A Simple, Convenient One-Pot Synthesis of Dithio-Carbamide Derivatives of Heterocyclic 1,3-Dicarbonyl Systems

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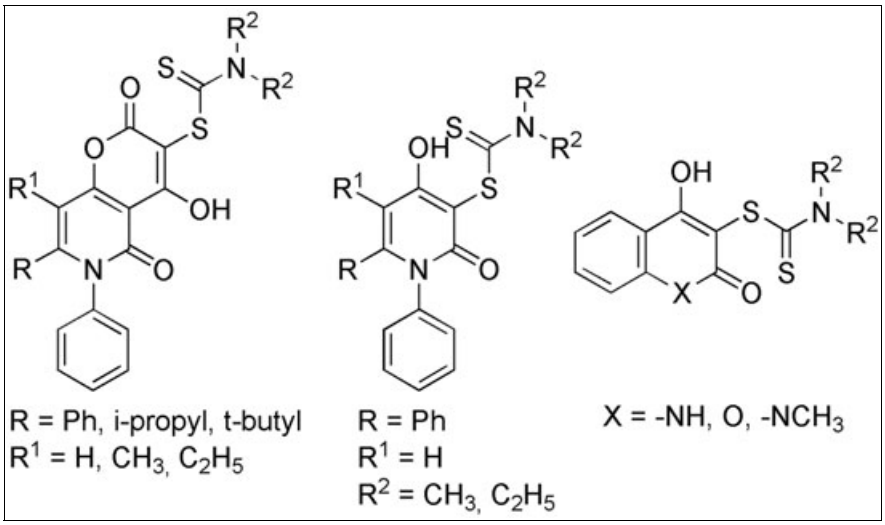

A various new dithi-ocarbamides were synthesized from heterocyclic six-membered 1,3-dicarbonyl systems, such as 4-hydroxy-2,5-pyranopyridines, 4-hydroxy-2-pyridones, 4-Hydroxy-2-quinolones, 4-hydroxy-coumarins, and 4-hydroxy-1-methyl-2-quinolones. The dicarbonyl compounds in the presence of anhydrous potassium carbonate in dimethyformamide react with tetraalkylthiuram disulfides to yield 3-dialkylaminothiocarbonylthio derivatives through a simple, convenient one-pot reaction. The structures were confirmed by using IR, NMR, and elemental analysis.

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INTRODUCTION

The sulfenylation of aryl compounds is an important issue in synthetic organic chemistry [1,2]. Nonactivated aromatic compounds can be sulfenylated by using electrophiles of disulfides in presence of Lewis acid catalysis (for instance $SbCl_5/AgSbF_6$) [3]. In the same way, sulfenylchlorides (*R*SCl) [4] and sulfinyltosylates (*R*S-SO_2-p-tolyl) [5] are also used for sulfenylation. However, the reaction with sulfenyltosylates proceeds best with phenolic substrates under basic conditions [5]. The condensed 5-alkyl-6-hydoxy-4-pyrimidone and 5-arylthio-6-hydoxy-4-pyrimidone show some anti-inflammatory activity [5]. Some of the 3-alkylthio-4-hydroxy-2-pyrones are effective HIV-protease inhibitors [6–9]. This and the known fungicidal and antiseptic activity of thiuram (tetramethylthiuram disulfide) [10] and disulfiram (antabuse, tetraethylthiuram disulfide) [11] prompted us to synthesize sulfenyl derivatives of 4-hydroxy-2,5-pyranopyridones, 4-hydroxy-2-pyridones, and 4-hydroxy-coumarins. Preliminary results relating to the sulfenylation of alicyclic 1,3-dicarbonyl systems have been published as a lecture abstract [12].

The sulfinylation of heterocyclic 1,3-dicarbonyl systems, such as 4-hydroxy-2-quinolones and 4-hydroxy-coumarins [13] and 4-hydroxy-2-pyrones, 6-hydroxy-4-pyrimidones, 4-hydroxy-2-pyridones, 4-hydroxy-6-pyridazones, and 5-hydroxy-3-pyrazolones [14], was reported earlier. The introduction of the dialkylaminothiocarbonylthio group directly at the 5-position of barbituric acid with tetraalkylthiuram disulfides is more effective than reactions via the 5-chloro derivative or 5-phenyliodonium yields [15]. The equimolar amount of the aliphatic tetraalkylthiuram disulfides is used for the sulfinylation. Aromatic thioethers are prepared by the reaction of 3-chloro-4-hydroxy-2-pyridones or their 3-phenyl-iodonium yields [12,14–17]. Oxidation of the aliphatic thioethers is not possible like the aromatic thioethers under similar reaction conditions.

As reported, the dialkylaminothiocarbonylthio derivatives can be obtained by two alternative routes. The

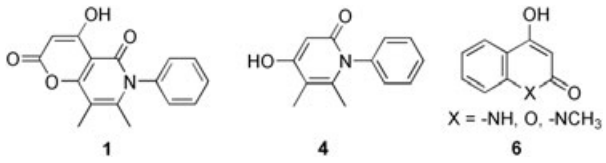


Figure 1. Heterocyclic 1,3-dicarbonyl system.

starting 1,3-dicarbonyl compounds of the type **1**, **4**, and **6** as shown Figure 1 are converted to their 3-chloro derivatives or their 3-phenyliodonium yields [18]. The commercially available thiuram disulfides are used for the sulfinylation of 1,3-dicarbonyl systems.

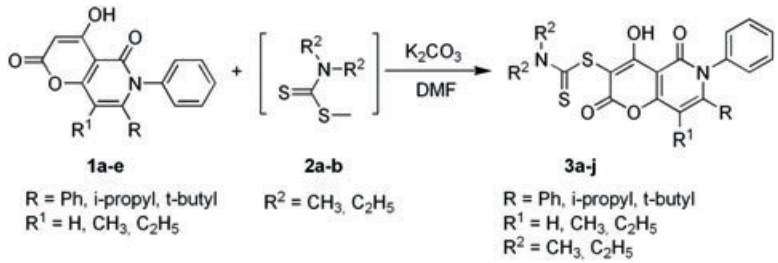
RESULTS AND DISCUSSION

Present article deals with the reactions of heterocyclic 1,3-dicarbonyl compounds, such as 4-hydroxy-2,5-pyranopyridines **1a–e**, 4-hydroxy-2-pyridones **4a–b**, 4-hydroxy-2-quinolones **6a**, 4-hydroxy-coumarins **6b**, and 4-hydroxy-1-methyl-2-quinolones **6c** with aliphatic disulfides **2a–b**. 4-Hydroxy-2,5-pyranopyridones [19] **1a–e** were reacted with sufficiently electrophilic alkylthiuram disulfides **2a–b** in presence of anhydrous potassium carbonate in dimethylformamide to yield 3-dial kylaminothiocarbonylthio-4-hydroxy-2,5-pyranopyridones **3a–j**. Here, equivalent amount of reagents **2a–b** was used to obtain aliphatic thioethers and not required to oxidize dialkylaminodithiocarbamates as illustrated in Scheme 1. In similar way, 4-hydroxy-2-pyridones [20] **4a–b**, 4-hydroxy-2-quinolones **6a**, 4-hydroxy-coumarins **6b**, and 4-hydroxy-1-methyl-2-quinolones **6c** reacted with alkylthiuram disulfides **2a–b** to yield respective 3-dialkylaminothiocarbonylthio derivatives **5a–b**, **7a–e** as shown in Schemes 2 and 3. The structures of the newly obtained compounds were elucidated on the basis of IR, NMR spectra, and elemental analysis.

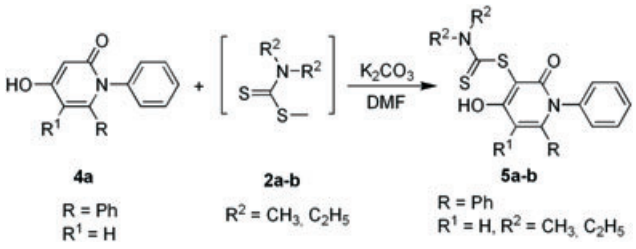
CONCLUSION

In conclusion, we have developed a simple, convenient one-pot synthesis method to prepare dithio-carbamide derivatives of heterocyclic 1,3-dicarbonyl systems, such as

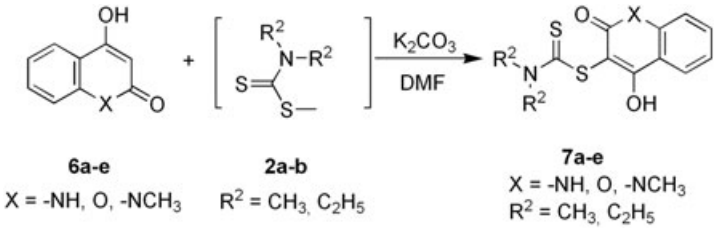
Scheme 1. Synthesis of 3-dialkylaminothiocarbonylthio-4-hydroxy-2,5-pyranopyridones 3.



Scheme 2. Synthesis of 3-dialkylaminothiocarbonylthio-4-hydroxy-2-pyridone derivatives 5.



Scheme 3. Synthesis of 3-dialkyaminothiocarbonylthio-4-hydroxy-quinolin-2H-ones (7a-b), -coumarin (7c-d), and -1-methyl-quinolin-2H-one (7e).



4-hydroxy-2,5-pyranopyridines, 4-hydroxy-2-pyridones, 4-hydroxy-2-quinolones, 4-hydroxy-coumarins, and 4-hydroxy-1-methyl-2-quinolones. The present method may be of value in organic synthesis because of operational simplicity, as well as good availability of the starting materials.

EXPERIMENTAL

All chemical were purchased from Merck (Darmstadt, Germany) and used without purification. The solvents were dried over appropriate drying agents and distilled prior to use. All reactions were monitored by TLC on pre-coated silica gel 60 PF_{254} (mesh). Melting points were recorded by using open glass capillaries on Gallenkamp MFB 595 melting point apparatus (USA) and were uncorrected. Infrared spectra were recorded on a Perkin-Elmer 298 spectrophotometer (PerkinElmer, Inc., Waltham, MA) by using KBr pellets. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Varian Gemini 200 MHz (Agilent Technologies, Lexington, MA) and 50 MHz, respectively, in DMSO-d_6 by using TMS as an internal standard. CHN analyses were recorded on a C,H,N-Automat Carlo Erba 1106 (CE Instruments Ltd, Wigan, UK) elemental analyzer.

Preparation of 3-dialkyaminocarbonylthio-4-hydroxy-6-phenyl-2H-pyrano[3,2-c]pyridine-2,5-diones (3a–j). General procedure. The appropriate 4-hydroxy-6,7-diphenyl-6*H*-pyrano-[3,2-*c*]-pyridine-2,5-dione **1** [19] (10 mmol), tetraalkylthiuramdisulphide **2** (11 mmol), and anhydrous potassium carbonate (30 mmol) in 75 mL dimethylformamide was refluxed at 90°C for 5 to 6 h. The solution was cooled, and dimethylformamide was removed on rotary evaporator. The concentrate obtained was added to 150 mL ice-water and filtered. The filtrate was precipitated by acidification with conc. hydrochloric acid, filtered by suction, dried, and recrystallized from acetic acid to give the corresponding derivative **3**. Physical data and yields are listed in Table 1.

3-Dimethylaminothiocarbonylthio-4-hydroxy-6,7-diphenyl-2H-pyrano[3,2-c]pyridine-2,5-dione (3a). IR (KBr, cm^{-1}): 3150–2960, 1750, 1665, 1600, 1570, 1480, 1310. ^{1}H-NMR (200 MHz, DMSO-d_6) δ (ppm): 3.45 (s, 3H, –CH_3), 3.50 (s, 3H, –CH_3), 6.95 (s, 1H, Ar–H_8), 7.20–7.50 (*m*, 10H, Ar–H). ^{13}C-NMR (50 MHz, DMSO-d_6) δ (ppm): 39.1, 84.5, 94.7, 110.4, 120.5, 125.3, 127.4, 128.3, 128.9, 129, 130.8, 132.4, 144.6, 154.2, 156.8, 160.5, 182.1, 198. *Anal*. calcd for $C_{23}H_{18}N_2O_4S_2$ (450.53): C 61.32, H 4.04, N 6.22%. Found: C 61.27, H 4.11, N 6.13%.

3-Diethylaminothiocarbonylthio-4-hydroxy-6,7-diphenyl-2H-pyrano[3,2-c]pyridine-2,5-dione (3b). IR (KBr, cm^{-1}): 3100–2980, 1740, 1670, 1600, 1570, 1490, 1300. ^{1}H-NMR (200 MHz, DMSO-d_6) δ (ppm): 1.20 (t, J=7, 3H, –CH_3), 1.35 (t, J=7, 3H, –CH_3), 3.90 (m, 4H, 2-CH_2), 6.95 (s, 1H, Ar–H_8), 7.20–7.40 (m, 10H, Ar–H). ^{13}C-NMR (50 MHz, DMSO-d_6) δ (ppm): 10.6, 44.5, 84.2, 94.6, 110.5, 120.4, 125.6, 127.3, 128.2, 128.8, 129, 130.9, 132.5, 144.5, 154.2, 156.7, 160.7, 182.2, 198.2. *Anal*. calcd for $C_{25}H_{22}N_2O_4S_2$ (478.58): C 62.74, H 4.63, N 5.85%. Found: C 62.68, H 4.55, N 5.78%.

3-Dimethylaminothiocarbonylthio-8-methyl-4-hydroxy-6,7-diphenyl-2H-pyrano[3,2-c]pyridine-2,5-dione (3c). IR (KBr, cm^{-1}): 3460, 2930, 1690, 1675, 1560, 1200. ^{1}H-NMR (200 MHz, DMSO-d_6) δ (ppm): 1.88 (s, 3H, CH_3); 3.46 (s, 3H, –CH_3), 3.48 (s, 3H, –CH_3), 7.15–7.35 (m, 10H, Ar–H). ^{13}C-NMR (50 MHz, DMSO-d_6) δ (ppm): 7.5, 39.2, 84.6, 104.5, 110.4, 120.4, 125.2, 127.2, 128.4, 128.6, 129.2, 130, 132.2, 134.7, 156.9, 158, 160.2, 182.8, 198. *Anal*. calcd for $C_{24}H_{20}N_2O_4S_2$ (464.56): C 62.05, H 4.34, N 6.03%. Found: C 62.01, H 4.32, N 6.01%.

3-Diethylaminothiocarbonylthio-8-methyl-4-hydroxy-6,7-diphenyl-2H-pyrano[3,2-c]pyridine-2,5-dione (3d). IR (KBr, cm^{-1}): 2980–2940, 1750, 1670, 1550, 1490, 1300, 1270, 1200. ^{1}H-NMR (200 MHz, DMSO-d_6) δ (ppm): 1.22 (t, J=7, 3H, –CH_3), 1.37 (t, J=7, 3H, –CH_3), 1.92 (s, 3H, –CH_3), 3.95 (m, 4H, 2-CH_2), 7.20–7.40 (m, 10H, Ar–H). ^{13}C-NMR (50 MHz, DMSO-d_6) δ (ppm): 7.4,

Table 1

Preparation of 3-dialkyaminocarbonylthio-4-hydroxy-6-phenyl-2H-pyrano[3,2-c]pyridine-2,5-diones **3.**

R	R^1	R^2	Compound no.	mp (°C)	Yield (%)
Ph	H	Me	**3a**	269–270	50
Ph	H	Et	**3b**	205–207	61
Ph	Me	Me	**3c**	266–267	60
Ph	Me	Et	**3d**	264–265	82
Ph	Et	Me	**3e**	250–252	60
Ph	Et	Et	**3f**	235–236	57
i-Propyl	H	Me	**3g**	243–244	87
i-Propyl	H	Et	**3h**	249–250	77
t-Butyl	H	Me	**3i**	249–250	58
t-Butyl	H	Et	**3j**	231–232	93

10.4, 44.4, 84.6, 104.4, 110.2, 120.5, 125.4, 127, 128.2, 128.4, 129, 130.7, 132.4, 134.6, 156.8, 158.2, 160.4, 182, 198.2. *Anal*. calcd for $C_{26}H_{24}N_2O_4S_2$ (492.61): C 63.39, H 4.91, N 5.69%. Found: C 63.36, H 4.93, N 5.63%.

3-Dimethylaminothiocarbonylthio-8-ethyl-4-hydroxy-6,7-diphenyl-2H-pyrano[3,2-c]pyridine-2,5-dione (3e). IR (KBr, cm^{-1}): 1740, 1670, 1550, 1390, 1300, 1170. ^{1}H-NMR (200 MHz, DMSO-d_6) δ (ppm): 1.00 (t, J = 8, 3H, –CH_3), 1.30 (q, J = 7.5, 2H, –CH_2), 3.46 (s, 3H, N–CH_3), 3.49 (s, 3H, N–CH_3), 7.21–7.30 (m, 10H, Ar–H), 14.45 (s, 1H, OH). ^{13}C-NMR (200 MHz, DMSO-d_6) δ (ppm): 10.4, 12.5, 39.4, 84.2, 108.8, 110.3, 120.4, 125.4, 127.2, 128.4, 128.8, 129, 130, 132.4, 134, 156.4, 158.7, 160, 182.4, 198. *Anal*. calcd for $C_{25}H_{22}N_2O_4S_2$ (478.58): C 62.74, H 4.63, N 5.85%. Found: C 62.69, H 4.66, N 5.82%.

3-Diethylaminothiocarbonylthio-8-ethyl-4-hydroxy-6,7-diphenyl-2H-pyrano[3,2-c]pyridine-2,5-dione (3f). IR (KBr, cm^{-1}): 3460, 2980, 1740, 1670, 1550, 1470, 1300, 1210. ^{1}H-NMR (200 MHz, DMSO-d_6) δ (ppm): 1.00 (t, J = 8, 3H, –CH_3), 1.19 (t, J = 7, 3H, –CH_3), 1.34 (t, J = 7, 3H, –CH_3), 2.25 (q, J = 7.5, 2H, –CH_2), 3.89 (m, 4H, 2 N–CH_2), 7.20–7.40 (m, 10H, Ar–H), 14.43 (s, 1H, OH). ^{13}C-NMR (50 MHz, DMSO-d_6) δ (ppm): 10.5, 12.6, 44.2, 84.6, 108.4, 110.2, 120.6, 125, 127.5, 128.1, 128.6, 129.4, 130, 132.4, 134.2, 155.6, 158, 160.6, 182, 198.2. *Anal*. calcd for $C_{27}H_{26}N_2O_4S_2$ (506.64): C 64.01, H 5.17, N 5.53%. Found: C 64.10, H 5.19; N 5.48%.

3-Dimethylaminothiocarbonylthio-4-hydroxy-7-i-propyl-6-phenyl-2H-pyrano[3,2-c]pyridine-2,5-dione (3g). IR (KBr, cm^{-1}): 3070–2940, 1750, 1670, 1380, 1150. ^{1}H-NMR (200 MHz, DMSO-d_6) δ (ppm): 1.15 (d, J = 7, 6H, 2–CH_3 *i*-propyl), 2.45 (m, 1H, –CH), 3.45 (s, 3H, –CH_3), 3.50 (s, 3H, –CH_3), 6.95 (s, 1H, Ar–H_8), 7.50–7.70 (m, 5H, Ar–H). ^{13}C-NMR (50 MHz, DMSO-d_6) δ (ppm): 18, 28.4, 38.9, 84.2, 90, 110.4, 120.5, 125.6, 128.8, 132, 150.2, 155.8, 158, 160.4, 182.4, 198. *Anal*. calcd for $C_{20}H_{20}N_2O_4S_2$ (416.51): C 57.67, H 4.84, N 6.73%. Found: C 57.74, H 4.88, N 6.65%.

3-Diethylaminothiocarbonylthio-4-hydroxy-7-i-propyl-6-phenyl-2H-pyrano[3,2-c]pyridine-2,5-dione (3h). IR (KBr, cm^{-1}): 3080–2940, 1740, 1670, 1570, 1480, 1280, 1200. ^{1}H-NMR (200 MHz, DMSO-d_6) δ (ppm): 1.15 (d, J = 7, 6H, 2-CH_3 *i*-propyl), 1.20 (t, J = 7, 3H, –CH_3), 1.34 (t, J = 7, 3H, –CH_3), 3.95 (m, 4H, 2-CH_2), 6.91 (s, 1H, Ar–H_8), 7.50–7.70 (m, 5H, Ar–H). ^{13}C-NMR (50 MHz, DMSO-d_6) δ (ppm): 10.4, 18.2, 28, 44.4, 84.4, 90.2, 110.4, 120.4, 125.2, 128.6, 132.2, 150.4, 155.4, 158, 160.4, 182, 198.4. *Anal*. calcd for $C_{22}H_{24}N_2O_4S_2$ (444.57): C 59.44, H 5.44, N 6.30%. Found: C 59.49, H 5.41, N 6.25%.

3-Dimethylaminothiocarbonylthio-4-hydroxy-7-t-butyl-6-phenyl-2H-pyrano[3,2-c]pyridine-2,5-dione (3i). IR (KBr, cm^{-1}): 3060–2930, 1745, 1670, 1590, 1530, 1460, 1290, 1250. ^{1}H-NMR (200 MHz, DMSO-d_6) δ (ppm): 1.15 (s, 9 3H, –CH_3 *t*-butyl), 3.45 (s, 3H, –CH_3), 3.48 (s, 3H, –CH_3), 6.90 (s, 1H, Ar–H_8), 7.55 (s, 5H, Ar–H), 13.85 (s, 1H, OH). ^{13}C-NMR (50 MHz, DMSO-d_6) δ (ppm): 28, 36.5, 39.2, 84.5, 88.4, 110.6, 120.5, 125, 128.6, 132, 155.6, 158.2, 158.6, 160, 182.5, 198.2. *Anal*. calcd for $C_{21}H_{22}N_2O_4S_2$ (430.54): C 58.58, H 5.15, N 6.51%. Found: C, 58.49; H 5.20, N 6.45%.

3-Diethylaminothiocarbonylthio-4-hydroxy-7-t-butyl-6-phenyl-2H-pyrano[3,2-c]pyridine-2,5-dione (3j). IR (KBr, cm^{-1}): 3110–2980, 1750, 1670, 1580, 1470, 1210. ^{1}H-NMR (200 MHz, DMSO-d_6) δ (ppm): 1.16 (s, 9H 3–CH_3 *t*-butyl), 1.20 (t, J = 7, 3H, –CH_3), 1.34 (t, J = 7, 3H, –CH_3), 3.90 (m, 4H, 2-CH_2), 6.92 (s, 1H, Ar–H_8), 7.56 (s, 5H, Ar–H), 13.85 (s, 1H, OH). ^{13}C-NMR (50 MHz, DMSO-d_6) δ (ppm): 10.4, 26.5, 36.6, 44.2, 84.8, 88, 110.5, 120.6, 125, 128.7, 132.4, 155.6, 158.1, 158.6, 160.4, 180.8, 198. *Anal*. calcd for $C_{23}H_{26}N_2O_4S_2$ (258.59): C 60.24, H 5.72, N 6.11%. Found: C 60.16, H 5.75, N 6.05%.

Preparation of 3-dialkyaminocarbonylthio-4-hydroxy-1-phenypyridin-2H-ones (5a–b). General procedure. The appropriate 4-hydroxy-1,6-diphenylpyridin-2(1*H*)-one **4** (10 mmol), tetraalkylthiuramdisulphides **2** (11 mmol), and anhydrous carbonate (30 mmol) in 50 mL dimethylformamide were refluxed at 90°C for 5 h. The solution was cooled, and dimethylformamide was removed on rotary evaporator. The concentrate obtained was added to 150 mL ice-water and filtered. The filtrate obtained was precipitated by acidification with conc. hydrochloric acid, filtered by suction, dried, and recrystallized from acetic acid to give **5a**. Physical data and yields are listed in Table 2.

3-Dimethylaminothiocarbonylthio-4-hydroxy-1,6-diphenylpyridin-2H-one (5a). IR (KBr, cm^{-1}): 2930, 2690, 2600, 1650, 1625, 1600, 1580, 1490, 1390. ^{1}H-NMR (200 MHz, DMSO-d_6) δ (ppm): 3.45 (s, 3H, –CH_3), 3.48 (s, 3H, –CH_3), 6.10 (s, 1H, Ar–H $_5$), 7.00–7.40 (m, 10H, Ar–H). ^{13}C-NMR (50 MHz, DMSO-d_6) δ (ppm): 40.2, 88.2, 94.4, 120.4, 123.7, 125.6, 128, 128.8, 130, 131.4, 135, 144.4, 156.8, 182.5, 194.3. *Anal*. calcd for $C_{20}H_{18}N_2O_2S_2$ (382.5): C 62.80, H 4.74, N 7.32%. Found: C 62.81, H, 4.79, N, 7.25%.

3-Diethylaminothiocarbonylthio-4-hydroxy-1,6-diphenylpyridin-2H-one (5b). IR (KBr, cm^{-1}): 3200–2980, 1625, 1600, 1550, 1500, 1420, 1200. ^{1}H-NMR (200 MHz, DMSO-d_6)

Table 2

Preparation of 3-dialkyaminocarbonylthio-4-hydroxy-1-phenypyridin-2H-ones **5.**

R	R^1	R^2	Compound no.	mp (°C)	Yield (%)
Ph	H	Me	**5a**	205–206	76
Ph	H	Et	**5b**	188–190	76

δ (ppm): 1.20 (t, $J=7$, 3H, $-CH_3$), 1.35 (t, $J=7$, 3H, $-CH_3$), 3.90 (m, 4H, 2-CH_2), 6.10 (s, 1H, Ar–H $_5$), 7.00–7.40 (m, 10H, Ar–H), 11.25 (s, 1H, OH). ^{13}C-NMR (50 MHz, DMSO-d_6) δ (ppm): 10.6, 44.6, 88, 94.6, 120.2, 123, 125.7, 128.2, 129, 129.6, 131.5, 135.4, 144, 156.4, 180.9, 194.2. *Anal*. calcd for $C_{22}H_{22}N_2O_2S_2$ (410.55): C 64.39, H 5.37, N 6.83%. Found: C 64.45, H 5.43, N 6.76%.

Preparation of 3-dialkyaminocarbonylthio-4-hydroxy-quinolin-2H-one (7a–b), 4-hydroxy-coumarin (7c–d)-one, and 4-hydroxy-1-methyl-quinolin-2H-one (7e). General procedure. The appropriate 4-hydroxy-quinolin-2*H*-one or 4-hydroxy-coumarin or 4-hydroxy-1-methyl-quinolin-2*H*-one **6** (20 mmol), corresponding tetraalkylthiuramdisulphides **2** (22 mmol) and anhydrous potassium carbonate (60 mmol) in 100 mL dimethylformamide, was refluxed at 90°C for 5 h. The solution was cooled, and dimethylformamide was removed on rotary evaporator. The concentrate obtained was added to 200 mL ice-water and filtered. The filtrate obtained was precipitated by acidification with conc. hydrochloric acid, filtered by suction, dried at reduced pressure, and recrystallized from acetic acid to give **7**. Physical data and yields are listed in Table 3.

3-Dimethylaminothiocarbonylthio-4-hydroxy-quinolin-2H-one (7a). Yield: 4.18 g (75%). mp 315° dec. (acetic acid). IR (KBr, cm^{-1}): 3360–2900, 1640, 1600, 1500, 1410, 1375, 1200. ^{1}H-NMR (200 MHz, DMSO-d_6) δ (ppm): 3.45 (s, 3H, $-CH_3$), 3.55(s, 3H, $-CH_3$), 7.22 (t, $J=7$, 1H, Ar–H), 7.32 (d, $J=8$, 1H, Ar–H), 7.61 (t, $J=7$, 1H, Ar–H), 7.92 (d, $J=7$, 1H, Ar–H), 11.02 (s, 1H -NH), 11.55 (s, 1H, OH). ^{13}C-NMR (50 MHz, DMSO-d_6) δ (ppm): 10.5, 44, 84.6, 114.5, 120.6, 125.4, 126, 128.8, 135.4, 159.7, 180.8, 192.4. *Anal*. calcd for $C_{12}H_{12}N_2O_2S_2$ (280.37): C 51.41, H 4.31, N 9.99%. Found: C 51.37; H, 4.29; N, 9.92%.

3-Diethylaminothiocarbonylthio-4-hydroxy-quinolin-2H-one (7b). Yield: 4.6 g (74%). mp 198–200° (acetic acid). IR (KBr, cm^{-1}): 3250–2980, 1700, 1600, 1500, 1420, 1270, 1210, 1150. ^{1}H-NMR (200 MHz, DMSO-d_6) δ (ppm): 1.20 (t, $J=7$, 3H, $-CH_3$), 1.40 (t, $J=7$, 3H, $-CH_3$), 3.95 (m, 4H, 2-CH_2), 7.20 (t, $J=7$, 1H, Ar–H), 7.35 (d, $J=8$, 1H, Ar–H), 7.63 (t, $J=7$, 1H, Ar–H), 7.95 (dd, $J=7$, 1.5, 1H, Ar–H), 11.00 (s, 1H, -NH), 11.50 (s, 1H, OH). ^{13}C-NMR (50 MHz, DMSO-d_6) δ (ppm): 10.4, 44.2, 84, 114.6, 120.4, 125, 126.4, 128.7, 135.6, 159, 180.4, 192.6. *Anal*. calcd for $C_{14}H_{16}N_2O_2S_2$ (308.42): C 54.52, H 5.23, N 9.08%. Found: C 54.60, H 5.21, N 9.12%.

3-Dimethylaminothiocarbonylthio-4-hydroxy-coumarin (7c). Yield: 5.2 g (93%). mp 180–181° (acetic acid). IR (KBr, cm^{-1}): 3180, 1680, 1620, 1550, 1495, 1400, 1380, 1290. ^{1}H-NMR (200 MHz, DMSO-d_6) δ (ppm): 3.50 (s, 3H, $-CH_3$), 3.55 (s, 3H, $-CH_3$), 7.40–7.50 (m, 2H, Ar–H), 7.75 (t, $J=7$, 1H, Ar–H), 8.00 (dd, $J=7$, 1.5, 1H, Ar–H). ^{13}C-NMR (50 MHz, DMSO-d_6) δ (ppm): 40.4, 80.6, 116.4, 120.4, 126, 127.2, 128.8, 148.9, 160.7, 184.4, 196.6. *Anal*. calcd for $C_{12}H_{11}NO_3S_2$(281.35): C 51.23, H 3.94, N 4.98%. Found: C 51.18, H 3.89, N 4.91%.

3-Diethylaminothiocarbonylthio-4-hydroxy-coumarin (7d). Yield: 4.66 g (75%). mp 170–172° (acetic acid). IR (KBr, cm^{-1}): 3200–2900, 1695, 1610, 1600, 1550, 1540, 1440, 1270. ^{1}H-NMR (200 MHz, DMSO-d_6) δ (ppm): 1.20 (t, $J=7$, 3H, $-CH_3$), 1.40 (t, $J=7$, 3H, $-CH_3$), 3.80–4.50 (m, 4H, 2-CH_2), 7.40–7.50 (m, 2H, Ar–H), 7.70–7.80 (m, 1H, Ar–H), 8.00 (dd, $J=7$, 1.5, 1H, Ar–H), 11.50 (s, 1H, OH). ^{13}C-NMR (50 MHz, DMSO-d_6) δ (ppm): 10.8, 42.6, 83.4, 116.8, 120.5, 126, 126.9, 127.4, 148.5, 160.8, 180.4, 196.7. *Anal*. calcd for $C_{14}H_{15}NO_3S_2$(309.4): C 54.35, H 4.89, N 4.53%. Found: C 54.27, H 4.84, N 4.53%.

3-Dimethylaminthioocarbonylthio-4-hydroxy-1-methyl-quinolin-2H-one (7e). Yield: 4.26 g (73%). mp 300° (acetic acid). IR (KBr, cm^{-1}): 3100, 1620, 1585, 1550, 1370, 1310, 1210. ^{1}H-NMR (200 MHz, DMSO-d_6) δ (ppm): 3.45 (s, 3H, $-CH_3$), 3.50 (s, 3H, $-CH_3$), 3.60 (s, 3H, N–CH_3), 7.35 (t, $J=7$, 1H, Ar–H), 7.55 (dd, $J=8$, 1H, Ar–H), 7.75 (t, $J=7$, 1H, Ar–H), 8.05 (dd, $J=8$, 1H, Ar–H). ^{13}C-NMR (50 MHz, DMSO-d_6) δ (ppm): 30.2, 40.8, 84.6, 114.4, 120.6, 125.5, 127, 128.6, 134.9, 158.4, 183.6, 192.6. *Anal*. calcd for $C_{13}H_{14}N_2O_2S_2$(294.39): C 53.04, H 4.79, N 9.52%. Found: C 52.98, H 4.72, N 9.45%.

Table 3

Preparation of 3-dialkyaminocarbonylthio-4-hydroxy-quinolin-2H-ones (**7a–b**), 4-hydroxy-coumarin-one (**7c–d**), and 4-hydroxy-1-methyl-quinolin-2H-one (**7e**).

X	R^2	Compound no.	mp (°C)	Yield (%)
NH	Me	**7a**	315 dec	75
NH	Et	**7b**	198–200	74
O	Me	**7c**	180–181	93
O	Et	**7d**	170–172	75
NMe	Me	**7e**	300	73

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