Reaction of (Cyano)thioacetamide with Arylhydrazones of β-Diketones: Novel Synthesis of 2(1*H*)-Pyridinethiones, Thieno[2,3-*b*]pyridines, and Pyrazolo[3,4-*b*]pyridines

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A novel synthesis of 2(1*H*)-pyridinethiones, thieno[2,3-*b*]pyridines and pyrazolo[3,4-*b*]pyridines utilizing (cyano)thioacetamide and arylhydrazones of 1,3-diketones as starting components is described.

Over the past five years, 2(1*H*)-pyridinethione compounds have gained considerable interest due to their importance as intermediates for the synthesis of the biologically active deazafolic acid and deazaaminopterin ring system.[1,2] As a part of our program directed for the development of new simple and efficient procedures for the synthesis of heterocyclic nitrogen compounds utilizing readily obtainable nitrile intermediates.[3—8] We have investigated the reaction of (cyano)thioacetamide (**1**) with readily accessible arylhydrazones of β-diketones. The investigation has resulted in the development of novel procedure for the synthesis of 2(1*H*)-pyridinethiones and their fused derivatives. The compounds obtained seem promising for further chemical transformations and for biological evaluation studies. Thus, it has been found that (cyano)thioacetamide (**1**) reacted with arylhydrazones **3** of both acetylacetone and benzoylacetone in boiling ethanolic sodium ethoxide to yield the 2(1*H*)-pyridinethione derivatives **7**. The structures of **7** were established and confirmed for the reaction products on the bases of their elemental analysis and spectral data (MS, IR, and ^{1}H NMR). The analytical data for **7a** revealed a molecular formula $C_{14}H_{12}N_4S$ ($M^+=268$), ^{1}H NMR was used to confirm this structure for the product. Thus, ^{1}H NMR revealed a broad band at $\delta=14.25$ assignable to NH group, a multiplet at $\delta=7.58$—7.87 assigned for aromatic protons and two singlets at $\delta=2.51$ and 2.74 assignable for two methyl groups (cf. Table 2). The formation of **7** is assumed to proceed via intermediacy of **5**, which loses two molecules of water to yield the stable sodium salts **6**. Subsequent addition of water and acidification gave the final isolable 2(1*H*)-pyridinethiones **7**. Compounds **7** can be converted into sodium salts **6** by treatment with sodium ethoxide at room temperature.

Compounds **7** bearing latent functional substituent were found useful for the synthesis of fused pyridines. Thus, it has been found that salts **6** or **7** reacted with ethyl iodide in DMF-NaOH to afford the corresponding *S*-alkyl derivatives **8**. The ^{1}H NMR spectra for **8a** showed a triplet at $\delta=1.41$ and a quartet at $\delta=2.58$ assigned to SCH_2CH_3 group. When salts **6** or **7** were subjected to the reaction of phenacyl bromide as alkylating agent, the *S*-alkylated derivatives could not be isolated, but cyclize to the thieno[2,3-*b*]pyridine derivatives **9**. The structure of compounds **9** was established on the bases of elemental analysis and spectral data. Thus, the IR spectrum of **9a** revealed the absence of a CN band, the mass was compatible with the molecular formula $C_{22}H_{18}N_4SO$ ($M^+=386$), and ^{1}H NMR contained a broad band at $\delta=7.26$ assignable to an amino function and a multiplet at $\delta=7.36$—7.88 assigned to the aromatic protons. A 2-chloro derivative corresponding to the compound **7** could be prepared by treating the 2(1*H*)-pyridinethiones **7** with chlorine gas in chloroform at room temerature. Structure **10** was established based on elemental analysis and spectral data (MS. IR, ^{1}H NMR). The IR spectra of compounds **10** showed absence of a NH band. Compounds **10** reacted with hydrazine hydrate in refluxing ethanol containing catalytic amounts of triethylamine for 3 h to give the 1*H*-pyrazolo[3,4-*b*]pyridine derivatives **11**. Compounds **11** could also be prepared by the reaction of **8** with hydrazine hydrate under the same conditions. The structure of **11** was established by mass spectroscopy, IR and ^{1}H NMR data. The IR spectra of compound **11b** showed absence of a CN band and its ^{1}H NMR spectra a band at $\delta=5.5$ assigned to an NH_2 group and broad band at $\delta=12.0$ assigned to an NH group. Hydrolysis of **10** with NaOH in ethanol led to the 1,2-dihydro-2-oxo-3-pyridinecarbonitriles (**12**). Compounds **12** could also be obtained in good yields by the reaction of **3** with (cyano)thioacetamide in boiling ethanolic sodium ethoxide (Scheme 1).

In summary, we have achieved a regiospecific synthesis of interesting 5-arylazo-2(1*H*)-pyridinethione derivatives by the reaction of (cyano) thioacetamide with arylhydrazones of β-diketones. These 2(1*H*)-pyridinethiones can be utilized as an excellent starting material for the preparation of other heterocyclic compounds which are not readily accessible.

Experimental

All melting points are uncorrected. IR spectra were obtained (KBr disc) on a Pye Unicam Spectra-1000 or on a Shimadzu IR 200 instrument. ^{1}H NMR spectra were mea-

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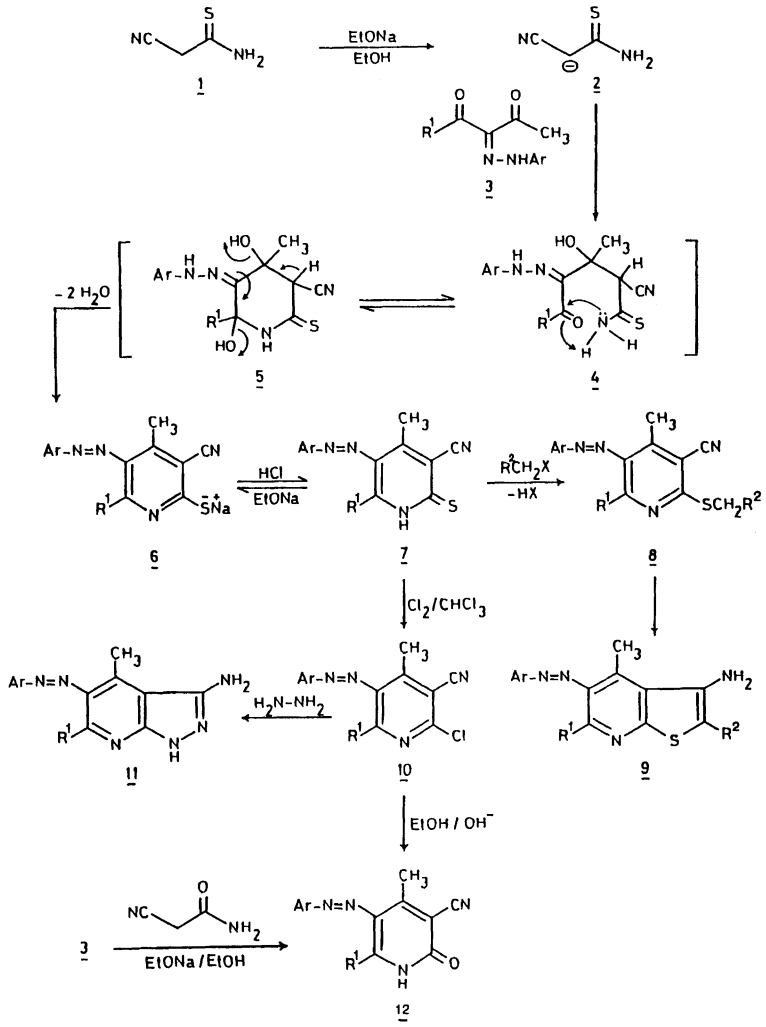
Table 1. Characterization Data for Compounds **7a**—**r**,**8a**—**h**, **9a**—**h**, **10a**—**h**,**11a**—**h**, and **12a**—**h**

Compound (color)	Recryst. (solvent)	Mp θ_m/°C	Yield %	Mol. formula	Found/calcd(%) C	H	N	M^+ m/z
7a	EtOH	220	68	$C_{14}H_{12}N_4S$	63.0	4.8	21.1	268
(brown)				(268)	62.7	4.5	20.9	
7b	EtOH/DMF	255	90	$C_{14}H_{11}ClN_4S$	55.3	3.9	18.2	302
(orange)				(302.5)	55.5	3.6	18.5	
7c	EtOH/DMF	222	90	$C_{14}H_{11}ClN_4S$	55.5	3.8	18.1	302
(yellow)				(302.5)	55.5	3.6	18.5	
7d	EtOH	245	95	$C_{14}H_{11}ClN_4S$	55.7	4.0	18.2	302
(yellow)				(302.5)	55.5	3.6	18.5	
7e	EtOH/DMF	227	85	$C_{15}H_{14}N_4S$	63.5	5.2	19.5	282
(brown)				(282)	63.8	5.0	19.9	
7f	AcOH	200	77	$C_{15}H_{14}N_4S$	63.8	5.3	20.0	282
(yellow)				(282)	63.8	5.0	19.9	
7g	EtOH/DMF	240	70	$C_{15}H_{14}N_4S$	64.0	5.0	19.6	282
(yellow)				(282)	63.8	5.0	19.9	
7h	AcOH	240	78	$C_{15}H_{14}N_4SO$	60.1	4.8	19.1	298
(yellow)				(298)	60.4	4.7	18.8	
7i	EtOH	210	78	$C_{15}H_{14}N_4SO$	60.0	5.0	19.1	
(yellow)				(298)	60.4	4.7	18.8	
7j	EtOH/DMF	205	78	$C_{15}H_{14}N_4SO$	60.5	4.5	18.4	298
(yellow)				(298)	60.4	4.7	18.8	
7k	EtOH/DMF	195	90	$C_{19}H_{14}N_4S$	68.8	4.4	16.8	330
(brown)				(330)	69.1	4.2	17.0	
7l	EtOH/$CHCl_3$	195	80	$C_{19}H_{13}ClN_4S$	62.7	4.0	15.6	364
(yellow)				(364.5)	62.6	3.6	15.4	
7m	DMF	212	90	$C_{19}H_{13}ClN_4S$	62.1	3.8	15.0	364
(yellow)				(364.5)	62.6	3.6	15.4	
7n	EtOH	183	95	$C_{20}H_{16}N_4S$	70.0	5.1	16.0	
(yellow)				(344)	69.8	4.7	16.3	
7o	EtOH/DMF	202	73	$C_{20}H_{16}N_4S$	69.8	4.9	15.9	
(orange)				(344)	69.8	4.7	16.3	
7p	AcOH	205	69	$C_{20}H_{16}N_4S$	69.4	4.4	15.9	
(yellow)				(344)	69.8	4.7	16.3	
7q	EtOH/DMF	197	82	$C_{20}H_{16}N_4SO$	66.3	4.7	15.3	360
(yellow)				(360)	66.7	4.4	15.6	
7r	EtOH/DMF	208	95	$C_{20}H_{16}N_4SO$	66.5	4.8	15.2	360
(yellow)				(360)	66.7	4.4	15.6	
8a	EtOH	110	65	$C_{16}H_{16}N_4S$	65.2	5.5	18.5	296
(orange)				(296)	64.9	5.4	18.9	
8b	EtOH	110	65	$C_{16}H_{15}ClN_4S$	57.7	4.2	16.6	330
(orange)				(330.5)	58.1	4.5	16.9	
8c	EtOH	130	50	$C_{17}H_{18}N_4S$	66.1	5.5	17.7	310
(orange)				(310)	65.8	5.8	18.1	
8d	EtOH	100	55	$C_{17}H_{18}N_4SO$	62.2	5.6	17.5	326
(orange)				(326)	62.6	5.5	17.2	
8e	EtOH	95	50	$C_{21}H_{18}N_4S$	70.0	4.8	15.2	358
(orange)				(358)	70.4	5.0	15.6	
8f	EtOH	135	60	$C_{21}H_{17}ClN_4S$	63.8	4.5	14.0	
(orange)				(392.5)	64.2	4.3	14.3	
8g	EtOH	102	50	$C_{22}H_{20}N_4S$	71.2	5.2	14.7	372
(yellow)				(372)	71.0	5.4	15.1	
8h	EtOH	148	50	$C_{22}H_{20}N_4SO$	67.7	5.4	14.0	388
(yellow)				(388)	68.0	5.2	14.4	
9a	EtOH	225	52	$C_{22}H_{18}N_4SO$	68.5	4.8	14.1	386
(yellow)				(386)	68.4	4.7	14.5	
9b	EtOH	197	55	$C_{22}H_{17}ClN_4SO$	63.0	4.4	12.9	420
(orange)				(420.5)	62.8	4.0	13.3	

Table 1. (Continued)

9c (red)	EtOH	185	50	$C_{23}H_{20}N_4SO$ (400)	68.8 69.0	4.8 5.0	13.6 14.0	400
9d (orange)	EtOH	192	56	$C_{23}H_{20}N_4SO_2$ (416)	66.7 66.4	5.2 4.8	13.1 13.5	416
9e (orange)	EtOH	235	50	$C_{27}H_{20}N_4SO$ (448)	71.9 72.3	4.7 4.5	12.3 12.5	
9f (yellow)	EtOH	240	58	$C_{27}H_{19}ClN_4SO$ (482.5)	66.8 67.2	4.2 3.9	11.2 11.6	
9g (red)	EtOH	220	50	$C_{28}H_{22}N_4SO$ (462)	72.3 72.7	4.4 4.8	11.8 12.1	462
9h (orange)	EtOH/DMF	207	50	$C_{28}H_{22}N_4SO_2$ (478)	70.1 70.3	4.4 4.6	11.3 11.7	
10a (brown)	EtOH	96	50	$C_{14}H_{11}ClN_4$ (270.5)	62.0 62.1	4.5 4.1	20.2 20.7	270
10b (brown)	EtOH	160	55	$C_{14}H_{10}Cl_2N_4$ (305)	54.7 55.1	3.6 3.3	18.0 18.4	
10c (brown)	EtOH	135	50	$C_{15}H_{13}ClN_4$ (284.5)	62.9 63.3	4.2 4.6	19.5 19.7	
10d (orange)	EtOH	190	55	$C_{15}H_{13}ClN_4O$ (300.5)	60.2 59.9	4.6 4.3	18.2 18.6	
10e (brown)	EtOH	140	60	$C_{19}H_{13}ClN_4$ (332.5)	69.0 68.6	4.2 3.9	16.4 16.8	332
10f (brown)	EtOH	135	50	$C_{19}H_{12}ClN_4$ (367)	61.8 62.1	3.7 3.3	14.9 15.3	
10g (brown)	EtOH	125	50	$C_{20}H_{15}ClN_4$ (346.5)	68.9 69.3	4.6 4.3	15.8 16.2	
10h (yellow)	EtOH	137	60	$C_{20}H_{15}ClN_4O$ (362.5)	65.9 66.2	4.4 4.1	15.0 15.4	
11a (yellow)	EtOH/DMF	295	60	$C_{14}H_{14}N_6$ (266)	62.8 63.2	4.9 5.3	31.2 31.6	266
11b (orange)	EtOH/DMF	280	65	$C_{14}H_{13}ClN_6$ (300.5)	56.2 55.9	4.0 4.3	27.7 28.0	
11c (red)	EtOH/DMF	270	80	$C_{15}H_{16}N_6$ (280)	64.0 64.3	5.5 5.7	29.7 30.0	280
11d (buff)	EtOH/DMF	290	70	$C_{15}H_{16}N_6O$ (296)	61.0 60.8	5.5 5.4	28.1 28.4	
11e (orange)	EtOH/DMF	270	60	$C_{19}H_{16}N_6$ (328)	69.2 69.5	5.0 4.9	25.2 25.6	
11f (green)	EtOH	320	70	$C_{19}H_{15}ClN_6$ (362.5)	63.1 62.9	4.5 4.1	22.8 23.2	
11g (orange)	EtOH/DMF	>300	60	$C_{20}H_{18}N_6$ (342)	69.8 70.2	5.6 5.3	24.3 24.6	342
11h (yellow)	EtOH/DMF	>300	70	$C_{20}H_{18}N_6O$ (358)	66.8 67.0	4.8 5.0	23.2 23.5	
12a (orange)	EtOH/DMF	285	80	$C_{14}H_{12}N_4O$ (252)	66.6 66.7	5.0 4.8	21.8 22.2	252
12b (yellow)	EtOH/DMF	>300	80	$C_{14}H_{11}ClN_4O$ (286.5)	58.6 58.6	4.2 3.8	19.3 19.5	
12c (yellow)	EtOH/DMF	290	70	$C_{15}H_{14}N_4O$ (266)	68.0 67.7	5.6 5.3	20.7 21.1	266
12d (yellow)	EtOH/DMF	300	75	$C_{15}H_{14}N_4O_2$ (282)	63.5 63.8	5.3 5.0	19.5 19.9	
12e (yellow)	EtOH	275	80	$C_{19}H_{14}N_4O$ (314)	72.3 72.6	4.8 4.5	17.5 17.8	314
12f (yellow)	EtOH	290	85	$C_{19}H_{13}ClN_4O$ (348.5)	65.2 65.4	4.0 3.7	15.7 16.1	
12g (orange)	EtOH/DMF	235	65	$C_{20}H_{16}N_4O$ (328)	73.2 73.2	5.1 4.9	16.7 17.1	
12h (yellow)	EtOH/DMF	290	70	$C_{20}H_{16}N_4O_2$ (344)	69.5 69.7	5.0 4.7	15.9 16.3	344



3,6,7	R^1	Ar
a,	CH_3	C_6H_5
b,	CH_3	2-ClC_6H_4
c,	CH_3	3-ClC_6H_4
d,	CH_3	4-ClC_6H_4
e,	CH_3	2-$CH_3C_6H_4$
f,	CH_3	3-$CH_3C_6H_4$
g,	CH_3	4-$CH_3C_6H_4$
h,	CH_3	2-$CH_3OC_6H_4$
i,	CH_3	3-$CH_3OC_6H_4$
j,	CH_3	4-$CH_3OC_6H_5$
k,	C_6H_5	C_6H_5
l,	C_6H_5	2-ClC_6H_4
m,	C_6H_5	4-ClC_6H_4
n,	C_6H_5	2-$CH_3C_6H_4$
o,	C_6H_5	3-$CH_3C_6H_4$
p,	C_6H_5	4-$CH_3C_6H_4$
q,	C_6H_5	3-$CH_3OC_6H_4$
r,	C_6H_5	4-$CH_3OC_6H_4$

8	R^1	R^2	Ar
a,	CH_3	CH_3	C_6H_5
b,	CH_3	CH_3	4-ClC_6H_4
c,	CH_3	CH_3	4-$CH_3C_6H_4$
d,	CH_3	CH_3	4-$CH_3OC_6H_4$
e,	C_6H_5	CH_3	C_6H_5
f,	C_6H_5	CH_3	4-ClC_6H_4
g,	C_6H_5	CH_3	4-$CH_3C_6H_4$
h,	C_6H_5	CH_3	4-$CH_3OC_6H_4$

9	R^1	R^2	Ar
a,	CH_3	COC_6H_5	C_6H_5
b,	CH_3	COC_6H_5	4-ClC_6H_4
c,	CH_3	COC_6H_5	4-$CH_3C_6H_4$
d,	CH_3	COC_6H_5	4-$CH_3OC_6H_4$
e,	C_6H_5	COC_6H_5	C_6H_5
f,	C_6H_5	COC_6H_5	4-ClC_6H_4
g,	C_6H_5	COC_6H_5	4-$CH_3C_6H_4$
h,	C_6H_5	COC_6H_5	4-$CH_3OC_6H_4$

10,11,12	R^1	Ar
a,	CH_3	C_6H_5
b,	CH_3	4-ClC_6H_4
c,	CH_3	4-$CH_3C_6H_4$
d,	CH_3	4-$CH_3OC_6H_4$
e,	C_6H_5	C_6H_5
f,	C_6H_5	4-ClC_6H_4
g,	C_6H_5	4-$CH_3C_6H_4$
h,	C_6H_5	4-$CH_3OC_6H_4$

Scheme 1.

Table 2. IR and ^{1}H NMR Data for Compounds Listed in Table 1

Compound	IR (KBr)/cm^{-1}	^{1}H NMR (DMSO) δ/ppm
7a	3480, 3350 (NH), 2225 (CN)	2.51 (s, 3H, CH_3), 2.74 (s, 3H, CH_3), 7.58—7.87 (m, 5H, C_6H_5), 14.25 (s, br, 1H, NH)
7b	3500, 3450 (NH), 2220 (CN)	2.68 (s, 3H, CH_3), 2.72 (s, 3H, CH_3), 7.47—7.72 (m, 4H, C_6H_4), 14.20 (s, br, 1H, NH)
7c	3460, 3400 (NH), 2230 (CN)	2.65 (s, 3H, CH_3), 2.67 (s, 3H, CH_3), 7.64—7.82 (m, 4H, C_6H_4), 14.28 (s, br, 1H, NH)
7d	3508, 3175 (NH), 2225 (CN)	2.64 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 7.48—7.75 (m, 4H, C_6H_4), 14.30 (s, br, 1H, NH)
7e	3565, 3173 (NH), 2234 (CN)	2.50 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 7.30—7.54 (m, 4H, C_6H_4), 14.26 (s, br, 1H, NH)
7f	3520, 3400 (NH), 2220 (CN)	2.42 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 7.37—7.68 (m, 4H, C_6H_4), 14.30 (s, br, 1H, NH)
7g	3502, 3176 (NH), 2225 (CN)	2.39 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 7.38—7.78 (m, 4H, C_6H_4), 14.20 (s. br, 1H, NH)
7h	3500, 3380 (NH), 2228 (CN)	2.61 (s, 3H, CH_3), 2.63 (s. 3H, CH_3), 3.91 (s, 3H, OCH_3), 7.02—7.58 (m, 4H, $C_6H_{,4}$), 14.20 (s, br, 1H, NH)
7i	3556, 3181 (NH), 2228 (CN)	2.62 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 3.88 (s, 3H, OCH_3), 7.14—7.52 (m, 4H, C_6H_4), 14.30 (s, br, 1H, NH)
7j	3450, 3270 (NH), 2225 (CN)	2.50 (s, 3H, CH_3), 2.61 (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 7.02—7.86 (m, 4H, C_6H_4), 14.25 (s, br, 1H, NH)
7k	3473 (NH), 2222 (CN)	2.62 (s, 3H, CH_3), 7.33—7.62 (m, 10H, 2 C_6H_5), 14.30 (s, br, 1H, NH)
7l	3629, 3172 (NH), 2223 (CN)	2.73 (s, 3H, CH_3), 7.35—7.55 (m, 9H, C_6H_5 and C_6H_4), 14.25 (s, br, 1H, NH)
7p	3478 (NH), 2223 (CN)	2.38 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 7.18—7.58 (m, 9H, C_6H_5 and C_6H_4), 14.60 (s, br, 1H, NH)
7q	3512, 3159 (NH), 2219 (CN)	2.64 (s, 3H, CH_3), 3.70 (s, 3H, OCH_3), 7.24—7.49 (m, 9H, C_6H_5 and C_6H_4), 14.40 (s, br, 1H, NH)
7r	3450, 3370 (NH), 2225 (CN)	2.61 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 7.16—7.42 (m, 9H, C_6H_5 and C_6H_4), 14.28 (s, br, 1H, NH)
8a	2215 (CN)	1.41 (t, 3H, CH_3), 2.58 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 3.32 (q, 2H, CH_2), 7.49—7.87 (m, 5H, C_6H_5)
8b	2219 (CN)	1.42 (t, 3H, CH_3), 2.60 (s, 3H, CH_3), 2.65 (s, 3H, CH_3), 3.30 (q, 2H, CH_2), 7.52—7.84 (m, 4H, C_6H_4)
8c	2215 (CN)	1.41 (t, 3H, CH_3), 2.46 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 3.31 (q, 2H, CH_2), 7.26—7.80 (m, 4H, C_6H_4)
8d	2220 (CN)	1.39 (t, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 3.38 (q, 2H, CH_2), 3.66 (s, 3H, OCH_3), 7.20—7.77 (m, 4H, C_6H_4)
8e	2221 (CN)	1.55 (t, 3H, CH_3), 2.63 (S, 3H, CH_3), 3.36 (q, 2H, CH_2), 7.11—7.75 (m, 10H, 2 C_6H_5)
8f	2220 (CN)	1.46 (t, 3H, CH_3), 2.70 (s, 3H, CH_3), 3.37 (q, 2H, CH_2), 7.26—7.59 (m, 9H, C_6H_5 and C_6H_4)
8g	2230 (CN)	1.45 (t, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 3.36 (q, 2H, CH_2), 7.25—7.54 (m, 9H, C_6H_5 and C_6H_4)
9a	3577, 3285 (NH_2), 1696 (CO)	2.61 (s, 3H, CH_3), 2.63 (s, 3H, CH_3), 7.26 (s, br, 2H, NH_2), 7.36—7.88 (m, 10H, 2 C_6H_5)
9b	3480, 3400 (NH_2), 1680 (CO)	2.57 (s, 3H, CH_3), 2.61 (s, 3H, CH_3), 7.15 (s, br, 2H, NH_2), 7.30—7.78 (m, 9H, C_6H_5 and C_6H_4)
9e	3500, 3380 (NH_2), 1685 (CO)	2.60 (s, 3H, CH_3), 7.28 (s, br, 2H, NH_2), 7.22—7.81 (m, 15 H, 3 C_6H_5)
9f	3500, 3380 (NH_2), 1690 (CO)	2.95 (s, 3H, CH_3), 7.26 (s, br, 2H, NH_2), 7.29—7.89 (m, 9H, C_6H_5 and C_6H_4)
10a	2228 (CN)	2.55 (s, 3H, CH_3), 2.68 (s, 3H, CH_3), 7.51—7.84 (m, 5H, C_6H_5)
10e	2220 (CN)	2.56 (s, 3H, CH_3), 7.20—7.79 (m, 10H, 2 C_6H_5)
10f	2235 (CN)	2.68 (s, 3H, CH_3), 7.25—7.59 (m, 9H, C_6H_5 and C_6H_4)
11a	3470, 3420, 3400 (NH_2 and NH)	2.41 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 4.82 (s, br, 2H, NH_2), 7.12—7.63 (m, 5H, C_6H_5), 11.40 (s, br, 1H, NH)

Table 2. (Continued)

11b	3577, 3565, 3414, 3296 (NH_2 and NH)	2.64 (s, 3H, CH_3), 2.68 (s, 3H, CH_3), 5.50 (s, br, 2H, NH_2), 7.23—7.67 (m, 4H, C_6H_4), 12.0 (s, br, 1H, NH)
11c	3548, 3404, 3306, 3197 (NH_2 and NH)	2.55 (s, 3H, CH_3), 2.63 (s, 3H, CH_3), 2.69 (s, 3H, CH_3), 5.48 (s, br, 2H, NH_2), 7.38—7.61 (m, 4H, C_6H_4), 12.18 (s, br, 1H, NH)
11d	3500, 3420 (NH_2 and NH)	2.45 (s, 3H, CH_3), 3.58 (s, 3H, CH_3), 3.68 (s, 3H, OCH_3), 4.90 (s, br, 2H, NH_2), 7.30—7.72 (m, 4H, C_6H_4), 11.81 (s, br, 1H, NH)
12a	3565, 3306 (NH), 2227 (CN)	2.58 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 7.35—7.82 (m, 5H, C_6H_5), 14.10 (s, br, 1H, NH)
12b	3430, 3400 (NH), 2225 (CN)	2.56 (s, 3H, CH_3), 2.65 (s, 3H, CH_3), 7.13—7.48 (m, 4H, C_6H_4), 13.88 (s, br, 1H, NH)
12d	3580, 3450 (NH), 2222 (CN)	2.52 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 7.07—7.59 (m, 4H, C_6H_4), 13.50 (s, br, 1H, NH)
12h	3520, 3470 (NH), 2220 (CN)	2.48 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 7.05—7.60 (m, 9H, C_6H_5 and C_6H_4), 13.70 (s, br, 1H, NH)

sured on a Wilmad 270 MHz or on a Varian 400 MHz spectrometer for solutions in $(CD_3)_2SO$ using $SiMe_4$ as an internal standard. Mass spectra were recorded on a Varian MAT 112 spectrometer. Analytical data were obtained from the Microanalytical Data Centre at Cairo University.

1-Substituted-2-arylhydrazono-1,3-butanediones (3a—r). A solution of acetylacetone or benzoylacetone (0.01 mol) in ethanol containing sodium acetate (3.0 g) was cooled to 0°C, stirred and treated gradually with a cooled solution of arenediazonium chloride (prepared from 0.01 mol of amine and the appropriate quantities of HCl and $NaNO_2$). The solid product formed on standing was collected and crystallized from the appropriate solvent.

2(1*H*)-Pyridinethiones (7a—r). A mixture of **3a—r** (0.01 mol) and (cyano)thioacetamide (0.01 mol) was dissolved in ethanol (30 ml) containing sodium ethoxide (0.01 mol). The mixture was refluxed for 1 h, and then allowed to cool to room temperature and acidified with cold dilute hydrochloric acid. The resulting solid product was collected by filtration and crystallized from the appropriate solvent (cf. Table 1).

Sodium 2-Pyridinethiolates (6a—r). To a solution of sodium ethoxide, prepared by dissolving 0.01 mol of sodium in ca. 6 ml of anhydrous ethanol, an equimolar amount of **7**, dissolved in ca. 15 ml of anhydrous ethanol, is added. The reaction mixture is stirred at room temperature for 30 min until the starting material is exhausted (TLC). The solvent is then removed under vacuum and compounds **6** are isolated as watersoluble solids in 70 95% yield; Mp>300°C, yellow crystals.

2-(Ethylthio)pyridines (8a—h). A mixture of **6** or **7** (0.01 mol), NaOH (0.01 mol), and ethyl iodide (0.01 mol) in dry DMF (50 ml) was stirred at room temperature for 24 h and then diluted with cold water (100 ml), and the resulting solid product was collected by filtration and crystallized from the appropriate solvent (cf. Table 1).

Thieno[2,3-*b*]pyridines (9a—h). A mixture of **6** or **7** (0.01 mol), sodium ethoxide (0.01 mol), and phenacyl bromide (0.01 mol) in dry ethanol (50 ml) was refluxed for 2 h, and then allowed to cool to room temperature and acidified with cold dilute hydrochloric acid. The resulting solid product was collected by filtration and crystallized from the appropriate solvent (cf. Table 1).

2-Chloro-3-pyridinecarbonitriles (10a—h). A solution of **7** (0.01 mol) in chloroform (50 ml) was stirred under a stream of dry chlorine gas for 2 h, and then set aside overnight. The resultant precipitate was filtered off and crystallized from the appropriate solvent (cf. Table 1).

3-Amino-1*H*-pyrazolo[3,4-*b*]pyridines (11a—h). To a mixture of **8** or **10** (0.01 mol) and hydrazine hydrate (0.01 mol) in ethanol (50 ml), triethylamine (0.5 ml) was added. The mixture was heated under reflux for 3 h, and then allowed to stand overnight. The resultant precipitate was isolated by suction and crystallized from the appropriate solvent (cf. Table 1).

2(1*H*)-Pyridinones (12a—h). Method a: To a solution of **10** (0.01 mol) in ethanol (30 ml) was added sodium hydroxide (5 ml, 20%). The mixture was refluxed for 3 h, the solvent is partially evaporated and the solution was poured into water and acidified with dilute hydrochloric acid. The resulting solid was collected by filtration and crystallized from the appropriate solvent (cf. Table 1).

Method b: A mixture of **3** (0.01 mol) and (cyano)-thioacetamide (0.01 mol) was dissolved in ethanol (30 ml), a few drops of piperidine were then added. The mixture was refluxed for 3 h, The resulting solid product was collected by filtration and crystallized from the appropriate solvent (cf. Table 1).

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