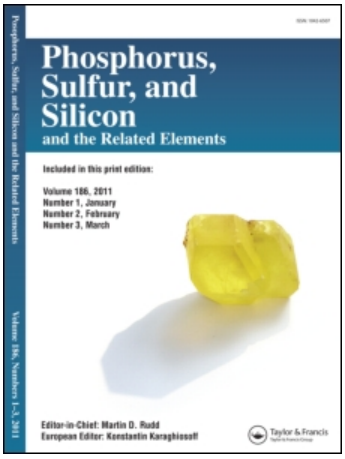

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REACTIONS WITH HYDRAZONOYL HALIDES XVII[1]. SYNTHESIS AND REACTIONS OF 1-BROMO-2-[4-(N-PIPERIDINO-SULFONYL)PHENYL]ETHANEDIONE-1-ARYLHYDRAZONE

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REACTIONS WITH HYDRAZONOYL HALIDES XVII[1]

Synthesis and Reactions of 1-Bromo-2-[4-(N-piperidinosulfonyl)phenyl]ethanedione-1-arylhydrazone

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The reaction of sulfamidohydrazonoyl bromide **3** with nucleophiles led to displacement of the bromide. Treatment of **3** with potassium thiocyanate or potassium selenocyanate gave 2-imino-1,3,4-thiadiazolines **5** and 2-iminoselenadiazolines **6** respectively. Reaction of **3** with thiourea and phenylthiourea yielded the thiazole derivatives **15** and **16**, while dithioesters **26**(or **27**) reacts with **3** to afford 2,3-dihydro-1,3,4-thiadiazoles **30–32**.

Keywords: Hydrazonoyl halides; 2,3-Dihydro-1,3,4-thiadiazole; 2,3-Dihydro-1,3,4-selenadiazole; dithioate esters; Nitrile imides

INTRODUCTION

Hydrazonoyl halides have been widely used as important tools for the synthesis of heterocyclic compounds, both as precursors of nitrile imides which undergo cycloaddition with various dipolarophiles and for condensation reactions.[2–7] Sulfonamides have been reported to have various types of biological activity, e.g. fungicidal,[8] pesticidal[9] and antibacterial action.[10,11] In addition, thiadiazolines showed a marked sedative and anaesthetic action.[12] However, the hydrazonoyl halides with sulfonamide moiety have not yet been reported.[13] The

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results of the synthesis and utilization of the hydrazonoyl halide **3** in heterocyclic synthesis is reported here.

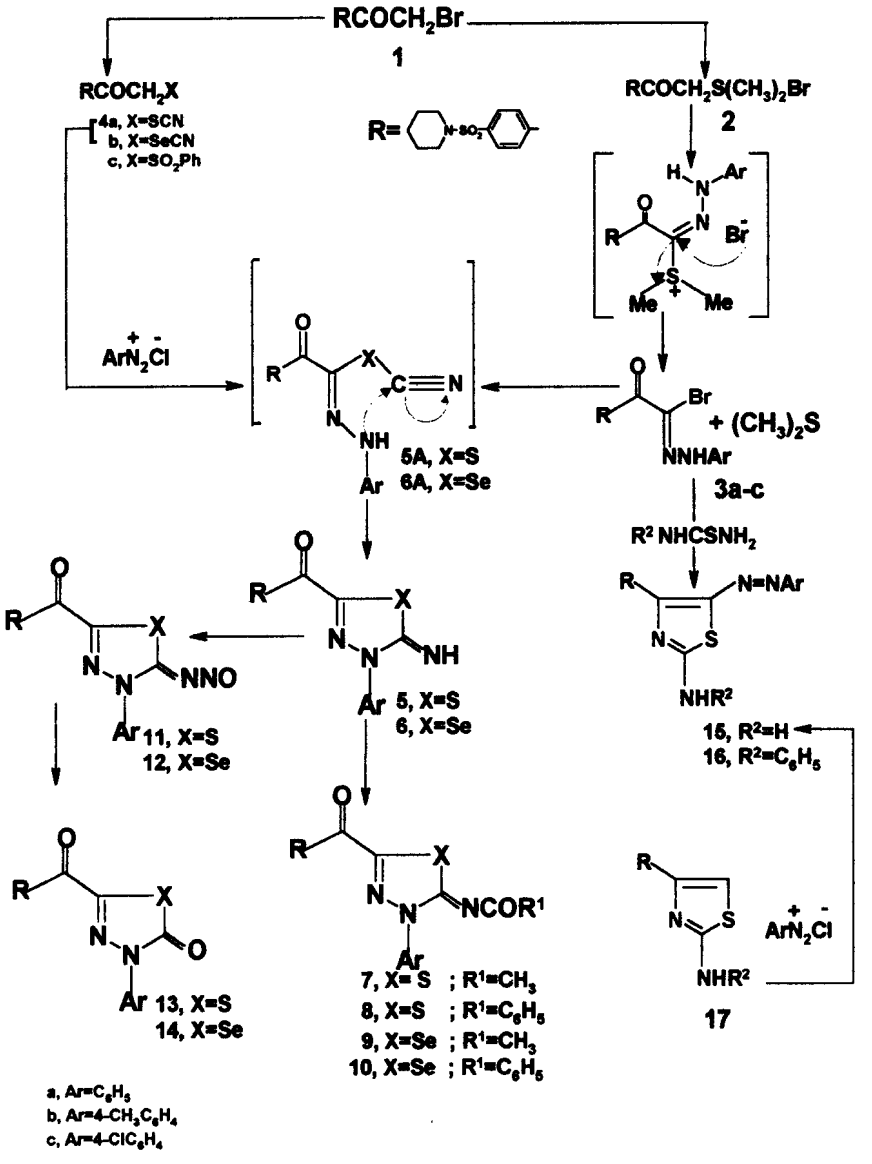
RESULTS AND DISCUSSION

Treatment of N-nitrosoarylacetamides[14,15] with sulfonium bromide **2** in ethanol gave 1-bromo-2-[4-(N-piperidinosulfonyl)phenyl]ethanedione-1-arylhydrazone (**3a–c**). The structure of **3** was confirmed by spectral data, microanalysis and reactions with different reagents. ^{1}H NMR (δ ppm) spectrum of **3b** showed signals at 1.60–1.64 (m, 6H, piperidine H-3, H-4 and H-5), 2.4 (s, 3H, 4-$CH_3C_6H_4$), 3.02 (t, 4H, piperidine H-2, H-6) and 7.34–8.52 (m, 9H, ArH's and NH). Its IR (cm^{-1}) spectrum revealed bands at 3269 (NH) and 1660 (CO). Compounds **3a–c** reacted with potassium thiocyanate and potassium selenocyanate to give **5a–c** and **6a,b** respectively. The structures of **5** and **6** were confirmed on the basis of elemental analyses, spectral data, alternative route and reaction of each with nitrous acid and acyl chlorides. The ^{1}H NMR (δ ppm) spectrum of **5b** for example showed signals at 1.61–1.64 (m, 6H, piperidine H-3, H-4 and H-5), 2.40(s, 3H, 4-$CH_3C_6H_4$), 3.02(t, 4H, piperidine H-2, H-6) and 7.34–8.52(m, 9H, ArH's and NH). The IR (cm^{-1}) of **5** and **6** revealed bands at 3380 (NH), 1643 (CO) and no absorption bands in the 2000–2200 due to free SCN or SeCN groups.[16] The absorption pattern of **5** and **6** in UV region was, in each case, characterized by three maxima in the 380–360, 280–250 and 230–210 nm regions. Thus, treatment of the 4-(N-piperidinosulfonyl)-phenacylthiocyanate (**4a**) and 4-(N-piperidinosulfonyl)phenacylselenocyanate (**4b**) with aryldiazonium chloride in ethanolic sodium acetate solution afforded the same products **5** and **6**, respectively.

These results indicated that both the reaction of **3** with potassium thiocyanate (potassium selenocyanate) and azo coupling of **4a**(b) proceed through one common intermediate, the hydrazones **5A** and **6A**, which cyclized readily to give **5** and **6**, respectively (cf. Scheme 1).

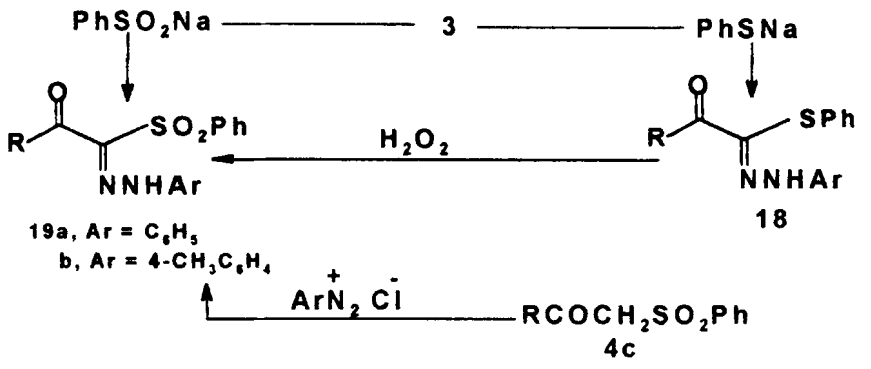
Acylation of **5** and **6** with acetic anhydride (and with benzoyl chloride in pyridine) afforded N-acetyl **7,9** and N-benzoyl **8,10**, respectively. Both spectral data and elemental analyses confirmed the structures of the products **7–10**. ^{1}H NMR (δ ppm) spectrum of **7** (Ar = 4-$CH_3C_6H_4$) showed signals at 1.61–1.63(m, 6H, piperidine H-3, H-4 and H-5), 2.31(s, 3H, CH_3CON), 2.41(s, 3H, 4-$CH_3C_6H_4$), 3.02(t, 4H, piperidine H-2, H-6) and 7.34–8.51(m, 8H, ArH's). IR (cm^{-1}) spectra of **7–10** revealed bands at 1660 (CO) and 1630 (RCON=).

Nitrosation of **5** and **6** gave the nitroso derivatives **11** and **12**, respectively. The UV of the latter revealed two common maxima in the region 510–470 nm



and 365–340 nm. These are assigned to n-n* and π-π* transition of the nitrosoimino group.

All compounds **11** and **12** decomposed to the corresponding 2,3-dihydrothiadiazolones **13** and 2,3-dihydroselenadiazolones **14**, upon being boiled in xylene. IR (cm^{-1}) spectra of **13** and **14** revealed two CO absorptions near 1685 and



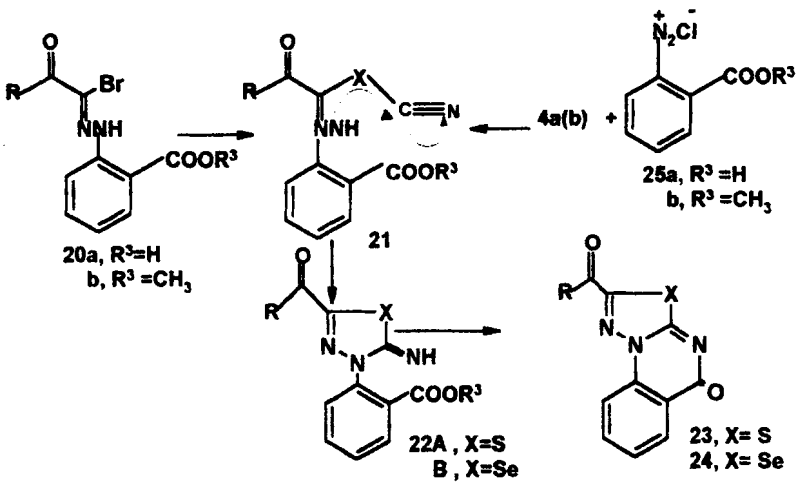
1665. ^{1}H NMR (δ ppm) spectra of **13**b showed signals at 1.60–1.64 (m, 6H, piperidine H-3, H-4 and H-5), 2.41(s, 3H, 4-$CH_3C_6H_4$), 3.10(t, 4H, piperidine H-2, H-6) and 7.12–8.51(m, 8H, ArH's).

Treatment of **3** with excess thiourea or phenylthiourea in ethanolic triethylamine afforded products which were identified as: 5-arylazo-4-[4-(N-piperidinosulfonyl)phenyl]-2-aminothiazoles (**15**) and 5-arylazo-4-[4-(N-piperidinosulfonyl)phenyl]-2-anilinothiazoles (**16**), respectively. The structure of products was confirmed by both elemental analysis and spectral data. The IR spectrum showed no CO absorption bands at 1650–1800.[16] The ^{1}H NMR (δ ppm) spectrum of **15**a showed signals at 1.61 (m, 6H, piperidine H-3, H-4 and H-5), 3.0(t, 4H, piperidine H-2, H-6), 5.91(s, br, 2H, NH_2) and 7.21–8.41 (m, 9H, ArH's). The UV of **15** exhibited two intense maxima in the 470–420 and 280–260 nm region. Unequivocal support of structure **15** was obtained by coupling aryldiazonium chloride with 2-amino-4-[4-(N-piperidinosulfonyl)phenyl]thiazole **17** in ethanolic sodium acetate solution.

Treatment of **3** with sodium benzenethiolate and with sodium benzenesulfinate afforded hydrazones **18** and **19**, respectively (Scheme 2). Compound **18** was easily oxidized by hydrogen peroxide in acetic acid to give an identical product in all respects (m.p., mixed m.p and spectra) with compound **19**. Compound **19** was also obtained via coupling of aryldiazonium chloride with ω-phenylsulfonoyl-4-(N-piperidinosulfonyl)acetophenone (**4**c) in ethanolic sodium acetate solution (cf Scheme 2).

Hydrazonoyl bromides **20**a,b reacted with potassium thiocyanate and potassium selenocyanate in ethanol to give a pale yellow colored products (Scheme 3).

Mass spectra and analytical data indicated the molecular formula as $C_{21}H_{18}N_4O_4S_2$ and $C_{21}H_{18}N_4O_4SSe$, respectively. IR (cm^{-1}) spectra of these products were free of SCN (or SeCN), NH and OH bands but revealed two carbonyl bands near 1690 and 1650. Thus, it is clear that hydrazone **21** was not

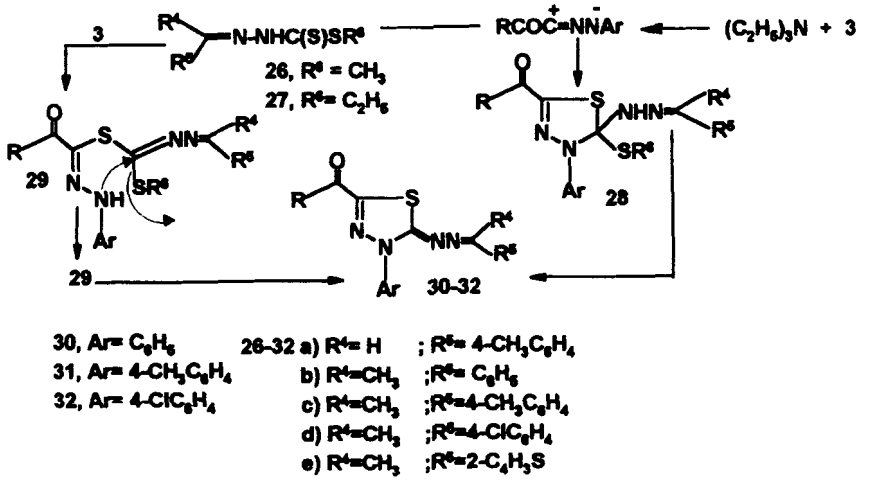


SCHEME 3

the end product of the reaction. It was thought that **21** undergoes spontaneous cycloaddition[17,18] to give the iminothiadiazoline **22A** and iminoselenadiazoline **22B**, which completed the reaction by loss of water or methanol to yield the final products thiadiazolo[3,2-a]quinazolinone **23** and selenadiazolo[3,2-a] quinazolinone **24**, respectively. The proposed structures **23** and **24** were confirmed by the finding that **23** and **24** were also obtained by coupling of **4**a,b with diazonium chloride **25**a, b (cf. Scheme 3).

Compound **3a**, reacted with dithioester **26a** in ethanolic triethylamine at room temperature, gave 2,3-dihydro-1,3,4-thiadiazole **30a** (Scheme 4). The structure of **30** was confirmed on the basis of elemental analysis, spectral data and alternative synthesis. Thus, ^{1}H NMR (δ ppm) spectrum of **30a** showed signals at 1.61(m, 6H, piperidine H-3, H-4 and H-5), 2.42 (s, 3H, 4-$CH_3C_6H_4$), 3.10(t, 4H, piperidine H-2, H-5), 7.15–8.21(m, 13 H, ArH's) and 9.15(s, 1H, CH=N). Its IR (cm^{-1}) revealed a band at 1660 (CO) and no absorption band due to the (NH) group. On the other hand, treatment of **3**a with **27**a in ethanolic triethylamine, produced the same product **30a**. Similarly, compounds **3**b,c reacted with **26**a–e to give **31**a–e and **32**a–e, respectively.

Products **30–32** are assumed to be formed via elimination of alkanethiol from the corresponding cycloadduct **28**, formed from 1,3-dipolar cycloaddition of nitrile imides (prepared in situ from **3** and triethylamine) to C=S of methyl or ethyl dithioester (Scheme 4). The formation of **30–32** can also be explained by a stepwise path involving substitutions to afford a cyclic hydrazone **29**, which was readily cyclized to give intermediate **28**, which subsequently eliminates alkanethiol to give the final products **30–32**a–e.



SCHEME 4

EXPERIMENTAL

All melting points were determined on a electrothermal melting point apparatus and are uncorrected. IR (KBr) spectra were recorded on FT-IR 8201 PC Schimadzu spectrophotometer. ^{1}H NMR spectra were recorded on a Varian Gemini 200-MHz spectrometer and chemical shifts were expressed in δ (ppm) units using TMS as internal reference. UV spectra (EtOH) were recorded on a Perkin-Elmer Lamda 4 spectrophotometer. Elemental analyses were performed by the Microanalytical Center at Cairo University, Giza, Egypt. Methyl and ethyl dithioate esters[19–21] were prepared according to previously described methods.

Synthesis of 4-(N-piperidinosulfonyl)phenacyl Bromide (1)

Bromine (16g, 0.1 mol) was added dropwise while stirring to 4-(N-piperidinosulfonyl)acetophenone[22] (26.7g, 0.1 mol) in dioxane-ether (100 ml; 1:1 v/v). The reaction mixture was stirred for 10 min., then poured onto an ice-cold water. The solid was collected, washed with water, then crystallized from ethanol to give **1**, 75% yield (cf. Table I).

Synthesis of 2-[4-(N-piperidinosulfonyl)phenyl-2-oxoethyl]dimethylsulfonium Bromide (2)

A mixture of **1** (34.6g, 0.1 mol) and dimethyl sulfide (3.4g, 0.11mol) in ethanol (50 ml) was refluxed for 45 min. The reaction mixture was cooled and the solid was collected, washed with diethyl ether, then recrystallized from ethanol to give **2**, 75% yield. (cf. Table I).

TABLE I Characterization data of the newly synthesised compounds.

Compd. No.	*M.P. °C*	*Mol. Formula (M.Wt.)*	*Analyses %*		*Calcd./Found*	
			C	*H*	*N*	*S*
1	85–6	$C_{13}H_{16}BrNO_3S$	45.10	4.66	4.05	9.26
		(346.25)	45.10	4.70	4.00	9.30
2	100–102	$C_{15}H_{22}BrNO_3S_2$	44.12	5.43	3.43	15.70
		(408.38)	44.10	5.50	3.40	15.80
3a	153–5	$C_{19}H_{20}BrN_3O_3S$	50.67	4.48	9.33	7.12
		(450.36)	50.70	4.50	9.40	7.20
3b	154–6	$C_{20}H_{22}BrN_3O_3S$	51.73	4.78	9.05	6.90
		(464.39)	51.80	4.80	9.00	6.90
3c	171–3	$C_{19}H_{19}BrClN_3O_3S$	47.07	3.95	8.67	6.61
		(484.80)	47.10	4.00	8.70	6.60
4a	87–8	$C_{14}H_{16}N_2O_3S_2$	51.83	4.97	8.63	19.77
		(324.42)	51.80	5.00	8.60	19.80
4b	103–5	$C_{14}H_{16}N_2O_3SSe$	45.29	4.34	7.54	8.64
		(371.32)	45.30	4.40	7.60	8.70
4c	136–7	$C_{19}H_{21}NO_5S_2$	56.00	5.19	3.44	15.74
		(407.512)	56.00	5.20	3.50	15.80
5a	160–2	$C_{20}H_{20}N_4O_3S_2$	56.06	4.70	13.07	14.96
		(428.53)	56.10	4.70	13.10	15.00
5b	163–4	$C_{21}H_{22}N_4O_3S_2$	56.99	5.01	12.66	14.49
		(442.56)	57.00	5.10	12.70	14.50
5c	169–71	$C_{20}H_{19}ClN_4O_3S_2$	51.89	4.14	12.10	13.85
		(462.98)	51.90	4.20	12.10	13.90
6a	160–61	$C_{20}H_{20}N_4O_3SSe$	50.53	4.24	11.78	6.74
		(475.43)	50.60	4.30	11.80	6.80
6b	138–40	$C_{21}H_{22}N_4O_3SSe$	51.53	4.53	11.45	6.55
		(489.45)	51.60	4.60	11.50	6.50
7a	219–20	$C_{22}H_{22}N_4O_4S_2$	56.15	4.71	11.91	13.63
		(470.57)	56.20	4.80	11.90	13.70
7b	218–9	$C_{23}H_{24}N_4O_4S_2$	57.01	4.99	11.56	13.23
		(484.60)	57.00	5.00	11.60	13.20
7c	205–7	$C_{22}H_{21}ClN_4O_4S_2$	52.32	4.19	11.09	12.70
		(505.01)	52.40	4.20	11.10	12.70
8a	238–40	$C_{27}H_{24}N_4O_4S_2$	60.88	4.54	10.52	12.04
		(532.64)	60.90	4.60	10.50	12.00
8b	245–7	$C_{28}H_{26}N_4O_4S_2$	61.52	4.79	10.25	11.73
		(546.67)	61.50	4.80	10.30	11.80
8c	230–2	$C_{27}H_{23}ClN_4O_4S_2$	57.19	4.09	9.88	11.31
		(567.09)	57.20	4.10	9.90	11.30
9a	163–4	$C_{22}H_{22}N_4O_4SSe$	51.06	4.29	10.83	6.20
		(517.47)	51.10	4.30	10.80	6.20
9b	158–60	$C_{23}H_{24}N_4O_4SSe$	51.98	4.55	10.54	6.03
		(531.49)	52.00	4.60	10.50	6.10
10a	213–5	$C_{27}H_{24}N_4O_4SSe$	55.96	4.17	9.67	5.53
		(579.54)	56.00	4.20	9.70	5.50
10b	225–7	$C_{28}H_{26}N_4O_4SSe$	56.66	4.42	9.44	5.40
		(593.56)	56.70	4.40	9.50	5.40
11a	135–6	$C_{20}H_{19}N_5O_4S_2$	52.50	4.19	15.31	14.02
		(457.53)	52.50	4.20	15.30	14.10
11b	128–9	$C_{21}H_{21}N_5O_4S_2$	53.49	4.49	14.85	13.60
		(471.56)	53.50	4.50	14.90	13.60
11c	133–5	$C_{20}H_{18}ClN_5O_4S_2$	48.83	3.69	14.24	13.03
		(491.98)	48.80	3.70	14.20	13.00

TABLE I *continued*

Compd. No.	*M.P. °C*	*Mol. Formula (M.Wt.)*	*Analyses %*		*Calcd./Found*	
			C	*H*	*N*	*S*
12a	80–2	$C_{20}H_{19}N_5O_4SSe$	47.62	3.80	13.88	6.36
		(504.43)	47.60	3.80	13.90	6.40
12b	109–10	$C_{21}H_{21}N_5O_4SSe$	48.65	4.08	13.51	6.18
		(518.45)	48.70	4.10	13.50	6.20
13a	164–5	$C_{20}H_{19}N_3O_4S_2$	55.93	4.46	9.78	14.93
		(429.52)	55.90	4.50	9.80	15.00
13b	195–7	$C_{21}H_{21}N_3O_4S_2$	56.87	4.77	9.47	14.46
		(443.548)	56.90	4.80	9.50	14.50
13c	188–90	$C_{20}H_{18}ClN_3O_4S_2$	51.78	3.91	9.06	13.82
		(463.966)	51.80	3.90	9.10	13.80
14a	170–3	$C_{20}H_{19}N_3O_4SSe$	50.42	4.02	8.82	6.73
		(476.41)	50.40	4.00	8.80	6.80
14b	165–7	$C_{21}H_{21}N_3O_4SSe$	51.43	4.32	8.57	6.54
		(490.44)	51.50	4.30	8.60	6.60
15a	264–5	$C_{20}H_{21}N_5O_2S_2$	56.19	4.95	16.38	15.00
		(427.55)	56.20	5.00	16.40	15.00
15b	233–5	$C_{21}H_{23}N_5O_2S_2$	57.12	5.25	15.86	14.52
		(441.57)	57.20	5.30	15.90	14.50
15c	274–6	$C_{20}H_{20}ClN_5O_2S_2$	52.00	4.36	15.16	13.88
		(461.99)	52.00	4.40	15.20	13.90
16a	123–5	$C_{26}H_{25}N_5O_2S_2$	62.00	5.00	13.91	12.73
		(503.64)	62.10	5.00	13.90	12.80
16b	236–8	$C_{27}H_{27}N_5O_2S_2$	62.64	5.26	13.53	12.39
		(517.67)	62.70	5.30	13.50	12.40
16c	241–3	$C_{26}H_{24}ClN_5O_2S_2$	58.04	4.50	13.02	11.92
		(538.09)	58.00	4.50	13.00	12.00
17	238–40	$C_{14}H_{17}N_3O_2S_2$	51.99	5.30	12.99	19.83
		(323.43)	52.00	5.30	13.00	19.80
18	124–5	$C_{23}H_{25}N_3O_3S_2$	62.61	5.25	8.76	13.37
		(479.62)	62.60	5.30	8.80	13.40
19a	190–91	$C_{25}H_{25}N_3O_5S_2$	58.69	4.93	8.21	12.53
		(511.62)	58.70	5.00	8.20	12.60
19b	208–9	$C_{26}H_{27}N_3O_5S_2$	59.41	5.18	7.99	12.20
		(525.65)	59.50	5.20	8.00	12.20
20a	208–10	$C_{20}H_{20}BrN_3O_5S$	48.59	4.08	8.50	6.49
		(494.37)	48.60	4.10	8.50	6.50
20b	145–7	$C_{21}H_{22}BrN_3O_5S$	49.61	4.36	8.27	6.31
		(508.40)	49.60	4.40	8.30	6.30
23	263–5	$C_{21}H_{18}N_4O_4S_2$	55.49	3.99	12.33	14.11
		(454.53)	55.50	4.00	12.40	14.20
24	278–80	$C_{21}H_{18}N_4O_4SSe$	50.30	3.62	11.17	6.39
		(501.42)	50.30	3.60	11.20	6.40
30a	219–20	$C_{28}H_{27}N_5O_3S_2$	61.63	4.99	12.83	11.75
		(545.68)	61.70	5.00	12.90	11.80
30b	214–5	$C_{28}H_{27}N_5O_3S_2$	61.63	4.99	12.83	11.75
		(545.68)	61.70	5.00	12.90	11.90
30c	188–9	$C_{29}H_{29}N_5O_3S_2$	62.23	5.22	12.51	11.46
		(559.71)	62.30	5.20	12.50	11.50
30d	220–21	$C_{28}H_{26}ClN_5O_3S_2$	57.97	4.52	12.07	11.05
		(580.13)	58.00	4.60	12.10	11.10
30e	216–8	$C_{26}H_{25}N_5O_3S_3$	56.60	4.57	12.69	17.44
		(551.71)	56.70	4.60	12.70	17.50
31a	189–91	$C_{29}H_{29}N_5O_3S_2$	62.32	5.22	12.51	11.46

TABLE I *continued*

Compd. No.	*M.P. °C*	*Mol. Formula (M.Wt.)*	*Analyses %*		*Calcd./Found*	
			C	*H*	*N*	*S*
		(559.71)	62.40	5.30	12.60	11.50
31b	204–6	$C_{29}H_{29}N_5O_3S_2$	62.32	5.22	12.51	11.46
		(559.71)	62.40	5.20	12.50	11.40
31c	203–5	$C_{30}H_{31}N_5O_3S_2$	62.80	5.45	12.21	11.18
		(573.74)	62.80	5.50	12.20	11.20
31d	193–5	$C_{29}H_{28}ClN_5O_3S_2$	58.62	4.75	11.79	10.79
		(594.15)	58.60	4.80	11.80	10.50
31e	203–4	$C_{27}H_{27}N_5O_3S_3$	57.32	4.81	12.38	17.00
		(565.74)	57.40	4.80	12.40	17.00
32a	231–3	$C_{28}H_{26}ClN_5O_3S_2$	57.97	4.52	12.07	11.05
		(580.13)	58.00	4.50	12.10	11.20
32b	243–5	$C_{28}H_{26}ClN_5O_3S_2$	57.97	4.52	12.07	11.05
		(580.13)	58.10	4.60	12.20	11.10
32c	215–6	$C_{29}H_{28}ClN_5O_3S_2$	58.62	4.75	11.79	10.79
		(594.15)	58.70	4.80	11.80	10.90
32d	227–9	$C_{28}H_{25}Cl_2N_5O_3S_2$	54.72	4.10	11.40	10.43
		(614.57)	54.70	4.10	11.50	10.50
32e	224–6	$C_{26}H_{24}ClN_5O_3S_3$	53.28	4.13	11.95	16.41
		(586.15)	53.30	4.20	12.00	16.50

Synthesis of 1-Bromo-2-[4-(N-piperidinosulfonyl)phenyl]ethanedione-1-arylhydrazone 3a–c and 20a,b

A mixture of **2** (20.4g, 0.05 mol) and the appropriate N-nitrosoarylacetamides (0.06 mol) was stirred in ethanol (50ml) for 1h at room temperature. The solid was collected washed with water and then crystallized from ethanol to give **3**a–c and **20**a,b, in 65–72% yield. (cf. Table I).

Synthesis of 4a–c and Thiazole 17

A mixture of **1** (17.3g, 0.05 mol) and the appropriate reagent (KSCN, KSeCN, $PhSO_2Na$ or NH_2CSNH_2) (0.06 mol) in ethanol (50 ml) was refluxed for 30 min (in the case of thiourea, 2h). The reaction mixture was cooled, diluted with water and the solid then was collected. Recrystallization from ethanol gave **4**a–c and **17** in almost quantitative yield (cf. Table I).

Reaction of 3 with nucleophiles, general method

Equimolecular quantities of the appropriate **3**a–c or **20**a,b and the appropriate reagent (KSCN or KSeCN or PhSNa or $PhSO_2Na$) (0.005 mol) in ethanol (20 ml) were stirred for 2–3h at room temperature. The solid which formed was

collected, washed with water and then recrystallized from ethanol to give **5**, **6**, **18**, **19**, **23** and **24**, respectively in 83–87% yields (cf. Table I).

Reaction of 4a–c with Aryldiazonium Chloride

A solution of the appropriate aryldiazonium chloride (0.005 mol) was added dropwise to a stirred solution of the appropriate reactant (**4**a–c) (0.005 mol) in ethanol (50 ml) containing sodium acetate (1 g) at 0–5°C. The reaction mixture was stirred for 3h at 0–5°C. The solid which formed was collected, washed with water and recrystallized from ethanol or acetic acid to give **5**, **6**, **19**, **23** and **24**, respectively. The products obtained were identical in all respects (m.p., mixed m.p. and spectra) with those prepared above.

Nitrosation of 5 and 6

A saturated solution of $NaNO_2$ (10 ml) was added dropwise to the appropriate solution of 2,3-dihydrothiadiazole **5** or 2,3-dihydroselenadiazole **6** (1 gm) in acetic acid (20 ml) while stirring at 0–5°C. The solid was collected by filtration, then crystallized from ethanol to give **11** and **12**, respectively in 79–83% yields. (cf. Table I).

Decomposition of 11 and 12

The N-nitroso derivative **11** or **12** (1g) in xylene (10 ml) was boiled for 10 min., then the solution was evaporated under reduced pressure. The solid was collected and crystallized to give 3-aryl-5-[4-(N-piperidineosulfonyl)phenyl]-2-oxo-2,3-dihydro-1,3,4-thiadiazole **13**a–c and 3-aryl-5-[4-(N-piperidineosulfonyl)phenyl]-2-oxo-2,3-dihydro-1,3,4-selenadiazole **14**a,b respectively in 72–73% yields (cf. Table I).

Acylation of 5 and 6

The appropriate **5** or **6** was stirred in acetic anhydride (20ml) for 10 min. The reaction mixture was left for 3h at room temperature. The solid which formed was collected and crystallized from acetic acid. The N-acetyl derivatives **7** and **9** were obtained in almost quantitative yields (cf. Table I). A mixture of equi-molecular amounts (0.005 mol) of **5** or **6** and benzoyl chloride in pyridine (10ml) was allowed to react at 80°C for 10 min. The reaction mixture was poured into ice cold water and acidified (HCl) and the solid product was collected, washed

with boiling water and then crystallized from acetic acid to afford **8** and **10**, respectively in 72–75% yields (cf. Table I).

Oxidation of 18

To the appropriate **18** (1g) in acetic acid (20 ml), hydrogen peroxide (5 ml, 30%) was added while stirring for 3h, then left at room temperature for 24h. The reaction mixture was diluted with water. The solid which formed was collected, washed with water and crystallized from acetic acid to give the same products **19** obtained from $PhSO_2Na$.

Synthesis of 5-Arylazo-4-[4-(N-piperidinosulfonyl)phenyl]-2-aminothiazole 15a–c

Equimolecular amounts of the appropriate hydrazonoyl bromide **3**a–c and thiourea (5 mmol of each) in ethanol (50 ml) were refluxed for 3h. The solid which formed after cooling was collected, washed with water and crystallized from acetic acid to give **15**a–c in 73–75% yields (cf. Table I).

Synthesis of 16a–c

To a mixture of the appropriate **3**a–c (0.005 mol) and phenylthiourea (0.006 mol) in ethanol (20 ml), triethylamine (0.7 ml, 0.005 ml) was added while stirring at room temperature. The solid which formed was collected and crystallized form acetic acid to give 5-arylazo-4-[4-(N-piperidinosulfonyl)-2-anilinothiazoles **16**a–c in 65–72% yields (cf. Table I).

Synthesis of 30–32a–e

To a mixture of the appropriate **26** or **27** (0.005 mol) and the appropriate hydrazonoyl bromide **3**a–c in ethanol (20 ml), triethylamine (0.7 ml, 0.005 mol) was added dropwise at room temperature while stirring. The reaction mixture was left to stir for 3h, then the solid which formed was collected and crystallized from acetic acid to give 2,3-dihydro-1,3,4-thiadiazoles **30**–**32**a–e in almost quantitative yields (cf. Table I).

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