 77 (57); Anal. Found (Calcd.) for $C_{23}H_{20}N_7ClO_2$ (461.90): C, 60.00 (59.81); H, 4.42 (4.36); N, 21.20 (21.23)%.

2,7-Dimethyl-8-phenylazo-3-[(*N*-(4-nitrophenyl)-2-oxopropane-hydrazonoyl)]-pyrazolo[1,5-*a*]pyrimidin-4(3*H*)-one (3e). Yellow solid (0.94 g, 80 %), m.p. 218-220°C (EtOH); IR (KBr) ν 3417, 1708, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.37 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 5.37 (s,1H, CH), 7.24-7.43 (m, 5H, ArH), 7.79 (d, J = 9 Hz, 2H, ArH), 7.91 (d, J = 9 Hz, 2H, ArH), 11.40 (s, 1H, NH); MS m/z (%) 473 (M^++1, 44), 472 (M^+, 68),382 (15), 381 (60), 266 (4), 265 (14), 191 (100), 148 (80), 133 (23), 121 (52), 117 (32), 105 (12), 95 (14), 77 (26); Anal. Found (Calcd.) for $C_{23}H_{20}N_8O_4$ (472.46): C, 58.53 (58.47); H, 4.09 (4.27); N, 23.58 (23.72)%.

2,7-Dimethyl-8-phenylazo-3-[*N*-phenyl-1-ethoxycarbonyl-methanehydrazonoyl-pyrazolo-[1,5-*a*]pyrimidin-4(3*H*)-one (3f). Yellow solid (0.91 g, 80 %), m.p. 244°C (dioxane); IR (KBr) ν 3423, 1739, 1703 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.06 (t, J = 7Hz, 3H, CH_3), 1.91 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 4.33 (q, J=7Hz, 2H, CH_2), 5.71 (s,1H, CH), 7.35-8.50 (m, 10H, ArH), 11.80 (s, 1H, NH); MS m/z (%) 456 (M^++1, 2), 457 (M^+, 5), 353 (3), 268 (22), 267 (100), 253 (13), 190 (34), 169 (10), 134 (7), 105 (9), 104 (33), 92 (20), 91 (17), 77 (35); Anal. Found (Calcd.) for $C_{24}H_{23}N_7O_3$ (457.48): C, 63.00 (63.01); H, 5.00 (5.07); N, 21.32 (21.43)%.

2,7-Dimethyl-8-phenylazo-3-[*N*-(4-methylphenyl)-1-ethoxycarbonyl-methane-hydrazonoyl)]pyrazolo[1,5-*a*]pyrimidin-4(3*H*)-one (3g). Yellow solid (0.94 g, 80 %), m.p. 230-232°C (dioxane/ EtOH); IR (KBr) ν 3447, 1743, 1661 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (t, J = 8 Hz, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 4.15 (q, J = 8 Hz, 2H, CH_2), 6.23 (s,1H, CH), 7.14-7.19 (m, 5H, ArH), 7.44 (d, J = 8 Hz, 2H, ArH), 7.67 (d, J = 8 Hz, 2H, ArH), 11.21 (s, 1H, NH); MS m/z (%) 473 (M^++2, 8), 472 (M^++1, 10), 471 (M^+, 15), 356 (7), 281 (100), 267 (13), 190 (31), 183 (13), 132 (11), 105 (40), 104 (46), 91 (36), 77 (65); Anal. Found (Calcd.) for $C_{25}H_{25}N_7O_3$ (471.51): C, 63.48 (63.68); H, 5.42 (5.34); N, 20.80 (20.79)%.

2,7-Dimethyl-8-phenylazo-3-[*N*-(4-chlorophenyl)-1-ethoxycarbonyl-methane-hydrazonoyl]pyrazolo[1,5-*a*]pyrimidin-4(3*H*)-one (3h). Yellow solid (1.07 g, 87 %), m.p. 228°C (dioxane/ MeOH); IR (KBr) ν 3498, 1740, 1697 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.15 (t, J= 8Hz, 3H, CH_3), 1.91 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 4.15 (q, J=8Hz, 2H, CH_2), 5.58 (s,1H, CH), 6.93 (d, J = 9 Hz, 2H, ArH), 7.03-7.76 (m, 5H, ArH), 8.24 (d, J = 9 Hz, 2H, ArH), 11.88 (s, 1H, NH); MS m/z (%) 493 (M^++2, 2), 492 (M^++1, 2), 491 (M^+, 4), 358 (3), 312 (64), 268 (6), 267 (4), 118 (37), 105 (7), 104 (12), 103 (24), 93 (23), 92 (30), 77 (100); Anal. Found (Calcd.) for $C_{24}H_{22}N_7ClO_3$ (491.93): C, 58.63 (58.60); H, 4.46 (4.51); N, 20.00 (19.93)%.

2,7-Dimethyl-8-phenylazo-3-[*N*-(4-nitrophenyl)-1-ethoxycarbonylmethanehydrazonoyl]-pyrazolo[1,5-*a*]pyrimidin-4(3*H*)-one (3i). Dark yellow solid (1.03 g, 82 %), m.p. 278-280°C (DMF/ EtOH); IR (KBr) ν 3445, 1739, 1699 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.05 (t, J = 9 Hz, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 4.35 (q, J = 9 Hz, 2H, CH_2), 5.78 (s,1H, CH), 7.30-7.99 (m, 5H, ArH), 8.02 (d, J = 8 Hz, 2H, ArH), 8.17 (d, J = 8 Hz, 2H, ArH), 11.71 (s, 1H, NH); MS m/z (%) 504 (M^++2, 8), 503 (M^++1, 16), 502 (M^+, 5), 355 (80), 267 (1), 207 (48), 180 (100), 152 (31), 151 (28), 122 (16), 105 (1), 95 (35), 81 (90), 77 (3); Anal. Found (Calcd.) for $C_{24}H_{22}N_8O_5$ (502.48): C, 57.21 (57.37); H, 4.35 (4.41); N, 22.41 (22.30)%.

2,7-Dimethyl-8-phenylazo-3-[(*N*-phenyl-2-oxo-2-phenyl-ethane-hydrazonoyl)]-pyrazolo[1,5-*a*]pyrimidin-4(3*H*)-one (3j). Yellow solid (1.05 g, 86 %), m.p. 262-264°C (dioxane); IR (KBr) ν 3318, 1702, 1660 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.23 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 5.51 (s,1H, CH), 7.23-7.90 (m, 15H, ArH), 12.58 (s, 1H, NH); MS m/z (%) 490 (M^++1, 12), 489 (M^+, 31), 268 (15), 267 (98), 222 (13), 190 (47), 162 (44), 131 (11), 105 (100), 93 (18), 91 (21), 77 (77); Anal. Found (Calcd.) for $C_{28}H_{23}N_7O_2$ (489.53): C, 68.76 (68.70); H, 4.73 (4.74); N, 20.00 (20.03)%.

2,7-Dimethyl-8-phenylazo-3-[(*N*-(4-methylphenyl)-2-oxo-2-phenyl-ethanehydrazonoyl]-pyrazolo[1,5-*a*]pyrimidin-4(3*H*)-one (3k). Yellow solid (0.94 g, 75 %), m.p. 240°C (dioxane/ MeOH); IR (KBr) ν 3151, 1699, 1655 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.90 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 5.69 (s,1H, CH), 7.40-7.51 (m, 10H, ArH), 8.05 (d, J = 8 Hz, 2H, ArH), 8.31 (d, J = 8 Hz, 2H, ArH), 12.19 (s, 1H, NH); MS m/z (%) 505 (M^++2, 14), 504 (M^++1, 15), 503 (M^+, 64), 312 (12), 292 (71), 267 (10), 225 (99), 220 (95), 218 (100), 201 (30), 179 (46), 161 (42), 151 (32), 123 (14), 105 (3), 91 (17), 77 (22); Anal. Found (Calcd.) for $C_{29}H_{25}N_7O_2$ (503.55): C, 69.00 (69.17); H, 5.03 (5.00); N, 19.42 (19.47)%.

2,7-Dimethyl-8-phenylazo-3-[*N*-(4-chlorophenyl)-2-oxo-2-phenyl-ethanehydrazonoyl)]-pyrazolo[1,5-*a*]pyrimidin-4(3*H*)-one (3l). Yellow solid (1.07g, 82 %), m.p. 260-262°C (DMF/ MeOH); IR (KBr) ν 3074, 1678, 1659 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 5.68 (s,1H, CH), 7.06-7.65 (m, 10H, ArH), 8.17 (d, J = 7 Hz, 2H, ArH), 8.44 (d, J = 7 Hz, 2H, ArH), 12.20 (s, 1H, NH); MS m/z (%) 524 (M^++1, 57), 523 (M^+, 62), 512 (100), 491 (52), 436 (48), 403 (62), 356 (48), 267 (67), 216 (57), 206 (81), 201 (43), 141 (81), 129 (52), 105 (57), 77 (43); Anal. Found (Calcd.) for $C_{28}H_{22}N_7ClO_2$ (523.97): C, 64.00 (64.18); H, 4.20 (4.23); N, 18.62 (18.71)%.

2,7-Dimethyl-8-phenylazo-3-[(*N*-(4-nitrophenyl)-2-oxo-2-phenyl-ethanehydrazonoyl)]-pyrazolo[1,5-*a*]pyrimidin-4(3*H*)-one (3m). Yellow solid (0.99 g, 74 %), m.p. 276-278°C (dioxane/ MeOH); IR (KBr) ν 3146, 1703, 1663 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.98 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 5.74 (s,1H, CH), 6.79 (d, J = 7 Hz, 2H, ArH), 7.85 (d, J = 7 Hz, 2H, ArH), 7.14-7.77 and 7.98-8.25 (m, 10H, ArH), 12.63 (s, 1H, NH); MS m/z (%) 536 (M^++2, 8), 535 (M^++1, 25), 534 (M^+, 53), 454 (4), 339 (11), 323 (64), 267 (25), 239 (30), 202 (2), 194 (59), 165 (14), 136 (32), 135 (19), 109 (21), 105 (7), 91 (74), 89 (73), 77 (100); Anal. Found (Calcd.) for $C_{28}H_{22}N_8O_4$ (534.53): C, 62.84 (62.92); H, 4.00 (4.15); N, 21.00 (20.96)%.

2,7-Dimethyl-8-phenylazo-3-[(*N*-phenyl-2-oxo-2-thienoyl-methanehydrazonoyl]-pyrazolo-[1,5-*a*]pyrimidin-4(3*H*)-one (3n). Yellow solid (1.05 g, 85 %), m.p. 290-292 °C (Dioxane); IR (KBr) ν 3182, 1705, 1680 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.18 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 6.28 (s,1H, CH), 7.08-7.51 (m, 13H, ArH), 11.56 (s, 1H, NH); MS m/z (%) 496 (M^++1, 16), 495

(M^+, 47), 268 (15), 267 (100), 190 (58), 134 (30), 93 (12), 92 (31), 91 (12), 77 (25); Anal. Found (Calcd.) for $C_{26}H_{21}N_7O_2S$ (495.56): C, 63.00 (63.02); H, 4.20 (4.27); N, 20.01 (19.79)%.

General procedure for synthesis of 1-aryl-3-substituted-4,7-dimethyl-6-phenylazo-bis-pyrazolo[1,5-*a*][4',3'-*e*]pyrimidine (4a-n)

To the appropriate 2,7-dimethyl-8-phenylazo-3-(N-aryl substituted alkane hydrazonoyl)pyrazolo[1,5-*a*]pyrimidin-4(3H)-one **3** (2.5 mmole), phosphorus oxychloride (10 ml) was added. The mixture was refluxed for 3 hr., then the excess $POCl_3$ was evaporated and the reaction mixture was poured onto crushed ice with stirring. The solid product that precipitated was filtered, washed with water and finally crystallized from the appropriate solvent to give the respective **4.** The physical constants of the products **4a-n** isolated are listed below.

1,3-Diphenyl-4,7-dimethyl-6-phenylazo-bis-pyrazolo[1,5-*a*][4',3'-*e*]pyrimidine (4a). Pale brown solid (0.93 g, 84 %), m.p. 210-212°C (EtOH); ^1H NMR ($CDCl_3$) δ 2.31 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 7.43-7.79 (m, 15H, ArH); ^{13}C NMR ($DMSO_6$) δ 14.25, 25.68, 120.63, 120.77, 120.83, 122.75, 123.01, 123.97, 126.97, 127.85, 128.19, 128.88, 128.99, 129.20, 139.57, 139.77, 139.89, 144.65, 148.00, 153.00, 165.01; MS m/z (%) 445 (M^++2, 10), 444 (M^++1, 35), 443 (M^+, 100), 290 (28), 272 (18), 245 (27), 187 (77), 174 (15), 147 (15), 116 (32), 105 (12), 103 (44), 77 (21); Anal. Found (Calcd.) for $C_{27}H_{21}N_7$ (443.50): C, 73.00 (73.12); H, 4.52 (4.77); N, 22.00 (22.11).

3-Acetyl-4,7-dimethyl-1-phenyl-6-phenylazo-bis-pyrazolo[[1,5-*a*][4',3'-*e*]pyrimidine (4b). Pale brown solid (0.85 g, 83 %), m.p. 198-200°C (EtOH); IR (KBr) ν 1689 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.02 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 7.33-7.64 (m, 10H, ArH); ^{13}C NMR ($DMSO_6$) δ 13.82, 25.36, 27.05, 117.63, 121.78, 126.75, 127.30, 128.68, 129.13, 129.26, 131.36, 136.00, 138.12, 141.37, 145.32, 148.12, 151.31, 162.33, 193.43; MS m/z (%) 411 (M^++2, 5), 410 (M^++1, 22), 409 (M^+, 37), 301 (26), 267 (1), 255 (25), 219 (12), 152 (10), 125 (100), 105 (3), 99 (18), 91 (52), 77 (46); Anal. Found (Calcd.) for $C_{23}H_{19}N_7O$ (409.44): C, 67.31 (67.47); H, 4.54 (4.68); N, 23.81 (23.95)%.

3-Acetyl-4,7-dimethyl-1-(4-methylphenyl)-6-phenylazo-bis-pyrazolo[1,5-*a*][4',3'-*e*]-pyrimidine (4c). Pale brown solid (0.91 g, 86 %), m.p. 218-220°C (dioxane/ MeOH); IR (KBr) ν 1697 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.99 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 6.97-7.54 (m, 5H, ArH), 7.74 (d, J = 9 Hz, 2H, ArH), 7.82 (d, J = 9 Hz, 2H, ArH); MS m/z (%) 424 (M^++1, 94), 423 (M^+, 100), 422 (34), 407 (17), 381 (20), 267 (23), 259 (25), 148 (29), 129 (18), 128 (11), 105 (4), 103 (26), 96 (22), 91 (65), 77 (67); Anal. Found (Calcd.) for $C_{24}H_{21}N_7O$ (423.47): C, 68.00 (68.07); H, 4.89 (5.00); N, 23.10 (23.15)%.

3-Acetyl-1-(4-chlorophenyl)-4,7-dimethyl-6-phenylazo-bis-pyrazolo[1,5-*a*][4',3'-*e*]-pyrimidine (4d). Pale brown solid (0.91 g, 82 %), m.p. 276-278°C (DMF/ MeOH); IR (KBr) ν 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.27 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 7.16-7.60 (m, 9H, ArH); MS m/z (%) 445 (M^++2, 26), 444 (M^++1, 17), 443 (M^+, 54), 296 (13), 250 (15), 188 (14), 187 (100), 174 (11), 139 (23), 116 (49), 111 (17), 103 (37), 90 (9), 77 (16); Anal.

Found (Calcd.) for $C_{23}H_{18}N_7ClO$ (443.89): C, 62.09 (62.23); H, 4.00 (4.09); N, 22.00 (22.09)%.

3-Acetyl-4,7-dimethyl-1-(4-nitrophenyl)-6-phenylazo-bis-pyrazolo[1,5-*a*][4',3'-*e*]-pyrimidine (4e). Pale brown solid (0.92 g, 81 %), m.p. 238-240°C (EtOH); IR (KBr) ν 1701 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 2.07 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 6.97-7.56 (m, 9H, ArH); MS m/z (%) 456 (M^++2, 18), 455 (M^++1, 25), 454 (M^+, 21), 267 (7), 225 (100), 218 (14), 206 (11), 186 (16), 179 (71), 151 (27), 105 (4), 103 (12), 91 (16), 77 (11); Anal. Found (Calcd.) for $C_{23}H_{18}N_8O_3$ (454.44): C, 60.83 (60.79); H, 3.74 (3.99); N, 24.63 (24.66)%.

4,7-Dimethyl-3-ethoxycarbonyl-1-phenyl-6-phenylazo-bis-pyrazolo[1,5-*a*][4',3'-*e*]-pyrimidine (4f). Dark red solid (0.93 g, 85 %), m.p. 180-182°C (EtOH); IR (KBr) ν 1716 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 1.06 (t, J = 7 Hz, 3H, CH_3), 1.94 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 4.32 (q, J = 7 Hz, 2H, CH_2), 7.36-7.48 and 7.79-7.83 (m, 10H, ArH); ^{13}C NMR (DMSO$_6$) δ 13.82, 15.36, 25.36, 61.10, 117.63, 121.78, 127.24, 128.19, 128.95, 129.13, 129.26, 132.09, 136.50, 138.12, 141.37, 142.32, 148.12, 151.31, 157.33, 170.43; MS m/z (%) 441 (M^++2, 28), 440 (M^++1, 23), 439 (M^+, 42), 257 (74), 155 (15), 148 (19), 144 (22), 143 (51), 132 (22), 127 (20), 106 (42), 93 (100), 92 (44), 87 (17), 77 (32); Anal. Found (Calcd.) for $C_{24}H_{21}N_7O_2$ (439.47): C, 65.42 (65.59); H, 4.64 (4.82); N, 22.01 (22.31)%.

4,7-Dimethyl-3-ethoxycarbonyl-1-(4-methylphenyl)- 6-phenylazo-bis-pyrazolo[1,5-*a*]-[4',3'-*e*]pyrimidine (4g). Dark red solid (0.91 g, 80 %), m.p. 172-174°C (EtOH); IR (KBr) ν 1705 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 1.09 (t, J = 7 Hz, 3H, CH_3), 1.85 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 4.18 (q, J = 7 Hz, 2H, CH_2), 6.91-7.73 (m, 5H, ArH), 8.10 (d, J = 8 Hz, 2H, ArH), 8.26 (d, J = 8 Hz, 2H, ArH),; MS m/z (%) 454 (M^++1, 24), 453 (M^+, 29), 291 (15), 267 (9), 227 (100), 225 (18), 220 (18), 218 (21), 191 (7), 185 (9), 179 (17), 151 (12), 118 (16), 91 (5), 77 (14); Anal. Found (Calcd.) for $C_{25}H_{23}N_7O_2$ (453.50): C, 66.00 (66.21); H, 5.23 (5.11); N, 21.32 (21.62)%.

1-(4-Chlorophenyl)-4,7-dimethyl-3-ethoxycarbonyl-6-phenylazo-bis-pyrazolo[1,5-*a*]-[4',3'-*e*]pyrimidine (4h). Dark red solid (1.01 g, 85 %), m.p. 190-192°C (EtOH); IR (KBr) ν 1705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.32 (t, J = 7 Hz, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 4.35 (q, J = 7 Hz, 2H, CH_2), 7.63 (d, J = 7 Hz, 2H, ArH), 7.12-7.32 (m, 5H, ArH), 8.00 (d, J = 7 Hz, 2H, ArH); MS m/z (%) 475 (M^++2, 21), 474 (M^++1, 67), 473 (M^+, 14), 341 (100), 340 (96), 207 (58), 180 (71), 152 (19), 133 (83), 111 (2), 105 (3), 103 (23), 90 (26), 80 (13), 77 (9); Anal. Found (Calcd.) for $C_{24}H_{20}ClN_7O_2$ (473.91): C, 60.74 (60.82); H, 4.20 (4.25); N, 20.71 (20.69)%.

4,7-Dimethyl-3-ethoxycarbonyl-1-(4-nitrophenyl)-6-phenylazo-bis-pyrazolo[1,5-*a*][4',3'-*e*]-pyrimidine (4i). Dark red solid (1.07 g, 88 %), m.p. 184-186°C (EtOH); IR (KBr) ν 1701 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 1.31 (t, J = 7 Hz, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 4.33 (q, J = 7 Hz, 2H, CH_2), 7.64 (d, J = 9 Hz, 2H, ArH), 7.14-7.55 (m, 5H, ArH), 8.14 (d, J = 9 Hz, 2H, ArH); MS m/z (%) 485 (M^++1, 20), 484 (M^+, 61), 375 (100), 335 (4), 267 (1), 256 (11), 228 (15), 187 (61), 180 (11), 174 (18), 146 (15), 119 (42), 103 (31), 91 (18), 77 (15); Anal. Found (Calcd.) for $C_{24}H_{20}N_8O_4$ (484.47): C, 59.43 (59.50); H, 4.00 (4.16); N, 23.20 (23.13)%.

3-Benzoyl-4,7-dimethyl-1-phenyl-6-phenylazo-bis-pyrazolo[1,5-*a*][4',3'-*e*]pyrimidine (4j). Buff solid (1.01 g, 86 %), m.p. 220-222 °C (Dioxane/ MeOH); IR (KBr) ν 1693 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 2.08 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 6.93-7.41 and 7.79-7.81 (m, 15H, ArH); ^{13}C NMR (DMSO$_6$) δ 20.37, 24.73, 114.93, 122.91, 123.96, 128.06, 128.18, 129.19, 129.58, 129.77, 132.76, 133.19, 136.24, 137.78, 137.99, 139.32, 139.49, 141.00, 143.58, 152.20, 153.67, 164.72, 195.42; MS m/z (%) 472 (M^++1, 2), 471 (M^+, 6), 325 (23), 324 (100), 323 (88), 267 (1), 208 (4), 180 (7), 165 (3), 105 (1), 90 (1), 89 (4), 77 (15); Anal. Found (Calcd.) for $C_{28}H_{21}N_7O$ (471.51): C, 71.00 (71.32); H, 4.51 (4.49); N, 20.59 (20.79)%.

3-Benzoyl-4,7-dimethyl-1-(4-methylphenyl)-6-phenylazo-bis-pyrazolo[1,5-*a*][4',3'-*e*]-pyrimidine (4k). Pale brown solid (0.99 g, 82%), m.p. 194-196°C (Dioxane/ MeOH); IR (KBr) ν 1701 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 2.29 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 7.17 (d, J = 9 Hz, 2H, ArH), 7.32 (d, J = 9 Hz, 2H, ArH), 7.57-7.72 (m, 10H, ArH); MS m/z (%) 487 (M^++2, 10), 486 (M^++1, 22), 485 (M^+, 78), 484 (44), 380 (14), 267 (6), 248 (15), 209 (100), 200 (3), 152 (16), 123 (22), 105 (7), 97 (24), 91 (6), 82 (88), 77 (8); Anal. Found (Calcd.) for $C_{29}H_{23}N_7O$ (485.54): C, 71.64 (71.74); H, 4.35 (4.77); N, 20.00 (20.19)%.

3-Benzoyl-1-(4-chlorophenyl)-4,7-dimethyl-6-phenylazo-bis-pyrazolo[1,5-*a*][4',3'-*e*]-pyrimidine (4l). Pale brown solid (1.08 g, 85 %), m.p. 222-224°C (Dioxane/ MeOH); IR (KBr) ν 1701 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 2.33 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 7.06 (d, J = 9 Hz, 2H, ArH), 7.27 (d, J = 9 Hz, 2H, ArH), 7.30-7.85 (m, 10H, ArH); MS m/z (%) 507 (M^++2, 23), 506 (M^++1, 24), 505 (M^+, 48), 323 (100), 267 (1), 220 (4), 201 (1), 192 (7), 111 (1), 105 (1), 91 (1), 89 (49), 77 (22); Anal. Found (Calcd.) for $C_{28}H_{20}N_7ClO$ (505.96): C, 66.44 (66.47); H, 3.76 (3.98); N, 19.00 (19.38)%.

3-Benzoyl-4,7-dimethyl-1-(4-nitrophenyl)-6-phenylazo-bis-pyrazolo[1,5-*a*][4',3'-*e*]-pyrimidine (4m). Pale brown solid (1.07 g, 83 %), m.p. 242 - 244 °C (Dioxane/ EtOH); IR (KBr) ν 1704 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.08 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 6.79 (d, J = 8 Hz, 2H, ArH), 7.03-7.51 (m, 10H, ArH), 7.52 (d, J = 8 Hz, 2H, ArH); MS m/z (%) 518 (M^++2, 17), 517 (M^++1, 74), 516 (M^+, 30), 267 (3), 266 (19), 225 (95), 218 (100), 216 (26), 204 (22), 191 (20), 179 (44), 151 (25), 118 (11), 105 (2), 91 (16), 77 (10); Anal. Found (Calcd.) for $C_{28}H_{20}N_8O_3$ (516.51): C, 65.01 (65.11); H, 3.72 (3.90); N, 21.54 (21.69)%.

4,7-Dimethyl-1-phenyl-6-phenylazo-3-thienoyl-*bis*-pyrazolo[1,5-*a*][4',3'-*e*]pyrimidine (4n). Pale brown solid (1.00 g, 84 %), m.p. 178 -180 °C (EtOH); IR (KBr) ν 1686 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.06 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 7.07-8.20 (m, 13H, ArH); ^{13}C NMR (DMSO$_6$) δ 14.00, 25.52, 114.72, 121.10, 123.19, 125.52, 127.28, 127.63, 128.49, 128.62, 129.07, 130.81, 137.66, 138.00, 140.50, 143.00, 144.00, 146.70, 152.83, 154.49, 162.50, 174.05; MS m/z (%) 478 (M^++1, 8), 477 (M^+, 42), 354 (69), 330 (26), 287 (22), 259 (9), 233 (16), 129 (19), 105 (4), 103 (43), 91 (100), 89 (13), 77 (92); Anal. Found (Calcd.) for $C_{26}H_{19}N_7OS$ (477.54): C, 65.48 (65.39); H, 4.00 (4.01); N, 20.34 (20.53)%.

Synthesis of 2,7-dimethyl-8-phenylazo-3-(substituted-methyl)-pyrazolo[1,5-*a*]-pyrimidin - 4(3*H*)-ones (5b,f). To a mixture of equimolar quantities of **1** and 3-chloro-2,4-pentanedione (2.5 mmole each) in dioxane (30 ml) was added triethylamine (2.5 mmole). The mixture was stirred at room temperature for 24 h, the solid that formed was collected and crystallized from dioxane/ ethanol to give the respective product **5b.**

When the same procedure was repeated using ethyl 2-chloro-3-oxobutanoate in place of 3-chloro-2,4-pentanedione, the product **5f** was obtained. The physical constants of the products isolated together with their spectral data are listed below.

2,7-Dimethyl-3-(2,3-dioxo-2-pentyl)-8-phenylazo-pyrazolo[1,5-*a*]pyrimidin-4(3H)-one (5b). Yellow solid (0.77 g, 84 %), m.p. 224-226^{o}C (EtOH); IR (KBr) ν 3421, 1702, 1691, 1662 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.06 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 5.39 (s,1H, CH), 7.06-7.74 (m, 5H, ArH), 11.51 (s, 1H, NH); MS m/z (%) 367 (M^++2, 1), 366 (M^++1, 2), 365 (M^+, 7), 364 (7), 339 (1), 280 (2), 268 (1), 260 (83), 218 (16), 207 (21), 141 (99), 131 (23), 121 (10), 106 (100), 105 (97), 90 (34), 83 (23), 77 (52); Anal. Found (Calcd.) for $C_{19}H_{19}N_5O_3$ (365.39): C, 62.41 (62.46); H, 5.25 (5.24); N, 19.20 (19.17)%.

2,7-Dimethyl-3-(1-ethoxycarbonyl-2-oxo-1-propyl)-8-phenylazo-pyrazolo[1,5-*a*]-pyrimidin-4(3*H*)-one (5f). Yellow solid (0.81 g, 82 %), m.p. 240-242^{o}C (EtOH); IR (KBr) ν 3445, 1740, 1699, 1652 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.04 (t, J = 6 Hz, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 4.42 (q, J = 6 Hz, 2H, CH_2), 5.26 (s,1H, CH), 7.08-7.37 (m, 5H, ArH), 11.19 (s, 1H, NH); MS m/z (%) 396 (M^++1, 25), 395 (M^+, 13), 394 (48), 318 (13), 268 (12), 178 (17), 153 (33), 151 (87), 139 (48), 137 (33), 111 (100), 101(27), 99 (44), 90 (14), 77 (4); Anal. Found (Calcd.) for $C_{20}H_{21}N_5O_4$ (395.41): C, 61.00 (60.75); H, 5.22 (5.35); N, 17.85 (17.71)%.

Alternate synthesis of 3b and 3f

To a solution of compound **5b** (10 mmol) in ethanol (40 ml) and DMF (10 ml) was added sodium acetate trihydrate (3 g) and the mixture was cooled in an ice bath at 0-5^{o}C while being stirred. To the resulting cold solution was added a cold solution of benzenediazonium chloride, prepared as usual by diazotizing aniline (10 mmol) in hydrochloric acid (6 ml, 6 M) with sodium nitrite (0.7 g, 10 mmol) in water (10 ml). After all of the diazonium salt solution was added, the reaction mixture was stirred for further 30 min while being cooled in an ice bath. The solid that precipitated was filtered off, washed with water, dried and finally crystallized from ethanol to give **3b** identical in all respects (mp., mixed mp., IR, MS and ^{1}H NMR spectra) with that one obtained from **1** and hydrazonoyl chloride **2b**.

When this procedure was repeated using **5f** *in lieu* **5b**, the respective **3f** was obtained. The latter product proved identical in all respects with **3f** obtained from reaction of **1** with **2f**.

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