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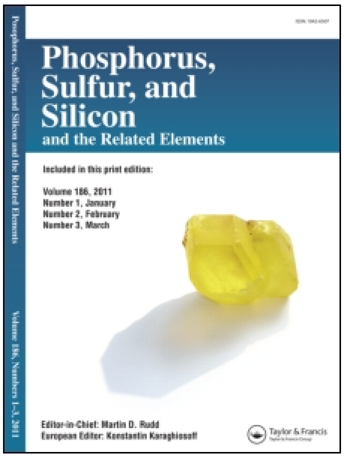

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SYNTHESIS OF 6-IMINO-6H-1,3-THIAZINES

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SYNTHESIS OF 6-IMINO-6H-1,3-THIAZINES

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The reaction of several substituted acrylonitriles **1** with arylthioamides **2** in acetic acid in the presence of perchloric acid yielding 2,4,5-trisubstituted 6-imino-6H-1,3-thiazine perchlorates **3a–3h** is described. The structures of these compounds were established by spectral data, mass spectrometic fragmentation behaviour, X-ray structure analysis as well as by chemical transformation to the corresponding 3-benzoylaminothioacrylic acid amides **6** and 4-thioxopyrimidines **7**.

INTRODUCTION

6-Imino-6H-1,3-thiazines have been assumed to be generated in the course of the synthesis of 3,4-dihydro-4-thioxopyrimidines, but the isolation of these intermediates has been unsuccessful, because of the strong tendency for Dimroth-rearrangement.[1–5] On the other hand, derivatives of 6-oxo- and 6-thioxo-6H-1,3-thiazines are well known.[6–8,14] In continuation to our studies on potential intermediates in the synthesis of 3,4-dihydro-4-thioxopyrimidines[9–11] we now report a convenient method for the preparation of the hitherto unknown 6-imino-6H-1,3-thiazine perchlorates **3**.

RESULTS AND DISCUSSION

2,4,5-Trisubstituted 6-imino-6H-1,3-thiazine perchlorates **3** were generated by reaction of 2,3-substituted acrylonitriles **1** with arylthioamides **2** in acetic acid in the presence of anhydrous perchloric acid (Scheme 1, Table I). A suitable leaving group in 3-position of the acrylonitril **1** such as X = —NH_2, —NHC_6H_5, —SCH_3 in the protonated state, on the one hand, as well as a relatively weak basicity of the arylthioamides **2**, on the other hand seemed to be essential for this reaction. The thiazine perchlorates **3** were obtained as yellow coloured stable compounds, only in a few cases the crude products were contaminated with small amounts of the corresponding 4-thioxopyrimidines **7**. Compound **3c** could not be isolated in a pure state because it was readily hydrolyzed in the presence of moisture to give

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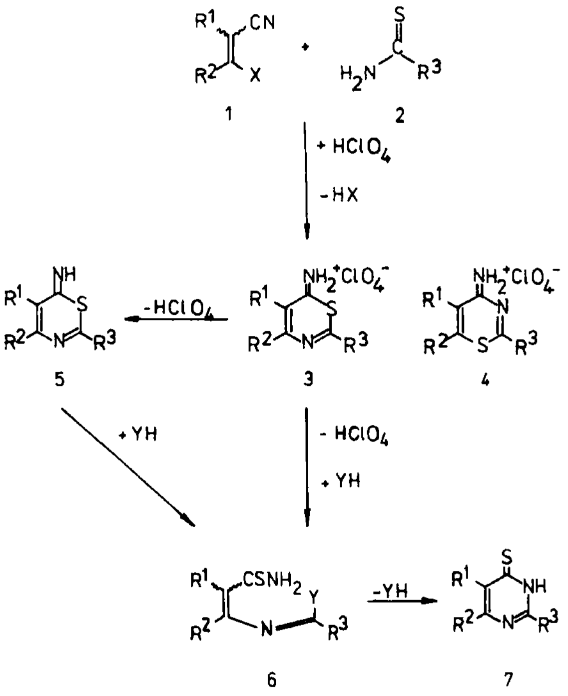

5d: $R^1 = COOEt$

$R^2 = SCH_3$

$R^3 = C_6H_5$

6c: $R^1 = CN$, $R^2 = H$, $R^3 = C_6H_5$, $Y = OH$

6i: $R^1 = COOEt$, $R^2 = OH$, $R^3 = C_6H_5$, $Y = OH$

SCHEME 1

TABLE I

Substrate				Product	
	1		2	3	7
X	R^1	R^2	R^3	(Methode/Yield: %)	
SCH_3	CN	SCH_3	C_6H_5	3a (A, 4h/41)	7a (A/78)
NH_2	CN	SCH_3	C_6H_5	3a (A, 4h/36)	
NH_2	CN	$SCH_2C_6H_5$	C_6H_5	3b (A, 6h/39)	7b (A/73)
NH_2	CN	H	C_6H_5	3c (A, 20 min/32)	7c (C/96)
SCH_3	COOEt	SCH_3	C_6H_5	3d (A, 21d/71 resp. B, 10 min/62)	7d (A/92 resp. B/72)
NHC_6H_5	COOEt	SCH_3	C_6H_5	3d (B, 10 min/38)	
SCH_3	COOEt	SCH_3	C_6H_4-4-CH_3	3e (B, 15 min/62)	7e (A/97)
SCH_3	COOEt	SCH_3	C_6H_4-4-OCH_3	3f (B, 15 min/57)	7f (A/59)
SCH_3	COOEt	SCH_3	C_6H_4-4-Cl	3g (B, 20 min/76)	7g (A/24)
NH_2	H	C_6H_4-4-CH_3	C_6H_5	3h (A, 12h/16)	7h (A/60)
—	COOEt[a]	OH[a]	C_6H_5[a]	—	7i (C/91)

[a] Substrate is compound **6i**.

the 3-benzoylamino-2-cyano-thioacrylic acid amid **6c**. The lack of an electron-donating substituent in 4-position of **3c** might be responsible for this instability.

Attempts to convert the thiazine perchlorates **3** into the free thiazine bases **5** under basic conditions were unsuccessful. Treatment of **3d** with equimolar amounts of bases yielded the thioxopyrimidin **7d** together with several side products. Surprisingly, the conversion of **3d** to the free thiazine base **5d** was accomplished by reaction with hydrochloric acid, as by-product the benzoylaminothioacrylic acid amid **6i** was formed. On treatment with an excess of a secondary amine as well as with NaOH the 6-imino-6H-1,3-thiazine perchlorates **3** underwent Dimroth-rearrangement to give the corresponding thioxopyrimidines **7** in high yields. Obviously, this rearrangement proceeded via the corresponding thiazine bases **5**, which by attack of nucleophile YH upon C-2 were transformed through the open-chain 3-benzoylaminothioacrylic acid amid intermediates **6** (Y = OH, NRR) into the thioxopyrimidines **7** (Scheme 1). **7c** and **7i** were obtained by treatment of **6c** and **6i**, respectively, with NaOH.

The structure of the 6-imino-6H-1,3-thiazine perchlorates **3** were confirmed on the basis of spectral properties and elementary analysis. The mass spectra of **3** exhibited the M^+-$HClO_4$-peaks with low intensities (1–12%). As expected, the main fragmentation leads to the fragment ions R^3CS^+, R^3CNH^+ and R^3CN^+. In the spectra of **3a–d**, **3f** and **3g** the R^3CS^+-ions represented the base peak, whereas in the case of **3h**, the compound without a substituent in 5-position, the elimination of HCN was the preferred fragmentation. The spectra of compounds

TABLE II

Bond lengths (Å) and bond angles (°)[a]

S(1)–C(1)	1.738(4)	S(1)–C(4)	1.755(6)
S(2)–C(2)	1.733(4)	S(2)–C(5)	1.787(7)
O(5)–C(12)	1.203(6)	O(6)–C(12)	1.309(8)
O(6)–C(13)	1.48(1)	N(1)–C(1)	1.299(6)
N(1)–C(2)	1.372(7)	N(2)–C(4)	1.308(7)
C(1)–C(6)	1.488(8)	C(2)–C(3)	1.421(7)
C(3)–C(4)	1.412(6)	C(3)–C(12)	1.495(9)
C(6)–C(7)	1.406(6)	C(6)–C(11)	1.388(7)
C(7)–C(8)	1.394(9)	C(8)–C(9)	1.380(8)
C(9)–C(10)	1.384(7)	C(10)–C(11)	1.390(9)
C(13)–C(14)	1.27(1)		
C(1)–S(1)–C(4)	102.2(2)	C(2)–S(2)–C(5)	102.1(3)
C(12)–O(6)–C(13)	116.9(5)	C(1)–N(1)–C(2)	124.1(4)
S(1)–C(1)–N(1)	125.4(4)	S(1)–C(1)–C(6)	114.9(3)
N(1)–C(1)–C(6)	119.7(4)	S(2)–C(2)–N(1)	113.2(3)
S(2)–C(2)–C(3)	121.6(4)	N(1)–C(2)–C(3)	125.1(4)
C(2)–C(3)–C(4)	120.8(5)	C(2)–C(3)–C(12)	117.9(4)
C(4)–C(3)–C(12)	121.3(5)	S(1)–C(4)–N(2)	111.1(4)
S(1)–C(4)–C(3)	122.2(4)	N(2)–C(4)–C(3)	126.7(5)
C(1)–C(6)–C(7)	121.2(4)	C(1)–C(6)–C(11)	118.7(4)
C(7)–C(6)–C(11)	120.1(5)	C(6)–C(7)–C(8)	119.0(5)
C(7)–C(8)–C(9)	120.6(5)	C(8)–C(9)–C(10)	120.2(6)
C(9)–C(10)–C(11)	120.2(5)	C(6)–C(11)–C(10)	119.9(4)
O(5)–C(12)–O(6)	122.8(6)	O(5)–C(12)–C(13)	122.6(6)
O(6)–C(12)–C(3)	114.5(4)	O(6)–C(13)–C(14)	113.8(6)

[a] The standard deviation in the last digit is in parentheses.

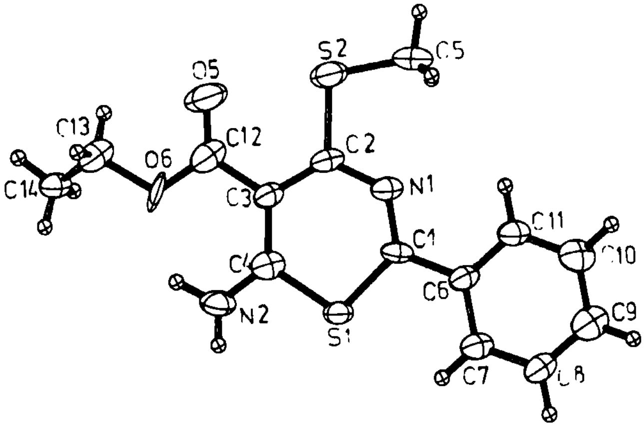

FIGURE 1 Stereoplot[13] of molecular structure of **3d**.

with the carbethoxy group in 5-position **3d–g**, contained the R^3CO^+-ion with high intensity (50–100%). The generation of this ion might be explained with a rearrangement involving the carbethoxy group. The mass spectrometric differentiation between the 6-imino-6H-1,3-thiazine perchlorates **3** and the isomeric 4-imino-4H-1,3-thiazine perchlorates **4** was not possible, and the chemical conversion of **3** into **6** and **7** excluded the alternative structure **4**.

Subsequently, the structure of **3d** was confirmed by X-ray structure analysis.[12] The bond length and angles are given in Table II. The molecular structure are illustrated in Figure 1. The two sixrings, including the atoms S(1), N(1), C(1)–C(4) and C(6)–C(11) are exactly planar. The greatest deviation from these planes is found for the atom C(2) with 0.021(5) Å. The torsion angles between the two rings is 1.4°. Remarkable is the fact, that also the atoms C(2), C(3), C(12), O(5) and S(2) give an exact planar arrangement. This can be explained by assumption of polar interactions between the O and S atoms. The intramolecular distance between the O(5) and S(2) atoms is 2.595 Å. This value lies between the sum of covalent radii (1.70 Å) and the sum of the van der Waals radii (3.25 Å).

A distinction between the benzoylaminothioacrylic acid amides **6** and the isomeric thiobenzoylaminoacrylic acid amides was made on the basis of the mass spectra and the uv-vis spectra. The mass spectrometric fragmentation of **6c** and **6i** leads to the R^3CO^+-ion, which was the base peak; in addition the spectrum of **6i** contained an intensive peak at *m*/*z* 121, due to the $R^3CONH_2^+$-ion. The R^3CS^+-ion could not be observed, excluding the presence of the isomeric thiobenzoylaminoacrylic acids amides. This finding was supported by the uv-vis spectra of **6**, which showed absorption maxima at 325 nm and 382 nm. The

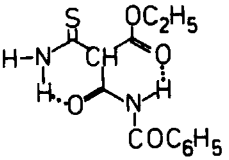

FIGURE 2 Compound **6i**.

isomeric compounds absorb in the region above 470 nm.[5,9] According to the ^{1}H-nmr spectrum **6c** and **6i** were assumed to exist in the oxo-form with intramolecular hydrogen bonding (Figure 2).

EXPERIMENTAL

Melting points are uncorrected.
UV spectra were recorded on a Specord UV-VIS
Mass spectra were recorded on a JEOL JMS-D 100 spectrometer at 75 eV. ^{1}H-NMR.
IR spectra were obtained on a UR-10 (VEB Carl Zeiss, Jena).
Spectra were measured with a Tesla BS 487C.
For details in X-ray structure analysis see Reference 12.

6-Imino-6H-1,3-thiazine perchlorates 3; *General Procedure*

The thioamide **2** (10 mmol) was added to the mixture of a substituted acrylonitril **1** (10 mmol) and a 2 m solution of anhydrous perchloric acid in acetic acid (10 ml, 20 mmol). The reaction mixture was shaken at room temperature (method A) or refluxed (method B) under the conditions indicated in Table I. The precipitated material was isolated by filtration, washed with ether and water and dried. To obtain analytically pure samples of **3a**, **3e** and **3f** the general procedure was modified. **3a**: Method A, 1 h in the presence of 50 ml $HClO_4$. **3e**: Method B, 5 min. **3c**: Immediately after addition of the thioamide, the precipitated **3c** was filtered off and dried without washing with water. **3c** could be obtained only as a crude product which was contaminated with ammonium perchlorate.

3a) mp 231–237°C (decomp.) (crude product). IR (KBr): 3330, 3175 (N—H), 2235 (C≡N), 1660 cm^{-1}. MS *m/z*(%): 259.0212 (12) (M$^+$—HClO$_4$) ($C_{12}H_9N_3S_2$ requires 259.0238); 121.0104 (100) ($C_6H_5CS^+$) (C_7H_5S requires 121.0104); 104 (28) ($C_6H_5CNH^+$); 103.0409 (16) ($C_6H_5CN^+$) (C_7H_5N requires 103.0422). Anal. Calcd. for $C_{12}H_9N_3S_2 \cdot HClO_4$: C 40.06; H 2.80; N 11.68; S 17.82. Found: C 39.98; H 3.03; N 11.92; S 17.96.

3b) mp 207–213°C (decomp.) (acetic acid, 80°C). IR (KBr): 3300, 3100 (N—H), 2225 (C≡N), 1655 cm^{-1}. MS *m/z*(%): 335 (10) (M—HClO$_4$)$^+$; 121 (100) ($C_6H_5CS^+$); 104 (49) ($C_6H_5CNH^+$); 103 (24) ($C_6H_5CN^+$). Anal. Calcd. for $C_{18}H_{13}N_3S_2 \cdot HClO_4$: C 49.60; H 3.24; N 9.64; S 14.71; Cl 8.13. Found: C 49.45; H 3.26; N 9.55; Cl 8.38.

3c) mp > 180°C (decomp.) (crude product). IR (KBr): 3270, 3100 (N—H), 2220 (C≡N), 1650 cm^{-1}. MS *m/z*(%): 213 (2) (M—HClO$_4$)$^+$; 121 (100) ($C_6H_5CS^+$); 104 (18) ($C_6H_5CNH^+$); 103 (54) ($C_6H_5CN^+$).

3d) mp 212–225°C (decomp.) (methanol). IR (KBr): 3360, 3260, 3175 (N—H), 1700 (C═O), 1610 cm^{-1}. MS *m/z*(%): 306 (3) (M—HClO$_4$)$^+$; 121 (100) ($C_6H_5CS^+$); 105.0301 (45) ($C_6H_5CO^+$) (C_7H_5O requires 105,0304); 104 (26) ($C_6H_5CNH^+$); 103 (10) ($C_6H_5CN^+$). Anal. Calcd. for $C_{14}H_{14}N_2O_2S_2 \cdot HClO_4$: C 41.33; H 3.72; N 6.89; S 15.76; Cl 8.71. Found: C 41.51; H 3.71; N 6.75; S 15.69; Cl 8.69.

3e) mp 197–213°C (decomp.) (acetic acid). IR (KBr): 3350–3000 (broad) (N—H), 1690 (C═O), 1615 cm^{-1}. MS *m/z*(%): 320.0654 (5) (M—HClO$_4$)$^+$($C_{15}H_{16}N_2O_2S_2$ requires 320.0654); 135 (36) ($CH_3C_6H_4CS^+$); 119.0490 (100) ($CH_3C_6H_4CO^+$) (C_8H_7O requires 119.0497); 118 (50) ($CH_3C_6H_4CNH^+$); 117 (58) ($CH_3C_6H_4CN^+$). Anal. Calcd. for $C_{15}H_{16}N_2O_2S_2 \cdot HClO_4$: C 42.80; H 4.07; N 6.66; S 15.24; Cl 8.42. Found: C 42.75; H 4.32; N 6.79; S 15.21; Cl 8.62.

3f) mp 230–239°C (decomp.) (acetic acid). IR (KBr): 3370, 3150 (N—H), 1705 (C═O), 1620 cm^{-1}. MS *m/z*(%): 336 (1) (M − HClO$_4$)$^+$; 151 (100) ($CH_3OC_6H_4CS^+$); 135.0452 ($CH_3OC_6H_4CO^+$) ($C_8H_7O_2$ requires 135.0446); 134 (27) ($CH_3OC_6H_4CNH^+$); 133 (29) ($CH_3OC_6H_4CN^+$). Anal. Calcd. for $C_{15}H_{16}N_2O_3S_2 \cdot HClO_4$: C 41.24; H 3.92; N 6.41; S 14.68; Cl 8.12. Found: C 41.40; H 4.03; N 6.80; S 14.56; Cl 8.16.

3g) mp 205–221°C (decomp.) (acetic acid). IR (KBr): 3275, 3150 (N—H), 1690 (C═O), 1610 cm^{-1}. MS *m/z*(%): 340 (11) (M—HClO$_4$)$^+$; 155 (100) ($ClC_6H_4CS^+$); 139 (45) ($ClC_6H_4CO^+$); 138 (17) ($ClC_6H_4CNH^+$); 137 (11) ($ClC_6H_4CN^+$). Anal. Calcd. for $C_{14}H_{13}ClN_2O_2S_2 \cdot HClO_4$: C 38, 10; H 3.20; N 6.35; S 14.53; Cl 16.07. Found: C 38.42; H 3.26; N 6.72; S 14.66; Cl 16.00.

3h mp 262–269°C (decomp.) (acetic acid). IR (KBr): 3305, 3140 (N—H), 1655 cm^{-1}. MS *m/z*(%): 278 (11) (M—HClO$_4$)$^+$; 251 (100) (M—HClO$_4$—HCN)$^+$; 121 (54) ($C_6H_5CS^+$); 104 (13) ($C_6H_5CNH^+$); 103 (11) ($C_6H_5CN^+$). Anal. Calcd. for $C_{17}H_{14}N_2S \cdot HClO_4$: C 53.90; H 3.99; N 7.40; S 8.46; Cl 9.36. Found: C 53.94; H 3.97; N 7.49; S 8.54; Cl 9.54.

6-Imino-4-(methylthio)-2-phenyl-6H-1,3-thiazine-5-carboxylic acid ethylester (**5d**) *and 2-(aminothiocarbonyl)-N-benzoylmalonic acid ethylester amide* (**6i**)

3d) (1.0 g; 2.5 mmol) was dissolved in a mixture of dimethylformamide (2 ml) and 4n HCl (1 ml), the solution was allowed to stand at 4°C for 3 h. The resulting precipitate was filtered off, washed with water and dried; yield: 0.2 g (26%).

5d. The filtrate was evaporated in vacuo, the oily residue was treated with water for crystallization. The crude product **6i** was recrystallized from benzene; yield: 0.2 g (27%).

5d) mp 130–135°C (methanol). IR (KBr): 3260, 3100 (N—H), 1680 (C═O), 1650 cm^{-1}. UV: λ_{max}^{EtOH} 315 (sh), 270 (log ε = 4.24) nm. MS *m/z*(%): 306.0494 (1) (M$^+$) ($C_{14}H_{14}N_2O_2S_2$ requires 306.0497); 105.0327 (100) ($C_6H_5CO^+$) (C_7H_5O requires 105.0340). Anal. Calcd. for $C_{14}H_{14}N_2O_2S_2$: C 54.89; H 4.61; N 9.14; S 20.93. Found: C 54.33; H 4.62; N 8.74; S 20.35. (Treatment of **5d** with perchloric acid gave **3d**).

6i) mp 128–143°C (benzen). IR (KBr): 3360, 3285, 3165, 1720, 1690, 1630 cm^{-1}. ^{1}H-NMR ($CDCl_3$/TMS): δ = 1.23 t(3), 4.09 q(2), 5.16 s(1), 7.40 m(3), 7.91 m(2), 9.00 s(1), 11.04 s(1). UV: λ_{max}^{EtOH} 325 (log ε = 4.16), 272 (4.34), 240 (4.85) nm. MS *m/z*(%): 294 (1) (M$^+$); 173.0141 (3) ($M—C_6H_5CONH_2)^+$ ($C_6H_7NO_3S$ requires 173.0147); 121.0541 (47) ($C_6H_5CONH_2^+$) (C_7H_7NO requires 121.0528); 105.0397 (100) ($C_6H_5CO^+$) (C_7H_5O requires 105.0340). Anal. Calcd. for $C_{13}H_{14}N_2O_4S$: C 53.05; H 4.79; N 9.52; S 10.89. Found: C 53.18; H 4.77; N 9.51; S 10.76.

3-(Benzoylamino)-2-cyanothioacrylic acid amide (**6c**)

3c (crude product) (1 g; 3.2 mmol) was treated with water, filtered off and crystallized from acetic acid to give **6c**; yield: 0.53 g (72%). mp 187–203°C (acetic acid). IR (KBr): 3360–3075, 2230, 1690, 1650 cm^{-1}. UV: λ_{max}^{EtOH} 382 (log ε = 3.93), 302 (4.24), 248 (4.14) nm. MS *m/z*(%): 231 (9) (M$^+$); 126.0104 (6) ($M—C_6H_5CO)^+$. ($C_4H_4N_3S$ requires 126.0126); 105.0322 (100) ($C_6H_5CO^+$) (C_7H_5O requires 105.0340). Anal. Calcd. for $C_{11}H_9N_3OS$: C 57.13; H 3.92; S 13.86. Found: C 57.35; H 3.90; S 13.85.

3,4-Dihydro-4-thioxopyrimidines **7**; *General Procedure*

Method A: A mixture of an 6-imino-6H-1,3-thiazine perchlorate **3** (5 mmol) and 1.74 ml (20 mmol) morpholine in 20 ml ethanol was refluxed for 15 min. The mixture was poured into 1 m HCl (200 ml) and recrystallized. For isolation of **7g** the reaction mixture was concentrated, the precipitated material was filtered off, suspended in a hot mixture of methanol/water (5:1), the insoluble material was separated and the filtrate was acidified with conc. HCl. The resulting precipitate was collected. **7h** precipitated from the hot reaction mixture, the product was filtered and recrystallized from benzene.

Method B: A solution of **3** (5 mmol) in 8 ml DMSO and 10 m NaOH (2 ml) was heated at 100°C for 5 min. The solution was cooled and 1 m HCl (5 ml) was added. The separated product was filtered off and washed with water.

Method C: **6c** and **6i**, respectively, were dissolved in 1 m NaOH, the solution was acidified with HCl and the precipitated products **7c** resp. **7i** were isolated and recrystallized.

7a) mp 226–233°C (2-Methoxyethanol). IR (KBr): 3160–3010 (N—H), 2210 (C≡N) cm^{-1}. UV: λ_{max}^{EtOH} 390 (log ε = 3.45), 309 (sh) (4.43), 290 (4.54), 268 (4.50) nm. Anal. Calcd. for $C_{12}H_9N_3S_2$: C 55.57; H 3.50; N 16.20; S 24.73. Found: C 55.52; H 3.76; N 16.19; S 24.50.

7b) mp 205–210°C (2-Methoxyethanol). IR (KBr): 3160–3030 (N—H), 2225 (C≡N) cm^{-1}. UV: λ_{max}^{EtOH} 396 (log ε = 3.54), 309 (sh) (4.34), 290 (4.52), 269 (4.43) nm. Anal. Calcd. for $C_{18}H_{13}N_3S_2$: C 64.45; H 3.91; N 12.53; S 19.12. Found: C 64.48; H 3.99; N 12.13; S 18.70.

7c) mp 217–230°C (acetonitrile). IR (KBr): 3150–3010 (N—H), 2235 (C≡N) cm^{-1}. UV: λ_{max}^{EtOH} 358 (sh) (log ε = 3.15), 310 (4.39), 274 (4.52) nm. MS *m/z*(%): 213 (100) (M$^+$). Anal. Calcd. for $C_{11}H_7N_3S$: C 61.95; H 3.31; N 19.70; S 15.04. Found: C 62.22; H 3.41; N 19.91; S 15.08.

7d) mp 163–174°C (methanol). IR (KBr): 3140 (N—H), 1725 (C═O) cm^{-1}. UV: λ_{max}^{EtOH} 369 (log ε = 3.63), 309 (4.20), 278 (4.36), 258 (4.43) nm. MS *m/z*(%): 306 (51 M$^+$), 104 (100, $C_6H_5CNH^+$). Anal. Calcd. for $C_{14}H_{14}N_2O_2S_2$: C 54.88; H 4.61; N 9.14; S 20.93. Found: C 54.64; H 4.52; N 9.19; S 20.96.

7e) mp 174–188°C (ethanol). IR (KBr): 3155 (N—H), 1715 (C═O) cm^{-1}. UV: λ_{max}^{EtOH} 373 (log ε = 3.69), 307 (sh) (4.23), 281 (4.47), 262 (4.45) nm. Anal. Calcd. for $C_{15}H_{16}N_2O_2S_2$: C 56.22; H 5.03; N 8.74; S 20.01. Found: C 56.31; H 5.05; N 8.64; S 20.24.

7f) mp 138–145°C (ethanol). IR (KBr): 3185 (N—H), 1725 (C═O) cm^{-1}. UV: λ_{max}^{EtOH} 380 (log ε = 3.76), 291 (4.55), 267 (sh) (4.43) nm. Anal. Calcd. for $C_{15}H_{16}N_2O_3S_2$: C 53.55; H 4.79; N 8.33; S 19.06. Found: C 53.74; H 4.85; N 8.83; S 19.32.

7g) mp 133–136°C (ethanol). IR (KBr): 1705 (C=O) cm^{-1}. UV: λ_{max}^{EtOH} 378 (log ε = 3.50), 311 (sh) (4.24), 283 (4.46), 261 (4.53) nm. MS m/z(%): 340 (82, M$^+$), 138 (100, $ClC_6H_4CNH^+$). Anal. Calcd. for $C_{14}H_{13}ClN_2O_2S_2$: C 49.33; H 3.84; N 8.22; S 18.81; Cl 10.40. Found: C 49.62; H 3.82; N 8.58; S 18.75; Cl 10.61.

7h) mp 197–222°C (benzen). IR (KBr): 3155 (N—H) cm^{-1}. UV: λ_{max}^{EtOH} 386 (log ε = 3.81), 300 (4.33), 258 (4.47) nm. Anal. Calcd. for $C_{17}H_{14}N_2S$: C 73.35; H 5.07; N 10.06; S 11.52. Found: C 73.29; H 5.06; N 10.43; S 11.52.

7i) mp 163–178°C (benzen). IR (KBr): 3210–2950, 1700, 1660 cm^{-1}. UV: λ_{max}^{EtOH} 303 (log ε = 4.18), 267 (sh) (4.20)m 240 (4.36) nm. MS m/z(%): 276 (11, M$^+$), 104 (100, $C_6H_5CNH^+$). Anal. Calcd. for $C_{13}H_{12}N_2O_3S$: C 56.51; H 4.38; N 10, 14; S 11.60. Found: C 56.86; H 4.42; N 9.88; S 11.55.

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