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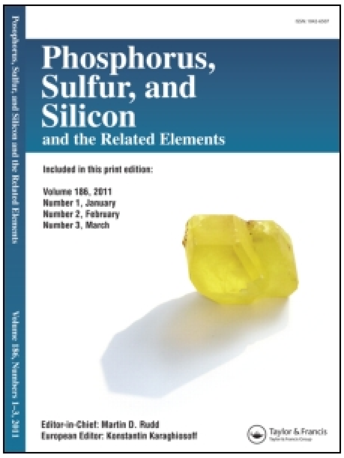

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Reactions of Hydrazonoyl Halides 56[1]: Synthesis and Reactions of 1-Bromo-2-(5-chloro-benzofuranyl)ethanedione-1-phenylhydrazone

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Reactions of Hydrazonoyl Halides 56[1]: Synthesis and Reactions of 1-Bromo-2-(5-chlorobenzofuranyl)ethanedione-1-phenylhydrazone

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2,3-Dihydro-1,3,4-thiadiazoles and triazolino[4,3-a]pyrimidines containing benzofuran moiety were prepared from reaction of 1-bromo-2-(5-chlorobenzofuranyl) ethanedione-1-phenylhydrazone with each of potassium thiocyanate, alkyl carbodithioates and pyrmidine-2-thiones. All newly synthesized were confirmed by elemental analysis, spectral data, and alternative route synthesis whenever possible.

Keywords 1,3-dipolar cycloaddition; 2,3-Dihydro-1,3,4-thiadiazoles; hydrazonoyl halides; triazolino[4,3-*a*]pyrimidines

INTRODUCTION

Hydrazonoyl halides have emerged as an important class of intermediates particularly for the synthesis of heterocyclic compounds.[1–7] The interesting pharmacological properties of furan derivatives,[8] in relation to various changes in the structures of these compounds, are worth studying in order to synthesize less toxic and more potent drugs. Thus, present investigation deals with the synthesis of some new 2,3-dihydro-1,3,4-thiadiazoles and triazolino[4,3-*a*]pyrimidines containing benzofuran moiety.

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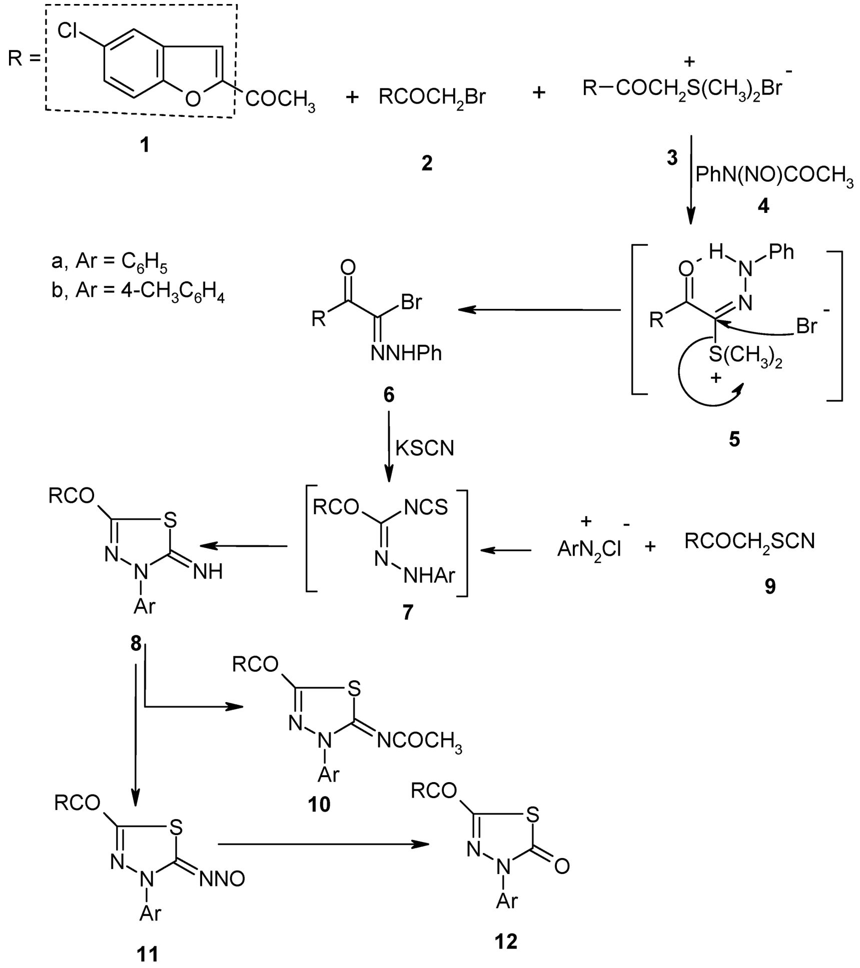
RESULTS AND DISCUSSION

Treatment of 5-chlorobenzofuranyl-2-oxoethylsulfonium bromide **(3)**[9] with N-nitrosoacetanilide **(4)**[10] in ethanol at room temperature to give 1-bromo-2-(5-chlorobenzofuranyl)ethanedione-1-phenylhydrazone **(6)**. Structure **6** was established by elemental analysis, spectral data, and chemical transformation. Thus, treatment of **6** with potassium thiocyanate in ethanol at room temperature afforded product which gave analytical and spectral in accord with their formation as: 5-chlorobenzo[*d*]furan-2-yl-2-imino-3-phenyl(1,3,4-thiadiazolin-5-yl)ketone (**8**). IR spectrum of **8** revealed the absence bands at 2156 (SCN) and showed bands at 3316 (NH), 1640 (CO conjugated). Its ^{1}HNMR spectrum showed signals at $\delta = 7.43–7.55$ (m, 5H), 7.59–7.88 (m, 4H), and 8.08 (s, 1H). Upon shaking with D_2O a new signal singlet appeared at $\delta = 4.55$ assignable to DOH proton and multiplicity signals at $\delta = 7.43–8.00$ ppm. Compound **8** was authentically sample by the reaction of [2-(5-chlorobenzo[*d*]furan-2-yl)-2-oxoethyl]thiocarbonitrile (**9**), with benzenediazonium chloride in ethanolic sodium acetate solution (Scheme 1). Such results indicate that both the azo coupling of **9** and the reaction of **6** with potassium thiocyanate proceed through one common intermediate. The latter is undoubtedly the hydrazone **7**, which cyclizes readily under the reaction conditions to give **8** (Scheme 1).

More evidence on the structure **8** can be come from the following chemical transformation. Thus, acetylation of **8** with acetic anhydride to yield the corresponding 1-aza-1-5-[(5-chlorobenzo[d]furan-2-yl)carbonyl]-3-phenyl](1,3,4-thiadiazolin-2-ylidene))acetone (**10**). ^{1}H NMR spectrum of **10** showed signals at $\delta = 2.38$ (s, 3H), 7.26–7.61 (m, 5H), 7.73–7.80 (m, 3H), and 8.20 (s, 1H). Nitrosation of **8** with sodium nitrite in acetic acid solution to give 2-(azanitrosomethylene)-3-phenyl(1,3,4-thiadiazolin-5-yl)-5-chlorobenzo-[*d*]furan-2-ylketone (**11**). The IR spectrum of **11** showed no band due to NH, but contained common bands at 1646 (CO) and 1490 (NO). Compound **11a** decomposed to 5-[(5-chlorobenzo[d]furan-2-yl)carbonyl]-3-phenyl-1,3,4-thiadiazolin-2-one (**12a**) upon boiling in xylene solution. The IR spectrum of **12** revealed two absorption bands near 1692 and 1645 cm^{-1}.

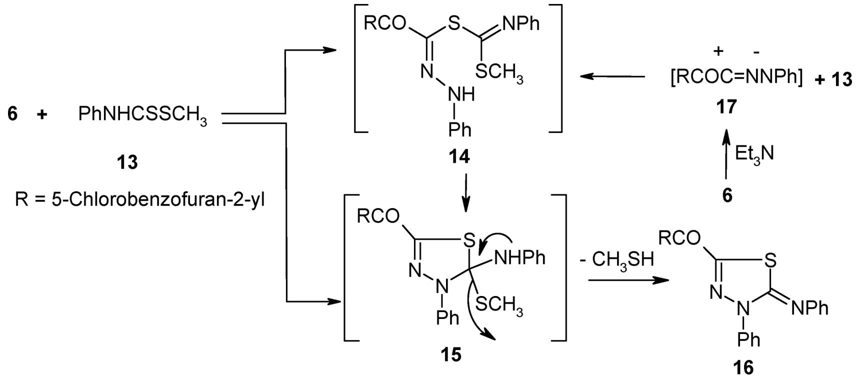
Compound **6** reacted with methyl phenylthiocarbamate[11] (**13**) in ethanolic triethylamine solution to give 2-(azaphenylmethylene)-3-phenyl(1,3,4-thiadiazolin-5-yl)-5-chlorobenzo[*d*]furan-2-yl ketone (**16**) (Scheme 2). Structure **16** was confirmed on the basis of spectral data and elemental analysis. Thus, ^{1}H NMR spectrum of **16** showed signals at $\delta = 6.46–7.01$ (m, 5H) and 7.20–7.59 (m, 9H).

In the light of the foregoing results, the mechanism outlined in scheme 2 seems to be the most plausible pathway for the formation



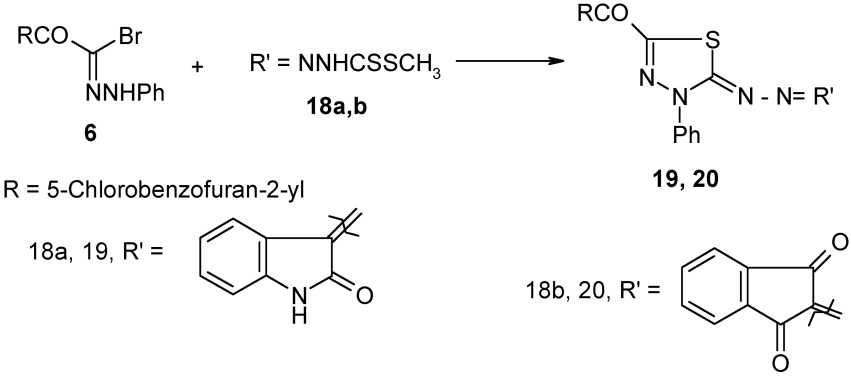
SCHEME 1

of **16** from the reaction of the **6** with **13**. The reaction involves initial formation of thiohydrazonate **14**, which undergoes intermolecular cyclization as soon as it is formed to yield the intermediate **15** or via 1,3-dipolar cycloaddition of nitrilimine **17**, (which prepared in situ from **6** with triethylamine) to C=S double bond of **13**. The formation of **14** and **15** are similar to the reaction of hydrazonoyl chloride with 1-phenyl-1,4-dihydrotetrazole-5-thione[12] and 5-phenyl-1,3,4-thiadiazole-2(3H)-thione[13].



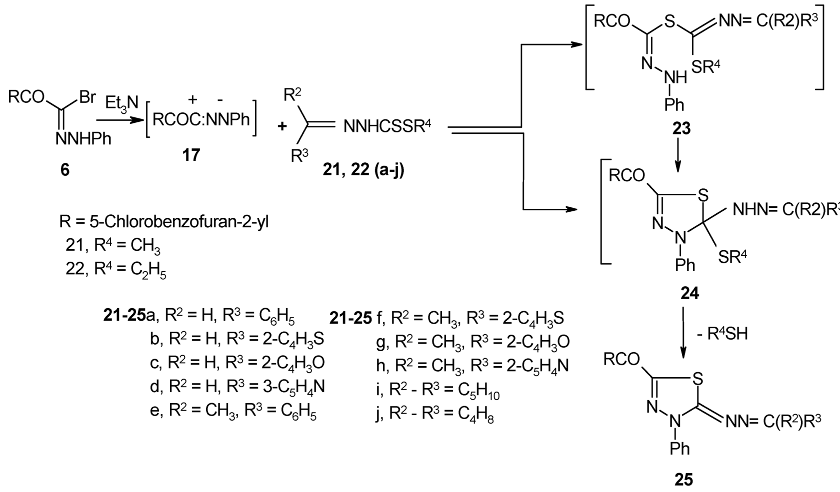
SCHEME 2

Analogously, **6** reacted with each of 3-{aza-[(methylthioxomethyl)-amino]methylene}indoline-2-one[14] and 3-{aza-[(methylthioxomethylamino]-methylene}indan-1,3-dione[15] to give 3-(1,2-diaza-2-{5-[(5-chlorobenzo[*d*]-furan-2-yl)carbonyl]-3-phenyl-(1,3,4-thiadiazolin-2-ylidene))-ethylidine}indolin-2-one (**19**) and 2-(1,2-diaza- 2-{5-[(5-chlorobenzo[*d*]furan-2-yl)carbonyl]-3-phenyl-(1,3,4-thiadiazolin-2-ylidene))ethylidine}indane-1,3-dione (**20**), respectively (Scheme 3).



SCHEME 3

Also, treatment of [(1-aza-phenylvinyl)amino]methylthiomethane-1-thione **21a**[16] with **6** in ethanolic triethylamine at room temperature, gave 2-(1,2-diaza-3-phenylprop-2-enylidene)-3-phenyl-(1,3,4-thiadiazolin-5-yl)-5-chlorobenzo[*d*]furan-2-ylketone **25a** (Scheme 4). Structure **25a** was confirmed by elemental analysis, spectral data, and alternative route synthesis. ^{1}H NMR spectra of **25a** showed signals at $\delta = 6.46$–7.30 (m, 10H), 7.42–7.59 (m, 3H), and 8.10 (s, 1H). Thus,



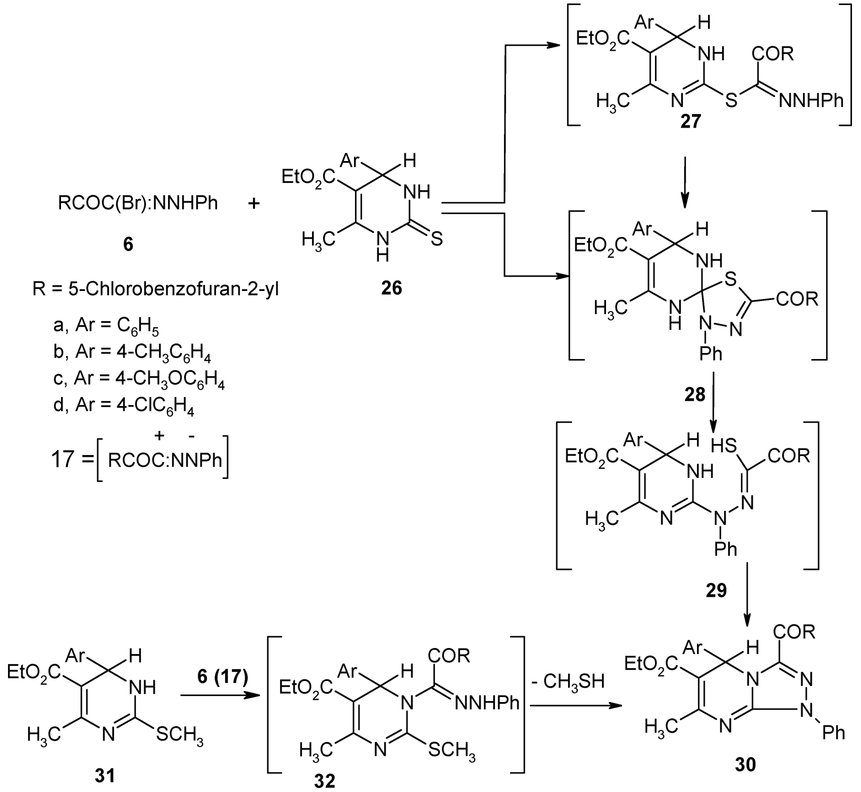
SCHEME 4

treatment of **6** with **22a** in ethanolic triethylamine gave product identical in all aspects (mp., mixed mp., and spectra) with **25a**.

Similarly, **6** reacted with other alkyl carbodithioates[17–19] **21–22 (b-j)** in ethanol containing triethylamine to afford 2,3-dihydro-1,3,4-thiadiazoles **25(b–j),** respectively (Scheme 4).

Also, treatment of **6** with the appropriate pyrimidine-2-thiones **26a-d**[20] in boiling chloroform gave triazolino[4,3-*a*]pyrimidines in a good yields **30a-d**, respectively (Scheme 5). Structure of **30** was elucidated on the basis elemental analysis, spectral data, and alternative synthesis route.

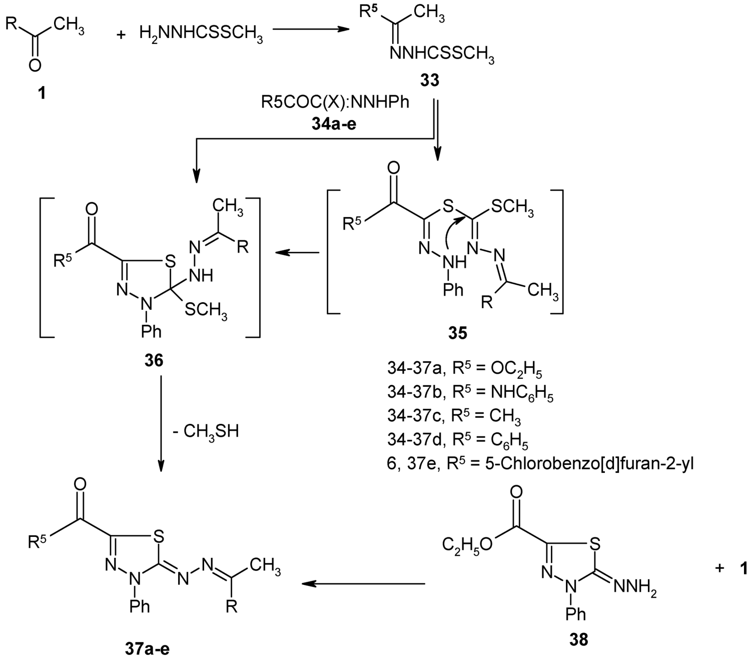
Thus, ^{1}H NMR spectrum of **30a** showed signals at $\delta = 1.23$ (t, 3H), 2.56 (s, 3H), 4.09 (q, 2H), 7.05 (s, 1H), 7.16–7.25 (m, 3H), 7.44–7.72 (m, 8H), 8.05 (s, 1H), and 8.24 (d, 2H). Its IR spectrum revealed bands at 1702 (CO ester), 1650 (CO conjugated) and 1615 (C=N). In addition, compound **30a** was obtained from the reaction of ethyl 6-methy-2-methylthio-4-phenyl-3,4-dihydropyrimidine-5-carboxylate[20] **31a** with **6** in boiling sodium ethoxide solution. The mechanism outlined in scheme 5 seems to be the most plausible pathway for the formation of **30** from the reaction of **6** with the appropriate **26a–d** or **31a–d**. Two possible pathways can account for the formation **30**: 1)- 1,3-addition of the thiol tautomer **26** to the nitrilium imide **17** to give the thiohydrazonate ester **27** which undergoes nucleophilic cyclization to yield spiro compounds **28**. The latter ring open to **29** which cyclized to yield **30** by loss hydrogen sulfide; and 2)- 1,3-cycloaddition of nitrilium imide to



SCHEME 5

C=S double bond of **26** can give directly **31** (Scheme 5). All attempts to isolate any intermediates are unsuccessful.

Also, 2-acetyl-5-chlorobenzo[*d*]furan was reacted with methyl hydrazine carbodithioate[21,22] in isopropyl alcohol to give {[1-aza-2-(5-chlorobenzo[*d*]furan-2-yl)prop-1-enyl]amino}methylthiomethane-1-thione **33** (Scheme 6). Structure **33** was confirmed by elemental analysis, spectral data, and its reaction with hydrazonoyl halides. Thus, ^{1}H NMR spectrum of **33** showed signals at $\delta = 2.34$ (s, 3H), 2.66 (s, 3H), 7.04–7.57 (m, 4H) and 9.99 (s, br., 1H). Thus, compound **33** reacted with *C*-ethoxycarbonyl-*N*-phenyl-hydrazonoyl chloride **34a**, in ethanol containing triethylamine at room temperature to afford ethyl 2-[1,2-diaza-3-(5-chlorobenzo[*d*]furan-2-yl)but-2-enylidene]-3-phenyl-1,3,4-thiadiazolin-5-carboxylate **37a** (Scheme 6). Structure **37** was elucidated by elemental analysis, spectral data and alternative method. Thus, ^{1}H NMR spectrum of **37a** showed signals at $\delta = 1.44$



SCHEME 6

(t, 3H), 2.45 (s, 3H), 4.46 (q, 2H) and 7.12–8.09 (m, 9H). Hydrazine **38** reacted with **1** in isopropyl alcohol to give product identical in all aspects (mp., mixed mp., and spectra) with **37a**. Thus, thiodiazoline **38**[23] reacted with 2-acetyl-5-chlorobenzofuran (**1**) in 2-propanol to give product identical in all aspect (mp., mixed mp., and spectra) with **37a**. Similarly, the appropriate hydrazonoyl halides **34b-d** and **6** reacted with carbodithioate **33** in ethanolic triethylamine at room temperature afforded 2,3-dihydro-1,3,4-thiadiazoles **37b-e**, respectively.

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}H NMR spectra were recorded in $CDCl_3$ and $(CD_3)_2SO$ solutions on a Varian Gemini 300 MHz spectrometer and chemical shifts are expressed in δ units using TMS as an internal reference. Elemental analyses were carried out at the Microanalytical Center of the Cairo University.

1-(5-Chlorobenzo[d]furan-2-oyl)methane dimethylsulfonium bromide (3)

A mixture of 2-bromo-1-(5-chlorobenzo[*d*]furan-2-yl)ethan-1-one (**2**) (13.63 g, 50 mmol) and dimethyl sulfide (3.2 g, 50 mmol) in ethanol (100 mL) was boiled for 30 min. The reaction mixture was cooled and diluted with ether (50 mL) for complete precipitation. The crude solid was collected and recrystallized from ethanol to give **3** (Table I).

3-Aza-2-bromo-1-(5-chlorobenzo[d]furan-2-yl)-3-(phenylamino)-prop-2-en-1-one (6)

A mixture of sulfonium bromide **3** (16.2 g, 50 mmol) and *N*-nitrosoacetanilide (10 g, 60 mmol) in ethanol (100 mL) was stirred for 2 h. The yellow solid was collected and recrystallized from acetic acid to give **6** (Table I).

[2-(5-chlorobenzeno[*d*]furan-2-yl)-2-oxoethyl]thiocarbonitrile (9)

A mixture of 2-bromo-1-(5-chlorobenzo[***d***]furan-2-yl)ethan-1-one (**2**) (1.36 g, 5 mmol) and potassium thiocyanate (0.49 g, 50 mmol) in ethanol (25 mL) was boiled for 30 min. The resulting solid, which formed after cooling, was collected, washed with water, and recrystallized from ethanol to give **9** (Tables I and II).

3-Aryl-5-chlorobenzo[*d*]furan-2-yl-2-imino-(1,3,4-thiadiazolin-5-yl)ketone 8a and 8b

Method A

A mixture of **6** (1.88 g, 5 mmol) and potassium thiocyanate (0.58 g, 6 mmol) in ethanol (25 mL) was stirred at room temperature for 3 h. The resulting solid was collected, washed with water and recrystallized from ethanol to give **8a** (Tables I and II).

Method B

The appropriate arenediazonium chloride (5 mmol) was added dropwise to a cold solution of ethanol (50 mL), containing a [2-(5-chlorobenzeno[*d*]furan-2-yl)-2-oxoethyl]thiocarbonitrile (**9**) (1.25 g, 5 mmol) and sodium acetate (1.3 g, 10 mmol), while stirring at 0–5°C. The resulting solid was collected and recrystallized from ethanol to give **8a** and **8b**, respectively (Tables I and II).

TABLE I Characterization Data of the Newly Synthesized Compounds

Compd. no.	Mp., °C solvent	Yield % color	Mol. formula mol. wt.	% Analyses, calcd./found			
				C	H	N	S
3	138-40	Yellow	$C_{12}H_{12}Br\,Cl\,O_2S$	42.94	3.60	—	9.55
	EtOH	75	335.64	42.88	3.41	—	9.37
6	194-6	Yellow	$C_{16}H_{10}Br\,Cl\,N_2O_2$	50.89	2.67	7.42	—
	EtOH	60	377.62	50.71	2.80	7.24	—
8a	171-3	Brown	$C_{17}H_{10}Cl\,N_3O_2S$	57.39	2.83	11.81	9.01
	EtOH	59	355.79	57.59	2.60	12.00	9.20
8b	179-82	Brown	$C_{18}H_{12}Cl\,N_3O_2S$	58.46	3.27	11.36	8.67
	EtOH	61	369.82	58.62	3.46	11.51	8.85
9	140-1	Yellow	$C_{11}H_6Cl\,N\,O_2S$	52.49	2.40	5.57	12.74
	EtOH	70	251.69	52.69	2.59	5.37	12.91
10a	254-5	Brown	$C_{19}H_{12}Cl\,N_3O_3S$	57.36	3.04	10.56	8.06
	AcOH	75	397.83	57.18	3.19	10.73	8.18
10b	233-5	Yellow	$C_{20}H_{14}Cl\,N_3O_3S$	58.32	3.43	10.20	7.79
	AcOH	73	411.86	58.49	3.28	10.39	7.59
11a	140-3	Brown	$C_{17}H_9Cl\,N_4O_3S$	53.06	2.36	14.56	8.33
	EtOH	60	384.79	53.18	2.55	14.39	8.52
11b	125-7	Brown	$C_{18}H_{11}Cl\,N_4O_3S$	54.21	2.78	14.05	8.04
	EtOH	54	398.82	54.40	2.62	14.20	7.89
12a	152-4	Brown	$C_{17}H_9Cl\,N_2O_3S$	57.23	2.54	7.85	8.99
	EtOH	50	356.78	57.42	2.39	7.66	9.10
12b	168-70	Brown	$C_{18}H_{11}Cl\,N_2O_3S$	58.30	2.99	7.55	8.65
	EtOH	52	370.81	58.50	3.11	7.70	8.48
16	268-71	Yellow	$C_{23}H_{14}Cl\,N_3O_2S$	63.96	3.27	9.73	7.42
	DMF	55	431.89	63.78	3.44	9.59	7.30
19	> 300	Orange	$C_{25}H_{14}Cl\,N_5O_3S$	60.06	2.82	14.01	6.41
	DMF	63	499.92	60.20	3.00	13.88	6.56
20	295-7	Brown	$C_{26}H_{19}Cl\,N_4O_4S$	60.17	3.69	10.80	6.18
	DMF	65	518.97	60.30	3.88	10.66	6.01
25a	279-80	Orange	$C_{24}H_{15}Cl\,N_4O_2S$	62.81	3.29	12.21	6.99
	DMF	71	458.92	62.66	3.45	12.40	7.16
25b	257-9	Red	$C_{22}H_{13}Cl\,N_4O_2S_2$	56.83	2.82	12.05	13.79
	DMF	63	464.94	56.66	3.00	12.20	13.59
25c	254-5	Brown	$C_{22}H_{13}Cl\,N_4O_3S$	58.87	2.92	12.48	7.14
	DMF	69	448.88	59.00	3.11	12.74	7.32
25d	142-5	Brown	$C_{23}H_{14}Cl\,N_5O_2S$	60.07	3.07	15.23	6.97
	DMF	57	459.90	59.82	3.22	15.41	7.16
25e	253-5	Red	$C_{25}H_{17}Cl\,N_4O_2S$	63.49	3.62	11.85	6.78
	DMF	75	472.94	63.66	3.44	11.99	6.58
25f	246-9	Red	$C_{23}H_{15}Cl\,N_4O_2S_2$	57.67	3.16	11.70	13.39
	DMF	72	478.97	57.79	3.36	11.89	13.18
25g	240-2	Brown	$C_{23}H_{15}Cl\,N_4O_3S$	59.68	3.27	12.10	6.93
	DMF	56	462.90	59.87	3.10	12.28	7.14
25h	233-5	Brown	$C_{24}H_{16}Cl\,N_5O_2S$	60.82	3.40	14.78	6.77
	DMF	60	473.93	61.00	3.21	14.59	6.91

(Continued on next page)

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

Compd. no.	Mp., °C solvent	Yield % color	Mol. formula mol. wt.	% Analyses, calcd./found			
				C	H	N	S
25i	215-8	Yellow	$C_{23}H_{19}Cl\,N_4O_2S$	61.26	4.25	12.42	7.11
	AcOH	66	450.94	61.44	4.08	12.59	7.31
25j	238-40	Yellow	$C_{22}H_{17}Cl\,N_4O_2S$	60.48	3.92	12.82	7.34
	DMF	64	436.91	60.67	4.10	12.66	7.41
30a	212-5	Red	$C_{30}H_{23}Cl\,N_4O_4$	66.85	4.30	10.39	—
	AcOH	70	538.98	66.99	4.11	10.19	
30b	168-9	Red	$C_{31}H_{25}Cl\,N_4O_4$	67.33	4.56	10.13	—
	EtOH	72	553.00	67.53	4.38	10.30	
30c	169-72	Red	$C_{31}H_{25}Cl\,N_4O_5$	65.44	4.43	9.85	—
	EtOH	68	569.00	65.29	4.59	9.99	
30d	218-21	Red	$C_{30}H_{22}Cl_2N_4O_4$	62.84	3.87	9.77	—
	DMF	63	573.42	63.00	3.70	9.94	
33	172-5	Yellow	$C_{12}H_{11}Cl\,N_2O\,S_2$	48.23	3.71	9.37	21.46
	EtOH	75	298.81	48.42	3.89	9.18	21.28
37a	169-72	Yellow	$C_{21}H_{17}Cl\,N_4O_3S$	57.21	3.89	12.71	7.27
	AcOH	74	440.90	57.41	4.06	12.58	7.40
37b	240-2	Orange	$C_{25}H_{18}Cl\,N_5O_2S$	61.54	3.72	14.35	6.57
	AcOH	65	487.96	61.71	3.57	14.20	6.74
37c	200-3	Yellow	$C_{20}H_{15}Cl\,N_4O_2S$	58.46	3.68	13.64	7.80
	AcOH	69	410.87	58.59	3.50	13.48	7.99
37d	203-6	Yellow	$C_{25}H_{17}Cl\,N_4O_2S$	63.49	3.62	11.85	6.78
	AcOH	70	472.947	63.66	3.80	11.69	6.98
37e	272-5	Red	$C_{27}H_{16}Cl_2N_4O_3S$	59.24	2.95	10.23	5.86
	DMF	74	547.412	59.44	3.15	10.44	6.04

3-Aryl-2-(azanitrosomethylene)(1,3,4-thiadiazolin-5-yl)-5-chlorobenzo[*d*]furan-2-ylketone 11a,b

A cold saturated solution of sodium nitrite (10 ml) was added dropwise to the appropriate**8a** and **8b** (1 g) in acetic acid (20 mL) in an ice bath while stirring. The reaction mixture was stirred for 30 min. The resulting solid was collected, washed with water, and recrystallized from acetone to give **11a** and **11b,** respectively (Tables I and II).

3-Aryl-5-[(5-chlorobenzo[d]furan-2-yl)carbonyl-1,3,4-thiadiazolin-2-one 12a,b

A solution of the appropriate **11a** or **11b** (0.5 g) in xylene (20 mL) was boiled for 15 min and then the solvent was evaporated under reduced pressure. The residue oil was triturated with petroleum ether (40–60°C) and the solid formed was collected and recrystallized from acetic

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

Compd. no.	^{1}H NMR (δ ppm)
6	IR: 3245 (NH), 1643 (CO conjugated) ^{1}HNMR: 6.25–7.81 (m, 9H) and 9.35 (s, 1H)
8b	IR: 3314 (NH), 1643 (CO conjugated) ^{1}HNMR: 2.44 (s, 3H), 6.26–7.71 (m, 8H), 8.06 (s, 1H)
9	IR: 2160 (CN), 1666 (CO) ^{1}HNMR: 4.54 (s, 2H), 7.44–7.72 (m, 4H)
10b	IR: 1645 (CO conjugated) ^{1}HNMR: 2.26 (s, 3H), 2.49 (s, 3H), 7.39–7.80 (m, 7H), 8.20 (s, 1H)
11a	IR: 1645 (CO conjugated) ^{1}HNMR: 6.26–7.71 (m, 9H), 8.06 (s, 1H)
11b	IR: 1645 (CO conjugated) ^{1}HNMR: 2.43 (s, 3H), 6.26–7.71 (m, 8H), 8.06 (s, 1H)
12a	IR: 1692, 1645 (CO) ^{1}HNMR: 6.26–7.71 (m, 9H), 8.06 (s, 1H)
12b	IR: 1692, 1645 (CO) ^{1}HNMR: 2.42 (s, 3H),6.26–7.71 (m, 8H), 8.06 (s, 1H)
25e	^{1}HNMR: 2.50 (s, 3H), 7.26–8.16 (m, 14 H)
25f	^{1}HNMR: 2.46 (s, 3H), 7.05–8.15 (m, 12 H)
25g	^{1}HNMR: 2.40 (s, 3H), 6.50–8.16 (m, 12 H)
25h	^{1}HNMR: 2.59 (s, 3H), 7.26–8.64 (m, 13 H)
30b	^{1}HNMR: 1.23 (t, 3H), 2.21 (s, 3H), 2.55 (s, 3H), 4.08 (q, 2H), 6.98 (s, 1H), 7.01–8.27 (m, 13 H)
30c	^{1}HNMR: 1.22 (t, 3H), 2.55 (s, 3H), 3.68 (s, 3H), 4.08 (q, 2H), 6.70 (s, 1H), 6.99–8.27 (m, 13 H)
30d	^{1}HNMR: 1.25 (t, 3H), 2.55 (s, 3H), 4.09 (q, 2H), 7.02 (s, 1H), 7.19–8.27 (m, 13 H)
33	IR: 3167 (NH), 1605 (C=C) ^{1}HNMR: 2.34 (s, 3H), 2.66 (s, 3H), 7.04–7.57 (m, 4H), 9.99 (s, br., 1H)
37a	IR: 1740 (CO) ^{1}HNMR: 1.46 (t, 3H), 2.34 (s, 3H), 3.21 (q, 2H), 7.12–8.09 (m, 9H)
37c	IR: 11680 (CO) ^{1}HNMR: 2.45 (s, 3H), 2.65 (s, 3H), 7.12–8.09 (m, 9H)

acid to give 1,3,4-thiadiazolinones **12a** and **12b,** respectively (Tables I and II).

3-Aryl-1-aza-1-{5-[(5-chlorobenzo[d]furan-2-yl)carbonyl]-(1,3,4-thiadiazolin-2-ylidene)}acetone 10a,b

A mixture of the appropriate **8a** or **8b** (1 g) in acetic acid (10 mL) and acetic anhydride (5 ml) was warmed for 5 min at 70°C. The reaction mixture was poured onto ice water (40 mL). The solid was collected and recrystallized to give the*N*-acetyl derivatives **10a** and **10b**, respectively (Tables I and II).

2,3-Dihydro-1,3,4-Thiadiazoles 16, 19–20, and 25a–j

Triethylamine [0.5 g (0.75 ml), 5 mmol] was added dropwise with stirring to a mixture of the appropriate alkyl carbodithioates **13, 17, 18, or (21-22)a-j** (5 mmol) and **6** (1.8 g, 5 mmol) in ethanol (20 mL). The resulting solid, which formed after 30 min, was collected and recrystallized from *N*, *N*-dimethylformamide to give 2,3-dihydro-1,3,4-thiadiazoles **16, 19, 20, 25a-j**, respectively, in a good yield (Tables I and II).

1,2,4-Triazolo[4,3-*a*]pyrimidines 30a-d

Method A

An equimolar amount of the hydrazonoyl bromide **6**, the appropriate of pyrimidines **31a–d,** and sodium ethoxide (5 mmol) in ethanol (20 mL) was heated under reflux for 3 h. The reaction mixture was cooled and the resulting solid was collected and recrystallized from ethanol to give **30a-d**, respectively (Tables I and II).

Method B

A mixture of the hydrazonoyl bromide **6** (5 mmol), the appropriate **26a-d** (5 mmol) and triethylamine [0.5 g, (0.75 mL), 5 mmol] in chloroform (20 mL) containing 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 aspects (mp., mixed mp., and spectra) with corresponding products obtained by method A.

{[1-Aza-2-2-(5-chlorobenzo[*d*]furan-2-yl)prop-1-en]amino}methyl-thiomethan-1-thion (33)

A mixture of 2-acetyl-5-chlorobenzo[*d*]furan (**1**)(0.92 gm, 5 mmol) and methyl hydraziocarbodithioate (0.66 g, 5 mmol) in 2-propanol (20 mL) was stirred at room temperature for 2 h. The resulting solid was collected and recrystallized to give **33** (Table I).

2-[1,2-Diaza-3-(5-chlorobenzo[d]furan-2-yl)but-2-enylidene]-3-phenyl(1,3,4-thiadiazolin-5-yl) 4-Substituted Ketenes 37a-e

Method A

Triethylamine [0.5 g (0.75 ml), 5 mmol] was added dropwise with stirring to a mixture of the appropriate methyl carbodithioate **33** and the appropriate hydrazonoyl halides **34a-d** or **6** (5 mmol) in ethanol (20 mL). The resulting solid, which formed after 30 min, was collected and crystallized from *N*, *N*-dimethylformamide to afford the corresponding thiadiazolines **37a-e**, respectively (Tables I and II).

Method B

A mixture of thiadiazoline **38** (1.32 g, 5 mmol) and 2-acetyl-5-chlorobenzofuran (0.92 g, 5 mmol) in 2-propanol (20 mL) was heated for 10 min then cooled. The resulting solid was collected and recrystallized from acetic acid to give **37a** (Tables I and II).

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