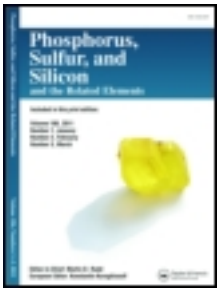

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UTILITY OF CYANOTHIOACETAMIDE AND ITS DERIVATIVES IN HETEROCYCLIC SYNTHESIS: SYNTHESIS AND CHARACTERIZATION OF SEVERAL NEW PYRIDINE, PYRAZOLO[3,4-b]PYRIDINE, THIENO[2,3-b] PYRIDINE AND PYRIDO[5,4-b]THIENO[3′,2′-d′] PYRIMIDINE DERIVATIVES

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Pyridinethione derivatives **5a,b** used as a reactive starting materials owing to its containing more than one active site. It reacted with several halogen-containing materials to give the corresponding 2-S-alkyl- or 2-S-aryl derivatives which cyclized to the corresponding thienopyridine derivatives. The obtained thienopyridine derivatives could be used for building new rings by their reaction with formic acid, nitrous acid, carbon disulfide or acetic anhydride.

Keywords: cyanothioacetamide; chloro-ketons; chloroacetyl derivatives; pyridine pyrazolo[3,4-b]pyridine; thiano[2,3-b]pyridine; pyrido[5,4-b]thiano[3′,2′ -d ′]pyrimidine

INTRODUCTION

Cyanothioacetamide **(1)** and its derivatives **3** are versatile reagents and their utility in heterocyclic synthesis has gained considerable recent attention.[1–11]The reported biological activities of pyridine and annelated pyridine as antimycotic[12], antipressant[13], fungicidal[14], antiarrhythmic[15] and antilipemic[16] agents stimulated our interest to synthseize a variety of these

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heterocycles. The arylidene of cyanothioacetamide **3a,b** seemed be excellent and unique to fulfill this objective.

RESULT AND DISCUSSION

It has been found that arylidene derivative **3a** reacts with acetylacetone **(4)** to afford a reaction product with molecular formula $C_{15}H_{13}N_3O_3S$ this formula corresponding to the formation of pyidinethione derivative **5a.** The IR spectrum of the isolated reaction product showed the presence of absorption band of NH at 3303. band of CN at 2225 and, band of CO at 1698cm^{-1}. Its ^{1}H-NMR spectrum revealed a broad signal of NH at δ 3.2–3.4. signal per of doublet corresponding to pyridine H-3 and Pyridine H-4 at 2.2–2.4, signals of methyl at δ1.9, sharp signal of acetyl at δ 2.3 in addition to a multiplet signal at 6.8–7.4 corresponding to aromatic protons. Its mass spectrum gave m/e = 315 based on the above data compound **5a** was formulated as 6-methyl-5-acetyl-4(4-nitrophenyl)-3-cyano-3,4-dihydropyridine-2-thione **(5a).** In the same manner compound **5b** could be prepared by the reaction of **3b** with **4** to give the corresponding pyridinethione derivative **5b.** This reaction product could be formulated based on elemental analysis and spectral data as **5a** previously prepared. Further elucidation of structures of **5a,b** via their synthesis from the reaction of yelidene of acetyl acetone **6a,b** with cyanothioacetamide **(1)** as previously reported[17] (c.f chart 1). The latter isolated products were taken as starting materials for the present study due to presence of more than one active site.

Thus compound **5a,b** reacts with hydrazine hydrate to afford sulfur- free reaction products. The IR spectra of these reaction products were free from the nitrile absorption bands. Their ^{1}H-NMR spectrum revealed the presence of NH and NH_2 signals at δ 4.8–5.0. On shaking compounds **9a,b** with deutrium oxide (D_2O) the singlet broad signal at 4.8–5.0 ppm which corresponding to the 3H of both NH and NH_2 groups disappear and two new signal appeared. The first is the singlet signal at δ 4.5 for 1H of DOH due to the exchanging protonat NH with D_2O and the second is the singlet signal at δ 4.7 for 2H of H_2O due to the exchanging protons at NH_2 with D_2O. The reaction products were identified as the pyrazolo[3,4-b]pyridine derivatives **9a,b** most likely formed via the intermediacy of the non isola-

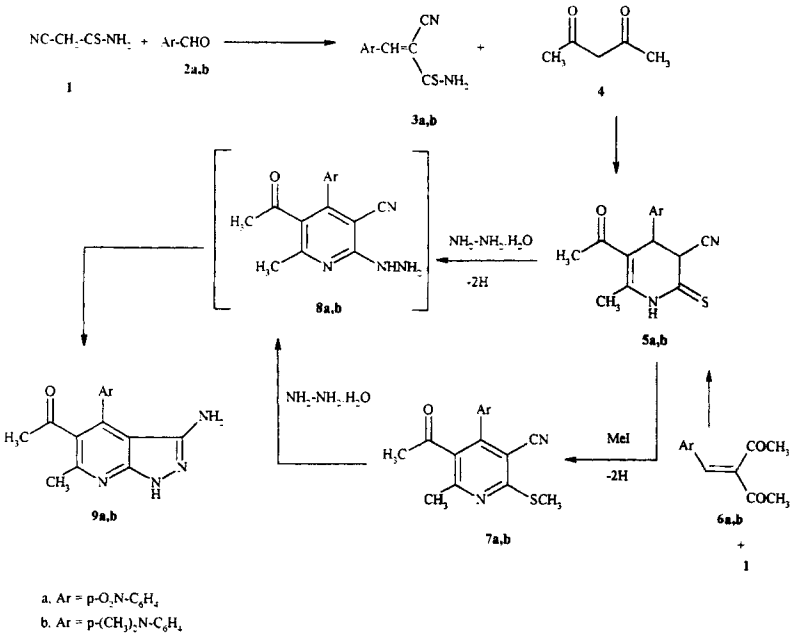

CHART 1

ble hydrazine **8a,b.** An unequivocal suport for the structures **9a,b** was achieved via their synthesis by first formation of the corresponding 2-S-methyl pyridine **7a,b** by the reaction of **5a,b** with methyl iodide. Compounds **7a,b** react with hydrazine hydrate with the loss of methyl mercaptan and cyclization under the applied reaction condition to give the corresponding **9a,b** (c.f. Chart 1).

Compound **5a** reacts with chloroacetamide **(10a)** to afford the isolated reaction product **13a.**The IR spectrum of the latter compound showed the absorption band at 3471, 3418, 3340 and 3277 corresponding to two NH_2 groups, band at 1701 due to CO of acetyl and band at 1660 corresponding to CO of amide group at thiophene ring and absence of nitrile function. Its ^1H NMR spectrum revealed the signals of two NH_2, methyl, methyl of acetyl in addition to an multiplet signal at δ 7.2–7.6 corresponding to aromatic protons. The formatin **of 13a** most likely proceeded via the initial formation of the non-isolable thieno[2,3-b]dihydropyridine **11a** which

underwent auto-oxidation into **13a** under the applied reaction conditions (c.f. Chart 2). Based on the above data the reaction product was identified as thieno[2,3-b]pyridine derivatives **13a.** Analogously, compound **5a** reacts with ethyl chloroacetate **(10b),** chloroacetone **(10c),** chloroacetonitrile **(10d)** and ω-bromoacetophenone **(10e)** to afford the reaction products **13b-e** respectively were based on correct elemental analysis and spectral data as for **13a** previously described (c.f. Chart 2). In the same manner compound **5b** reats with each of **10a-e** to give the corresponding thieno[2,3-b]pyridine derivative **13f-j** respectively. The structures of **13f-j** were also based on both spectral data and elemental analysis as previously reported for **13a-e** (c.f. Chart 1and Experimental Part). Using compounds **13a,** f as starting materials to synthesis new several heterocyclic derivatives by using different reagents extended our investigation. Thus, it has been found that compound **13a** reacts with aceticanhydride to give a reaction product **14a.** Its IR spectrum showed the presence of absorption band at 3329 corresponding to NH, band of CO of acetyl at pyridine ring at 1697 and band of CO of pyrimidine at 1675 cm^{-1}. Its ^{1}H-NMR spectrum revealed the signal at δ 4.2–4.5 due to NH, signal at δ 1.9 corresponding to methylat pyridine, signal at 2.1 corresponding to methyl of acetyl at pyridine ring signal at δ 1.7 corresponding to methyl of pyrimidine ring and multiplet signal at δ 6.9–7.4 corresponding to aromatic protons. Based on the above data compound **14a** was identified as pyrido[5,4-b]thieno[3′,2′-d′]pyrimidinone derivative **14a.** Treatment of **13a** with formic acid gave **15a.** The IR spectrum of the latter product showed the presence of absorption band of NH at 3330, band of carbonyl of acetyl at pyridine at 1697. Its ^{1}H-NMR spectrum revealed the signal of NH at δ 4.3–4.5 and sharp singlet at δ 2.3 due to pyrimidne H-2, signal at δ 1.8 corresponding to methyl at pyridine and signal at δ 2. 1 corresponding to methyl of acetyl at pyridine. Based on the above data the latter isolated product could be formulated pyrido[5,4-b]thieno[3′ ,2′ -d′]-pyrimidinone derivative **15a.** Moreover compound **13a** reacts with nitrous acid to give the self-cyclized reaction product **16a.** The IR spectrum of the latter compound showed the band of NH triazine at 3329 and CO of acetyl of pyridine at 1697 cm^{-1} Its ^{1}H-NMR spectrum revealed a broad signal at δ 4.3–4.5 corresponding to NH, sharp signal at δ 1.8 corresponding to methyl at pyrimidine, signal at δ 2.1 of methyl of acetyl at pyridine in addition to a multiplet signal at δ 6.9–7.4 corresponding to aromatic protons. Based on the elemental analysis and spectral data. The latter isolated product was

identified as pyrido[5,4-b]thieno[3′,2′-d′]triazinone derivatives **16a.** Compound **13a** also reacted with ethyl chloroformate and gave a reaction product **17a.** Its IR spectrum showed the band of two NH, CO of acetyl at pyridine and two carbonyl group of pyrimidinone. Its ^{1}H-NMR spectrum revealed the signals of two NH, methyl of acetyl of pyridine, methyl of pyridine in addition to protons of aromatic ring at 6.9–7.3. Based on the above data the reaction product could be formulated as pyrido[3,2-b]thieno[3′,2′-d]pyrimidinone derivative **17a.** Finaly compound **13a** reacts with carbon disulphide to afford a reaction product **18a.** Its IR spectrum showed the presence of band at 3330 and 3280 corresponding to two NH, band at 1697 corresponding to CO of a cetyl of pyridine ring and band at 1673 corresponding to CO, of pyrimidine ring. Its ^{1}H-NMR spectrum revealed a broad signal at δ 4.3–4.5 corresponding to NH, signal at δ 1.8 corresponding to methyl of pyridine, signal at δ 2. 1 corresponding to methyl of acetyl of pyridine ring and a multiplet signal at δ 6.9–7.4 corresponding to aromatic protons. Based on the above data the latter isolated product was identified as pyrido[5,4-b]thieno[3′,2′-d′]pyrimidine derivative **18a.** In the same manner. compound **13f** reacts with aceticanhydride, formic acid. nitrous acid, ethyl chloroformate and carbon disulphide to yield **14b. 15b, 16b, 17b** and **18b** respectively. The structures **14b-18b** were also based on both elemental analysis and spectral data previously reported for **14a-18a** respectively.

EXPERIMENTAL

All melting points are uncorrected. IR (KBr discs) were recorded on a Pye-Unicam sp-1100 spectrophotometer. ^{1}H-NMR spectra were recorded on Varian EM 390 MHz. Gemnai-200 MHz and Brucker WP-80 spectrometers using TMS as an internal standard and $CDCl_3$, DMSO-d_6 and $(CD_3)_2CO$ as solvents and chemical shifts are expressed as ppm units. Mass spectra were recorded on Hewlett-Packard GC-MS type 2988 using inlet type at 70 eV. Microanalyses were performed by the Microanalytical Center of Cairo University using Pekin-Elmer 2400 CHN Analyzer.

General method (A) for preparation of 3,4-dihydropyridine-2-thione derivatives 5a,b

A solution of cinnamonitrile derivatives **3a,b** (0.01 mol) and acetylacetone **(4)** (0.01 mol) in methanol (30 ml) and triethyl amine (0.4 ml) was heated

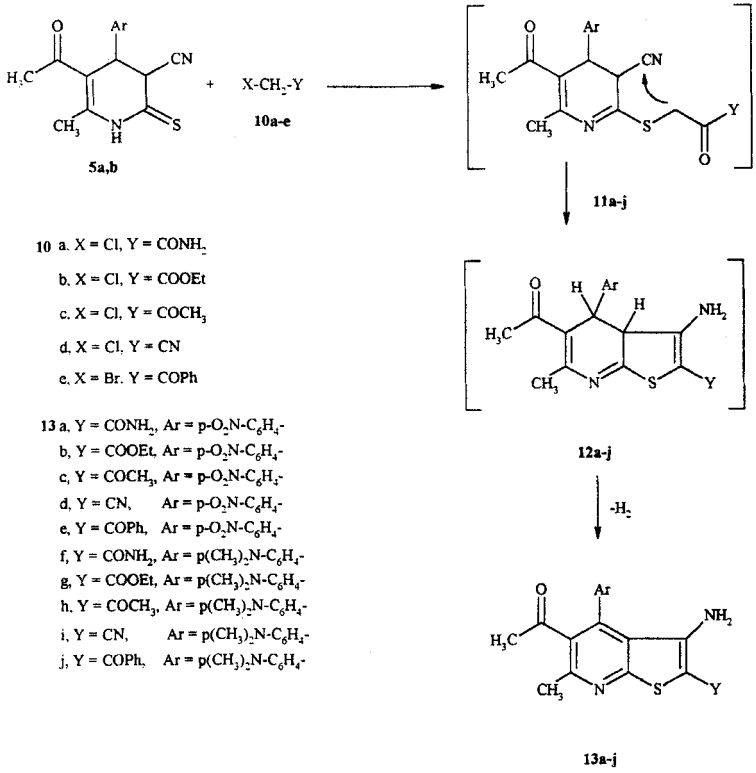

CHART 2

under reflux for 6 hours. The solid products obtained were collected by filtration washed with ethanol, dried then crystallized from the proper solvent to give **5a,b** respectively.

General method (B) for preparation of 2-S-alkyl pyridine derivatives 7a.b

A solution of **5a,b** (0.01 mol) and methyl iodide (0.01 mol) in sodium methoxide (prepared by 0.01 mol sodium metal in 20 ml methanol) was heated under reflux for 45 min. Cool, pour on to ice bath, then acidified with concentrated hydrochloric acid. The solid products were collected by filtration, washed with cold water, dried then crystallized from the proper solvent to afford **7a,b** respectively.

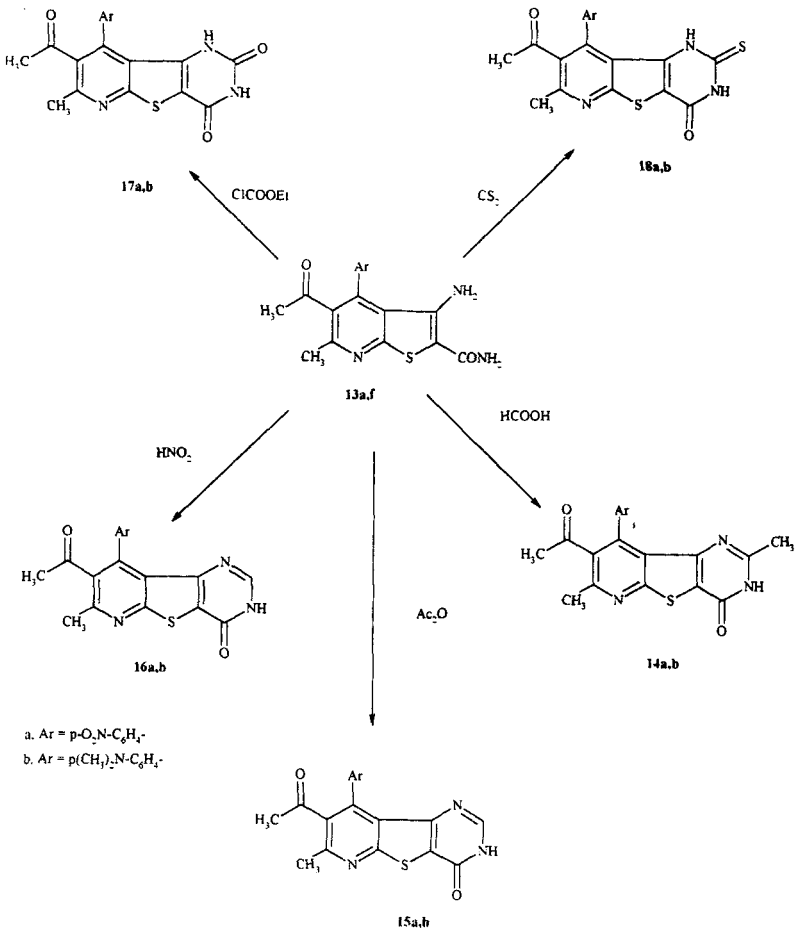

CHART 3

General method (C) for preparation of pyrazolo[4,5-b]pyridine derivatives 9a,b

A solution of **5a,b** or **7a,b** (0.01 mol) and hydrazine hydrate (0.01 mol) in methanol (15 ml) and pyridine (2 ml) was heated under reflux for 6 hours. The solid products were collected by filtration, washed with ethanol, dried then crystallized from the proper solvent to afford **9a,b** respectively.

TABLE I

Comp. Color	*Mol. Formula*	*Yield % m.p. °C*	*General Method of Prep.*	*Solvent Of Cryst.*	*IR (cm^{-1})*	*^1H NMR (ppm)*
13b Y	$C_{19}H_{17}N_3SO_5$	77 290–2	D	Ethanol	3482, 3356 (NH_2); 3101 (CH, aromatic); 2983 (CH sat.); 1695 (CO acetyl); 1675 (CO ester); 1617 (C=N); and 1587 (C=C).	1.9 (s, 3H, CH_3); 2.3 (s, 3H, CH_3-CO); 2.5 (t, 3H, $\underline{CH_3}$-CH_2); 3.8 (q, 2H, CH_3-$\underline{CH_2}$); 5.5–5.7 (br., 2H, NH_2) and 7.7–8.3 (m, 4H, ArH's).
13c O	$C_{18}H_{15}N_3SO_4$	75 272–4	D	Ethanol	3479, 3331 (NH_2); 3073 (CH, aromatic); 2987 (CH sat.); 1696 (CO acetyl at pyridine); 1680 (CO acetyl at thiophene); 1617 (C=N); and 1588 (C=C).	2.1 (s, 3H, CH_3); 2.4 (s, 3H, CH_3-CO at pyridine); 2.7 (s, 3H, $\underline{CH_3}$-CO at thiophene); 6.0–6.2 (br, 2H, NH_2) and 7.4–8.4 (m, 4H, ArH's).
13d G-B	$C_{17}H_{12}N_4SO_3$	70 220–2	D	Ethanol	3321, 3290 (NH_2); 3050 (CH, aromatic); 2981 (CH sat.); 2196 (CN); 1696 (CO acetyl); 1628 (C=N); and 1595 (C=C).	1.9 (s, 3H, CH_3); 2.4 (s, 3H, CH_3-CO); 5.3–5.5 (br, 2H, NH_2) and 7.8–8.4 (m, 4H, ArH's)
13e B	$C_{23}H_{17}N_3SO$	69 228–30	D	Ethanol	3482, 3297 (NH_2); 3074 (CH, aromatic); 2983 (CH sat.); 1703 (CO acetyl); 1660 (CO benzoyl); 1625 (C=N); and 1590 (C=C).	1.8 (s, 3H, CH_3); 2.4 (s, 3H, CH_3-CO); 5.2–5.4 (br, 2H, NH_2) and 7.8–8.3 (m, 9H, ArH's).
13f Y	$C_{19}H_{20}N_4SO_2$	78 290–2	D)	Ethanol	3464, 3327, 3259 and 3151 (two NH_2); 3080 (CH, aromatic); 2980 (CH sat.); 1695 (CO acetyl); 1651 (CO amide); 1621 (C=N); and 1608 (C=C).	1.8 (s, 3H, CH_3); 2.4 (s, 3H, CH_3-CO); 3.3 (s, 6H, $(CH_3)_2N$); 5.3–5.5 (br, 4H, two NH_2) and 6.8–7.3 (m, 4H, ArH's).
13g Y	$C_{21}H_{23}N_3SO_3$	75 216–18	D	Ethanol	3379, 3213, (NH_2); 3001 (CH, aromatic); 2987 (CH sat.); 1697 (CO acetyl); 1680 (CO ester); 1630 (C=N); and 1606 (C=C).	1.9 (s, 3H, $\underline{CH_3}$); 2.2 (t, 3H, $\underline{CH_3}$-CH_2); 2.5 (s, 3H, CH_3-CO); 3.2 (s, 6H, $(CH_3)_2N$); 3.9 (q, 2H, CH_3-$\underline{CH_2}$-); 5.7–5.9 (br., 2H, NH_2) and 6.7–7.4 (m, 4H, ArH's).

Comp. Color	*Mol. Formula*	*Yield % m.p. °C*	*General Method of Prep.*	*Solvent Of Cryst.*	*IR (cm^{-1})*	*^1H NMR (ppm)*
13h O	$C_{20}H_{21}N_3SO_2$	73 256–8	D	Ethanol	3479, 3333, (NH_2); 3060 (CH, aromatic); 2989 (CH sat.); 1697 (CO acetyl at pyridine); 1675 (CO acetyl at thiophene); 1618 (C=N); and 1589 (C=C).	1.7 (s, 3H, CH_3); 2.3 (s, 3H, CH_3-CO at pyridine); 2.8 (s, 3H, CH_3-CO at thiophene); 3.2 (s, 6H, $(CH_3)_2N$); 5.3 (br., 2H, NH_2) and 6.8–7.3 (m, 4H, ArH's).
131 B	$C_{19}H_{18}N_4SO$	67 240–2	D	Ethanol	3337, 3217 (NH_2); 3065 (CH, aromatic); 2979 (CH sat.); 2193 (CN); 1703 (CO acetyl); 1627 (C=N) and 1608 (C=C).	1.8 (s, 3H, CH_3); 2.4 (s, 3H, CH_3-CO); 3.2 (s, 6H, $(CH_3)_2N$); 5.2–5.4 (br., 2H, NH_2) and 6.8-7.5 (m, 4H, ArH's).
13j B	$C_{25}H_{23}N_3SO_2$	65 181–3	D	Ethanol	3452, 3275 (NH_2); 3040 (CH, aromatic); 2981 (CH sat.); 1701 (CO acetyl); 1677 (CO benzoyl); 1630 (C=N) and 1603 (C=C)	1.8 (s. 3H, CH_3); 2.4 (s, 3H, CH_3-CO); 3.2 (s, 6H, $(CH_3)_2N$); 5.3–5.5 (br., 2H, NH_2) and 6.7-7.3 (m, 9H. ArH's).
14a B	$C_{19}H_{14}N_4SO_4$	60 > 340	E	Acetic acid	3430 (NH); 3100 (CH, aromatic); 2981 (CH sat.); 1705 (CO acetyl); 1680 (CO pyrimidine); 1650 (C=N) and 1603 (C=C).	1.7 (s, 3H, CH_3 at pyridine); 1.9 (s, 3H, CH_3 at pyrimidine); 2.4 (s, 3H, CH_3-CO); 5.1–5.2 (br., 1H, NH) and 7.7–8.3 (m, 4H, ArH's).
14b Gr	$C_{21}H_{20}N_4SO_2$	61 > 330	E	Ethanol	3430 (NH); 3100 (CH, aromatic); 2981 (CH sat.); 1705 (CO acetyl); 1680 (CO pyrimidine); 1650 (C=N) and 1603 (C=C).	1.8 (s, 3H, CH_3 at pyridine); 2.0 (s, 3H, CH_3 at pyrimidine); 2.3 (s, 3H, CH_3-CO); 3.2 (s, 6H, $(CH_3)_2N$); 5.3–5.5 (br., 1H, NH) and 6.7–7.4 (m, 4H, ArH's).
15a B	$C_{18}H_{12}N_4SO_4$	61 > 340	F	Acetic acid	3448 (NH); 3109 (CH, aromatic); 2987 (CH sat.); 1703 (CO acetyl); 1667 (CO pyrimidine); 1625 (C=N) and 1599 (C=C)	1.8 (s, 3H, CH_3); 2.4 (s, 3H, CH_3-CO); 5.1–5.2 (br., 1H, NH) and 7.8–8.4 (br, 5H, ArH's).
15b Y	$C_{20}H_{18}N_4SO_2$	62 324–6	F	Ethanol	3448 (NH); 3109 (CH, aromatic); 2987 (CH sat.); 1703 (CO acetyl); 1667 (CO pyrimidine); 1625 (C=N) and 1599 (C=C)	1.8 (s, 3H, CH_3); 2.3 (s, 3H, CH_3-CO); 3.2 (s, 6H, $(CH_3)_2N$); 5.1–5.2 (br., 1H, NH) and 6.7-7.3 (m, 5H, ArH's)

Comp. Color	*Mol. Formula*	*Yield % m.p. °C*	*General Method of Prep.*	*Solvent Of Cryst.*	*IR (cm^{-1})*	*^1H NMR (ppm)*
16a B	$C_{17}H_{11}N_5SO_4$	65 314–6	G	Acetic acid	3342 (NH); 3072 (CH, aromatic); 2983 (CH sat.); 1707 (CO acetyl); 1663 (CO triazine); 1623 (C=N) and 1590 (C=C).	1.8 (s, 3H, CH_3); 2.3 (s, 3H, CH_3-CO); 5.1–5.2 (br., 1H, NH) and 7.8–8.3 (m. 4H, ArH's).
16b B	$C_{19}H_{17}N_5SO_2$	66 226–8	G	Acetic acid	3206 (NH); 3101 (CH, aromatic); 2988 (CH sat.); 1694 (CO acetyl); 1670 (CO triazine); 1622 (C=N) and 1608 (C=C).	1.9 (s, 3H, CH_3); 2.4 (s, 3H, CH_3-CO); 3.2 (s, 6H, $(CH_3)_2N$); 5.2–5.3 (br., 1H, NH) and 6.8-7.3 (m, 4H, ArH's).
17a Y	$C_{18}H_{12}N_4SO_5$	62 308–10	H	Acetic acid	3416, 3342 (two NH); 3080 (CH, aromatic); 2980 (CH sat.); 1702 (CO acetyl); 1675, 1659 (two CO at pyrimidine); 1622 (C=N) and 1608 (C=C).	1.8 (s, 3H, CH_3); 2.3 (s, 3H, CH_3-CO); 5.2–5.4 (br., 2H, two NH) and 7.6–8.2 (m, 4H, ArH's).
17b Y	$C_{20}H_{18}N_4SO_3$	63 261–3	H	Ethanol	3463, 3328 (two NH); 3075 (CH, aromatic); 2983 (CH sat.); 1698 (CO acetyl); 1670 and 1660 (two CO of pyrimidine); 1622 (C=N) and 1605 (C=C).	1.9 (s, 3H, CH_3); 2.5 (s, 3H, CH_3-CO); 3.2 (s, 6H, $(CH_3)_2N$); 5.2–5.4 (br., 2H, two NH) and 6.7–7.3 (m, 4H, ArH's)
18a Y	$C_{18}H_{12}N_4S_2O_4$	63 322–4	I	Acetic acid	3415, 3342 (two NH); 3060 (CH. aromatic); 2981 (CH sat.); 1703 (CO acetyl); 1660 (CO of pyrimidine); 1623 (C=N); 1593 (C-C) and 1546 (C=S)	1.8 (s, 3H, CH_3); 2.4 (s, 3H, CH_3-CO); 5.1–5.3 (br., 2H, two NH) and 7.7–8.4 (m, 4H, ArH's).
18b Y	$C_{20}H_{18}N_4S_2O_2$	62 281–3	I	Ethanol	3329, 3261 (two NH); 3065 (CH. aromatic); 2985 (CH sat.); 1695 (CO acetyl); 1651, (CO of pyrimidine); 1623 (C=N); 1608 (C=C) and 1542 (C=S).	1.8 (s, 3H, CH_3); 2.4 (s, 3H, CH_3-CO); 3.2 (s, 6H, $(CH_3)_2N$); 5.1–5.3 (br., 2H, two NH) and 6.8–7.4 (m, 4H, ArH's).

Y = Yellow; O = Orange; B = Brown; G-B = Greenish-blue; Gr = Grey

General method (D) for preparation of thieno[2,3-b]pyridine derivatives 13a-j

A solution **of 5a,b** (0.01 mol) in sodium methoxide (0.01 mol prepared from 0.01 mol sodium metal in 30 ml methanol) and each of **10a-e** was heated under reflux for 5 hours. Cool, poured on to ice bath, then acidified with concentrated hydrochloric acid. The solid products were collected by filtration, washed with cold water. dried then crystallized from the proper solvent to afford **13a-j** respectively.

General method (E) for preparation of pyrido[4,5-b]thieno[3',2'-d]pyrimidinone derivatives 14a,b

A solution of **13a,f** (0.01 mol) and acetic anhydride (20ml) was heated under reflux for 4 hour. The solid products were collected by filtration. washed with water, dried, then crystallized from the proper solvent to give **14a,b** respectively.

General method (F) for preparation of pyrido[4, 5-b]thieno[3',2'-d]pyrimidinone derivatives 15a,b

A solution of **13a,f** (0.01 mol) and formaic acid (20 ml) was heated under reflux for 4 hour. The solid products were collected filtrated washed with ethanol. dried then crystallized from the proper solvent to give 15a,b respectively.

General method (G) for preparation of pyrido[5,4-b]thieno[3',2'-d]trizinone derivatives 16a,b

A cold solution of sodium nitrile (0.01 mol) was added to a cold solution of **13a,f** ethanol (20ml) and conc. hydrochloric acid (0.5 ml) portionwise during period of 30 min. The reaction mixture was stirred for further 1h. in ice bath. After stirring was completed, the solid product obtained was collected by filtration, washed with water, dried, then crystallized from the proper solvent to give **16a,b** respectively.

General method for preparation of pyrido[5,4-b]thieno[3',2'-d']pyrimidinone derivatives 17a,b

A solution of **13a,f** (0.01 mol) and ethyl chloroformate (0.01 mol) in ethanol (20ml) and triethyl amine (0.3 ml) was heated under reflux for 4 hour.

The solid product obtained was collected by filtration. washed with water, dried, then crystallized from the proper solvent to give **17a,b** respectively.

General method for preparation of pyrido[5,4-b]thieno[3',2'-d]pyrimidinthione derivatives 18a,b

A solution of **13a,f** (0.01 mol) and carbon disulphide (0.01 mol) in pyridine (30ml) was heated under reflux for 5 hour. The solid product obtained was collected by filtration, washed with water, dried, then crystallized from the proper solvent to give **18a,b** respectively.

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