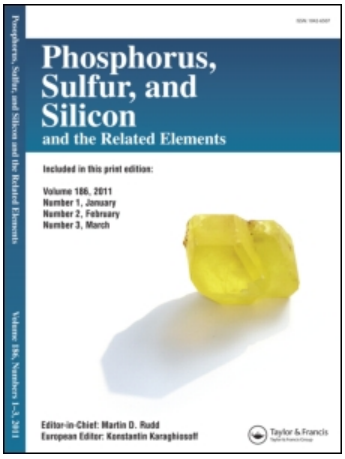

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REACTIONS OF HYDRAZONOYL HALIDES 39[1]: SYNTHESIS OF SOME NEW TRIAZOLES AND 2,3-DIHYDRO-1,3,4-THIADIAZOLES

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C-*acyl*-N-*phenyllhydrazonoyl halides* ***1a–g*** *have been caused to react with 3-(aminomethylthiomethyl)-2H-chromen-2-one in the presence of triethylamine to give triazoles. Also,* C-*acyl*-N-*pyrazolylhydrazonoyl chlorides* ***13a,b*** *react with alkyl carbodithioates (****14*** *or* ***15)a–m*** *afforded 2,3-dihydro-1,3,4-thiadiazoles 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: 1,2,4-triazoles; 1,3-dipolar cycloaddition; 1,3,4-thiadiazoles; 2H-chromen-2-one; carbodithioates; hydrazonoyl halides; thiocarbamates

INTRODUCTION

Pyrazoles and annelated pyrazoles have long been known to exhibit diverse biological activities.[2–7] Among these activities include their use as CAMP phosphodiesterase inhibitors, antipyretic,antitumor, hypnotic and herbicidal agents. Moreover, 1,3,4-thiadiazole and its derivatives have become very useful compound in medicine, agriculture and in many fields of technology.[8] It was of value to combine the two moieties in a series of derivatives with the objective of investigating their expected biological activities.

RESULTS AND DISCUSSIONS

Treatment of hydrazonoyl chloride **1a** with 3-(aminothioxomethyl)-2H-chromen-2-one (**2**) in ethanolic triethylamine afforded three products

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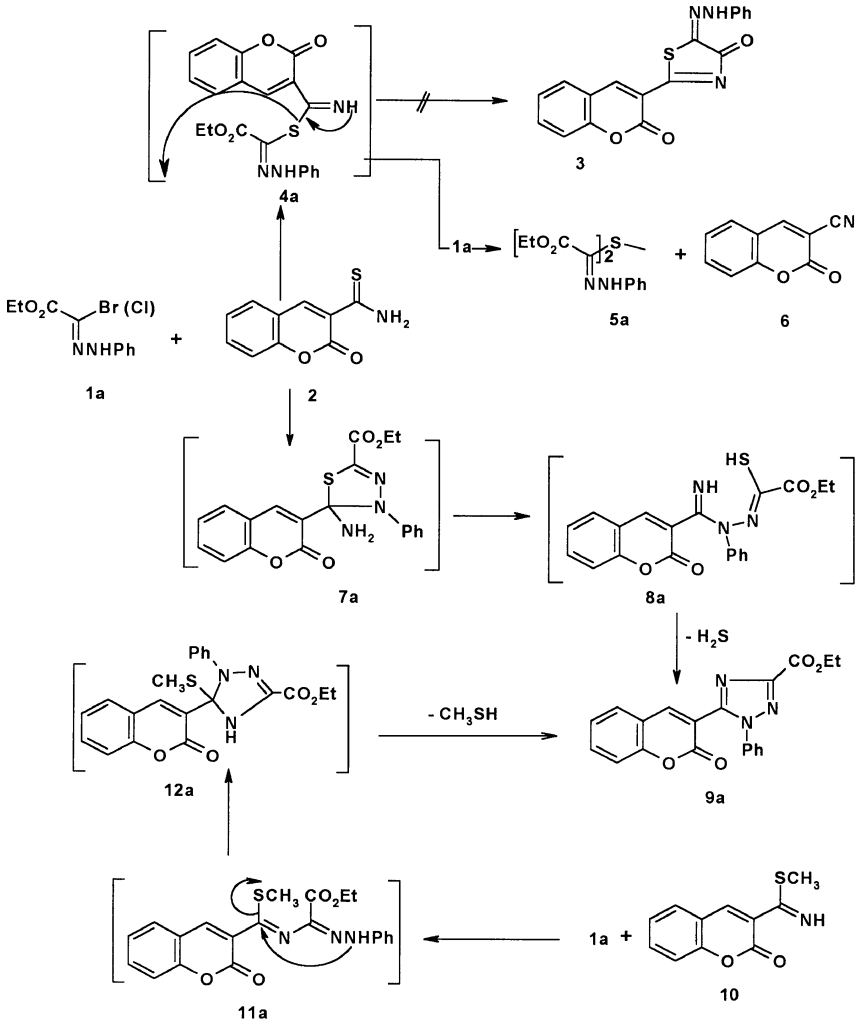
according to TLC. The structures of these products elucidated on the basis of elemental analyses, spectral data, and alternative synthesis method. Thus, IR spectrum of the first product revealed bands at 3330 (NH) and 1701 (CO), and its ^{1}H NMR (δ ppm) spectrum showed signals at $\delta = 1.22$ (t, 6H), 4.20 (q, 4H), 7.01–7.47 (m, 10H), and 10.83 (s, br., 2H). Based on these data the product formulated as ethyl 2-[2-aza-1-(ethoxycarbonyl)-2-(phenylamino)vinylthio]-3-aza-3-(phenylamino)prop-2-enoate (**5**). Structure **5** was further confirmed by independent synthesis. Thus, cyanothioacetamide treated with **1a** to produce a product[9] proved to be identical in all respects (m.p., mixed m.p., and spectra) with **5**. IR spectrum of the second product revealed bands at 2190 (CN) and 1720 (CO) and its ^{1}H NMR (δ ppm) spectrum showed signals at $\delta = 7.23$–7.78 (m, 4H, ArHs) and 9.30 (1H, coumarin 4-H). Also, this compound showed no depression in m.p. with authentic sample.[10] Based on these data, the product formulated as 2-oxo-2-H-chromene-3-carbonitrile (**6**). IR spectrum of the third product revealed bands at 1740, 1715 (COs), and its ^{1}H NMR (δ ppm) spectrum showed signals at $\delta = 1.32$ (t, 3H, CH_2CH_3), 4.29 (q, 2H, CH_2CH_3), 7.21–7.63 (m, 9H, ArHs) and 8.16 (1H, coumarin 4-H). Based on these data, the product formulated as ethyl 5-(2-oxo(2H-chromen-3-yl))-1-phenyl-1,2,4-triazole-3-carboxylate (**9**). Structure **9** was further confirmed by independent synthesis. Thus, treated S-methyl 2-oxo-2H-chromene-3-carboximidothioate (**10**)[11] with **1a** produced a product proved to be identical in all respects (m.p., mixed m.p., and spectra) with **9a**.

The formation of these products can be explained via stepwise path involving substitution via 1,3–addition of thiol **2** to nitrile imide (generated in situ by treatment of **1a** with triethylamine) or 1,3-dipolar cycloaddition of nitrile imide to C=S double bond of **2** to give intermediates **4**, **7**, and **8** which transformed to final products **5**, **6**, and **9**, respectively. All attempts to isolate any intermediates were unsuccessful. Structure **3** was ruled out on the basis of previous data (Scheme 1). Analogy, the hydrazonoyl halides **1b–g** reacts with S-methyl 2-oxo-2H-chromene-3-carboximidothioate (**10**) afforded 5-(2-oxo(2H-chromen-3-yl))-1-phenyl-1,2,4-triazole derivatives **9b–g**, respectively (Scheme 1).

Hydrazonoyl chloride **13a** reacted with each alkyl carbodithioates[12–14] **14a** or **15a** gave the same product **18a** via elimination of alkyl mercaptan. Structure **18a** was elucidated on the basis of elemental analysis and spectral data. Thus, IR spectrum of **18a** revealed bands at 3050, 2939 (CH), 1710 (CO), 1620 (C=N), and 1600 (C=C). Its ^{1}H NMR spectrum showed signals at $\delta = 1.32$ (t, 3H, CH_3CH_2), 4.21 (q, 2H, CH_2CH_3), 6.51 (s, pyrazole C-4), 7.16–7.95 (m, 11H, ArH and NH), and 8.34 (s, 1H, =CH). Structure **18a** was further confirmed



RCOC(X):NNHPh

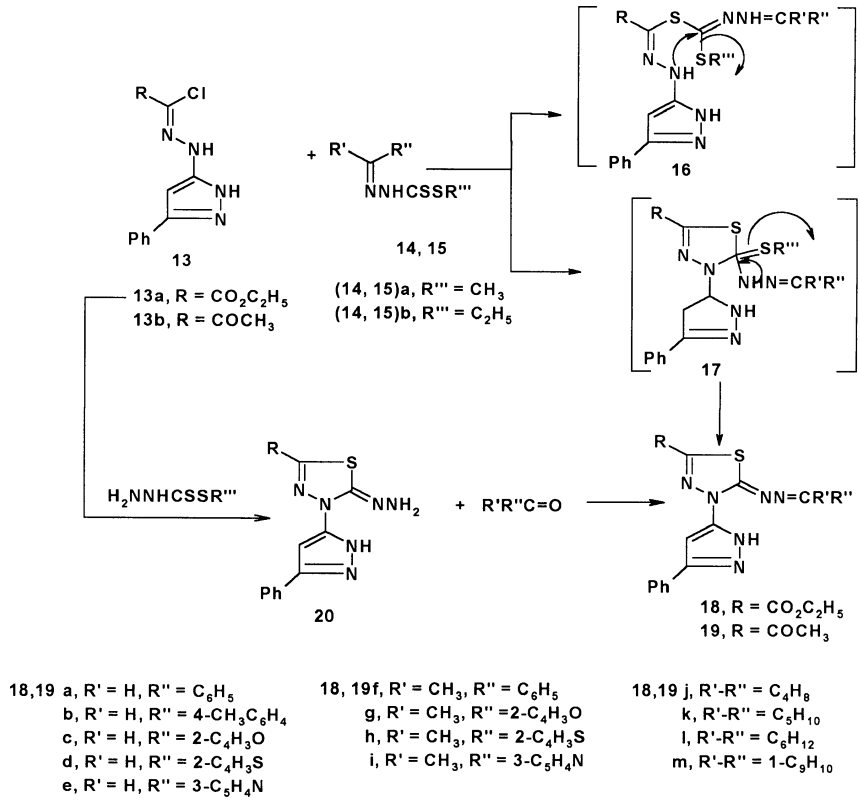
1

1, 4, 5,7-9,11,12 a, R = $CO_2C_2H_5$
b, R = CO_2CH_3
c, R = $COCH_3$
d, R = $CONHC_6H_5$

1, 4, 5,7-9,11,12 e, R = COC_6H_5
f, R = 2-C_4H_3S
g, R = 2-$C_{10}H_7$

SCHEME 1

by independent synthesis. Thus, 1-[5-hydrazono-4-(5-phenyl-2-H-pyrazol-3-yl)-4,5-dihydro-[1,3,4]thiadazol-2-yl]ethanone (**20**), which prepared from hydrazonoyl chloride **13a** and the appropriate alkyl hydrazinecarbodithioates,[15] treated with benzaldehyde to produce a product proved to be identical in all respects (m.p., mixed m.p., and spectra) with **18a** (Scheme 2). Similar hydrazonoyl chloride **13a** reacted with the appropriate alkyl carbodithioates **14b–m** or **15b–m** in ethanolic triethylamine afforded 2,3-dihydro-1,3,4-thiadiazoles **18b–m**, respectively, in a good yield.

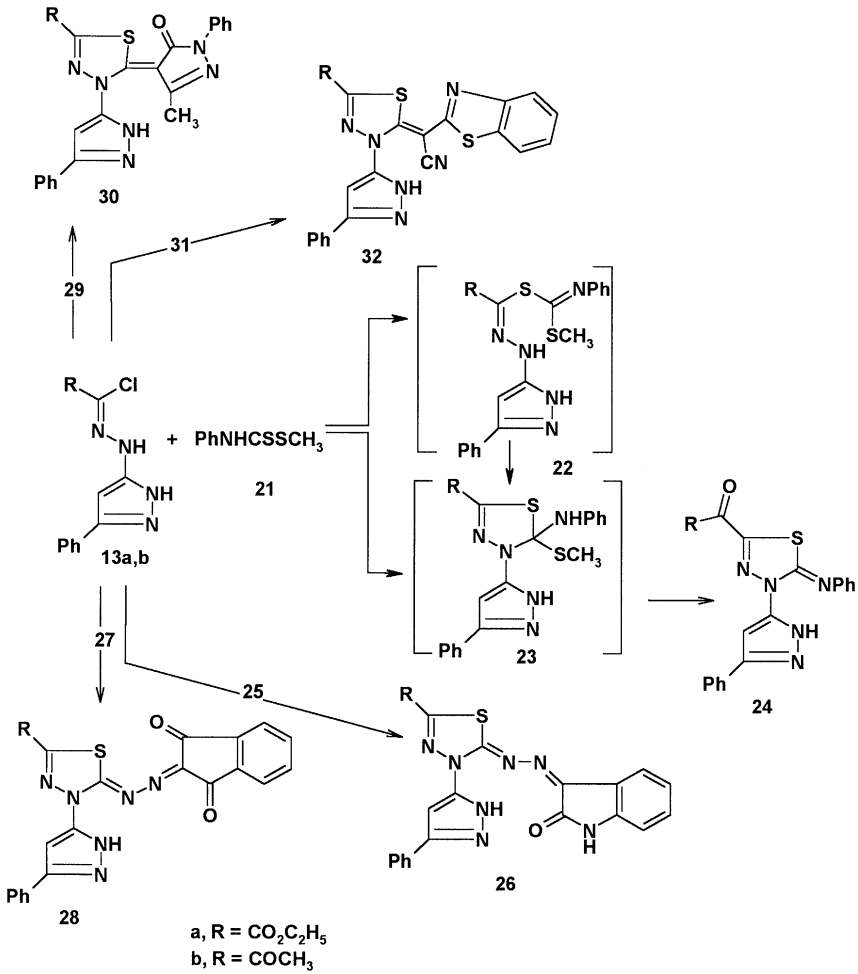


SCHEME 2

Products **18a–m** are assumed to be formed via elimination of alkanethiol from the corresponding cycloadduct **17**, which formed from 1,3-dipolar cycloaddition (or 1,3-addition) of nitrile imide (generated in situ from **13a** and triethylamine) to C=S **14a** or **15a** (Scheme 2). By similar route, the appropriate **14a–m** or **15a–m** reacts with hydrazonoyl

chloride **13b** in ethanolic triethylamine gave 2,3-dihydro-1,3,4-thiadiazoles **19a–m**, respectively (Scheme 2).

Treatment of hydrazonoyl chloride **13b** with methyl dithiocarbamate **21**[16] in ethanolic triethylamine at room temperature afforded one isolable product **24** (Scheme 3). Structure **24** was confirmed by elemental analysis and spectral data. ^{1}H NMR spectrum of **24b** showed signals at $\delta = 2.34$ (s, 3H, CH_3), and 6.99–8.57 (m, 11H, ArH and pyrazole C-4). Formation of **24** can be explained via stepwise path involving substitution via 1,3-addition of thiol **21** to nitrile imide (generate in situ by



SCHEME 3

treatment of **13** with triethylamine) or 1,3-dipolar cycloaddition of nitrile imide to C=S double bond of **21** to give intermediates **22** and **23**, which transformed to final products **24** via elimination of methyl mercaptan (Scheme 3).

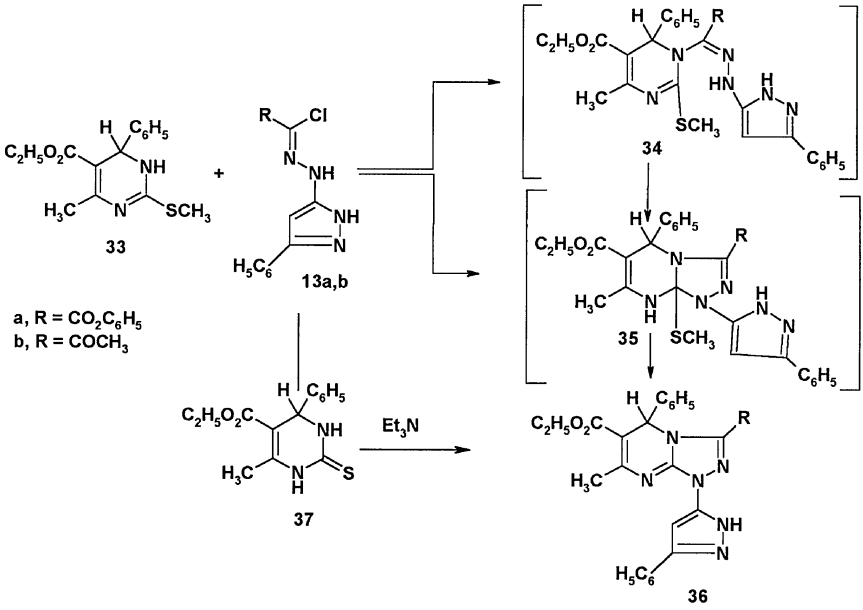
Analogy, hydrazonoyl chloride **13a** reacted with each 3-{aza-[(methylthiothioxomethyl)amino]methylene}indolin-2-one[17] (**25**) or 2-{aza[(methylthiothioxomethyl)amino]methylene}indane-1,3-dione[17] (**27**) or 3-methyl-4-(methylthiothioxomethyl)-1-phenyl-2-pyrazolin-5-one[18] (**29**) or 2-benzothiazol-2-yl-3-methylthio-3-thioxopropanenitrile[19] (**31**) in ethanolic triethylamine to afford ethyl 2-[1,2-diaza-2-(2-oxoindolin-3-ylidene)ethylidene]-3-(3-phenylpyrazol-5-yl-1,3,4-thiadiazoline-5-carboxylate (**26a**), ethyl 2-[1,2-diaza-2-(1,3-dioxoindan-2-ylidene)ethylidene]-3-(3-phenylpyrazol-5-yl)-1,3,4-thiadiazoline-5-carboxylate (**28a**), ethyl 2-(3-methyl-5-oxo-1-phenyl(2-pyrazolin-4-ylidene))-3-(3-phenylpyrazo;-5-yl)-1,3,4-thiadiazoline-5-carboxylate(**30a**), and ethyl 2-(benzothiazol-2-ylcyanomethylene)-3-phenyl-1,3,4-thiadiazolin-5-carboxylate (**32a**), respectively (Scheme 3). By a similar route, hydrazonoyl chlorides **13b** reacted with the appropriate **25**, **27**, **29**, or **31** afforded 2,3-dihydro-1,3,4-thiadiazoles **26b**, **28b**, **30b** and **32b**, respectively.

Finally, the appropriate hydrazonoyl chlorides **13a**,**b** reacted with ethyl 6-methyl-2-methylthio-4-phenyl-3,4,5,6,-teterahydropyrmidine-5-carboxylate[27] (**33**) in ethanolic sodium ethoxide gave triazolo[4,3-*a*]pyrimidine **36a** and **36b**, respectively (Scheme 4).

The structure of **36** was elucidated on the basis of elemental analyses, spectral data, and independent method synthesis. IR spectra of **36** revealed bands near 1712, 1665 (CO), 1625 (C=N), and 1595 (C=C). ^{1}H NMR spectra of **36b** showed signals at $\delta = 1.18$ (t, 3H, CH_2CH_3), 2.32 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 4.09 (q, 2H, CH_2CH_3), 5.14 (s, 1H, Pyrimidine C-4), 6.12 (s, 1H, pyrazole C-4), 7.20–7.96 (m, 10H, ArHs), and 8.10 (s, 1H, NH). The formation of **36** can be explained via 1,3-dipolar cycloaddition or 1,3-addition of nitrile imides (prepared in situ from hydrazonoyl halides **13** with triethylamine or sodium ethoxide) to **33** to give intermediates **34** and **35**, which gave final products **36** by elimination of methyl mercaptan (Scheme 4).

EXPERIMENTAL

All melting points were determined on an electrothermal apparatus and are uncorrected. IR spectra were recorded (KBr discs) on a Shimadzu FTIR 8201 PC spectrophotometer. ^{1}H NMR spectra were recorded in $CDCl_3$ and $(CD_3)_2SO$ on a Varian Gemini 200 MHz spectrometer, and



SCHEME 4

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. Hydrazonoyl halides **1a–g**,[21–26] **13a**,**b**,[27] and alkyl carbodithioates (**14–15**)**a–m**[12–14] were prepared as previously reported.

Reaction of 1 with 3-(Aminothioxomethyl)-2H-chromen-2-one (2)

Triethylamine (0.5 g, 0.75 ml, 5 mmol) was added dropwise while stirring to a mixture of the hydrazonoyl chloride **1a** (1.13 g, 5 mmol) and 3-(aminothioxomethyl)-2H-chromen-2-one (**2)** (1.03 g, 5 mmol) in ethanol (20 ml) at room temperature for 30 min. The yellow solid formed was collected and crystallized from ethanol to give **5**. The filtrate evaporates to its half volume under reduced pressure and cooling. The solid was collected and crystallized from acetic acid to afford compound **6**. The final filtrate was evaporated, and the residue oil was triturated with methanol afforded **9a** (which crystallized from ethanol).

Synthesis of 1.2,4-Triazole 9a–g

Triethylamine (0.5 g, 0.75 ml, 5 mmol) was added dropwise while stirring to a mixture of the appropriate hydrazonoyl halides **1a–g** and S-methyl 2-oxo-2H-chromene-3-carboximidothioate (**10**) (5 mmol each) in ethanol (20 ml) for 2 h. The solid formed was collect, washed with water and crystallized from ethanol to give 1,2,4-triazoles **9a–g**, respectively (Tables I–III).

Synthesis of 2,3-Dihydro-1,3,4-thiadiazoles (18,19)a–m

Method A

Triethylamine (0.5 g, 0.75 ml, 5 mmol) was added dropwise with stirring to a mixture of the appropriate alkyl carbodithioates (**14–15**)**a–m** (5 mmol) and appropriate hydrazonoyl chlorides **13a**,**b** (5 mmol) in ethanol (20 ml). The resulting solid, which formed after 30 min, was collected and crystallized from acetic acid gave the corresponding 2,3-dihydro-1,3,4-thiadiazoles **18a–m** and **19a–m**, respectively in a good yield (Tables I–III).

Method B

A mixture of hydrazine derivative **20a** (1.65 g, 5 mmol) and benzaldehyde (0.53 g, 5 mmol) in ethanol (20 ml) was stirred for 30 min. The solid formed was collect, washed with water, and crystallized from ethanol gave products identical in all respects (m.p., mixed m.p., and spectra) with **18a**.

Synthesis of 2,3-Dihydro-1,3,4-thiadiazoles 24, 26, 28, 30, and 32

Triethylamine (0.5 g, 0.75 ml, 5 mmol) was added dropwise while stirring to a mixture of the appropriate hydrazonoyl chlorides **13a**,**b** and the appropriate S-methyl phenylthiocarbamate—3-{aza[(methylthiothioxomethyl)amino]methylene}indolin-2-one (**25**), 2{aza[(methylthiothioxomethyl)amino]methylene}indane-1,3-dione (**27**), 3-methyl-4-(methylthiothioxomethyl)-1-phenyl-2-pyrazolin-5-one (**29**), 2-benzothiazol-2-yl-3-methylthio-3-thioxopropanenitrile (**31**) (5 mmol each)—in ethanol (20 ml) for 2 h. The solid formed was collected, washed with water and crystallized from ethanol to give 2,3-dihydro- 1,2,4-thiadiazoles **24**, **26**, **28**, **30**, and **32**, respectively (Tables I and II).

TABLE I Characterization Data of the Newly Synthesized Compounds

Comp. no.	m.p. (°C) solvent	Color yield (%)	Mol. formula mol. wt.	Calcd./found (%)			
				C	H	N	S
9a	211–212	Pale brown	$C_{20}H_{15}N_3O_4$	66.48	4.18	11.36	—
	EtOH	50	361.36	66.62	4.00	11.50	
9b	224–225	Pale brown	$C_{19}H_{13}N_3O_4$	65.70	3.44	12.10	—
	EtOH	55	347.33	65.92	3.45	12.30	
9c	189–190	Brown	$C_{19}H_{13}N_3O_3$	68.87	3.95	12.68	—
	EtOH	52	331.34	68.78	4.10	12.80	
9d	218–219	Pale brown	$C_{24}H_{16}N_4O_3$	70.58	3.95	13.72	—
	EtOH	60	408.42	70.70	3.75	13.56	
9e	205–207	Pale orange	$C_{24}H_{15}N_3O_3$	73.27	3.84	10.68	—
	EtOH	55	393.41	73.30	3.90	10.70	
9f	175–176	Green	$C_{22}H_{13}N_3O_3S$	66.15	3.28	9.48	10.82
	EtOH	25	399.43	66.25	3.40	9.70	
9g	168–169	Deep brown	$C_{28}H_{17}N_3O_3$	75.84	3.86	9.48	—
	EtOH	40	443.47	75.98	3.60	9.62	
18a	170–172	Yellow	$C_{21}H_{18}N_6O_2S$	60.27	4.34	20.08	7.66
	EtOH	73	418.48	60.70	4.34	20.20	7.50
18b	142–144	Yellow	$C_{22}H_{20}N_6O_2S$	61.10	4.66	19.34	7.41
	EtOH	70	432.51	60.90	4.65	19.43	7.32
18c	151–152	Yellow	$C_{19}H_{16}N_6O_3S$	55.87	3.95	20.58	7.85
	EtOH	80	408.44	55.65	4.10	20.70	7.90
18d	202–203	Yellow	$C_{19}H_{16}N_6O_3S_2$	53.76	3.80	19.80	15.11
	EtOH	60	424.51	53.60	4.10	19.90	14.95
18e	201–203	Yellow	$C_{20}H_{18}N_7O_2S$	57.13	4.32	23.32	7.63
	EtOH	66	420.48	57.14	4.39	23.20	7.30
18f	237–238	Yellow	$C_{22}H_{20}N_6O_2S$	61.10	4.66	19.43	7.41
	AcOH	75	432.51	61.24	4.87	19.34	7.30
18g	222–223	Gold	$C_{20}H_{18}N_6O_3S$	56.86	4.29	19.89	7.59
	EtOH	68	422.47	56.98	4.13	19.90	7.65
18h	224–226	Yellow	$C_{20}H_{18}N_6O_2S_2$	54.78	4.14	19.16	14.62
	AcOH	85	438.53	54.80	4.06	19.30	14.40
18i	248–250	Yellow	$C_{21}H_{19}N_7O_2S$	58.19	4.42	22.62	7.40
	AcOH	60	433.50	58.26	4.61	22.42	7.52
18j	243–244	Yellow	$C_{19}H_{20}N_6O_2S$	57.56	5.08	21.20	8.09
	AcOH	65	396.48	57.42	5.26	21.10	7.90
18k	212–214	Yellow	$C_{20}H_{22}N_6O_2S$	58.52	5.40	20.47	7.81
	EtOH	68	410.50	58.63	5.55	20.30	7.70
18l	239–240	Yellow	$C_{21}H_{24}N_6O_2S$	59.41	5.70	19.80	7.55
	AcOH	80	424.53	59.50	5.40	19.65	7.52
18m	218–220	Yellow	$C_{24}H_{22}N_6O_2S$	62.86	4.84	18.33	6.99
	AcOH	78	458.55	62.72	4.80	18.52	6.78
19a	223–225	Yellow	$C_{20}H_{16}N_6OS$	61.84	4.15	21.63	8.25
	AcOH	75	388.45	61.90	4.30	21.80	8.50
19b	165–167	Yellow	$C_{21}H_{18}N_6OS$	62.67	4.51	20.88	7.97
	AcOH	65	402.47	62.75	4.60	20.75	8.20
19c	160–161	Orange	$C_{18}H_{14}N_6O_2S$	57.13	3.73	22.21	8.47
	EtOH	72	378.42	57.25	3.90	22.40	8.60

(Continued on next page)

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

Comp. no.	m.p. (°C) solvent	Color yield (%)	Mol. formula mol. wt.	Calcd./found (%) C	H	N	S
19d	188–189	Brown	$C_{18}H_{14}N_6OS_2$	54.81	3.58	21.30	16.26
	EtOH	65	394.48	54.60	3.70	21.10	16.30
19e	179–181	Pale brown	$C_{19}H_{15}N_7OS$	58.60	3.88	25.18	8.23
	EtOH	60	389.44	58.50	4.00	25.40	8.28
19f	235–236	Yellow	$C_{21}H_{18}N_6OS$	62.67	4.51	20.88	7.97
	AcOH	74	402.47	62.70	4.60	21.10	8.20
19g	233–234	Yellow	$C_{19}H_{16}N_6O_2S$	58.15	4.11	21.42	8.17
	AcOH	62	392.44	58.30	4.20	21.20	8.00
19h	190–192	Brown	$C_{19}H_{16}N_6OS_2$	55.86	3.95	20.57	15.70
	AcOH	65	408.51	55.60	3.80	20.70	15.60
19i	>300	Yellow	$C_{20}H_{17}N_7OS$	59.54	4.25	24.30	7.95
	AcOH	71	403.47	59.60	4.30	24.50	8.00
19j	148–149	Yellow	$C_{18}H_{18}N_6OS$	59.00	4.95	22.93	8.75
	EtOH	68	366.45	59.20	4.80	23.10	8.90
19k	148–150	Yellow	$C_{19}H_{20}N_6OS$	59.98	5.30	22.10	8.34
	EtOH	58	380.48	59.30	5.10	22.00	8.40
19l	133–134	Yellow	$C_{20}H_{22}N_6OS$	60.89	5.62	21.30	8.13
	EtOH	67	394.50	61.10	5.70	21.10	8.10
19m	233–234	Yellow	$C_{23}H_{20}N_6OS$	64.47	4.70	19.61	7.48
	AcOH	75	428.52	64.50	4.60	19.40	7.60
20	85–87	Yellow	$C_{14}H_{14}N_6O_2S$	50.90	4.27	25.44	9.71
	EtOH	65	330.37	50.66	4.40	25.15	9.80
24a	234–245	Yellow	$C_{20}H_{17}N_5O_2S$	61.37	4.38	17.89	8.19
	EtOH	55	391.46	61.56	4.25	17.90	8.24
24b	172–173	Yellow	$C_{19}H_{15}N_5OS$	63.14	4.18	19.38	8.87
	EtOH	65	361.43	63.12	3.10	19.40	8.70
26a	289–291	Orange	$C_{22}H_{17}N_7O_3S$	57.51	3.73	21.34	6.98
	DMF	78	459.49	57.72	3.94	21.45	7.24
26b	>315	Orange	$C_{21}H_{15}N_7O_2S$	58.73	3.52	22.83	7.47
	DMF	80	429.46	58.90	3.30	22.70	7.60
28a	200–202	Red	$C_{23}H_{16}N_6O_4S$	62.15	3.63	12.61	7.21
	AcOH	60	444.47	62.24	3.50	12.52	7.10
28b	213–215	Red	$C_{22}H_{14}N_4O_3S$	58.47	3.41	17.79	6.79
	AcOH	70	472.49	58.20	3.50	17.90	7.10
30a	152–154	Yellow	$C_{24}H_{20}N_6O_3S$	61.00	4.27	17.79	6.79
	AcOH	75	472.53	60.80	4.30	17.50	6.62
30b	289–291	Yellow	$C_{23}H_{18}N_6O_2S$	62.43	4.10	18.99	7.25
	AcOH	70	442.50	62.50	4.20	18.90	7.00
32a	274–246	Yellow	$C_{23}H_{16}N_6O_2S_2$	58.46	3.14	17.78	13.57
	DMF	68	472.55	58.60	3.30	17.60	13.60
32b	279–281	Yellow	$C_{22}H_{14}N_6OS_2$	59.71	3.19	18.99	14.49
	DMF	55	442.52	59.90	2.90	18.65	14.52
36a	206–207	Yellow	$C_{27}H_{26}N_6O_4$	65.05	5.26	16.89	—
	EtOH	65	498.55	55.90	5.10	16.70	
36b	148–150	Yellowish-	$C_{26}H_{26}N_6O_4$	66.65	5.16	17.94	—
	EtOH	brown	468.52	66.50	5.00	18.10	

TABLE II ^{1}H NMR Spectra of Some Selected Synthesized Compounds

Compd. no.	^{1}H NMR (δ ppm)
9b	3.88 (s, 3H), 7.20–7.63 (m, 9H) and 8.16 (s, 1H)
9c	2.55 (s, 3H), 7.20–7.63 (m, 9H) and 8.16 (s, 1H)
9d	7.20–7.63 (m, 14 H), 8.16 (s, 1H) and 9.25 (s, br., 1H)
9e	7.20–7.65 (m, 14 H) and 8.16 (s, 1H)
9f	7.06–7.65 (m, 12 H) and 8.16 (s, 1H)
9g	7.20–7.63 (m, 15 H), 8.16 (s, 1H) and 8.22 (s, 1H)
18b	1.30 (t, 3H), 2.35 (s, 3H), 4.20 (q, 2H), 6.50 (s, 1H), 7.10–7.50 (m, 9H), 8.10 (s, 1H), and 8.45 (s, 1H)
18c	1.30 (t, 3H), 4.20 (q, 2H), 6.30 (d, 1H), 6.35 (t, 1H), 6.5 (s, 1H), 7.22–7.48 (m, 7H), and 8.32 (s, 1H)
18d	1.30 (t, 3H), 4.20 (q, 2H), 6.50 (s, 1H), 7.22–7.48 (m, 9H), and 8.32 (s, 1H)
18e	1.3 (t, 3H), 4.20 (q, 2H), 6.50 (s, 1H), and 7.21–9.32 (m, 11H)
18f	1.30 (t, 3H), 2.00 (s, 3H), 4.22 (q, 2H), 6.5 (s, 1H), 7.22–7.60 (m, 10 H), and 8.62 (s, 1H)
18g	1.30 (t, 3H), 2.00 (s, 3H), 4.20 (q, 2H), 6.3 (m, 2H), 6.5 (s, 1H), 7.22–7.48 (m, 6 H), and 8.90 (s, 1H)
18h	1.30 (t, 3H), 2.10 (s, 3H), 4.22 (q, 2H), 6.50 (s, 1H), 7.00–7.48 (m, 8 H), and 8.80 (s, 1H)
18i	1.30 (t, 3H), 2.09 (s, 3H), 4.22 (q, 2H), 6.50 (s, 1H), and 7.00–9.12 (m, 10 H)
18j	1.22 (t, 3H), 1.35 (t, 4H), 1.37 (m, 4H), 4.41 (q, 2H), 6.50 (s, 1H), 7.22–7.48 (m, 5 H) and 8.82 (s, 1H)
19a	2.20(s, 3H), 6.50 (s, 1H), 7.20–7.63 (m, 10H), 8.16 (s, 1H), and 8.45 (s, br., 1H)
19b	2.20 (s, 3H), 2.35 (s, 3H), 6.50 (s, 1H), 7.10–7.50 (m, 9H), 8.10 (s, 1H), and 8.45 (s, 1H)
19c	2.20 (s, 3H), 6.30 (d, 1H), 6.35 (t, 1H), 6.5 (s, 1H), 7.22–7.48 (m, 7H), and 8.32 (s, 1H)
19d	2.20 (s, 3H), 6.50 (s, 1H), 7.22–7.48 (m, 9H), and 8.32 (s, 1H)
19e	2.21 (s, 3H), 6.53 (s, 1H), and 7.21–9.32 (m, 11H)
19f	2.00 (s, 3H), 2.20 (s, 3H), 6.5 (s, 1H), 7.22–7.60 (m, 10 H), and 8.62 (s, 1H)
19g	2.10 (s, 3H), 2.30 (s, 3H), 6.50 (s, 1H), 7.00–7.48 (m, 8 H), and 8.80 (s, 1H)
19h	2.10 (s, 3H), 2.23 (s, 3H), 6.50 (s, 1H), 7.00–7.48 (m, 8 H), and 8.80 (s, 1H)
19i	2.09 (s, 3H), 2.20 (s, 3H), 6.50 (s, 1H), and 7.00–9.12 (m, 10 H)
36a	1.30 (t, 6H), 1.71 (s, 3H), 4.19 (q, 2H), 4.20 (q, 2H), 4.59 (s, 1H), 6.50 (s, 1H), 7.06–7.48 (m, 10 H), and 9.50 (s, 1H)

TABLE III ^{13}C NMR Spectra of Some Selected Synthesized Compounds

Compd. no.	^{13}C NMR (δ ppm)
9a	13.6, 59.1, 121, 125, 126, 127, 128, 129, 140, 150, 154, 162, 167
18a	13.3, 58.9, 90, 127, 128, 129, 130, 131, 136, 149, 154, 155, 161, 163, 164
18c	13.3, 58, 91, 110, 127, 128, 129, 136, 143, 149, 154, 155, 161, 163, 164
36a	13.3, 13.7, 17, 59.3, 59.9, 91, 123, 126, 127, 128, 129, 136, 142, 161, 163, 165

Synthesis of Ethyl 5-Hydrazono-4-(5-phenyl-2H-pyrazol-3-yl)-4,5-dihydro-[1,3,4-]thiadiazole-2-carboxylate (20)

Triethylamine (0.5 g, 0.75 ml, 5 mmol) was added dropwise to amixture of equimolar quantities of C-ethoxycarbonyl-N-(5-phenyl)pyrazol-3-ylhydrazonoyl chloride (**13a**) and methyl hydrazinecarbodithioate (5 mmol each) in ethanol (15 ml) while stirring for 2 h. The resulting solid was collected and crystallized from ethanol to give **20** (Tables I and II).

Synthesis of Triazolo[4,3-*a*]Pyrimidines 36a,b

Method A

An equimolar amount of each of the appropriate hydrazonoyl chlorides **13a**,**b** and sodium ethoxide (5 mmol) in ethanol (20 ml) was refluxed for 3 h. The reaction mixture was cooled, and the resulting solid was collected and crystallized from ethanol to give **36a** and **36b**, respectively (Tables I–II).

Method B

A mixture of the appropriate hydrazonoyl chlorides **13a**,**b** (5 mmol) and compound **37** (1.37 g, 5 mmol) in chloroform (20 ml) containing triethylamine (0.5 g, 0.75 ml, 5 mmol) was refluxed for 10 h. Chloroform was evaporated under reduced pressure, and the residue solid was crystallized from ethanol to give products identical in all respects (m.p., mixed m.p., and spectra) with corresponding products obtained by method A.

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