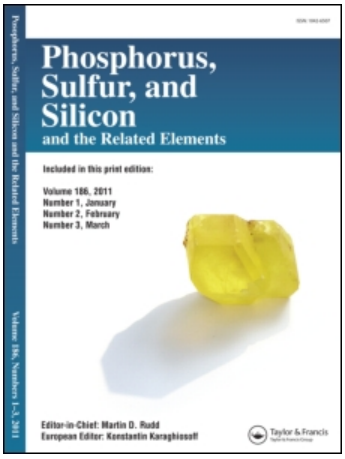

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Reactions of Hydrazonoyl Halides 35 1 : Synthesis of Some New 1,2,4-Triazolino[4,3-a]pyrimidines, 2,3-Dihydro-1,3,4-thiadiazoles and 2,3-Dihydro-1,3,4-selenadiazoles

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REACTIONS OF HYDRAZONOYL HALIDES 35[1]: SYNTHESIS OF SOME NEW 1,2,4-TRIAZOLINO[4,3-a]PYRIMIDINES, 2,3-DIHYDRO-1,3,4-THIADIAZOLES AND 2,3-DIHYDRO-1,3,4-SELENADIAZOLES

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*Hydrazonoyl halides have been caused to react with each of ethyl 4-(2*H*-benzo[3,4-*d*]1,3-dioxolen-5-yl)-6-methyl-2-methylthio-3,4-dihydropyrimidin-5-carboxylate, potassium thiocyanate (or thiourea), potassium selenocyanate, and alkyl carbodithioate in the presence of triethylamine to give 4,3-dihydro-1,2,4-triazolino[4,3-a]pyrimidine, 1,3,4-thiadiazoline, 1,2,4-selenadiazoline, and unsymmetrical azine derivatives in good yields. Structures of the new compounds were elucidated on the basis of elemental analyses, spectral data, and alternative methods of synthesis whenever possible.*

Keywords: 1,3,4-selenadiazolines; 1,3,4-thiadiazolines; hydrazonoyl halides; triazolo[4,3-a]pyrimidine

Hydrazonoyl halides have been used widely as important tools for the synthesis of heterocyclic compounds.[2–5] In continuation of our interest in the chemistry of hydrazonoyl halides,[6–10] we report herein their utility in the convenient and efficient synthesis of triazolino[4,3-*a*]pyrimidine and 1,3,4-thiadiazole derivatives.

The reaction of equimolar amount of ethyl 4-(2*H*-benzo[3,4-*d*]1,3-dioxolen-5-yl)-6-methyl-2-methylthio-3,4-dihydropyrimidin-5-carboxylate (**4**), C-methoxycarbonyl-*N*-phenylhydrazonoyl chloride (**1a**) and sodium ethoxide in boiling ethanol furnished exclusively the corresponding methyl 4-(2*H*-benzo[*d*]1,3-dioxolen-5-yl)-5-ethoxycarbonyl)-6-methyl-1-phenyl-4,3-dihydro-1,2,4-triazolino-[4,3-*a*]pyrimidine-3-carboxylate (**7a**) in excellent yield. Structure **7a** was elucidated on the

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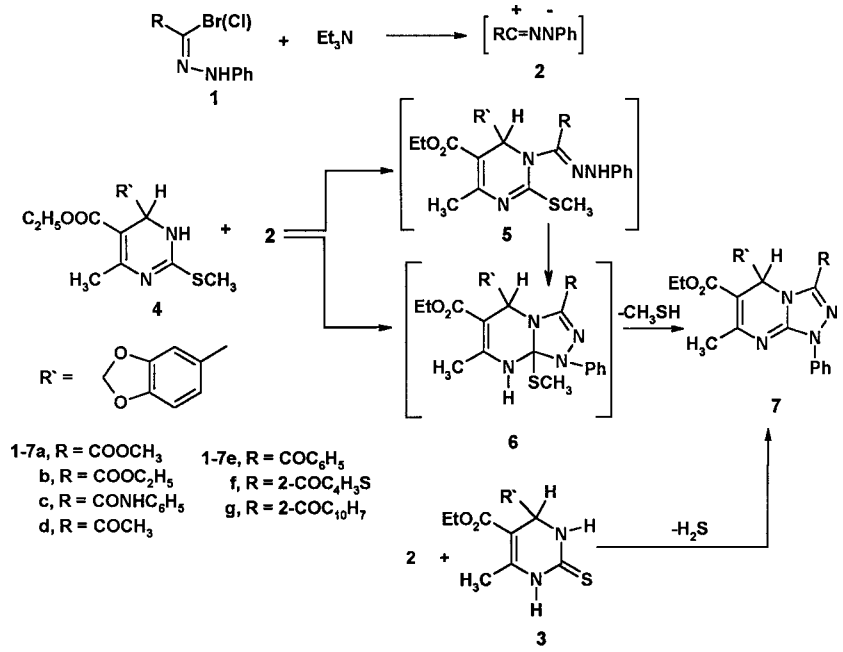
basis of analytical, spectral data, and alternative synthesis route. ^{1}H NMR spectrum showed signals at δ 1.23 (t, 3H, CH_2CH_3), δ 2.51 (s, 3H, CH_3), δ 3.96 (s, 3H, OCH_3), δ 4.12 (q, 2H, CH_2CH_3), δ 5.88 (s, 2H, CH_2), δ 6.64 (s, 1H, CH), and δ 6.87–8.20 (m, 8H, ArH's). IR spectrum revealed peaks at 1735 (CO's esters), 1666 (C=N) and 1604 C=C).

Moreover, ethyl 6-(2*H*-benzo[3,4-*d*]1,3-dioxolen-5-yl)-4-methyl-2-thioxo-1,3,6-trihydropyrimidine-5-carboxylate (**3**) reacted with **1a** in boiling chloroform in the presence of triethylamine gave the identical product in all respects (m.p., mixed m.p., and spectra) with compound **7a**. The formation of **7a** can be explained by a stepwise path involving substitution to give amidrazone **5a**, which readily cyclized to give intermediate **6a**. The intermediate **6a** can be formed via 1,3-dipolar cycloaddition of nitrile imide **2a** (which formed in situ by the treatment of hydrazonoyl chloride **1a** with triethylamine) to C=N of pyrimidine **4**. The intermediate **6a** was converted to **7a** via elimination of methyl mercaptan (cf. Scheme 1).



SCHEME 1

Similarly, the appropriate **3** or **4** reacted with the appropriate hydrazonoyl halides **1b–g** to give the corresponding 1,2,4-triazolino[4,5-*a*]pyrimidines **7b–g** respectively.

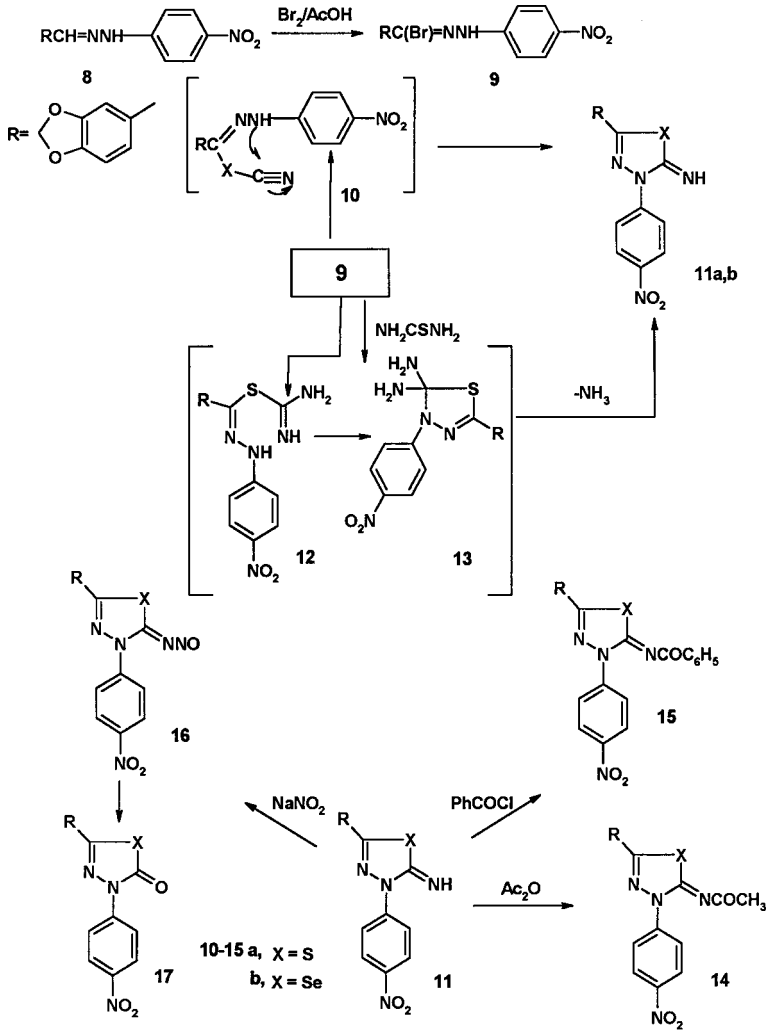
Bromination of, ((1E)2-(2*H*-benzo[3,4-*d*]1,3-dioxolen-5-yl)-1-azavinyl)(4-nitrophenyl-1-aza-amine (**8**) in acetic acid gave ((1E)-2-(2*H*-benzo[3,4-*d*]1,3-dioxolen-5-yl)-aza-2-bromovinyl)(4-nitrophenyl)amine (**9**) (72%). Structure of **9** was confirmed on the basis of microanalyses, spectral data, and its reactions with different reagents. ^{1}HNMR spectrum of **9** showed signals at δ 4.30 (s, 2H, CH_2) and δ 7.28–8.19 (m, 8H, ArH's and NH). Compounds **9** reacted with potassium thiocyanate and potassium selenocyanate in ethanol to give **11a** and **11b** respectively. The structures **11a** and **11b** were confirmed on the basis of elemental analyses, spectral data, alternative synthesis route, and the reaction of each with nitrous acid and acetic anhydride (or benzoyl chloride). The ^{1}HNMR spectrum of **11a** showed signals at δ 6.62 (s, 2H, CH_2) and δ 7.00–8.31 (m, 8H, ArH's and NH). The IR spectra of **11a** and **11**b revealed bands at 3380 (NH) and no absorption bands in the region 2000–2200 due to the absence of SCN or SeCN groups.[11] Thus treatment of **9** with thiourea in boiling ethanol gave identical product in all respects (mp, mixed mp and spectra) with **11a**. These results indicated that both the reaction of **9** with potassium thiocyanate or thiourea proceed through the intermediate **10** or (**12** and **13**), which cyclized readily to give **11a** (cf. Scheme 2).

Acylation of **11a** and **11b** with acetic anhydride (and with benzoyl chloride in pyridine) afforded *N*-acetyl **14a**,**b** and *N*-benzoyl **15a**,**b** respectively. Both spectral data and elemental analyses confirmed the structures of the products **14a**,**b** and **15a**,**b**. ^{1}HNMR spectrum of **14a** showed signals at δ 2.43 (s, 3H, CH_3CO), δ 6.07 (s, 2H, CH_2), and δ 6.88–8.39 (m, 7H, ArH's). IR spectra of **14a**,**b** and **15a**,**b** revealed bands at 1650 cm^{-1} (RCON=).

Nitrosation of **11a** and **11b** with nitrous acid gave the nitroso derivatives **16a** and **16b** respectively. The UV of the latter revealed two common maxima in the region 510–570 nm and 365–340 nm assigned to n-n* and π-π^* transition of the nitrosoimino groups.

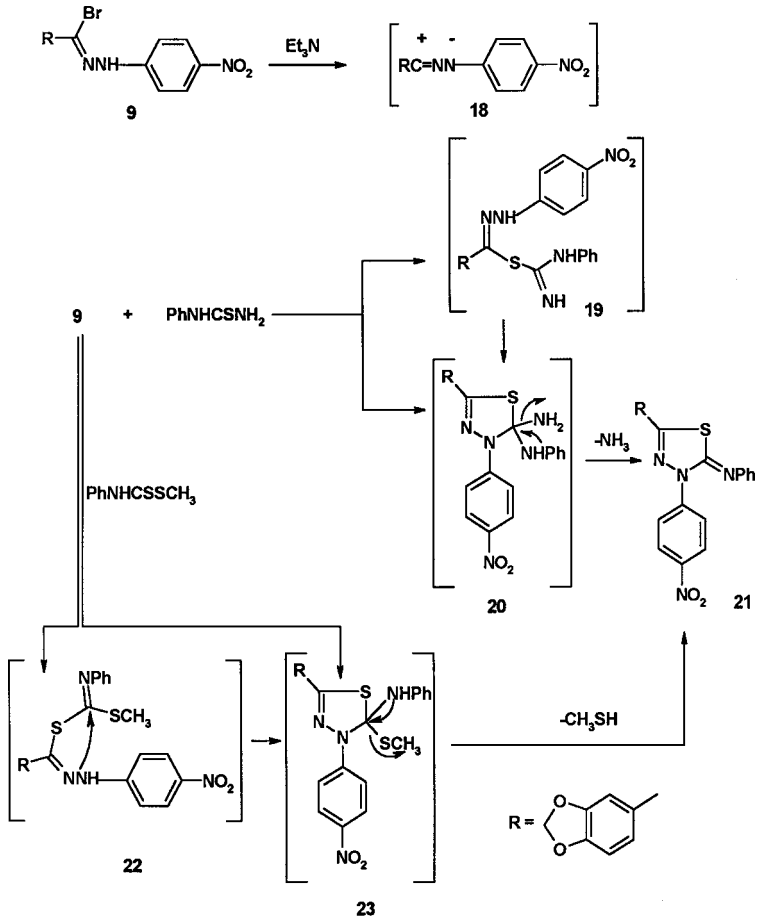
Compounds **16a** and **16b**, upon being boiled in xylene, decomposed to the corresponding 2,3-dihydrothiadiazolinones **17a** and **17b**. IR spectra of **17a** and **17b** revealed an absorption band near 1680 cm^{-1}. ^{1}H NMR spectrum of **17a** showed signals at δ 6.18 (s, 2H, CH_2) and δ 7.13–8.43 (m, 7H, ArH's).

Treatment of **9** with phenylthiourea in ethanol afforded **21** (66%). Structure of **21** was elucidated on the basis of elemental analyses, spectral data, and an alternative synthesis method. Thus treatment of **9** with methyl phenylthiocarbamate[12] in ethanolic triethylamine gave identical product in all respects m.p., mixed m.p., and spectra) with **21**. Scheme 3 explains the formation of **21**.



SCHEME 2

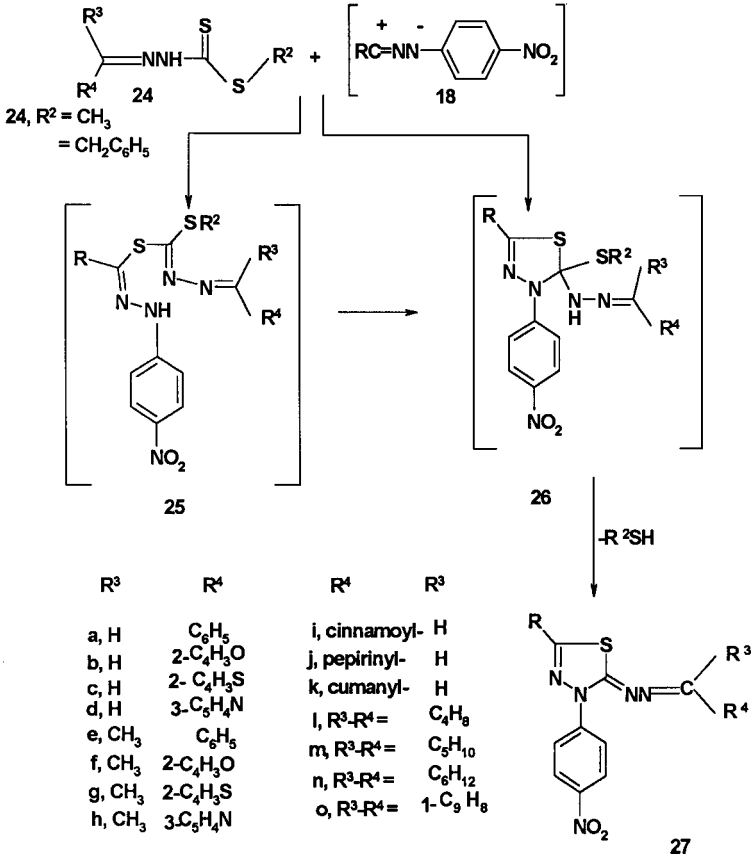
Compound **9** reacted with the appropriate dithioesters **24a–o** in ethanolic triethylamine at room temperature to give the corresponding 2,3-dihydro-1,3,4-thiadiazole derivatives **27a–o**, respectively (cf. Scheme 4). Structure of **27** was confirmed on the basis of elemental analyses, spectral data, and an alternative synthesis route. Thus, ^{1}HNMR spectrum of **27a** showed signals at δ 6.07(s, 2H, CH_2) and δ 6.87–8.54 (m, 13H, ArH's and vinyl —CH=). Products **27a–o** are assumed to be formed via elimination of alkanethiol from the corresponding cycloadduct **26**,



SCHEME 3

formed from 1,3-dipolar cycloaddition of nitrile imide **18** (formed in situ from **9** and triethylamine) to the C=S of the alkyl dithioester. The formation of **27** also can be explained by 1,3-addition of thiol tautomer of **24** with nitrile imide **18** to afford a cyclic hydrazone **25**, which was readily cyclized to give intermediate **26** and which subsquently eliminated an alkanethiol to give the final products **27a–o** (cf. Scheme 4).

Moreover, treatment of hydrazonoyl bromide **9** with the appropriate alkyl benzoylhydrazinecarbodithioates in ethanolic triethylamine gave 2,3-dihydro-1,3,4-thiadiazole derivative **30**. Structure of **30** was confirmed on the basis of elemental analysis, spectral data, and an alternative synthesis route. ^{1}HNMR spectrum showed signals at δ 6.09 (s, 2H,

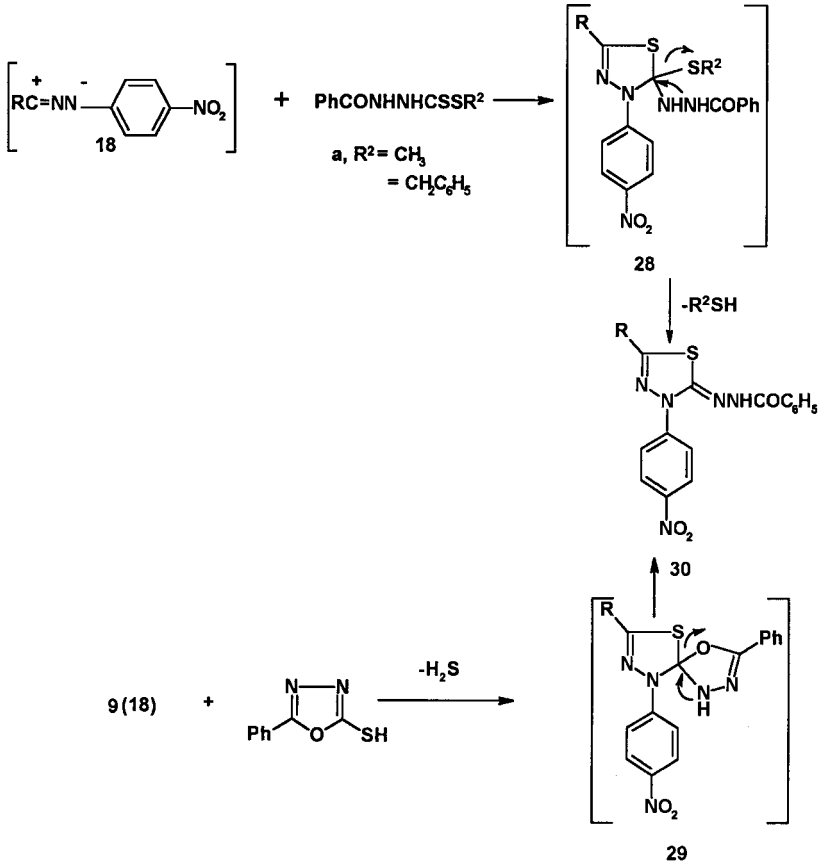


SCHEME 4

CH_2), δ 6.14–8.54 (m, 12H, ArH's), and δ 11.39 (s, br., 1H, NH). Thus, hydrazonoyl bromide **9** reacted with 5-phenyl-1,3,4-oxadiazol-2-thione in chloroform containing triethylamine to afford an identical product in all respects (mp, mixed mp and spectra) with **30** (cf. Scheme 5).

EXPERIMENTAL

All melting points were determined on an electrothermal apparatus and are uncorrected. IR spectra were recorded (KBr) discs on a Shimadzu FT-IR 8201 PC spectrophotometer. ^{1}HNMR spectra were recorded in $CDCl_3$ and $(CD_3)_2SO$ solution on a Varian Gemini 300 MHz spectrometer, and chemical shifts were expressed in δ units using



SCHEME 5

tetramethylsilane (TMS) as an internal reference. Elemental analyses were carried out at the Microanalytical Center of Cairo University. Hydrazonoyl halides[13–21] **1a–g** and alkyl carbodithioates[22,23] were prepared as previously reported.

Synthesis of Ethyl 6-(2*H*-Benzo[3,4-*d*]1,3-dioxolen-5-yl)-4-methyl-2-thioxo-1,3-6-trihydropyrimidine-5-carboxylate (3)

A mixture of ethyl acetoacetate (0.1 mol, 13 g), thiourea (0.11 mol, 8.2 g) and piperinal (0.1 mol, 15 g) in ethanol (30 ml) containing a catalytic amount of concentrated hydrochloric acid (10 drops) was refluxed for 3 h. The reaction mixture then was allowed to stand at room

TABLE I Characterization Data of the Newly Synthesized Compounds

Compd. no.	M.p.,°C	Yield (%) color	Mol. formula mol. wt.	% Analyses calcd./found			
				C	H	N	S
3	175–176	78	$C_{15}H_{16}N_2O_4S$	56.24	5.03	8.74	10.01
		Pale brown	320.37	56.40	4.90	8.50	10.10
4	230–231	78	$C_{16}H_{18}N_4O_4S$	57.47	5.43	8.38	9.59
		Pale brown	334.38	57.70	5.30	8.50	9.70
7a	148–149	70	$C_{24}H_{22}N_4O_6$	62.33	4.80	12.11	
		Pale brown	462.47	62.50	5.00	12.90	
7b	162–164	68	$C_{25}H_{24}N_4O_6$	63.02	5.08	11.76	
		Pale yellow	476.49	62.90	5.10	11.50	
7c	200–201	72	$C_{29}H_{25}N_5O_5$	66.53	4.81	13.38	
		Yellow	523.55	66.70	5.00	13.50	
7d	185–186	75	$C_{24}H_{22}N_4O_5$	64.57	4.97	12.55	
		Yellow	446.47	64.80	5.10	12.70	
7e	174–175	69	$C_{29}H_{24}N_4O_5$	68.49	4.76	11.02	
		Yellow	508.54	68.70	4.90	10.80	
7f	162–164	65	$C_{27}H_{22}N_4O_5S$	63.02	4.31	10.89	6.23
		Brown	514.56	63.50	4.60	11.00	6.40
7g	172–173	63	$C_{33}H_{26}N_4O_5$	70.96	4.69	10.03	
		Brown	558.59	71.20	4.90	10.30	
9	140–143	70	$C_{14}H_{10}BrN_3O_4$	46.18	2.77	11.54	
		Brown	364.16	46.30	2.50	11.70	
11a	173–175	63	$C_{15}H_{10}N_4O_4S$	52.63	2.94	16.37	9.37
		Brown	342.34	52.80	3.00	16.50	9.50
11b	147–150	65	$C_{15}H_{10}N_4O_4Se$	46.29	2.59	14.39	
		Brown	389.23	46.50	2.70	14.50	
14a	262–263	60	$C_{17}H_{12}N_4O_5S$	53.12	3.15	14.58	8.34
		Yellow	384.37	53.30	3.40	14.70	8.50
14b	223–225	68	$C_{17}H_{12}N_4O_5Se$	47.35	2.80	12.99	
		Brown	431.27	47.50	3.00	13.00	
15a	262–264	70	$C_{22}H_{14}N_4O_5S$	59.19	3.16	12.55	7.18
		Orange	446.44	59.40	3.20	12.70	7.30
15b	243–245	68	$C_{22}H_{14}N_4O_5Se$	53.56	2.86	11.36	
		Brown	493.34	53.70	3.00	11.60	
16a	165–167	65	$C_{15}H_9N_5O_5S$	48.52	2.44	18.86	8.63
		Rose	371.33	48.70	2.60	19.00	8.80
16b	185–187	60	$C_{15}H_9N_5O_5Se$	43.08	2.17	16.75	
		Pink	418.23	43.20	2.30	16.50	
17a	288–290	65	$C_{15}H_9N_3O_5S$	52.48	2.64	12.24	9.34
		Yellow	343.32	52.60	2.80	12.00	9.50
17b	208–210	55	$C_{15}H_9N_3O_5Se$	46.17	2.32	10.77	
		Brown	390.22	46.30	2.50	10.50	
21	170–172	65	$C_{21}H_{14}N_4O_4S$	60.28	3.37	13.39	7.66
		Red	418.43	60.40	3.50	13.60	7.80
27a	266–268	65	$C_{22}H_{15}N_5O_4S$	59.32	3.39	15.72	7.20
		Pale brown	445.46	59.60	3.60	15.90	7.40
27b	213–215	62	$C_{20}H_{13}N_5O_5S$	55.17	3.01	16.08	7.36
		Yellow	435.42	55.30	3.20	16.30	7.50

(Continued on next page)

TABLE I Characterization Data of the Newly Synthesized Compounds *(Continued)*

Compd. no.	M.p.,°C	Yield (%) color	Mol. formula mol. wt.	% Analyses calcd./found C	H	N	S
27c	260–263	63	$C_{20}H_{13}N_5O_4S_2$	53.21	2.90	15.51	14.20
		Pale brown	451.49	53.00	3.00	15.30	14.00
27d	297–299	65	$C_{21}H_{14}N_6O_4S$	56.50	3.16	18.82	7.18
		Yellow	446.45	56.70	3.30	19.00	7.40
27e	215–217	67	$C_{23}H_{17}N_5O_4S$	60.12	3.73	15.24	6.98
		Brown	459.49	60.00	3.50	15.00	7.10
27f	240–242	65	$C_{21}H_{15}N_5O_5S$	56.12	3.36	15.58	7.13
		Brown	449.45	56.30	3.60	15.80	7.00
27g	230–233	60	$C_{21}H_{15}N_5O_4S_2$	45.18	3.25	15.04	13.78
		Orange	465.51	45.30	3.50	15.20	13.90
27h	260–263	58	$C_{22}H_{16}N_6O_4S$	57.39	3.50	18.25	6.96
		Yellow	460.47	57.60	3.70	18.40	7.00
27i	198–200	63	$C_{24}H_{17}N_5O_4S$	61.14	3.63	14.85	6.80
		Brown	471.50	61.40	3.80	15.00	6.90
27j	178–180	60	$C_{23}H_{15}N_5O_6S$	56.44	3.09	14.31	6.55
		Pale brown	489.47	56.60	3.30	14.50	6.70
27k	180–182	68	$C_{25}H_{21}N_5O_4S$	61.59	4.34	14.36	6.58
		Yellow	487.54	61.80	4.50	14.60	6.80
27l	218–220	58	$C_{20}H_{17}N_5O_4S$	56.73	4.05	16.54	7.57
		Yellow	423.45	56.90	4.20	16.70	7.70
27m	210–211	61	$C_{21}H_{19}N_5O_4S$	57.66	4.38	16.01	7.33
		Brown	437.48	57.90	4.70	16.30	7.50
27n	180–183	56	$C_{22}H_{21}N_5O_4S$	58.53	4.69	15.51	7.10
		Yellow	451.51	58.70	4.90	15.70	7.30
27o	195–197	50	$C_{25}H_{19}N_5O_4S$	61.85	3.94	14.42	6.60
		Yellow	485.53	62.00	4.00	14.60	6.80
30	275–277	75	$C_{22}H_{15}N_5O_5S$	57.26	3.28	15.18	6.95
		Orange	461.46	57.40	3.40	15.30	7.00

temperature overnight, whereby the solid precipitate so formed was collected by filtration, washed with ethanol, and crystallized from ethanol to give **3** (cf. Tables I and II).

Synthesis of Ethyl 4-(2*H*-Benzo[3,4-*d*]1,3-dioxolen-5-yl)-6-methyl-2-methythio-3,4-dihydropyrimidine-5-carboxylate (4)

Iodomethane (0.005 mol) was added portionwise with stirring to a mixture of compound **3** (1.6 g, 0.005 mmol) and sodium ethoxide solution (prepared by dissolving sodium metal [0.005 mmol, 0.11 g-atom]) in ethanol (15 ml) for 4 h. The reaction mixture was left overnight at room temperature and then the precipitate was collected and crystallized from ethanol to give **4** (cf. Tables I and II).

TABLE II Spectroscopic Data of Some Newly Synthesized Compounds

Compound No.	δ (ppm)
3	1.25 (t, 3H, CH_2CH_3), 2.51 (s, 3H, CH_3), 4.10 (q, 2H, CH_2CH_3), 5.89 (s, 2H, CH_2), 6.64 (s, 1H, CH), 7.25–8.20 (m, 3H, ArH's), 9.61 (s, 1H, NH), and 10.35 (s, 1H, NH)
4	1.20 (t, 3H, CH_2CH_3), 2.50 (s, 3H, CH_3), 2.8 (s, 3H, CH_3), 4.10 (q, 2H, CH_2CH_3), 5.89 (s, 2H, CH_2), 6.64 (s, 1H, CH), 7.25–8.20 (m, 3H, ArH's), and 9.60 (s, 1H, NH)
7a	1.23 (t, 3H, CH_2CH_3), 2.51 (s, 3H, CH_3), 3.96 (s, 3H, OCH_3), 4.12 (q, 2H, CH_2CH_3), 5.88 (s, 2H, CH_2), 6.64 (s, 1H, CH), and 6.87–8.20 (m, 8H, ArH's)
7b	1.25 (t, 3H, CH_2CH_3), 1.37 (t, 3H, CH_2CH_3) 2.51 (s, 3H, CH_3), 4.12 (q, 2H, CH_2CH_3), 4.42 (q, 2H, CH_2CH_3), 5.89 (s, 2H, CH_2), 6.64–8.20 (m, 9H, ArH's and CH pyrimidine)
7c	1.24 (t, 3H, CH_2CH_3), 2.54 (s, 3H, CH_3), 4.12 (q, 2H, CH_2CH_3), 5.87 (s, 2H, CH_2), 6.64 (s, 1H, CH pyrimidine), and 7.01–8.39 (m, 14H, ArH's and NH)
7d	1.25 (t, 3H, CH_2CH_3), 2.51 (s, 3H, CH_3), 2.54 (s, 3H, CH_3), 4.42 (q, 2H, CH_2CH_3), 5.88 (s, 2H, CH_2), 6.63 (s, 1H, pyrimidine CH), and 6.90–8.23 (m, 8H, ArH's)
7e	1.22 (t, 3H, CH_2CH_3), 2.55 (s, 3H, CH_3), 4.12 (q, 2H, CH_2CH_3), 5.83 (s, 2H, CH_2), 6.56 (s, 1H, pyrimidine CH), 6.83–8.24 (m, 13H, ArH's)
7f	1.23 (t, 3H, CH_2CH_3), 2.54 (s, 3H, CH_3), 4.12 (q, 2H, CH_2CH_3), 5.84 (s, 2H, CH_2), 6.59–8.26 (m, 12H, ArH's, and pyrimidine CH)
7g	1.25 (t, 3H, CH_2CH_3), 2.57 (s, 3H, CH_3), 4.11 (q, 2H, CH_2CH_3), 5.80 (s, 2H, CH_2), 6.56–8.67 (m, 16H, ArH's, and pyrimidine CH)
9	4.30 (s, 2H, CH_2) and 7.28–8.19 (m, 8H, ArH's, and NH)
11a	6.62 (s, 2H, CH_2) and 7.00–8.31 (m, 8H, ArH's, and NH)
11b	4.30 (s, 2H, CH_2) and 7.28–819 (m, 8H, ArH's, and NH, exchangeable)
14a	2.43 (s, 3H, CH_3CO), 6.07 (s, 2H, CH_2), and 6.88–8.39 (m, 7H, ArH's)
14b	2.43 (s, 3H, CH_3CON═), 6.08 (s, 2H, CH_2), and 7.26–8.39 (m, 7H, ArH's)
15a	6.08 (s, 2H, CH_2) and 6.95–8.46 (m, 12H, ArH's)
15b	6.08 (s, 2H, CH_2) and 6.95–8.46 (m, 12H, ArH's)
16a	6.09 (s, 2H, CH_2) and 6.85–8.19 (m, 7H, ArH's)
16b	6.09 (s, 2H, CH_2) and 6.85–8.19 (m, 7H, ArH's)
17a	6.18 (s, 2H, CH_2) and 7.13–8.43 (m, 7H, ArH's)
17b	6.05 (s, 2H, CH_2) and 6.85–8.24 (m, 7H, ArH's)
27a	6.07 (s, 2H, CH_2) and 6.87–8.54 (m, 13H, ArH's, and vinyl —CH═)
27c	6.08 (s, 2H, CH_2) and 6.88–8.62 (m, 11H, ArH's, and vinyl —CH═)
27e	2.48 (s, 3H, CH_3), 6.13 (s, 2H, CH_2), and 6.99–8.52 (m, 12H, ArH's)
27g	2.51 (s, 3H, CH_3), 6.09 (s, 2H, CH_2), and 6.86–8.52 (m, 10H, ArH's)
27h	2.45 (s, 3H, CH_3), 6.07 (s, 2H, CH_2), and 6.53–8.54 (m, 11H, ArH's)
27i	6.13 (s, 2H, CH_2) and 6.87–7.55 (m, 12H, ArH's), 8.29 (d, 1H, —CH═CH—), 8.50 (s, 1H, vinyl CH), and 8.51 (d, 1H, —CH═CH—)
27k	1.26 (d, 6H, $(CH_3)_2CH$), 2.95 (sept, 1H, $(CH_3)_2CH$—), 6.09 (s, 2H, CH_2), and 6.09–8.50 (m, 12H, ArH's, and CH vinyl)
27l	2.55 (t, 4H), 2.6 (pent. 4H), 6.07 (s, 2H, CH_2), and 7.87–8.52 (m, 7H, ArH's)

Synthesis of 1,2,4-Triazolino[4,3-*a*]pyrimidines 7a-g

Method A

A mixture of the appropriate hydrazonoyl halides **1a–g** (0.005 mol), compound **3** (1.6 g, 0.005 mol), and triethylamine (0.75 ml, 0.005 mol) in chloroform (20 ml) was refluxed for 10 h. The reaction mixture was evaporated under reduced pressure; the oil residue was triturated with ethanol (10 ml). The resulting solid collected and crystallized from ethanol to give **7a–g** respectively (cf. Tables I and II).

Method B

Equimolar amounts (0.005 mol) of the appropriate hydrazonoyl halides **1a–g**, compound **4**, and sodium ethoxide in ethanol (20 ml) was refluxed for 3 h. The reaction mixture was cooled; the resulting solid was collected and crystallized from ethanol to give identical products in all respects (m.p., mixed m.p., and spectra) with corresponding products obtained by Method A.

Synthesis of ((1E)-2-(2*H*-Benzo[3,4-*d*]1,3-dioxolen-5-yl)-1-aza-2-bromovinyl)(4-nitrophenyl)amine (9)

A solution of bromine (16g, 5 ml, 0.1 mol) in acetic acid (10 ml) was added dropwise while stirring to a solution of piperinal-4-nitrophenylhydrazone (**8**) (g, 28.5 mol) in acetic acid (100 ml) at room temperature. The reaction mixture was stirred for 2 h, the resulting solid was collected and crystallized from ethanol to give **9** (cf. Tables I and II).

Synthesis of 5-(2*H*-Benzo[*d*]1,3-dioxolen-5-yl)-3-(4-nitrophenyl)-1,3,4-thiadiazolin-2-imine (11a) and 5-(2*H*-benzo[*d*]1,3-dioxolen-5-yl)-3-(4-nitrophenyl)-1,3,4-selenadiazolin-2-imine (11b)

Method A

A mixture of **9** (0.005 mol) and potassium thiocyanate or potassium selenocyanate (0.005 mol) in ethanol (30 ml) was stirred at room temperature for 4 h. The crude precipitate was collected, washed with water, and then crystallized from ethanol to give **11a** and **11b** respectively (cf. Tables I and II).

Method B

A mixture of equimolar amount of **9** and thiourea (0.005 mol) in ethanol (20 ml) was refluxed for 30 min. The resulting solid after cooling was collected, washed with water, and crystallized from ethanol to give

identical product in all respects (m.p., mixed m.p., and spectra) with **11a**.

Acylation of 11a and 11b

The appropriate **11a** or **11b** (0.5 g) was stirred in acetic anhydride (10 ml) for 10 min. The reaction mixture was left for 3 h at room temperature. The solid so formed was collected and crystallized from acetic acid to give 1-[5-(2*H*-benzo[*d*]1,3-dioxolen-5-yl)-3-(4-nitrophenyl)-1,3,4-thiadiazolin-2-ylidene]-1-azaacetone (**14a**) and 1-[5-(2*H*-benzo[*d*]1,3-dioxolen-5-yl)-3-(4-nitrophenyl)-1,3,4-selenodiazolin-2-ylidene]-1-azaacetone (**14b**) respectively (cf. Tables I and II).

Benzoylation of 11a and 11b

A mixture of equimolar amounts (0.005 mol) of **11a** or **11b** and benzoyl chloride in pyridine (10 ml) was heated at 80°C for 10 min. The reaction mixture was poured into ice-cold water and acidified with hydrochloric acid. The resulting product was collected, washed with boiling water, and then crystallized from acetic acid to afford 2-[5-(2*H*-benzo[*d*]1,3-dioxolen-5-yl)-3-(4-nitrophenyl)-1,3,4-thiadiazolin-2-ylidene]-2-aza-1-phenylethan-1-one (**15a**) and 2-[5-(2*H*-benzo[*d*]1,3-dioxolen-5-yl)-3-(4-nitrophenyl)-1,3,4-selenodiazolin-2-ylidene]-2-aza-1-phenylethan-1-one (**15b**) respectively (cf. Tables I and II).

Synthesis of 5-(2*H*-Benzo[*d*]1,3-dioxolen-5-yl)-2-(azanitrosomethylene)-3-(4-nitrophenyl)-1,3,4-thiadiazoline (16a) and 5-(2*H*-Benzo[*d*]1,3-dioxolen-5-yl)-2-(azanitrosomethylene)-3-(4-nitrophenyl)-1,3,4-selenadiazoline (16b)

A solution of **11a** (or **11b**) (0.005 mol) in acetic acid (30 ml) was treated with a saturated solution of sodium nitrite (20 ml) while stirring (30 min). The solid so formed was collected and crystallized from acetone (cf. Tables I and II).

Synthesis of 5-(2*H*-Benzo[*d*]1,3-dioxolen-5-yl)-3-(4-nitrophenyl)-1,3,4-thiadiazolin-2-one (17a) and 5-(2*H*-Benzo[*d*]1,3-dioxolen-5-yl)-3-(4-nitrophenyl)-1,3,4-selenadiazolin-2-one (17b)

The appropriate nitroso derivatives **16a** (or **16b**) (0.005 mol) were refluxed in xylene (30 ml) for 30 min and then left overnight at room

temperature. The solvent was removed and the mixture was triturated with ethanol. The so formed solid was collected by filtration and then crystallized from ethanol (cf. Tables I and II).

Synthesis of 5-(2*H*-Benzo[*d*]1,3-dioxolen-5-yl)-3-(4-nitrophenyl)-*N*-phenylimino-2,3-dihydro-1,3,4-thiadiazole (21) and Unsymmetrical Azines 27a–o

Triethylamine (0.75 ml, 0.005 mol) was added while stirring at room temperature to a solution of the hydrazonoyl bromide **9** (0.005 mol) and the appropriate methyl phenyldithiocarbamate (or phenylthiourea) or alkyl carbodithioates **24a–o** (0.005 mol) in ethanol (20 ml). The reaction mixture was stirred for 2 h, the so formed solid was collected and crystallized from acetic acid to give **21** or **27a–o** respectively (cf. Tables I and II).

Synthesis of 2,3-Dihydro-1,3,4-thiadiazole Derivative 30

Method A

Triethylamine (0.75 ml, 0.005 mol) was added while stirring at room temperature to a mixture of the hydrazonoyl bromide **9** (1.8 g, 0.005 mol) and benzoylhydrazinecarbodithioate in ethanol (20 ml). The reaction mixture was stirred for 2 h. The so formed solid was collected and crystallized from acetic acid (cf. Tables I and II).

Method B

A mixture of hydrazonoyl bromide **9** (1.8 g, 0.005 mol), 5-phenyl-1,3,4-oxadiazol-2-thione (0.89 g, 0.005 mol) and triethylamine (0.75 ml, 0.005 mol) in chloroform (20 ml) was refluxed for 10 h; the solvent then was evaporated under reduced pressure. The oil residue was triturated with ethanol (10 ml); the resulting solid was collected and crystallized from acetic acid to give identical product in all respects (m.p., mixed m.p., and spectra) with compound **30** which was obtained from Method A.

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