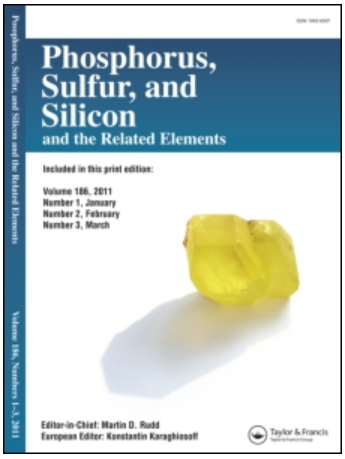

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REACTIONS WITH HYDRAZONOYL HALIDES XXIV[1]: SYNTHESIS OF SOME NEW UNSYMMETRICAL AZINES AND DIHYDRO-1,3,4-THIADIAZOLES

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REACTIONS WITH HYDRAZONOYL HALIDES XXIV[1]: SYNTHESIS OF SOME NEW UNSYMMETRICAL AZINES AND DIHYDRO-1,3,4-THIADIAZOLES

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(In final form January 25, 1999)

Unsymmetrical azines were synthesized from reaction of C-coumarinoyl-N-arylformohydrazonoyl bromide with different alkyl carbodithioates. In addition, reactions of hydrazonoyl halides with thioanilide and methyl dithioates were studied. The structures of newly synthesized compounds were confirmed by elemental analyses, spectroscopic tools, and alternative syntheses whenever possible.

Keywords: Hydrazonoyl halides; Unsymmetrical azines; Thiadiazolines; Alkyl dithioates; Thioanilides

Hydrazonoyl halides are versatile and have been extensively utilized in heterocyclic synthesis.[2–4] In continuation of our interest in the chemistry of hydrazonoyl halides,[5–10] we report herein their utility in the synthesis of unsymmetrical azines and 2,3-dihydro-1,3,4-thiadiazoles.

Thus, treatment of hydrazonoyl bromide **1** with methyl arylmethylenehydrazinecarbodithioate[11–13] **2a** in ethanolic triethylamine solution at room temperature gave readily the product **6a.** The structure of **6** was elucidated on the basis of elemental analyses and spectral data. The IR (cm^{-1}) spectrum of the product revealed no bands near 3500–3100 corresponding to an NH group. The ^1H NMR spectrum of **6a** showed signals at δ 7.21–8.01 (m, 15H, ArH's and CH=) and δ 8.31 (s, 1H, coumarin H-4). Based on the above data, the product was formulated as 5-coumarin-3′-oyl-3-phenyl-2-benzaldeydehydrazono-2,3-dihydro-1,3,4-thiadiazole (**6a**). The structure **6** was further confirmed by the reaction of

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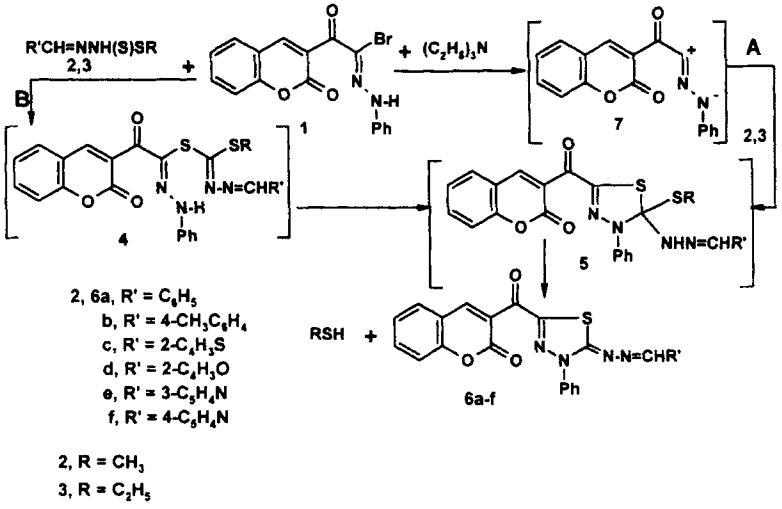
hydrazonoyl bromide **1** with ethyl arylmethylenehydrazinecarbodithioate **3a,** in ethanolic triethylamine solution to give a product identical in all respects (mp, mixed mp, and spectra) with **6a.** (cf. Scheme 1).



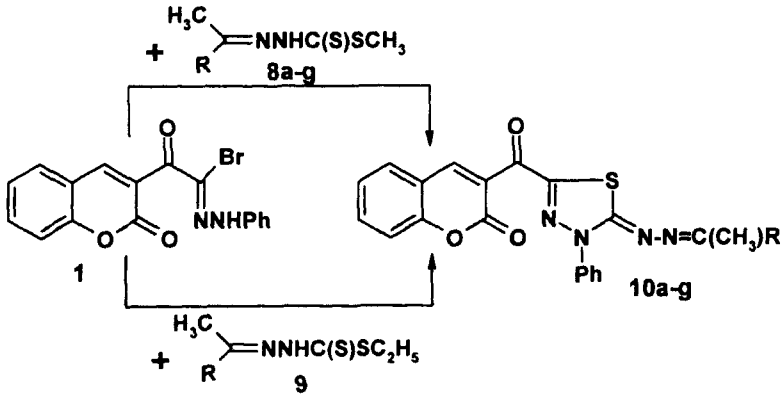
SCHEME 1

The formation of unsymmetrical azine **6** can be explained via elimination of methanethiol (or ethanethiol) from the cycloadduct **5,** which is assumed to be formed from 1,3-dipolar cycloaddition of nitrile imide **7** (generated in situ by treatment of **1** with triethylamine) to the CS double bond of the dithioate **2** (or **3**) (pathway A) or by its the stepwise path involving substitution to give a cyclic hydrazone **4** (pathway B), which spontaneously converts **5.** Cyclization of the latter is achieved by elimination of methanethiol (or ethanethiol) to yield the final product **6a.** All attempts to isolate either intermediate cycloadduct or open hydrazone were unsuccessful.

Similarly, unsymmetrical azines **6b-f** were obtained in a good yields via the reaction of hydrazonoyl bromide **1** with methyl arylmethylenehydrazinecarbodithioate **2b-f** or ethyl arylmethylenehydrazinecarbodithioate **3b-f** in ethanolic triethylamine solution at room temperature.

Moreover, the reactions of hydrazonoyl bromide **1** with methyl phenylmethylenehydrazinecarbodithioate (**8a**),[14] in ethanolic triethylamine,

afforded a product, which analyzed correctly for $C_{26}H_{18}N_4O_3S$. The structure of the product was inferred from its spectral data. Thus, ^1H NMR spectrum of the product showed signals at δ 2.39 (s, 3H, CH_3C=), δ 7.02–8.03 (m, 14H, ArH's), and δ 8.30 (s, 1H, coumarin H-4). The structure of the product was further confirmed by the reaction of ethyl phenylmethylenehydrazinecarbodithioate **9a**[115] with coumarinoylhydrazonoyl bromide **1** in ethanolic triethylamine solution at room temperature, and afforded a product identical in all respects (mp, mixed mp, and spectra) with above sample obtained (cf. Scheme 2). Based on the above results, the product formulated as 2-acetophenonehydrazone-5-coumarin-3′-oyl-3-phenyl-2,3-dihydro-1,3,4-thiadiazole (**10a**).



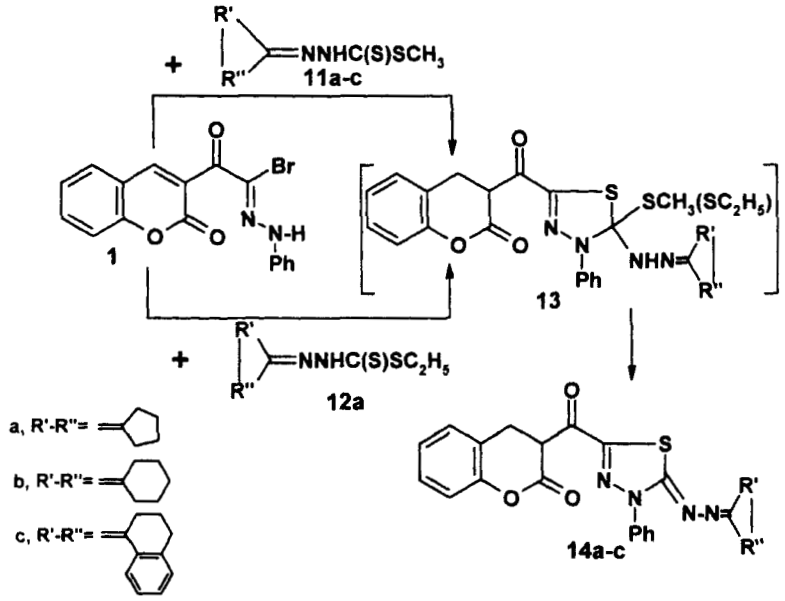
8, 10a, R = C_6H_5 **8, 10 e**, R = 2-C_4H_3O
b, R = 4-$CH_3C_6H_4$ **f**, R = 2-C_6H_4N
c, R = 4-ClC_6H_4 **g**, R = 3-C_6H_4N
d, R = 2-C_4H_3S

SCHEME 2

Similarly, the carbodithioate derivatives **8b-g** or **9b-g** reacted with hydrazonoyl **1** in ethanolic triethylamine to give the corresponding 2,3-dihydro-1,3,4-thidiazoles **10b-g,** respectively (cf. Scheme 2).

The hydrazonoyl bromide **1** also reacted with dithioate **11a** in ethanolic triethylamine to afford a yellow solid, which analyzed for these formula $C_{23}H_{18}N_4O_3S$. ^1H NMR showed signals at δ 1.81 (m, 4H, $2CH_2$), 2.52(t, 4H, $2CH_2$), δ 7.21–7.97 (m, 9H, ArH's), and δ 8.31 (s, 1H, coumarin H-4).

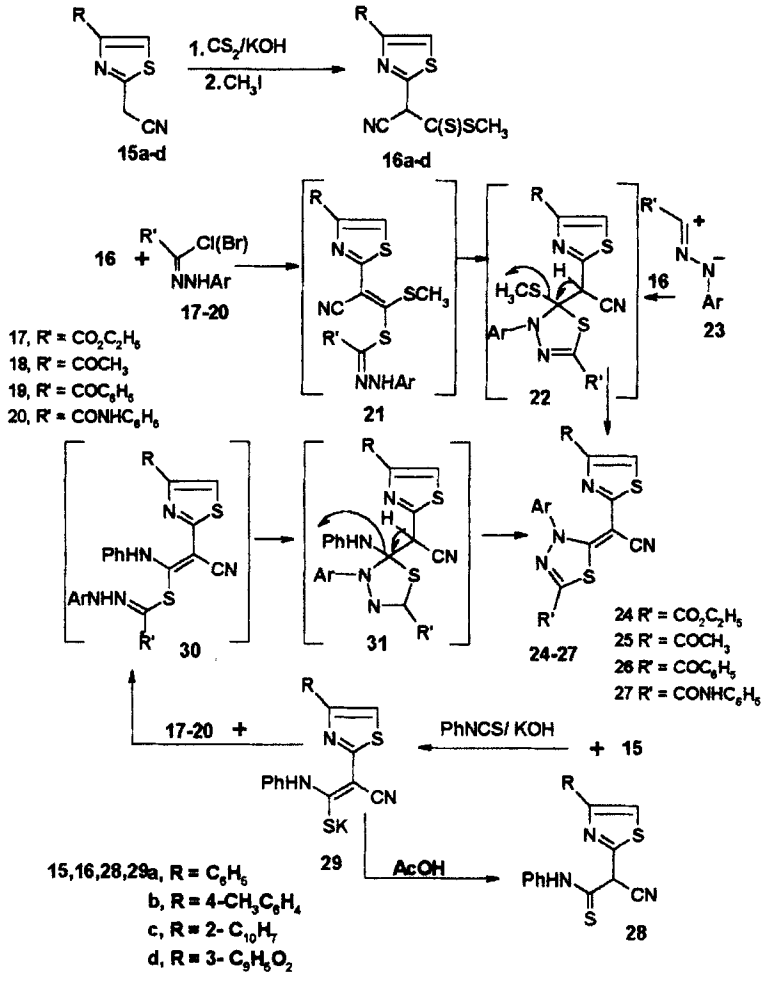
The structure of the product was further confirmed by the reaction of **1** with dithioate **12a** which gave a product identical in all respects (mp, mixed mp, and spectra) with that prepared before. Based on the above data, the product was formulated as 2-cyclopentylhydrazono-5-coumarin-3′-oyl-3-phenyl-2,3-dihydro-1,3,4-thiadiazole (**14a**) (cf. Scheme 3).



SCHEME 3

Similarly, dithioate **11b,c** reacted with hydrazonoyl bromide **1** in ethanolic solution to give 2,3-dihydro-1,3,4-thiadiazoles **14b** and **14c,** respectively.

Treatment of methyl 1-cyano-1-(4′-phenyl)thiazol-2′-ylethanedithioate (**16**) with the appropriate hydrazonoyl halides[16–19] **17–20** in ethanolic triethylamine (or in N,N-dimethylformamide containing triethylamine) afforded one product according TLC. Thus, C-ethoxycarbonyl-N-phenylhydrazonoyl chloride (**17a**) reacted with **16a** to give a product with signals at δ 1.49 (t, 3H, CH_3CH_2O), δ 4.57 (q, 2H, CH_3CH_2O), δ 7.34–7.68 (m, 10H, ArH's) and δ 8.65 (s, 1H, thiazole H-5) in the ^1H NMR spectrum. The IR spectrum revealed bands at 2191 (CN) and 1735 (CO ester) cm^{-1}.



	R	Ar		R	Ar
24-27 a,	C_6H_5	C_6H_5	24-27 e,	$CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$
b,	C_6H_5	$4\text{-}CH_3C_6H_4$	f,	$CH_3C_6H_4$	$4\text{-}ClC_6H_4$
c,	C_6H_5	$4\text{-}ClC_6H_4$	g,	$2\text{-}C_{10}H_7$	C_6H_5
d,	$CH_3C_6H_4$	C_6H_5	h,	$3\text{-}C_9H_6O_2$	C_6H_5

SCHEME 4

Based on the above results, the structure was formulated as 2,3-dihydro-1,3,4-thiadiazole derivative **24a.** The structure **24** was further confirmed by the reaction of hydrazonoyl chloride **17a** with the potassium salt of 1-(4′-phenyl)thiazol-2′-ylcyanothioacetanilide (**29a**) in N,N-dimethylformamide, and afforded an identical product in all respects (mp, mixed mp, and spectra) with **24a** (cf. Scheme 4). The formation of the product **24a** can be explained via elimination of methanethiol from the cycloadduct of nitrile imide **23a** (which is generated in situ by treatment of hydrazonoyl chloride **17a** with triethylamine) to the CS double bond of dithioate **16a** or by a stepwise path involving substitution to give a cyclic hydrazone **21a,** which was converted to cyclic intermediate **22a.** Elimination of methanethiol from **22a** gave the final product **24a.** On the other hand, one molecule of the potassium salt of thioanilide **29a** could react with one molecule of the hydrazonoyl chloride **17a** to form intermediate **30a**, which would be readily converted to another cyclized intermediate **31.** The latter would lose one molecule of aniline to give the final product **24a.**

Similarly, the reaction of the appropriate **16a-d** with the appropriate hydrazonoyl halides **17–20** in the presence of a base, such as triethylamine or potassium hydroxide, gave the 2,3-dihydro-1,3,4-thiadiazoles **24–27,** respectively, in a good yields.

EXPERIMENTAL

All melting points were determined on a Electrothermal apparatus and are uncorrected. IR spectra were recorded (KBr discs) on a Shimadzu FT-IR 8201 PC spectrophotometer. ^{1}H NMR spectra were recorded in $CDCl_3$ and $(CD_3)_2SO$ on a Varian Gemini 200 MHz spectrometer, and chemical shifts were expressed in δ units using TMS as internal reference. Elemental analyses were carried out at the Microanalytical Center of the University of Cairo, Giza, Egypt.

Synthesis of 2,3-dihydro-1,3,4-thiadiazoles 6, 10 and 14

General Procedure

To a solution of the appropriate dithiocarbazate **2a-f** (or **3**), **8a-g** (or **9**), **11a-c** (or **12**), and hydrazonoyl bromide **1** (5 mmol each) in ethanol

(20 ml) was added triethylamine (0.7 ml, 5 mmol), at room temperature with stirring. Stirring was continued for 2 hr, and the solid which formed was collected, washed with water, and crystallized from acetic acid to give **6a-g, 10a-g** and **14a-c,** respectively, in 80–85% yields (cf. Tables I & II).

TABLE I Characterization data of the newly synthesized compounds

			% Analyses, Calcd./Found			
Compd no.	*M.P. °C/colour*	*Mol.Formula/Mol.Wt.*	*C*	*H*	*N*	*S*
6a	203–5	$C_{25}H_{16}N_4O_3S^a$	66.36	3.56	12.38	7.09
	Orange	452.50	66.20	3.60	12.30	7.00
6b	196–8	$C_{26}H_{18}N_4O_3S^a$	66.94	3.89	12.01	6.87
	Yellow	466.52	66.80	3.90	12.00	6.80
6c	202–4	$C_{23}H_{14}N_4O_3S_2{}^a$	60.25	3.08	12.22	13.99
	Red	458.53	60.10	3.20	12.30	13.80
6d	193–5	$C_{23}H_{14}N_4O_4S^a$	62.44	3.19	12.66	7.25
	Brown	442.46	62.40	3.20	12.60	7.20
6e	199–200	$C_{24}H_{15}N_5O_3S^a$	63.57	3.33	15.44	7.07
	Brown	453.49	63.60	3.30	15.40	7.00
6f	206–8	$C_{24}H_{15}N_5O_3S^e$	63.57	3.33	15.44	7.07
	Red	453.49	63.50	3.40	15.40	7.10
10a	193–5	$C_{26}H_{18}N_4O_3S^a$	66.94	3.88	12.01	6.87
	Orange	466.52	66.90	3.90	12.10	6.80
10b	226–8	$C_{27}H_{20}N_4O_3S^a$	67.49	4.20	11.66	6.67
	Red	480.55	67.40	4.10	11.70	6.60
11c	236–8	$C_{26}H_{17}Cl\ N_4O_3S^a$	62.34	3.42	11.18	6.40
	Orange	500.97	62.20	3.30	11.20	6.40
10d	180–1	$C_{24}H_{16}N_4O_3S_2{}^d$	61.00	3.41	11.86	13.57
	Yellow	472.55	61.10	3.40	11.80	13.60
10e	196–8	$C_{24}H_{16}N_4O_4S^a$	63.15	3.53	12.27	7.02
	Red	456.48	63.10	3.60	12.10	7.10
10f	243–5	$C_{25}H_{17}N_5O_3S^a$	64.23	3.67	14.98	6.86

Compd no.	M.P. °C/colour	Mol.Formula/Mol.Wt.	% Analyses, Calcd./Found C	H	N	S
	Orange	467.51	64.30	3.60	14.90	6.80
10g	216–8	$C_{25}H_{17}N_5O_3S$[a]	64.22	3.66	14.98	6.85
	Orange	467.51	64.20	3.60	14.90	6.70
14a	228–30	$C_{23}H_{18}N_4O_3S$[a]	64.17	4.21	13.01	7.45
	Orange	430.49	64.20	4.30	13.00	7.40
14b	178–9	$C_{24}H_{20}N_4O_3S$[a]	64.85	4.54	12.60	7.21
	Red	444.52	64.70	4.50	12.70	7.20
14c	225–7	$C_{28}H_{20}N_4O_3S$[a]	68.28	4.09	11.37	6.51
	Yellow	492.56	68.20	4.20	11.40	6.40
16a	248–50	$C_{13}H_{10}N_2S_3$[c]	53.76	3.47	9.65	33.12
	Orange	290.43	53.60	3.50	9.50	33.00
16b	253–5	$C_{14}H_{12}N_2S_3$[c]	55.23	3.97	9.20	31.59
	Orange	304.46	55.10	3.90	9.30	31.70
16c	248–50	$C_{17}H_{12}N_2S_3$	59.97	3.55	8.23	28.25
	Orange	340.49	59.60	3.40	8.00	28.40
16d	312–3	$C_{16}H_{10}N_2O_2S_3$[c]	53.61	2.81	7.81	26.83
	Orange	358.46	53.50	2.80	7.70	26.80
24a	248–50	$C_{22}H_{16}N_4O_2S_2$[a]	61.09	3.73	12.95	14.83
	Yellow	432.53	60.80	3.50	12.80	14.50
24b	275–7	$C_{23}H_{18}N_4O_2S_2$[a]	61.86	4.06	12.55	14.36
	Greenish yellow	446.55	61.80	4.20	12.50	14.20
24c	293–5	$C_{22}H_{15}ClN_4O2S_2$[c]	56.59	3.23	12.00	13.73
	Yellow	466.98	56.50	3.30	11.90	13.60
24d	285–7	$C_{23}H_{18}N_4O_2S_2$[c]	61.86	4.06	12.54	14.36
	Orange	446.67	61.70	4.20	12.50	14.30
24f	263–5	$C_{23}H_{17}ClN_4O_2S_2$[c]	57.43	3.56	11.65	13.33
	Orange	481.01	57.40	3.50	11.50	13.30
24g	271–4	$C_{26}H_{18}N_4O_2S_2$[a]	64.71	3.76	11.61	13.29

			% Analyses, Calcd./Found			
Compd no.	*M.P. °C/colour*	*Mol.Formula/Mol.Wt.*	*C*	*H*	*N*	*S*
	Yellow	482.59	64.50	3.60	11.80	13.40
24h	280–2	$C_{25}H_{16}N_4O_4S_2$[c]	59.99	3.22	11.19	12.81
	Yellow	500.56	59.90	3.40	11.20	12.70
25a	319–20	$C_{21}H_{14}N_4OS_2$	62.67	3.51	13.92	15.93
	Orange	(402.50)	62.60	3.60	14.10	15.80
25b	283–5	$C_{22}H_{16}N_4OS_2$[c]	63.44	3.87	13.45	15.40
	Orange	416.53	63.40	3.80	13.30	15.40
25c	278–80	$C_{21}H_{13}ClN_4OS_2$[c]	57.72	3.00	12.82	14.67
	Orange	436.94	57.60	2.90	12.70	14.50
25d	238–40	$C_{22}H_{16}N_4OS_2$[c]	63.44	3.87	13.45	15.40
	Orange	416.53	63.40	3.80	13.30	15.50
25e	268–70	$C_{23}H_{18}N_4OS_2$[c]	64.16	4.21	13.01	14.89
	Brown	430.55	64.10	4.10	13.00	14.90
25f	236–8	$C_{22}H_{15}ClN_4OS_2$[c]	58.59	3.35	12.42	14.22
	Orange	450.97	58.30	3.20	12.60	14.10
25g	290–1	$C_{25}H_{16}N_4OS_2$[a]	66.35	3.56	12.38	14.17
	Orange	452.52	66.40	3.60	12.50	14.30
25h	308–10	$C_{24}H_{14}N_4O_3S_2$[c]	61.26	3.00	11.90	13.63
	Orange	470.53	61.20	2.90	11.80	13.70
26a	239–41	$C_{26}H_{16}N_4OS_2$[a]	67.22	3.47	12.06	13.80
	Yellow	464.57	66.90	3.20	11.90	13.60
26c	220–2	$C_{26}H_{15}ClN_4OS_2$[a]	62.58	3.03	11.23	12.85
	Orange	(499.02)	62.70	2.90	11.40	12.70
26d	289–90	$C_{27}H_{18}N_4OS_2$[a]	67.76	3.79	11.70	13.40
	Orange	478.60	67.60	3.60	11.50	13.20
26e	295–7	$C_{28}H_{20}N_4OS_2$[c]	68.27	4.09	11.37	13.02
	Red	492.63	68.20	4.20	11.30	13.00
26f	285–7	$C_{27}H_{17}ClN_4OS_2$[c]	63.21	3.34	10.92	12.50

			% Analyses, Calcd./Found			
Compd no.	*M.P. °C/colour*	*Mol.Formula/Mol.Wt.*	*C*	*H*	*N*	*S*
	Orange	513.04	63.20	3.20	10.80	12.60
26g	241–3	$C_{30}H_{18}N_4OS_2$[a]	70.02	3.52	10.89	12.46
	Red	514.63	70.10	3.30	10.70	12.60
26h	308–10	$C_{29}H_{16}N_4O_3S_2$[c]	65.40	3.02	10.52	12.04
	Red	532.60	65.40	3.00	10.70	11.90
27a	281–2	$C_{26}H_{17}N_5OS_2$[a]	65.12	3.57	14.60	13.37
	Orange	479.59	65.00	3.40	14.40	13.20
27g	269–71	$C_{30}H_{19}N_5OS_2$[a]	68.03	3.61	13.22	12.11 1
	Orange	529.60	68.10	3.80	13.10	11.90
28b	212–4	$C_{19}H_{15}N_3S_2$[c/e]	65.30	4.33	12.02	18.35
	Golden	349.48	65.20	4.40	12.10	18.20
29b	312–15	$C_{19}H_{14}N_3S_2K$	58.88	3.64	10.84	16.54
	Page	387.57	58.70	3.40	10.90	16.40

Crystallization Solvents: a = Acetic acid; b = Benzene; c = N,N-dimethylformamide; d = Dioxane; e = ethanol.

Synthesis of 2-cyanomethylthiazole 15d

Equimolar amounts of 3-(ω-bromoacetyl)coumarin[20] and cyanothioacetamide (0.1 mol) in ethanol (50 ml) were refluxed for 30 minutes. The reaction mixture was cooled, and then poured onto ice cold water containing two drops of ammonium hydroxide (100 ml). The solid was collected and crystallized from ethanol to give thiazole **15d,** in 60 % yield.

Synthesis of methyl 1-cyano-1-(4′-substituted)thiazol-2′-ylethanedithioate 16a-d

A mixture of the appropriate 2-cyanomethylthiazoles **15a-d,** carbon disulfide, and potassium hydroxide (5 mmol) in N,N-dimethylformamide (15 ml) was stirred at room temperature for 2 hr. (or until the potassium hydroxide dissolved), and then methyl iodide (0.005 mol, 0.35 ml) was

added dropwise with stirring. Stirring was continued for 30 minutes, and the solid formed was collected and crystallized from acetic acid to give **16a-d** in 70–74% yields, respectively (cf. Tables I & II).

Synthesis of 2,3-dihydro-1,3,4-thidiazoles 24–27

Method (A)

A mixture of the appropriate 2-cyanomethylthiazoles **15a-d,** potassium hydroxide and carbon disulfide (5 mmol) in N,N-dimethylformamide (20 ml) was stirred at room temperature for 3 hr and methyl iodide (0.32 ml) was added. The appropriate hydrazonoyl halides **17–20** (5 mmol) and triethylamine (0.7 ml, 5 mmol), was added dropwise with stirring, and the stirring was continued for 4 hr. The solid was collected, washed with ethanol, and crystallized from the proper solvent to give 2,3-dihydrothidiazoles **24–27,** in 60–65% yields, respectively. (cf. Tables I & II).

Method (B)

A mixture of the appropriate 2-cyanomethylthiazoles **15a-d,** potassium hydroxide, and phenyl isothiocyanate (5 mmol each) in N,N,-dimethylformamide (20 ml) was stirred at room temperature for 4 hr. The appropriate hydrazonoyl halides **17–20** (5 mmol) was added, and stirring was continued for 6 hr. The solution was then diluted with water. The solid formed was collected and crystallized from the proper solvent. The products prepared were identical in all respects (mp, mixed mp, and spectra) with those corresponding in Method (A).

Synthesis of potassium thiazol-2′-ylthioanilides 29a-d

Potassium ethoxide solution [which was prepared via reaction of potassium metal (1 g) in absolute ethanol (10 ml)] was added to the mixture of the appropriate thiazoles **15a-d** and phenyl isothiocyanate (10 mmol) in ethanol (20 ml) while stirring. The solid formed was collected, washed with diethyl ether, and crystallized from ethanol-diethyl ether mixture.

TABLE II IR and ^{1}H NMR of the newly synthesised compounds

Comp.	*IR (cm^{-1})*	*^{1}H NMR (δ)*
6a	1735, 1647(CO's) and 1608(C=N).	7.21–8.01 (m, 15H, ArH's and CH=) and 8.31 (s, 1H, coumarin H-4).
6b	1751, 1648(CO's) and 1606(C=N).	2.45 (s, 3H, $CH_3C_6H_4$), 7.21–8.01 (m, 14H, ArH's and CH=) and 8.31 (s, 1H, coumarin H-4).
6c	1741, 1649(CO's) and 1606(C=N).	7.01–8.01 (m, 13H, ArH's and CH=) and 8.31 (s, 1H, coumarin H-4).
6d	1750, 1650(CO's) and 1606(C=N).	6.78–8.01 (m, 13H, ArH's and CH=) and 8.31 (s, 1H. coumarin H-4).
6e	1732, 1654(CO's) and 1610(C=N).	7.22–8.22 (m, 14H, ArH's and CH=) and 8.31 (s, 1H, coumarin H-4).
6f	1743, 1635(CO's) and 1608(C=N).	7.26–8.11 (m, 14H, ArH's and CH=) and 8.31 (s, 1H, coumarin H-4).
10a	1735, 1649(CO's) and 1608(C=N).	2.39 (s, 3H, CH_3C=), 7.02–8.03 (m, 14H, ArH's) and 8.30 (s, 1H, coumarin H-4).
10b	1741, 1649(CO's) and 1608(C=N).	2.39 (s, 3H, CH_3C=), 2.46 (s, 3H, 4-$CH_3C_6H_4$), 7.20–8.03 (m, 13H, ArH's) and 8.30 (s, 1H, coumarin H-4).
10c	1735, 1646(CO's) and 1606(C=N).	2.39 (s, 3H, CH_3C=), 7.02–8.03 (m, 13H, ArH's) and 8.30 (s, 1H, coumarin H-4).
10d	1735, 1652(CO's) and 1606(C=N).	2.45 (s, 3H, CH_3C=), 7.03–8.00 (m, 12H, ArH's) and 8.30 (s, 1H, coumarin H-4).
10e	1728,1652(CO's) and 1608(C=N).	2.38 (s, 3H, CH_3C=), 6.49 (t, 1H, furan H-4), 6.90 (d, 1H, Furan H-3), 7.26–8.01 (m, 10H, ArH's and furan H-5) and 8.31 (s, 1H, coumarin H-4).
10f	1735, 1645(CO's) and 1610(C=N).	2.57 (s, 3H, CH_3C=), 7.26–8.33 (m, 13H, ArH's) and 8.64 (s, 1H, coumarin H-4).
10g	1737, 1646(CO's) and 1610(C=N).	2.55 (s, 3H, CH_3C=), 7.22–8.28 (m, 13H, ArH's) and 8.59 (s, 1H, coumarin H-4).
14a	1755, 1650(CO's) and 1614(C=N).	1.81 (m, 4H, $2CH_2$), 2.52 (t, 4H, $2CH_2$), 7.21–7.97 (m, 9H, ArH's) and 8.31 (s, 1H, coumarin H-4).
14b	1730, 1651(CO's) and 1610(C=N).	1.81 (m, 6H, $3CH_2$), 2.52 (t, 4H, $2CH_2$), 7.21–7.97 (m, 9H, ArH's) and 8.31 (s, 1H, coumarin H-4).
14c	1728, 1650(CO's) and 1608(C=N).	1.81 (m, 2H, CH_2), 2.52 (t, 4H, $2CH_2$), 7.21–7.97 (m, 13H, ArH's) and 8.31 (s, 1H, coumarin H-4).
24a	2191 (CN) and 1735 (CO ester).	1.49 (t, 3H, CH_3CH_2O), 4.57 (q, 2H, CH_3CH_2O), 7.34–7.68 (m, 10H, ArH's) and 8.65 (s, 1H, thiazole H-5).

Comp.	*IR (cm^{-1})*	*^1H NMR (δ)*
24d	2192 (CN) and 1735 (CO ester).	1.49 (t, 3H, CH_3CH_2O), 2.45 (s, 3H, CH_3), 4.57 (q, 2H, CH_3CH_2O), 7.34–7.68 (m, 9H, ArH's) and 8.65 (s, 1H, thiazole H-5).
24f	2190 (CN) and 1735 (CO ester).	1.49 (t, 3H, CH_3CH_2O), 2.45 (s, 3H, CH_3), 4.57 (q, 2H, CH_3CH_2O), 7.34–7.68 (m, 8H, ArH's) and 8.65 (s, 1H, thiazole H-5).
24g	2192 (CN) and 1735 (CO).	1.49 (t, 3H, CH_3CH_2O), 4.57 (q, 2H, CH_3CH_2O), 7.34–7.68 (m, 12H, ArH's) and 8.65 (s, 1H, thiazole H-5).
24h	2192 (CN) and 1735 (CO).	1.04 (t, 3H, CH_3CH_2), 4.57 (q, 2H, CH_2CH_3), 7.36–7.68 (m, 9H, ArH's) and 8.32 (s, 1H, coumarin H-4) and 8.66 (s, 1H, thiazole H-5).
25a	2187(CN), 1695(CO) and 1600(C=N).	2.37 (s, 3H, CH_3), 7.26–7.73 (m, 10H, ArH's) and 8.55 (s, 1H, thiazole H-5).
25d	2190(CN), 1692(CO) and 1604(C=N)	2.27 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 7.26–7.73 (m, 9H, ArH's) and 8.55 (s, 1H, thiazole H-5).
25f	2185(CN), 1692(CO) and 1600(C=N).	2.45 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 7.26–7.73 (m, 8H, ArH's) and 8.55 (s, 1H, thiazole H-5).
25g	2185(CN), 1692(CO).	2.37 (s, 3H, CH_3), 7.26–7.73 (m, 12H, ArH's) and 8.55 (s, 1H, thiazole H-5).
25h	2185(CN), 1692(CO) and 1600(C=N).	2.67 (s, 3H, CH_3), 7.26–7.75 (m, 9H, ArH's), 8.31 (s, 1H, coumarin H-4) and 8.65 (s, 1H, thiazole H-5).
26a	2216(CN) and 1659(CO).	7.26–7.73 (m 15H, ArH's) and 8.55 (s, 1H, thiazole H-5).
26d	2216(CN) and 1659(CO).	2.45 (s, 3H, CH_3), 7.26–7.73 (m, 14H, ArH's) and 8.55 (s, 1H, thiazole H-5).
26e	2216(CN) and 1659(CO).	2.45 (s, 6H, $_2CH_3$), 7.26–7.73 (m, 13H, ArH's) and 8.55 (s, 1H, thiazole H-5).
26f	2216(CN) and 1659(CO).	2.45 (s, 3H, CH_3), 7.26–7.73 (m, 13H, ArH's) and 8.55 (s, 1H, thiazole H-5).
26g	2216(CN) and 1659(CO).	7.26–7.73(m, 17H, ArH's) and 8.55(s. 1H, thiazole H-5).
26h	2216(CN) and 1659(CO),	7.36–7.68 (m, 14H, ArH's) and 8.32 (s, 1H, coumarin H-4) and 8.66 (s, 1H, thiazole H-5).
27a	3350(NH), 2218(CN), 1682(CO) and 1610(C=N).	7.34–7.68 (m, 15H, ArH's), 8.34 (s, 1H, NH) and 8.65 (s, 1H, thiazole H-5).

Synthesis of 1-Cyano-2-(4-p-tolyl)thiazolylthioacetanilide 28b

Acetic acid (5 ml) was added to a solution of the potassium of 1-cyano-2-(4-p-tolyl)thiazolylthioacetanilide **28b** (1 g) in water (15 ml) while stirring at room temperature. The resulting solid was collected and crystallized from N,N-dimethylformamide and ethanol solution to give 1-cyano-2-(4-p-tolyl)thiazolylthioacetanilide **28b** in 72% yield (cf. Tables I & II).

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