

Hantzsch synthesis of 5-Indolylpyrimidopyrido[2,3-*d*]pyrimidinones using PTSA under ultrasonic irradiation in aqueous medium

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Abstract:

Various derivatives of 5-Indolylpyrimidopyrido[2,3-*d*]pyrimidinone have been synthesized by multicomponent Hantzsch reaction of one mole of 3-formylindole, two moles of barbituric/thiobarbituric acid and one mole of ammonium acetate using *p*-toluene sulfonic acid in aqueous medium under ultrasonic irradiation. Compared with conventional procedure, reaction carried out under ultrasonic irradiation in lesser time providing higher yields. Structures of these compounds have been deduced upon the basis of elemental analysis and spectral data (IR, NMR, mass).

Keywords:

5-Indolylpyrimidopyrido[2,3-*d*]pyrimidinones, ultrasonication, Hantzsch syntheses, *p*-Toluenesulfonic acid, Aqueous medium.

1. Introduction

Pyrido[2,3-*d*]pyrimidinones and their oxo and thioxo derivatives have been recognized as important organic materials in drug design [1-2] which display wide range of potentially useful biological applications *viz.* antimicrobial [3-4], antihistaminic [5], diuretic [6], antifolate [7], calcium-channel-antagonist [8], anti-inflammatory [9], anti-allergic [10], anti-herpes [11] antihypertensive [12] activities. Motoo *et al.* has suggested that dioxo derivatives of pyrido[2,3-*d*]pyrimidine are useful bases for the synthesis of anticancer nucleosides [13].

The synthesis of 1,4-dihydropyridine by Hantzsch [14] method generally involves the reaction of one mole of aldehyde and two moles of β -keto ester and one mole of nitrogen donor compound such as ammonium acetate or ammonia by refluxing in ethanol. Different approaches have been proposed for

the syntheses of 1,4-DHP's which involve variation in aldehyde, β -keto ester and in amine component [15-17] *viz.* Kidwai *et al.* synthesized pyrimidopyrido[2,3-*d*]pyrimidinones using acidic alumina as solid support under microwave irradiation [18]. In various other hantzsch reactions acetic acid [19], PTSA [20], methane sulfonic acid [20] Phenylboronic Acid [21], camphor-10-sulfonic acid [20], Yb(OTf)₃ [22], *t*-BuOK [23], Nickel nanoparticle [24], etc [25] were used in catalytic amount. However, some of these methods have several drawbacks such as harsh reaction conditions, longer reaction times and low yields of products. Thus improved synthesis of Hantzsch products are in demand.

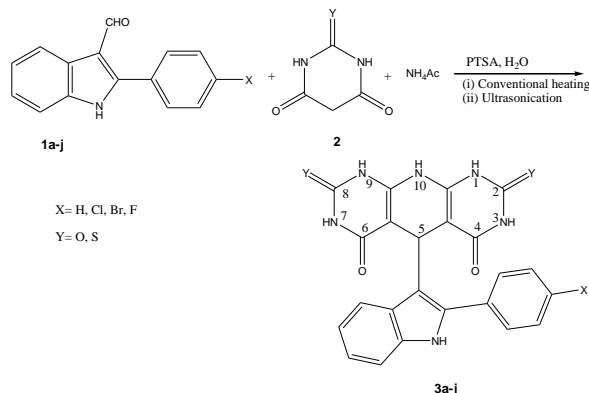
Therefore, Here, in our research programme devoted to the synthesis of different heterocycles incorporated indole moiety [26-29], we planned to synthesize novel 5-Indolylpyrimidopyrido[2,3-*d*]pyrimidinones by multicomponent reaction of one mole of 3-formylindole **1**, two moles of barbituric/thiobarbituric acid **2** and one mole of ammonium acetate using *p*-toluene sulfonic acid (10 mol%) in aqueous medium under ultrasonic irradiation in better yields and lesser reaction time as compared to conventional heating method. We also carried out the reaction in various solvents but aqueous medium gave better yields than in solvents such as methanol, ethanol or THF.

2. Results and Discussion

One mole of each 3-formylindole **1**, two moles of barbituric/thiobarbituric acid **2** and ammonium acetate, were grinded together with catalytic amount of PTSA and further exposed to ultrasonic waves in aqueous medium to obtain an orange red product *i.e.*

5-Indolylpyrimidopyrido[2,3-*d*]pyrimidinones (**3a-j**). Products were obtained in good to excellent yields in

25-35 min of irradiation (**Scheme 1**) as depicted in **Table 1**. Various 3-formylindoles (**1a-j**) were prepared by the method of Joshi *et al.*[30].



Scheme 1: Synthesis of various 5-Indolylpyrimidopyrido[2,3-d]pyrimidinones (**3a-j**) using conventional heating and ultrasonication.

In the IR spectra of 3-formylindole **1** characteristic absorption due to $>C=O$ group appears at 1625 cm^{-1} . This downfield shift from the normal $>C=O$ absorption (1720 cm^{-1}) is attributed to the presence of high degree of conjugation in the formylated indole. An upfield shift in $>C=O$ ($1690\text{-}1670\text{ cm}^{-1}$) absorption band of 5-Indolylpyrimidopyrido[2,3-d]pyrimidinones **3** is observed. Absorption bands due to $>C=S$ and N-H stretching frequencies are observed at $1580\text{-}1540\text{ cm}^{-1}$ and $3500\text{-}3135\text{ cm}^{-1}$, respectively.

^1H NMR spectra of compounds **3** showed singlets at δ 5.24-5.67 ppm due to methine proton at C-5 position of 5-Indolylpyrido[2,3-d]pyrimidinones moiety. Aromatic protons are observed as multiplet from δ 7.10 to 7.82 ppm. The disappearance of signals at δ 10 ppm (indolic formyl) **1**, and δ 3.2 ppm (CH_2) **2** confirmed the formation of title compounds (**3a-j**). Final confirmation was obtained from FAB-Mass spectra which agreed well with their molecular formulae.

Table 1: Synthesis of 5-Indolylpyrimidopyrido[2,3-d]pyrimidinones (**3a-j**) using Hantzsch reaction using PTSA as catalyst in aqueous medium.

Compd.	X	Y	Conventional heating		Ultrasonic irradiation		M.P. (°C)
			Time (h)	Yield (%)	Time (min)	Yield (%)	
3a	H	O	2	60	30	78	280
3b	Cl	O	2.5	65	35	86	290
3c	Br	O	2	64	30	86	298
3d	F	O	1.5	70	25	75	315
3e	CH ₃	O	2	74	30	80	305
3f	H	S	2	68	35	82	295
3g	Cl	S	2.5	70	25	85	300
3h	Br	S	2	75	32	80	305
3i	F	S	2	68	27	85	296
3j	CH ₃	S	2.5	70	34	89	306

3. Conclusion

In summary, we have synthesized novel 5-Indolylpyrimidopyrido[2,3-d]pyrimidinone derivatives (**3a-j**) using PTSA under ultrasonic irradiation by the multicomponent reaction of 3-formyl indole **1**, barbituric/thiobarbituric acid **2** and ammonium acetate which provided higher yields in shorter reaction time with the simplicity of the procedure.

4. Experimental

Melting points were determined in open glass capillaries and are uncorrected. The IR spectra (ν_{max} in cm^{-1}) were recorded on FT-IR SHIMADZU-8400S Spectrophotometer using KBr pellets. ^1H NMR spectra were recorded on JEOL-AL 300 spectrophotometer (300 MHz) using $\text{CDCl}_3/\text{DMSO-d}_6$ as solvents. TMS was taken as internal standard. FAB mass spectra were recorded on JEOL SX-102/DA-6000 (FAB) mass spectrometer / data system using Argon / Xenon (6 kV, 10 mA) as the FAB gas at Central Drug Research Institute (CDRI), Lucknow using m-nitrobenzyl alcohol as matrix. Elementar Vario EL III automatic CHN analyzer was used for elemental analyses. The FAB mass spectra and CHN analyses were recorded at central drug research institute (CDRI), Lucknow, India. Sonication was performed in a Toshcon model SW 4 cleaner (with a frequency of 37 KHz and operating at maximum power of 150 W). The purity of compounds was checked by TLC using silica gel (60-120 mesh) as adsorbent, UV light, or iodine accomplished

visualization. All common reagents and solvents were used as obtained from commercial suppliers without further purification. Starting materials were (1) prepared by method given in literature [30].

General procedure for the preparation of 5-Indolylpyrimidopyrido[2,3-d]pyrimidinone derivatives (3a-j).

- (i) **Conventional method:** In a 25 mL round-bottomed flask, 3-formylindole (1 mmol), barbituric/thiobarbituric acid (2 mmol), NH_4OAc (1 mmol), and PTSA (0.1 mmol) was added with small amount of water. The reaction flask was then placed on a water bath and refluxed for 1.5-2.5 hours (Table 1). The progress of the reaction was monitored by TLC using C_6H_6 : EtOAc : 95:5 as solvent system. After completion of the reaction, the reaction mixture was diluted with brine and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to give a crude product. The pure product was obtained by crystallization of the crude material from MeOH.
- (ii) **Ultrasonic irradiation:** In a 25 mL round-bottomed flask, 3-formylindole (1 mmol), barbituric/thiobarbituric acid (2 mmol), NH_4OAc (1 mmol), and PTSA (0.1 mmol) was added with small amount of water. The reaction flask was then placed in the maximum energy area in an ultrasonic cleaning bath (observation of the surface of the reaction solution during vertical adjustment of flask depth shows the optimum position by the point at which maximum surface disturbance occurs). The bath temperature was controlled (30-35 °C) by addition or removal of water. The progress of the reaction was monitored by TLC using C_6H_6 : EtOAc : 95:5 as solvent system. Sonication was continued until starting reactants disappeared as indicated by TLC. A orange-red solid product was obtained within 25-35 mins of irradiation (Table 1). After completion of the reaction, the reaction mixture was diluted with brine and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to give a crude product. The

pure product was obtained by crystallization of the crude material from MeOH.

5-(2-Phenyl-1H-indol-3-yl)-5,10-dihydropyrimido[5',4':5,6]pyrido[2,3-d]pyrimidine-2,4,6,8(1H,3H,7H,9H)-tetrone (3a).

Mp 280 °C; IR (cm^{-1} , KBr) 3450 (N-H str.), 3280 (N-H str.), 3130 (N-H str), 3045 (aromatic C-H str.), 1670 (C=O), 1630 (aromatic C=C), 1520 (C=S); MS (m/z) 440; ^1H NMR (300 MHz, CDCl_3) δ 5.25 (s, H (5), 1H), 6.45 (s, NH (1), NH (9), 2H), 7.10-7.81(m, ArH, 9H), 7.95 (s, NH (3), NH (7), 2H), 8.46 (s, NH (indole) 1H), 9.65 (s, NH (10) 1H). Anal. Calcd. for $\text{C}_{23}\text{H}_{16}\text{N}_6\text{O}_4$: C, 62.72; H, 3.66; N, 19.08. Found: C, 62.75; H, 3.67; N, 19.07.

5-[2-(4-Chlorophenyl)-1H-indol-3-yl]-5,10-dihydropyrimido[5',4':5,6]pyrido[2,3-d]pyrimidine-2,4,6,8(1H,3H,7H,9H)-tetrone (3b).

Mp 290 °C; IR (cm^{-1} , KBr) 3460 (N-H str.), 3270 (N-H str.), 3140 (N-H str), 3050 (aromatic C-H str.), 1675 (C=O), 1635 (aromatic C=C), 1550 (C=S); MS (m/z) 474; ^1H NMR (300 MHz, CDCl_3) δ 5.65 (s, H (5), 1H), 6.65 (s, NH (1), NH (9), 2H), 7.12-7.80 (m, ArH, 8H), 7.98 (s, NH (3), NH (7), 2H), 8.47 (s, NH (indole) 1H), 9.61 (s, NH (10) 1H). Anal. Calcd. for $\text{C}_{23}\text{H}_{15}\text{ClN}_6\text{O}_4$: C, 58.17; H, 3.18; N, 17.70 Found: C, 58.15; H, 3.17; N, 17.71.

5-[2-(4-Bromophenyl)-1H-indol-3-yl]-5,10-dihydropyrimido[5',4':5,6]pyrido[2,3-d]pyrimidine-2,4,6,8(1H,3H,7H,9H)-tetrone (3c).

Mp 298 °C; IR (cm^{-1} , KBr) 3475 (N-H str.), 3230 (N-H str.), 3170 (N-H str), 3055 (aromatic C-H str.), 1690 (C=O), 1620 (aromatic C=C), 1590 (C=S); MS (m/z) 518; ^1H NMR (300 MHz, CDCl_3) δ 5.28 (s, H (5), 1H), 6.45 (s, NH (1), NH (9), 2H), 7.15-7.82 (m, ArH, 8H), 8.10 (s, NH (3), NH (7), 2H), 8.49 (s, NH (indole) 1H), 9.77 (s, NH (10) 1H). Anal. Calcd. for $\text{C}_{23}\text{H}_{15}\text{BrN}_6\text{O}_4$: C, 53.20; H, 2.91; N, 16.18. Found: C, 53.21; H, 2.90; N, 16.17.

5-[2-(4-Fluorophenyl)-1H-indol-3-yl]-5,10-dihydropyrimido[5',4':5,6]pyrido[2,3-d]pyrimidine-2,4,6,8(1H,3H,7H,9H)-tetrone (3d).

Mp 315 °C; IR (cm^{-1} , KBr) 3480 (N-H str.), 3250 (N-H str.), 3175 (N-H str), 3065 (aromatic C-H str.), 1685 (C=O), 1625 (aromatic C=C), 1575 (C=S); MS (m/z) 458; ^1H NMR (300 MHz, CDCl_3) δ 5.35 (s, H (5), 1H), 6.52 (s, NH (1), NH (9), 2H), 7.12-7.81 (m, ArH, 8H), 7.98 (s, NH (3), NH (7), 2H), 8.47 (s, NH (indole) 1H), 9.74 (s, NH (10) 1H). Anal. Calcd. for $\text{C}_{23}\text{H}_{15}\text{FN}_6\text{O}_4$: C, 60.26; H, 3.30; N, 18.33; Found: C, 60.27; H, 3.29; N, 18.32.

5-[2-(4-Methylphenyl)-1H-indol-3-yl]-5,10-dihydropyrimido[5',4':5,6]pyrido[2,3-d]pyrimidine-2,4,6,8(1H,3H,7H,9H)-tetrone (3e).
Mp 305 °C; IR (cm⁻¹, KBr) 3470 (N-H str.), 3255 (N-H str.), 3165 (N-H str.), 3035 (aromatic C-H str.), 1690 (C=O), 1630 (aromatic C=C), 1580 (C=S); MS (m/z) 454; ¹H NMR (300 MHz, CDCl₃) δ 1.12 (s, CH₃, 3H), 5.35 (s, H (5), 1H), 6.52 (s, NH (1), NH (9), 2H), 7.13-7.81 (m, ArH, 11H), 7.96 (s, NH (3), NH (7), 2H), 8.46 (s, NH (indole) 1H), 9.73 (s, NH (10) 1H). Anal. Calcd. for C₂₄H₁₈N₆O₄: C, 63.43; H, 3.99; N, 18.49; Found: C, 63.42; H, 3.97; N, 18.51.

5-[2-(4-Phenyl)-1H-indol-3-yl]-2,8-dithioxo-2,3,5,8,9,10-hexahydropyrimido[5',4':5,6]pyrido[2,3-d]pyrimidine-4,6(1H,7H)-dione (3f)
Mp 295 °C; IR (cm⁻¹, KBr) 3475 (N-H str.), 3270 (N-H str.), 3130 (N-H str.), 3010 (aromatic C-H str.), 1695 (C=O), 1640 (aromatic C=C), 1570 (C=S); MS (m/z) 472; ¹H NMR (300 MHz, CDCl₃) δ 5.54 (s, H (5), 1H), 6.62 (s, NH (1), NH (9), 2H), 7.10-7.81 (m, ArH, 9H), 7.98 (s, NH (3), NH (7), 2H), 8.49 (s, NH (indole) 1H), 9.78 (s, NH (10) 1H). Anal. Calcd. for C₂₃H₁₆N₆O₂S₂: C, 58.46; H, 3.41; N, 17.78; Found: C, 58.45; H, 3.40; N, 17.79.

5-[2-(4-Chlorophenyl)-1H-indol-3-yl]-2,8-dithioxo-2,3,5,8,9,10-hexahydropyrimido[5',4':5,6]pyrido[2,3-d]pyrimidine-4,6(1H,7H)-dione (3g)
Mp 300 °C; IR (cm⁻¹, KBr) 3450 (N-H str.), 3280 (N-H str.), 3135 (N-H str.), 3015 (aromatic C-H str.), 1690 (C=O), 1645 (aromatic C=C), 1560 (C=S); MS (m/z) 506; ¹H NMR (300 MHz, CDCl₃) δ 5.64 (s, H (5), 1H), 6.51 (s, NH (1), NH (9), 2H), 7.10-7.82 (m, ArH, 8H), 8.02 (s, NH (3), NH (7), 2H), 8.46 (s, NH (indole) 1H), 9.68 (s, NH (10) 1H). Anal. Calcd. for C₂₃H₁₅ClN₆O₂S₂: C, 54.49; H, 2.98; N, 16.58; Found: C, 54.49; H, 2.98; N, 16.58.

5-[2-(4-Bromophenyl)-1H-indol-3-yl]-2,8-dithioxo-2,3,5,8,9,10-hexahydropyrimido[5',4':5,6]pyrido[2,3-d]pyrimidine-4,6(1H,7H)-dione (3h)
Mp 305 °C; IR (cm⁻¹, KBr) 3455 (N-H str.), 3270 (N-H str.), 3155 (N-H str.), 3020 (aromatic C-H str.), 1695 (C=O), 1640 (aromatic C=C), 1565 (C=S); MS (m/z) 551; ¹H NMR (300 MHz, CDCl₃) δ 5.67 (s, H (5), 1H), 6.60 (s, NH (1), NH (9), 2H), 7.12-7.82 (m, ArH, 8H), 7.96 (s, NH (3), NH (7), 2H), 8.45 (s, NH (indole) 1H), 9.71 (s, NH (10) 1H). Anal. Calcd. for C₂₃H₁₅BrN₆O₂S₂: C, 50.10; H, 2.74; N, 15.24; Found: C, 50.10; H, 2.74; N, 15.24.

5-[2-(4-Fluorophenyl)-1H-indol-3-yl]-2,8-dithioxo-2,3,5,8,9,10-hexahydropyrimido[5',4':5,6]pyrido[2,3-d]pyrimidine-4,6(1H,7H)-dione (3i)
Mp 296 °C; IR (cm⁻¹, KBr) 3435 (N-H str.), 3275 (N-H str.), 3150 (N-H str.), 3030 (aromatic C-H str.), 1695 (C=O), 1645 (aromatic C=C), 1540 (C=S); MS (m/z) 490; ¹H NMR (300 MHz, CDCl₃) δ 5.62 (s, H (5), 1H), 6.61 (s, NH (1), NH (9), 2H), 7.11-7.81 (m, ArH, 8H), 7.93 (s, NH (3), NH (7), 2H), 8.45 (s, NH (indole) 1H), 9.72 (s, NH (10) 1H). Anal. Calcd. for C₂₃H₁₅FN₆O₂S₂: C, 56.32; H, 3.68; N, 17.13; Found: C, 56.32; H, 3.68; N, 17.13.

5-[2-(4-Methylphenyl)-1H-indol-3-yl]-2,8-dithioxo-2,3,5,8,9,10-hexahydropyrimido[5',4':5,6]pyrido[2,3-d]pyrimidine-4,6(1H,7H)-dione (3j)
Mp 306 °C; IR (cm⁻¹, KBr) 3455 (N-H str.), 3255 (N-H str.), 3140 (N-H str.), 3040 (aromatic C-H str.), 1675 (C=O), 1665 (aromatic C=C), 1545 (C=S); MS (m/z) 486; ¹H NMR (300 MHz, CDCl₃) δ 1.11 (s, CH₃, 3H), 5.66 (s, H (5), 1H), 6.69 (s, NH (1), NH (9), 2H), 7.11-7.82 (m, ArH, 8H), 7.94 (s, NH (3), NH (7), 2H), 8.46 (s, NH (indole) 1H), 9.74 (s, NH (10) 1H). Anal. Calcd. for C₂₄H₁₈N₆O₂S₂: C, 59.24; H, 3.73; N, 17.27; Found: C, 59.24; H, 3.73; N, 17.27.

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6. References

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