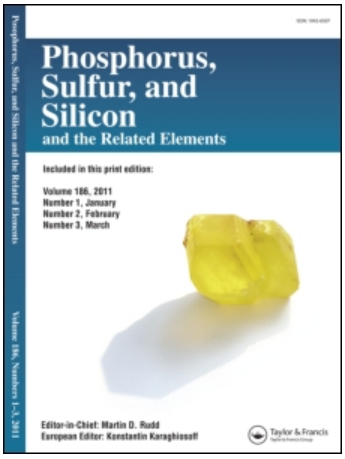

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REACTIONS WITH HYDRAZIDOYL HALIDES. IX: A NOVEL SYNTHESIS OF SOME HYDRAZIDOYL SULFIDES, THIADIAZOLINES,THIAZOLES AND COUMARINES

Abdou O. Abdelhamid[a]; Sadek E. Abdou[b]; Fathia H. El-shiaty[b]
[a] Department of Science, King Khalid Military Academy, Riyadh, Saudi Arabia [b] Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

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REACTIONS WITH HYDRAZIDOYL HALIDES. IX[1]: A NOVEL SYNTHESIS OF SOME HYDRAZIDOYL SULFIDES, THIADIAZOLINES, THIAZOLES AND COUMARINES

ABDOU O. ABDELHAMID[2]*
Department of Science, King Khalid Military Academy, P.O. Box 22140, Riyadh 11495, Saudi Arabia

and

SADEK E. ABDOU and FATHIA H. EL-SHIATY
Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

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The reactions of hydrazidoyl halides with N-phenylcyanothioacetamide and α-cyanothioacetamide gave unexpected hydrazidoyl sulfides, thiadiazolines and thiazole derivatives. The structures of these products were confirmed by elemental analyses and spectral data and wherever possible, alternate synthesis.

Key words: Hydrazidoyl sulfides; thiadiazolines; thiazoles; coumarines; hydrazidoyl halides; N-phenylcyanothiacetamide.

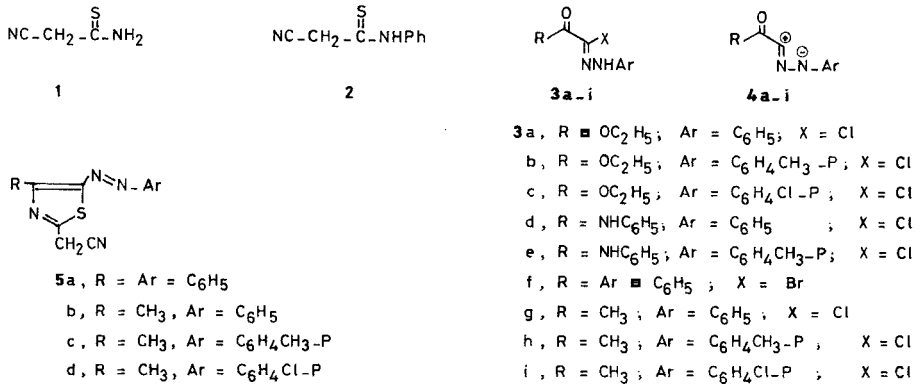
INTRODUCTION

Several reactions of hydrazidoyl halides with thioamides[3–5] and β-keto thioamides[6] have been already investigated. In a preceding paper,[7] α-cyanothioacetamide (1) was shown to react with hydrazidoyl halides **3a**, **d** and **3f** to give hydrazidoyl sulfides **10** and thiazoles **5**, respectively. The results of an examination of the reactions of N-phenylcyanothioacetamide (2) with hydrazidoyl halides **3a–i** is reported here. This examination was undertaken to extend our knowledge of the reactions of hydrazidoyl halides with CS double bonds of the thioacid derivatives and to examine whether hydrazidoyl halides in those systems react with a displacement mechanism or via 1,3-dipolar species, nitrilimine **4**.

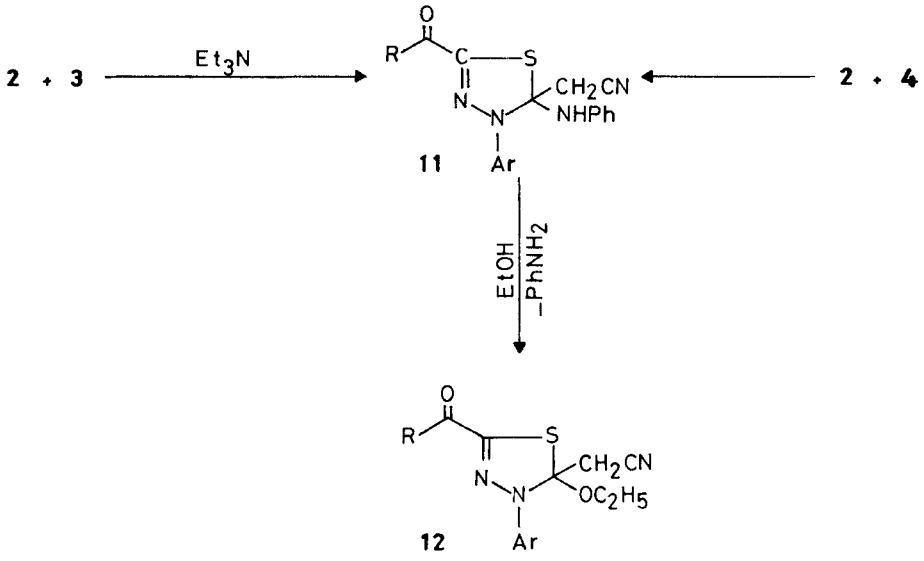
RESULTS AND DISCUSSION

It has been found that N-phenylcyanothioacetamide (2) reacted with the hydrazidoyl chloride **3a** in ethanolic triethylamine solution to afford two products (according to TLC). Elemental analyses indicated the products have molecular formulas $C_{20}H_{22}N_4SO_4$ and $C_{15}H_{17}N_3SO_3$, respectively. The mass spectra show the expected m/e 414 and m/e 319. The ^{1}H-NMR spectrum in $CDCl_3$ of the first product contains four signals at δ 1.3 (t, 6H, two $CH_2\underline{CH_3}$); δ 4.3 (q, 4H, $\underline{CH_2}CH_3$); δ 7.1–

7.4 (m, 10H, ArH's) and δ 10.2 (s, br., 2H, two NH) ppm. The IR spectra of this product revealed bands at 3250 (NH), 1690 (CO) and 1600 (C=C) cm^{-1}. On the basis of the above data, the product was assigned structure **10a**. Unequivocal support of the structure **10a** was achieved by its independent synthesis through the reaction of hydrazidoyl chloride **3a** with cyanothioacetamide.[7] The initial step is believed to be the formation of a mixed hydrazidoyl imidoyl sulfide **6** which may arise either by displacement of hydrazidoyl halogen atom by thioamide anion or by thioamide itself (to give a protonated form of mixed sulfide), or the addition of nitrilimine **4a**, formed in situ by dehydrohalogenation of **3a**, to the thiol form of the thioamide, analogous to the reaction of nitrilimine with thiophenols.[8,9] Reaction between the hydrazidoyl halide or nitrilimine and the mixed sulfide, gave rise to the 1,2,4-triazolium ion **7** and thiohydrazide anion **8**. The latter may react further with hydrazidoyl halide to produce the hydrazidoyl sulfide **10a** (cf. Scheme 1). This reaction is analogous to the reaction of hydrazidoyl halides with the secondary thioamides,[4] and the formation of 1,2,4-triazolines from nitrilimine and various Schiff's base.[8,9] The ^{1}H-NMR spectrum of the second product in $CDCl_3$ contains six signals at δ 1.3 (t, 3H, $CH_2\underline{CH_3}$); δ 1.4 (t, 3H, $CH_2\underline{CH_3}$); δ 2.2 (s, 2H, $\underline{CH_2}CN$); δ 4.2 (q, 2H, $\underline{CH_2}CH_3$); δ 4.4 (q, 2H, $\underline{CH_2}CH_3$) and δ 7.4–7.8 (m, 5H, ArH's) ppm. The IR spectrum revealed bands at 2200 (CN), 1715 (CO) and 1600 (C=C) cm^{-1}. From the above data and elemental analysis, the product was assigned structure **12a**. The formation of **12a** is assumed to proceed via ring closure



SCHEME 1



SCHEME 2

TABLE I

Characterization of the newly synthesized derivatives

Comp.	Colour (Solvent)	M.P. °C	Yield %	Mol. formula (m/e)	% Analysis Calcd./found C	H	N	S
5b	Brown	142	80	$C_{12}H_{10}N_4S$	59.48	4.16	23.12	13.2
	(AcOH)				59.60	4.00	23.30	13.4
5c	Brown	155	71	$C_{13}H_{12}N_4S$	60.91	4.71	21.85	12.5
	(AcOH)				61.10	4.80	21.60	12.3
5d	Brown	168	69	$C_{12}H_9ClN_4S$	46.16	2.90	17.94	10.3
					46.30	3.10	17.80	10.4
10a	Yellow	135[7]	85	$C_{20}H_{22}N_4SO_4$	57.95	5.35	13.51	7.73
	(EtOH)			(414)	58.20	5.20	13.60	7.50
10b	Yellow	170	70	$C_{22}H_{26}N_4SO_4$	59.71	5.92	12.66	7.24
	(AcOH)			(442)	59.50	6.10	12.50	7.30
10c	Yellow	183	75	$C_{20}H_{20}Cl_2N_4SO_4$	49.69	4.17	11.59	6.63
	(AcOH)			(483)	50.00	4.10	11.70	6.70
10d	Yellow	227[7]	82	$C_{28}H_{24}N_6SO_2$	66.12	4.75	16.52	6.30
	(DMF)			(508)	66.30	4.70	16.70	6.10
10e	Yellow	205	83	$C_{30}H_{28}N_6SO_2$	67.14	5.25	15.66	5.97
	(dioxan)			(536)	67.30	5.10	15.30	6.20
10f	Yellow	205	86	$C_{28}H_{22}N_4SO_2$	70.27	4.63	11.70	6.69
	(AcOH)			(478)	70.20	4.70	11.90	6.50
10g	Yellow	236	77	$C_{18}H_{18}N_4SO_2$	61.00	5.11	15.80	9.04
	(EtOH)			(354)	60.80	5.20	16.00	8.80
10h	Yellow	215	74	$C_{20}H_{22}N_4SO_2$	62.80	5.79	14.64	8.38
	(EtOH)			(382)	62.60	5.80	14.30	8.40
10i	Yellow	208	68	$C_{18}H_{16}Cl_2N_4SO_2$	51.10	3.80	13.23	7.57
	(EtOH)			(423)	51.30	3.70	13.40	7.30
12a	Yellow	196	66	$C_{15}H_{17}N_3SO_3$	56.41	5.36	13.15	10.0
	(EtOH)			(319)	56.20	5.20	13.00	9.90
12b	Yellow	175	62	$C_{16}H_{19}N_3SO_3$	57.64	5.74	12.60	9.61
	(EtOH)			(333)	57.80	5.90	12.50	9.40

TABLE I (*Continued*)

Comp.	Colour (Solvent)	M.P. °C	Yield %	Mol. formula (m/e)	% Analysis Calcd./found C	H	N	S
12c	Yellow	185	71	$C_{15}H_{16}ClN_3SO_3$	50.91	4.55	11.82	9.06
	(AcOH)				51.10	4.40	12.00	8.80
12d	Yellow	296	65	$C_{19}H_{18}N_4SO_2$	62.27	4.95	15.29	8.75
	(AcOH)			(366)	62.30	5.10	15.40	8.70
12e	Orange	273	50	$C_{20}H_{20}N_4SO_2$	63.14	5.30	14.72	8.42
	(EtOH)			(380)	63.20	5.20	14.60	8.30
12f	Yellow	175	74	$C_{19}H_{17}N_3SO_2$	64.94	4.87	11.95	9.12
	(AcOH)			(351)	65.10	4.70	12.10	9.30
12g	Yellow	236	72	$C_{14}H_{15}N_3SO_2$	58.11	5.22	14.52	11.0
	(AcOH)			(289)	58.40	5.10	14.70	10.8
12h	Yellow	215	63	$C_{15}H_{17}N_3SO_2$	59.38	5.64	13.85	10.6
	(AcOH)			(303)	59.50	5.60	13.70	10.3
12i	Yellow	208	70	$C_{14}H_{14}ClN_3SO_2$	51.93	4.35	12.97	9.90
	(AcOH)			(323)	51.70	4.50	13.20	10.5
13a	Brown	177	62	$C_{18}H_{14}N_6S$	62.41	4.07	24.26	9.25
	(DMF)				62.20	4.20	24.40	9.40
13b	Brown	185	74	$C_{19}H_{16}N_6S$	63.31	4.47	23.31	8.89
	(DMF)				63.20	4.60	23.30	9.10
13c	Brown	205	77	$C_{18}H_{13}ClN_6S$	56.77	3.44	22.06	8.41
	(dioxan)				56.80	3.50	22.20	8.30
14a	Brown	188	75	$C_{15}H_{13}N_3SO_2$	65.69	3.77	12.09	9.22
	(DMF)				65.70	3.90	12.20	9.50
14b	Brown	235	79	$C_{20}H_{15}N_3SO_2$	66.46	4.18	11.62	8.87
	(DMF)				66.50	3.90	11.40	9.10
14c	Brown	208	80	$C_{15}H_{12}ClN_3SO_2$	59.76	3.16	11.01	8.39
	(AcOH)				59.81	3.00	10.96	8.20

of **6** or addition of the C=S of the thioamide to nitrolimine to give 5-anilino-1,3,4-thiadiazolins **11**, which upon alcoholysis produces the corresponding 5-alkoxy-1,3,4-thiadiazolines **12** (cf. Scheme 2). A similar treatment of the appropriate **3b–i** with **2** in ethanolic triethylamine solution at room temperature afforded the products **10b–i** and **12b–i**, respectively.

Cyanothioacetamide (1) reacted with hydrazidoyl chlorides **3b**, **c** and **3e** in ethanolic triethylamine to give hydrazidoyl sulfides **10b**, **c** and **10e**, respectively. The formation of **10** in this reaction is assumed to proceed via the formation of the mixed sulfide **6** (NPh=NH) which cleaved under the applied condition to give malononitrile and the thiohydrazide **8**. Compound **8** reacted readily with hydrazidoyl halide **3b**, **c**, and **3e** to give the final isolable product **10b**, **c** and **10e**, respectively (cf. Scheme 1, Tables I and II).

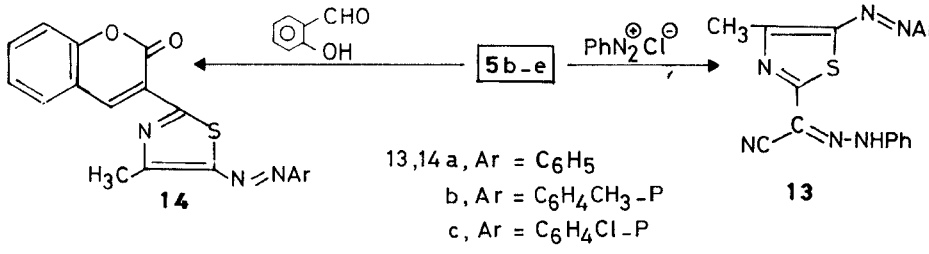
The hydrazidoyl bromides **3f–i** reacted also with α-cyanothioacetamide (1) in ethanolic triethylamine solution to give the thiazole derivatives **5a–d**. The reaction takes place by losing one molecule of water from intermediate **6** (NPH=NH, Scheme 1). The structure was confirmed by elemental analyses and spectral data (cf. Tables I and II). Compound **5b–c** reacted with benzenediazonium chloride in pyridine solution at 0–5°C to give the corresponding hydrazones **13a–c**. Thiazoles **5** are easily converted into the 3-thiazolylcoumarin derivatives **14a–c** by boiling with salicylaldehyde in ethanolic sodium ethozide solution. The

TABLE II
IR and ^{1}H-NMR spectral data

Comp.	IR [cm^{-1}]	^{1}H-NMR [δ ppm]
5b	2220(CN), 1630(C=N), 1600 (C=C)	2.4(s,3H,$\underline{CH_3}$); 3.29(s, 2H,$\underline{CH_2}$CN) and 6.9-8.1(m,5H,ArH's).
5c	2220(CN), 1620(C=N), 1600 (C=C)	2.2(s,3H,$C_6H_4\underline{CH_3}$-p);2.4(s,3H,$\underline{CH_3}$) 3.2(s,2H,$\underline{CH_2}$CN) and 6.9-7.8(m,4H, ArH,s).
5d	2220(CN), 1620(C=N), 1600 (C=C)	2.4(s,3H,$\underline{CH_3}$);3.3(s,2H,$\underline{CH_2}$CN) and 6.8-7.9(m,4H,ArH's).
10a	3250(NH), 1690(CO), 1630 (C=N) and 1600(C=C)	1.3(t,6H,two $CH_2\underline{CH_3}$);4.3(q,4H,two $\underline{CH_2}CH_3$);7.1-7.4(m,10H,ArH's) and 10.2(s,br.,2H,two NH).
10b	3250(NH), 1685(CO), 1620 (C=N) and 1600(C=C)	1.3(t,6H,two $CH_2\underline{CH_3}$);2.4(s,6H,two C_6H_4-$\underline{CH_3}$-p);4.3(q,4H,two $\underline{CH_2}CH_3$); 7.1-7.4(m,8H,ArH's) and 10.1(s,br 2H,two NH).
10c	3270(NH), 1690(CO), 1630 (C=N) and 1600(C=C)	1.3(t,6H,two $CH_2\underline{CH_3}$);4.3(q,4H,two $\underline{CH_2}CH_3$);7.1-7.5(m,8H,ArH's) and 10.2(s,br.,two NH).
10d	3380(NH), 1670(CO), 1620 (C=N) and 1600(C=C)	7.1-7.8(m,20H,ArH's);10.2(s,br., 2H,two NH) and 11.8(s,br.,2H,two NH).
10e	3360(NH), 1670(CO), 1620 (C=N) and 1600(C=C).	2.4(s,6H,two C_6H_4-$\underline{CH_3}$-p);7.1-7.8 (m,18H,ArH's);10.2(s,br.,two NH) and 11.7(s,br.,two NH).
10f	3350(NH), 1660(CO), 1620	7.2-7.8(m,20H,ArH's) and 11.4(s, br.,two NH).
10g	33350(NH), 1650(CO), 1610 (C=N) and 1600(C=C)	2.4(s,6H,$\underline{CH_3}$CO), 7.1-7.6(m,10H, ArH's) and 11.2(s,br.,2H,two NH).
10h	3350(NH), 1650(CO), 1620 (C=N) and 1600(C=C)	2.3(s,6H,C_6H_3-$\underline{CH_3}$-p), 2.4(s, 6H, $\underline{CH_3}$CO);7.1-7.5(m,8H,ArH's) and 11.3(s,br.,2H,two NH).
10i	3360(NH), 1650(CO), 1610 (C=N) and 1600(C=C)	2.4(s, 6H,$\underline{CH_3}$CO);7.1-7.5(m ,8H, ArH's) and 11.4(s,br.,2H,two NH).
12a	2220(CN), 1715(CO), 1630 (C=N) and 1600(c=C).	1.3(t,3H,$CH_2\underline{CH_3}$);1.4(t,3H,$CH_2\underline{CH_3}$) 2.2(s,2H,$\underline{CH_2}$CN);4.2(q,2H,$\underline{CH_2}CH_3$); 4.4(q,2H,$\underline{CH_2}CH_3$) and 7.4-7.8(m,5H ArH's).
12b	2220(CN), 1715(CO), 1620 (C=N) and 1600(C=C)	1.3(t.3H,$CH_2\underline{CH_3}$);1.4(t,3H,$CH_2\underline{CH_3}$) 2.2(s,2H,$\underline{CH_2}$CN);2.4(s,3H,C_6H_4-$\underline{CH_3}$ -p);4.2(q,2H.$\underline{CH_2}CH_3$);4.4(q,2H,$\underline{CH_2}$ CH_3) and 7.3-7.6(m,4H,ArH's).
12c	2220(CN), 1715(CO), 1620 (C=N) and 1600(C=C)	1.3(t,3H,$CH_2\underline{CH_3}$);1.4(t,3H,$CH_2\underline{CH_3}$) 2.2(s,2H,$\underline{CH_2}$CN);4.2(q,2H,$\underline{CH_2}CH_3$) 4.4(q,2H,$\underline{CH_2}CH_3$) and 7.4-7.8(m,4 H,ArH's).
12d	3350(NH), 2220(CN), 1690	1.3(t,3H,$CH_2\underline{CH_3}$);2.2(s,2H,$\underline{CH_2}$CN);

TABLE II (*Continued*)

Comp.	IR [cm^{-1}]	^{1}H-NMR [δ ppm]
	(CO),1630(C=N) and 1600 (C=C)	4.2(q,2H,$\underline{CH_2}CH_3$) and 7.2-7.9(m, 11H,ArH's and NH).
12e	3340(NH), 2220(CN), 1680 (CO), 1620(C=N) and 1600 (C=C).	1.3(t,3H,$\underline{CH_2}CH_3$);2.2(s,2H,$\underline{CH_2}CN$) 2.4(s,3H,$C_6H_4\underline{CH_3}$-p);4.2(q,2H,$\underline{CH_2}$ CH_3) and 7.1-8.0(m,10H,ArH's and NH).
12f	2220(CN), 1660(CO), 1620 (C=N) and 1600 (C=C)	1.3(t,3H,$CH_2\underline{CH_3}$);2.4(s,2H,$\underline{CH_2}CN$) 4.4(q,2H,$\underline{CH_2}CH_3$) and 7.8-8.0(m, 10H,ArH's).
12g	2220(CN), 1660(CO), 1620 (C=N) and 1600(C=C)	1.3(t,3H,$CH_2\underline{CH_3}$),2.3(s,2H,$\underline{CH_2}CN$) 2.4(s,3H,$\underline{CH_3}CO$);4.3(q,2H,$\underline{CH_2}CH_3$) and 7.1-7.5(m,5H,ArH's).
12h	2220(CN), 1650(CO), 1620 (C=N) and 1600(C=C)	1.3(t,3H,$CH_2\underline{CH_3}$);2.2(s,2H,$\underline{CH_2}CN$) 2.3(s,3H,$\underline{CH_3}CO$);2.4(s,3H,$C_6H_4\underline{CH_3}$-P);4.2(q,2H,$\underline{CH_2}CH_3$) and 7.2-7.5 (m,4H,ArH's).
12i	2210(CN), 1650(CO), 1610 (C=N) and 1600(C=C)	1.3(t,3H,$CH_2\underline{CH_3}$);2.2(s,2H,$\underline{CH_2}CN$) 2.3(s,3H,$\underline{CH_3}CO$);4.3(q,2H,$\underline{CH_2}CH_3$) and 6.9-8.1(m,4H,ArH's).
13a	3350(NH), 2220(CN), 1620 (C=N) and 1600(C=C)	2.2(s,3H,$\underline{CH_3}$);6.8-7.8(m,10H,ArH's and 9.6(1H,NH).
13b	3300(NH), 2220(CN), 1620 (C=N) and 1600(C=C)	2.1(s,3H,$\underline{CH_3}$);2.4(s,3H,$C_6H_4\underline{CH_3}$-p) 6.9-8.0(m,9H,ArH's) and 9.7(s,br. 1H,NH).
13c	3400(NH), 2220(CN), 1620 (C=N) and 1600 (C=C)	2.2(s,3H,$\underline{CH_3}$);6.8(m,9H,ArH's) and 9.6(s,br.,1H,NH).
14a	1680(CO), 1620(C=N) and 1600(C=C)	2.2(S,3H,$\underline{CH_3}$) and 6.8-8.2(m,10H, ArH's).
14b	1690(CO), 1620(C=N) and 1600(C=C)	2.2(s,3H,$\underline{CH_3}$);2.4(s,3H,$C_6H_4\underline{CH_3}$-p) and 6.9-8.2(m,9H,ArH's).
14c	1670(CO), 1620(C=N) and 1600(C=C)	2.1(s,3H,$\underline{CH_3}$) and 6.7-7.9(m,9H, ArH's).



SCHEME 3

structures of the newly synthesized derivatives were established on the basis of elemental analyses and spectral data (cf. Scheme 3 and Tables I and II).

EXPERIMENTAL

Melting points are uncorrected. IR spectra were recorded (KBr) on a Pye-Unicam SP-1100 spectrophotometer. ^{1}H-NMR spectra were obtained in $CDCl_3$ or DMSO-d_6 on IBM NR 200 AF spectrometer, with $(CH_3)_4Si$ as internal reference and chemical shift are expressed as δ ppm. The mass spectra were taken on a Du Part 491 mass spectrometer. Elemental analyses were performed by the Microanalytical Centre of Cairo University. N-Phenylcyanothioacetamide **2**,[12] 2-chloro-2-ethylglyoxalate-2-arylhydrazones **3a–c**,[13] phenylcarbamoylhydrazonyl chlorides **3d, e**,[14] 2-bromophenylglyoxal-2-arylhydrazone **3f**[15] and 2-chloromethylglyoxal-2-arylhydrazones **3g–i**[16] were prepared according to literature procedures.

Reaction of hydrazidoyl halides **3a–f** *with N-phenylcyanothioacetamide (2)*: General procedure. The appropriate hydrazidoyl halide **3a–f** (0.005 mol) was added to a solution of **2** (0.88 g, 0.005 mol) in absolute ethanol (20 ml). The reaction mixture was warmed to 40°C. Triethylamine (0.5 ml, 0.005 mol) was then added dropwise to the above mixture with stirring and the reaction mixture was allowed to stand at room temperature for 15 min. The solid was collected by filtration, washed with water, dried and then recrystallized from an appropriate solvent to give the corresponding hydrazidoyl sulfides **10a–i**, respectively. The filtrate was diluted with water (20 ml) and the solid was collected and crystallized from the proper solvent to yield the corresponding 1,3,4-thiadiazolines **12a–i**, respectively (cf. Tables I and II).

Another method of hydrazidoyl sulfides **10a–e**. A solution of triethylamine (0.5 ml, 0.005 mol) was added dropwise to a stirred solution of the appropriate hydrazidoyl chlorides **3a–c**, **3a–b** (0.005 mol) and α-cyanothioacetamide (1) (0.5 g, 0.005 mol) in ethanol (20 ml) at room temperature. The reaction mixture was stirred for 30 min. The product separated was collected and crystallized from the proper solvent to give **10a–e** (cf. Tables I and II).

Synthesis of the 5-arylazo-4-methyl-2-thiazolylacetonitriles **5b–d**. A solution of 0.5 N sodium hydroxide (10 ml) was added dropwise to a stirred solution of the appropriate hydrazidoyl chlorides **3g–i** and α-cyanothioacetamide (1) (0.5 g, 0.005 mol) in ethanol (30 ml) at room temperature. The reaction mixture was stirred for 2 h. Then, diluted with water (100 ml). The solid, so formed, was collected and crystallized from dioxan or acetic acid to give **5b–d**, respectively (cf. Tables I and II).

Reaction of benzenediazonium chloride with compound **5b–d**. An aqueous solution of benzene diazonium chlorides (0.005 mol) was added dropwise to a stirred solution of the appropriate thiazoles **5a–d** (0.005 mol) in pyridine (30 ml) at 0–5°C. The reaction mixture was stirred for 3 h, and the solid collected, washed with water and crystallized from dioxan or acetic acid to give corresponding **13a–c**, respectively (cf. Tables I and II).

Synthesis of 3-thiazolyl coumarin **14a–c**. A mixture of the appropriate 5 (0.0005 mol) and salicylaldehyde (0.6 g, 0.005 mol) in absolute ethanol (35 ml) containing sodium ethoxide (0.005 mol) was refluxed for 4 h. The reaction mixture was cooled and then acidified with dilute hydrochloric acid. The solid, so formed, was collected and crystallized from the proper solvent to give **14a–c**, respectively (cf. Tables I and II).

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