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A CONVENIENT SYNTHESIS OF 1,3-DIARYL-1,2,3,4,-TETRAHYDRO-5,7,7-TRIMETHYL-4-OXO-2-THIOXO-7H-PYRANO[2,3-d]PYRIMIDINES

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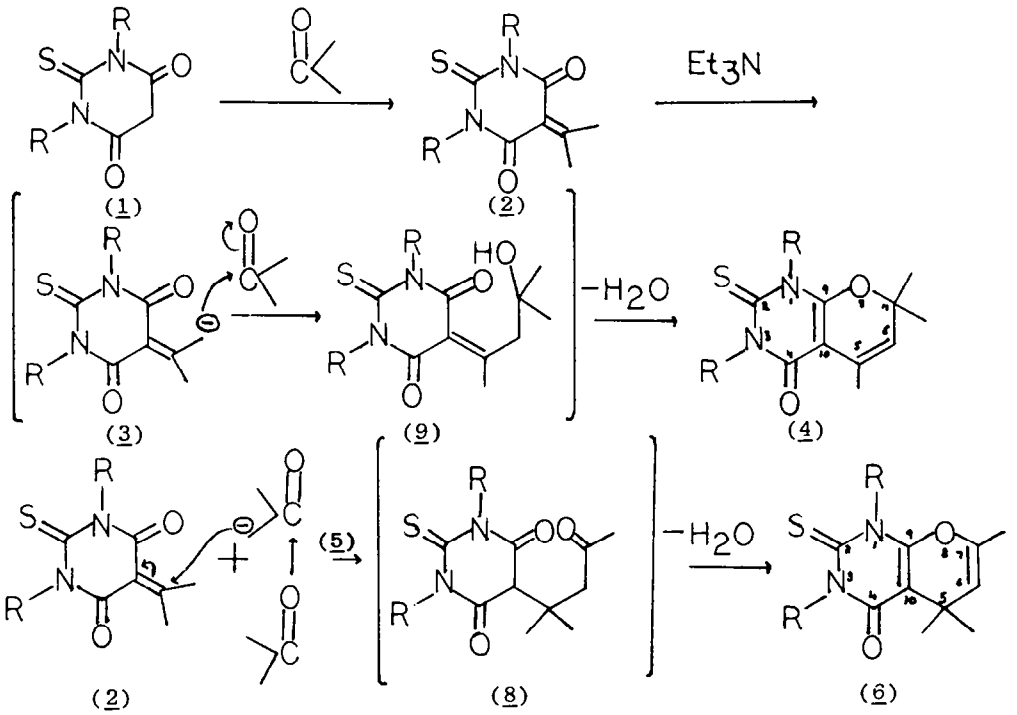
Abstract: A novel synthesis of 1,3-diaryl-1,2,3,4-tetrahydro-5,7,7-trimethyl-4-oxo-2-thioxo-7H-pyrano[2,3-d]pyrimidines (4) and the isomeric 1,3-diaryl-1,2,3,4,-tetrohydro-5,5,7-trimethyl-4-oxo-2-thioxo-5H-pyrano [2,3-d]pyrimidines (6) is described.

The synthesis of pyranopyrimidines is of great interest in view of the biological activities associated with this system. A number of methods for the synthesis of these compounds have been described[1-7]. The majority of these involve a number of steps and the yields are poor. The title compounds were synthesised earlier[8] by the reaction of 1,3-diarythiobarbituric acids (1) with acetone in the presence of triethylamine. The reaction was believed to take place[8] by the formation of the isopropylidene derivative (2) which lost a proton to give the intermediate (3); this then reacted further with another molecule of acetone to give the title compound 4 . Subsequently an alternative course of reaction has come to our attention in which the intermediate 2 reacts with the species 5 (which could be generated by the abstration of proton from acetone) to give the isomeric structure 6 as shown in Chart-1. In view of the above it was considered of interest to decide the exact pathway by which the above reaction takes place. Since mesityl oxide could be derived from acetone, the reaction of mesityl oxide with 1,3-diarylthiobarbituric acids (1) was investigated as a first step. Mesityl oxide can in principle react with 1,3-diarylthiobarbituric acids (1) either by addition to its carbonyl group followed by cyclisation of intermediate compound (route A; Chart - 2) to give the structure 4 or by the Michael type addition (route B, Chart - 3) to give the isomeric structure 6.

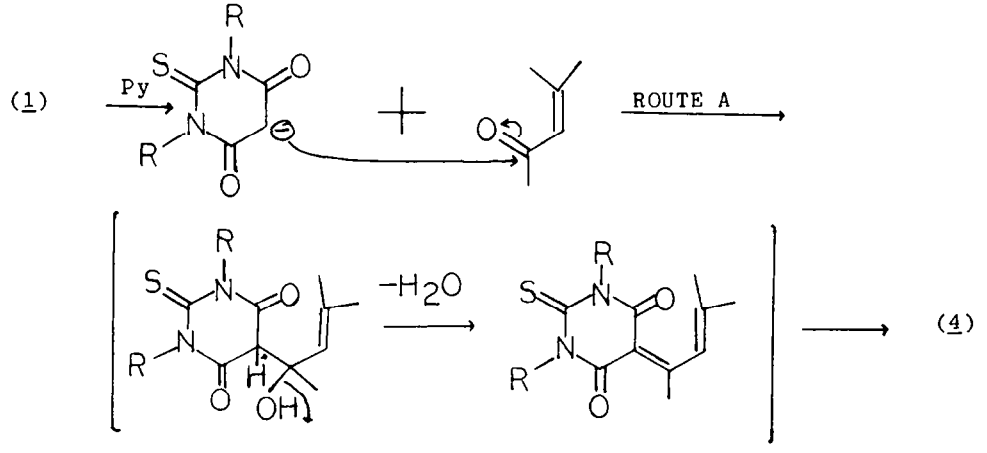
Normally the reaction of mesityl oxide with 1,3-diarylthiobarbituric acid (1) is expected to proceed via Michael addition (route B) to give the isomeric compound 6. The question was therefore whether the reaction had proceeded via route A giving 4 or via route B giving 6. For this it was necessary to differentiate between structure 4 and 6. It was difficult to differentiate between the two structures 4 & 6 on the basis of ^{1}H and ^{13}C NMR. Hence it was essential to make one of the structures by an unambiguous method.



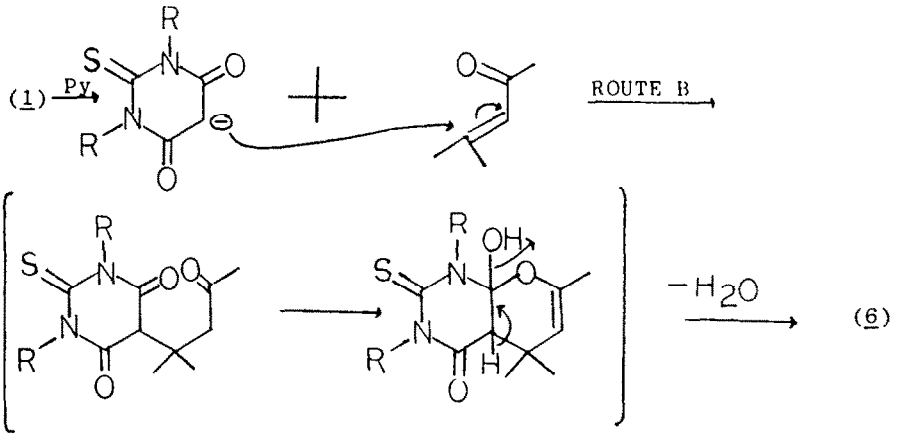
(a) R = C_6H_5
(b) R = o-$CH_3C_6H_4$
(c) R = m-$CH_3C_6H_4$
(d) R = p-$CH_3C_6H_4$
(e) R = o-$CH_3OC_6H_4$
(f) R = m-$CH_3OC_6H_4$
(g) R = p-$CH_3OC_6H_4$

(Chart - 1)

The authentic sample of 4 was obtained as follows: The reaction of 1,3-diarylthiobarbituric acid (1) with ethyl acetoacetate gave 1,3-diaryl-1,2,

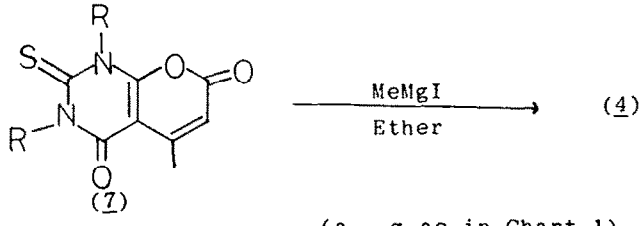


(Chart - 2)



(Chart - 3)

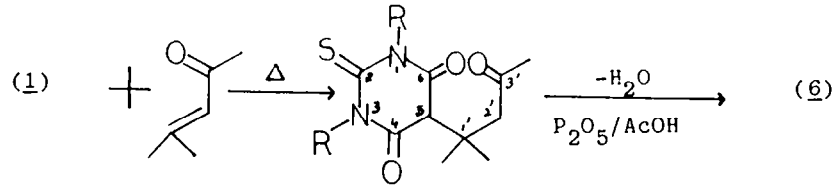
3,4,-tetrahydro-5-methyl-4,7-dioxo-2-thioxo-7H-pyrano[2,3-d]pyrimidine (7). Its Grignard reaction with methylmagnesium iodide gave[9] the required 4 The product obtained by the reaction of 1,3-diarylthiobarbituric acid (1) with acetone or with mesityl oxide in the presence of pyridine was found to



(a - g as in Chart 1)

be identical with the authentic sample of 4 obtained above. This shows the condensation of mesityl oxide with 1,3-diarylthiobarbituric acids proceed via route A & not via route B. This abnormal behaviour can be attributed to the steric interference caused by the presence of two methyl groups of the mesityl oxide and the bulky N-aryl group of 1,3-diarylthiobarbituric acid which do not allow the orientation needed for normal michael addition. The isomeric structure viz 1,3-diaryl-1,2,3,4,-tetrahydro-5,5,7-trimethyl-4-oxo-2-thioxo-5H-pyrano[2,3-d]pyrimidine (6) was obtained as follows: The reaction of 1,3-diarylthiobarbituric acid (1) with mesityl oxide in the absence of base gave a product, which gave positive 2,4-dinitrophenyl hydrazine test indicating the presence of open chain structure. On the basis of spectral & elemental analysis, it was given the structure 8. Cyclisation of 8 under acidic conditions gave 6 (Chart - 4).

Once the authentic samples of these two structures 4 and 6 have been obtained, it is now possible to differentiate between the two structures on



(Chart - 4)

(a - g as in Chart 1)

the basis of ^{1}H (table 1) and ^{13}C (table 2) NMR spectral data.

Table-1

^{1}H NMR spectral data of 4a and 6a ($CDCl_3$, δ)

Compounds	5/7-CH_3	6-H	7/5-$C(CH_3)_2$	Ar-H
4a	2.15(s, 5-CH_3)	4.90(s)	1.30(s, 7-$C(CH_3)_2$	7.10-7.51(m)
6a	1.55(s, 7-CH_3)	4.70(s)	1.45(s, 5-$C(CH_3)_2$	7.30-7.70(m)

On the basis of above data it is possible to differentiate between the two structures 4a and 6a. The signal for methyl group at C-7 in structure 6a appeared at the usual position i.e. δ 1.55. The appearance of signal at δ 2.15 for methyl at C-5 in structure 4a can be explained due to the deshielding effect of carbonyl group at C-4.

On the basis of ^{13}C NMR spectral data (table 2) it is concluded that the main difference between the structures 4a and 6a is the chemical shift of tertiary carbon atom at C-7 in structure 4a or at C-5 in structure 6a δ 83.80, whereas in 6a it appeared at δ 31.90. In view of the above, it is concluded that the reaction of 1,3-diarylthiobarbituric acids (1) with mesityl oxide in the presence of pyridine takes place via route A (Chart-2). However it is now confirmed that the reaction of 1,3-diarylthiobarbituric acids (1) with acetone in the presence of triethylamine gives 4 which is also obtained from the intermediate 2 under the same conditions. Therefore the formation of 4 shows that the intermediate structure can not be 8 (Chart-1) but must be 9 which alone can give 4 on cyclisation. Formation of 9 can only proceed through the formatien of carbanion 3 which is preferred to carbanion 5.

EXPERIMENTAL

All melting points are uncorrected. ^{1}H-NMR spectra were recorded on Perkin Elmer R-32 (90 MHz) instrument using TMS as the internal standard (chemical shifts in δ). ^{13}C-NMR spectra were recorded on Jeol JNM-FX 100 (25.0 MHz) spectrometer using TMS as the internal standard (chemical shifts in δ).

Table - 2

^{13}C NMR spectral data of 4a and 6a ($CDCl_3$, δ , proton decoupled)

Compounds	C-1',1"	C-10	C-2',3',4',5' 6',2",3",4",5" & 6"	C-2	C-4	C-5	C-6	C-7	C-9	5/7-CH_3	5/7 2xCH_3
4a	138.16* (s)	129.30(s)	128.27 128.39(each) 128.80 d 129.15	177.30 (s)	159.20 (s)	140.0* (s)	119.70 (d)	83.80 (s)	157.20 (s)	22.20 (q,5-CH_3)	27.48 (q,7-2xCH_3)
6a	138.37 (s)	129.39(s)	128.28 128.51 128.86(each) 129.10 d	164.51 (s)	153.29 (s)	31.90 (s)	111.60 (d)	139.90 (s)	142.50	17.67 (q,7-CH_3)	29.47 (q,5-2xCH_3)

*Assignments may be reversed

1,2,3,4,-Tetrahydro-5,7,7-trimethyl-4-oxo-1,3-diphenyl-2-thioxo-7H-pyrano [2,3-d] pyrimidine (4a) Method (1) 1a (1.48 g, 5 mmol), mesityl oxide (0.49 ml, 5 mmol) in dry pyridine (50 ml) was refluxed for 10-12 hr. The reaction mixture was cooled and treated with crushed ice. It was neutralized with dil HCl. The separated slid was crystallised from methanol to yield 4a as light yellow crystals (1.60 g); m.p. 206-207°C (lit[8] m.p. 206-207°); ^{1}H NMR ($CDCl_3$) δ:1.30(6H, s, $C(CH_3)_2$), 2.15(3H, s, 5-CH_3), 4.96(1H, s, 6-H), 7.10-7.51(10H, m, ArH), ^{13}C NMR($CDCl_3$) δ : 20.20(q, 5-CH_3), 27.48 (q, 7-2xCH_3), 83.80(s, 7-C), 119.70(d, 6-C), 128.27, 128.39, 128.80, 129.15(each d, Ar-C), 129.30(s, 10-C), 138.16(s, 1' & 1"-C), 140.0(s, 5-C), 159.20(s, 4-C), 177.30(s, 2-C), 157.20(s, 9-C). Found : C, 70.0; H, 5.2; N, 7.4. Calcd. for $C_{22}H_{20}N_2O_2S$: C, 70.2; H, 5.3; N, 7.4%.

Compounds 4b-g were obtained in a similar way.

4b: Yield 84.5%, m.p. 158-159° (Lit.[8] m.p. 158-59°C); ^{1}H NMR($CDCl_3$) δ : 1.31(6H, s, $C(CH_3)_2$), 2.20(3H, s, 5-CH_3), 2.50(6H, s, 2 x CH_3), 5.00(1H, s, 6-H), 7.10-7.40 (8H, m, Ar H). Found: C, 71.1; H, 5.9; N, 6.8 Calcd. for $C_{24}H_{24}N_2O_2S$: C, 71.2; H, 5.9; N, 6.9%.

4c: Yield 82%, m.p. 189-190°; ^{1}H NMR($CDCl_3$) δ:1.31(6H, s, $C(CH_3)_2$), 2.20(3H, s, 5-CH_3), 2.40(6H, s, 2 x CH_3), 5.08(1H, s, 6-H), 7.20-7.70(8H, m, Ar H). Found: C, 71.1; H, 5.9; N, 6.7. Calcd for $C_{24}H_{24}N_2O_2S$: C, 71.2; H, 5.9; N, 6.9%.

4d: Yield 86.8%, m.p. 190-191° (Lit.[8]m.p. 190-191°C); ^{1}H NMR($CDCl_3$) δ: 1.29 (6H, s, $C(CH_3)_2$), 2.19(3H, s, 5-CH_3), 2.40(6H, s, 2 x CH_3), 4.90(1H, s, 6-H), 7.30(4H, d, J=9 Hz, 3',5',3" and 5"-H), 7.35(4H, d, J=9 Hz, 2',6',2" and 6"-H); Found: C, 71.0; H, 5.8; N, 6.8. Calcd for $C_{24}H_{24}N_2O_2S$: C, 71.2; H, 5.9; N, 6.9%.

4e: Yield 85.5%, m.p. 199-200°; ^{1}H NMR($CDCl_3$) δ: 1.20(6H, s, $C(CH_3)_2$), 2.25(3H, s, 5-CH_3), 3.85(6H, s, 2x OCH_3), 5.10(1H, s, 6-H), 7.10-7.70(8H, m, Ar H). Found: C, 66.1; H, 5.4; N, 6.4. Calcd for $C_{24}H_{24}N_2O_4S$: C, 66.0; H, 5.5; N, 6.4%.

4f: Yield 76.5%, m.p. 204-206°; ^{1}H NMR($CDCl_3$) δ:1.30(6H, s, $C(CH_3)_2$), 2.20 (3H, s, 5-CH_3), 3.88(6H, s, 2 x OCH_3), 5.10(1H, s, 6-H), 6.90-7.70(8H, m, Ar H); Found: C,59.9; H, 5.4; N, 6.5. Calcd for $C_{24}H_{24}N_2O_4S$: C, 66.0; H, 5.5; N, 6.4%.

4g: Yield 78%, m.p. 245-46° (Lit.[8] m.p. 245-246°C); ^{1}H NMR($CDCl_3$) δ:1.22(6H, s, $C(CH_3)_2$), 2.15(3H, s, 5-CH_3), 3.75(6H, s, 2 x OCH_3), 4.90(1H, s, 6H), 6.85(4H, d, J=9 Hz, 3',5',3" and 5"-H), 7.16(4H, d, J=9 Hz, 2',6',2" and 6"-H). Found: C, 59.8; H, 5.4; N, 6.4. Calcd for $C_{24}H_{24}N_2O_4S$: C, 66.0; H, 5.5; N, 6.4%.

Method II

Step 1 : 1,2,3,4,-Tetrahydro-5-methyl-4,7-dioxo-1,3-diphenyl-2-thioxo-7H-pyrano[2,3-d]pyrimidine (7a) 1a (1 g) was dissolved in ethyl acetoacetate (5 ml) and sulphuric acid (0.5 ml) was added to it. The above mixture was heated on a steam bath for 30 min., viscous oil so obtained was treated with crushed ice. A pale yellow solid separated out which was filtered and crystallised from benzene to give 7a as light yellow crystals, yield 1.0 g (82%); m.p. 245-246°C. ^{1}H NMR($CDCl_3$)δ: 2.70(3H, s, 5-CH_3), 6.25(1H, s, 6H), 7.60-7.78(10H, m, Ar H). Found : C, 66.3; H, 3.9; N, 7.8. Calcd for $C_{20}H_{14}N_2O_3S$: C, 66.2; H, 3.8; N, 7.7%.

7b-g were obtained in a similar way.

7b: Yield 85%; m.p. 245-46°C; ^{1}H NMR ($CDCl_3$)δ: 2.25(6H, s, 2 x CH_3), 2.60 (3H, s, 5-CH_3), 5.85(1H, s, 6-H), 7.20-7.60(8H, m, Ar H); Found : C, 67.7; H, 4.5; N, 7.2. Calcd. for $C_{22}H_{18}N_2O_3S$: C, 67.6; H, 4.6; N, 7.1%.

7c: Yield 84%; m.p. 202-203°; ^{1}H NMR ($CDCl_3$) δ : 2.40(6H, s, 2 x CH_3), 2.60 (3H, s, 5-CH_3), 5.90(1H, s, 6-H), 6.70-7.50(8H, m, Ar H). Found : C, 67.7; H, 4.5; N, 7.2 Cacld for $C_{22}H_{18}N_2O_3S$: C, 67.6; H, 4.6; N, 7.1%.

7d: Yield 89% m.p. 258-259°; ^{1}H NMR($CDCl_3$)δ: 2.40(6H, s, 2 x CH_3), 2.58(3H, s, 5-CH_3), 5.85(1H, s, 6-H), 7.25-7.50(8H, m, Ar H); Found C, 67.5; H, 4.5; 7.2 Calcd for $C_{22}H_{18}N_2O_3S$: C, 67.6; H, 4.6; N, 7.1%.

7e: Yield 83%, m.p. 233-234°; ^{1}H NMR($CDCl_3$)δ: 2.60(3H, s, 5-CH_3), 3.90(6H, s, 2 x OCH_3), 5.96(1H, s, 6-H), 7.20-7.40(8H, m, Ar H). Found : C, 62.4; H, 4.3; N, 6.5. Calcd for $C_{22}H_{18}N_2O_5S$: C, 62.5; H, 4.2; N, 6.6%.

7f: Yield 81%; m.p. 238-239°; ^{1}H NMR($CDCl_3$)δ: 2.70(3H, s, 5-CH_3), 3.97(6H, s, 2 x OCH_3), 6.28(1H, s, 6-H), 7.0-7.90(8H, m, Ar H). Found : C, 62.6; H, 4.1; N, 6.5. Calcd. for $C_{22}H_{18}N_2O_5S$: C, 62.5; H, 4.2; N, 6.6%.

7g: Yield 72%; m.p. 206-07°; ^{1}H NMR($CDCl_3$)δ : 2.70 (3H, s, 5-CH_3), 4.0(6H, s, 2 x OCH_3), 6.25(1H, s, 6-H), 7.10-7.40(8H, m, Ar H). Found : C, 62.6; H, 4.3; N, 6.5. Calcd for $C_{22}H_{18}N_2O_5S$: C, 62.5; H, 4.2; N, 6.6%.

Step II: A solution of 7a (1.5 g, 5 mmol) in benzene (100 ml) was added slowly (1 hr) to a stirred Grignard solution of methyl iodide (2.41 g, 1.7 mmol), magnesium (0.40 g, 1.7 mg atom) and ether (50 ml). The solution was refluxed for 5 hr and set aside overnight. Decomposition with 25% ammonium chloride solution (50 ml) and extraction with ether gave an etheral solution which was washed with water and dried (Na_2SO_4). Removal of solvent and crystallization from methanol gave 4a as light yellow crystals, yield 1.01 g (65%); m.p. 206-207°C;

Using similar method, compounds 4b-g were obtained in 60-65% yield and their m.p. and spectral data agreed with products obtained by method I above.

5(1',1'-dimethyl-3'-oxobutyl)-1,3-diphenyl-2-thiobarbituric acid (8a) : 1a (1 g) and mesityl oxide (5 ml) were heated on steam bath for 5 hr. The reaction mixture was cooled and macerated with petroleum ether (4x10 ml). The solid product thus obtained was crystalised from methanol to yield 8a as white crystals, yield 1.19g (90%); m.p. 164-165°; ^{1}H NMR($CDCl_3$) : 1.50 (6H, s, $C(CH_3)_2$), 2.20(3H, s, $C(O)CH_3$), 2.80(2H, s, CH_2), 4.50(1H, s, 5-H), 7.0-7.50(10H, m, Ar H), ^{13}C NMR($CDCl_3$) δ : 25.81(q, 2 x 1'-CH_3), 30.93(q, CH_3), 40.21(s, 1'-C), 52.07(t, 2'-CH_2), 56.18(d, 5-C), 127.74, 128.03, 128.68, 129.15, 129.32(each d, Ar-C), 138.66(s, 1" and 1"'-C), 166.02(s, 4 & 6-C), 181.16(s, 2-C), 206.06(s, 3'-C). Found : C, 66.9; H, 5.5; N, 7.0 Calcd. for $C_{22}H_{22}N_2O_3S$: C, 67.0; H, 5.5; N, 7.0%.

Compounds 8b-g were obtained in a similar way.

8b: Yield 88.5%; m.p. 139-140°; ^{1}H NMR($CDCl_3$) δ : 1.45(6H, s, $C(CH_3)_2$), 2.20 (3H, s, $C(O)CH_3$), 2.30(6H, s, 2 x CH_3), 2.72(2H, s, CH_2), 4.70(1H, s, 5-H), 7.50-7.70(8H, m, Ar H). Found : C, 68.1; H, 6.0; N, 6.5. Calcd. for $C_{24}H_{26}N_2O_3S$: C, 68.2; H, 6.1; N, 6.6%.

8c: Yield 85%; m.p. 201-202°; ^{1}H NMR($CDCl_3$) δ : 1.40(6H, s, $C(CH_3)_2$), 2.30 (9H, m, 2 x CH_3 & $C(O)CH_3$), 2.60(2H, s, CH_2), 4.32(1H, s, 5-H), 6.85-7.40 (8H, m, Ar-H); Found : C, 68.0; H, 6.0; H, 6.7. Calcd. for $C_{24}H_{26}N_2O_3S$: C, 68.2; H, 6.1; N, 6.6%.

8d: Yield 90%; m.p. 179-180°; ^{1}H NMR($CDCl_3$) δ: 1.40(6H, s, $C(CH_3)_2$), 2.15 (3H, s, $C(O)CH_3$), 2.42(6H, s, 2 x CH_3), 2.60(2H, s, CH_2), 4.48(1H, s, 5-H) 7.10-7.70(8H, m,Ar-H). Found : C, 68.1; H, 6.1; N,6.6. Calcd for $C_{24}H_{26}N_2O_3S$: C, 68.2; H, 6.1; N, 6.6%.

8e: Yield 89%, m.p. 212-213°; ^{1}H NMR($CDCl_3$) δ : 1.50(6H, s, $C(CH_3)_2$), 2.16 (3H, s, $C(O)CH_3$), 2.75(2H, s, CH_2), 3.92(6H, s, 2 x OCH_3), 4.48(1H, s, 5-H) 7.20-7.70(8H, m, Ar H). Found: C, 63.3; H, 5.7; N, 6.0. Calcd. for $C_{24}H_{26}N_2O_5S$: C, 63.4; H, 5.7; N, 6.1%.

8f: Yield 82.5%; m.p. 152-153°; ^{1}H NMR($CDCl_3$) δ : 1.40(6H, s, $C(CH_3)_2$), 2.10 (3H, s, $C(O)CH_3$), 2.65(2H, s, CH_2), 3.80(6H, s, 2 x OCH_3), 4.35(1H, s, 5-H), 6.70-7.40(8H, m, Ar-H). Found: C, 63.3; H, 5.6; N, 6.0 Calcd. for $C_{24}H_{26}N_2O_5S$: C, 63.4; H, 5.7; N, 6.1%.

8g: Yield 86.5%; m.p. 146-147°; ^{1}H NMR($CDCl_3$) δ : 1.40(6H, s, $C(CH_3)_2$), 2.15 (3H, s, $C(O)CH_3$), 2.75(2H, s, CH_2), 3.90(6H, s, 2 x OCH_3), 4.55(1H, s, 5-H), 7.10-7.40(8H, m, Ar-H). Found: C, 63.2; H, 5.7; N, 6.0. Calcd. for $C_{24}H_{26}N_2O_5S$: C, 63.4; H, 5.7; N, 6.1%.

1,2,3,4-Tetrahydr-5,5,7-trimethyl-4-oxo-1,3-diphenyl-2-thio-5H-pyrano[2,3-d] pyrimidine (6a): To a solution of phosphorus pentoxide (4 g) in glacial acetic acid (16 ml) was added the compound 8a (1 g) and the mixture was

stirred at 120° for 1 hr. Subsequently the reaction mixture was cooled and treated with crushed ice. The product separated was filtered and crystallized from methanol to yield 6a as light yellow crystals, yield 0.85 g (90°); m.p. 249-250°; ^{1}H NMR($CDCl_3$) δ : 1.45(6H, s, $C(CH_3)_2$), 1.55(3H, s, 7-CH_3), 4.70(1H, s, 6-H), 7.30-7.70(10H, m, Ar-H); ^{13}C-NMR($CDCl_3$) : 17.67(q, 7-CH_3), 29.47(q, 5-2xCH_3), 31.90(s, 5-C), 111.60(d, 6-C), 128.28, 128.51, 128.86, 129.10(each d, Ar-C), 129.39(s, 10-C), 138.37(s,1',and 1"-C), 139.90(s, 7-C), 153.29(s, 4C), 164.51(s, 2-C), 142.50(s, 9-C). Found: C, 70.1; H, 5.2; N, 7.4. Calcd for $C_{22}H_{20}N_2O_2S$: C, 70.2; H, 5.3; N, 7.4%.

Compounds 6b-g were obtained in a similar way.

6b: Yield87.0%; m.p. 187-188°; ^{1}H NMR($CDCl_3$) δ : 1.50(6H, s, $C(CH_3)_2$), 1.59 (3H, s, 7-CH_3), 2.25(6H, s, 2xCH_3), 4.75(1H, s, 6-H), 7.40-7.60(8H, m, Ar-H). Found: C, 71.2; H, 5.8; N, 6.8. Calcd. for $C_{24}H_{24}N_2O_2S$: C, 71.2; H, 5.9; N, 6.9%.

6c: Yield 85.5%; m.p. 191-192°; ^{1}H NMR($CDCl_3$) δ : 1.48(6H, s, $C(CH_3)_2$), 1.58 (3H, s, 7-CH_3), 2.40(6H, s, 2 x CH_3), 4.55(1H, s, 6-H), 6.90-7.28(8H, m, Ar-H); Found: C, 71.0; H, 5.8; N, 6.9. Calcd. for $C_{24}H_{24}N_2O_2S$: C, 71.2; H, 5.9; N, 6.9%.

6d: Yield 86.0%; m.p. 205-206°; ^{1}H NMR($CDCl_3$) δ : 1.48(6H, s, $C(CH_3)_2$), 1.60 (3H, s, 7-CH_3), 2.40(6H, s, 2 x CH_3), 4.68(1H, s, 6-H), 7.20-7.50(8H, m, Ar-H). Found: C, 71.1; H, 5.8; N, 6.8. Calcd. for $C_{24}H_{24}N_2O_2S$: C, 71.2; H, 5.9; N, 6.9%.

6e: Yield 85.4%, m.p. 210-211°; ^{1}H NMR($CDCl_3$) δ : 1.50(6H, s, $C(CH_3)_2$), 1.60 (3H, s, 7-CH_3), 3.90(6H, s, 2 x OCH_3), 4.70(1H, s, 6-H), 7.10-7.60(8H, m, Ar-H); Found: C, 65.9; H, 5.4; N, 6.4. Calcd. for $C_{24}H_{24}N_2O_4S$: C, 66.0; H, 5.5; N, 6.4%.

6f: Yield 88.0%; m.p. 169-170°; ^{1}H NMR($CDCl_3$) δ : 1.45(6H, s, $C(CH_3)_2$), 1.58 (3H, s, 7-CH_3), 3.78(6H, s, 2 x OCH_3), 4.55(1H, s, 6-H), 6.80-7.40(8H, m, Ar-H); Found: C, 66.1; H, 5.5; N, 6.5 Calcd. for $C_{24}H_{24}N_2O_4S$: C, 66.0 H, 5.5; N, 6.4%.

6g: Yield 90.5%; m.p. 254-255°; ^{1}H NMR($CDCl_3$) δ : 1.45(6H, s, $C(CH_3)_2$), 1.57 (3H, s, 7-CH_3), 3.85(6H, s, 2 x OCH_3), 4.55(1H, s, 6-H), 7.10-7.40(8H, m, ArH); Found : C, 66.1; H, 5.4; N, 6.4. Calcd. for $C_{24}H_{24}N_2O_4S$: C, 66.0; H, 5.5; N, 6.4%.

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