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### Reactions with Hydrazonoyl Halides 42<sup>1</sup>: Synthesis of Some New 2,3-Dihydro-1,3,4thiadiazoles, 2,3-Dihydro-1,3,4-selenadiazoles and Triazolino<sup>[4], [3]</sup>pyrimidines

Abdou O. Abdelhamid<sup>a</sup>; Mohamed A. M. Alkhodshi<sup>a</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

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## Reactions with Hydrazonoyl Halides 42<sup>1</sup>: Synthesis of Some New 2,3-Dihydro-1,3,4- thiadiazoles, 2,3-Dihydro-1,3,4-selenadiazoles and Triazolino[4,3-*a*]pyrimidines

Abdou O. Abdelhamid  
Mohamed A. M. Alkhodshi

Department of Chemistry, Faculty of Science, Cairo University,  
Giza 12316, Egypt

*2,3-Dihydro-1,3,4-thiadiazoles, 2,3-dihydro-1,3,4-selenadiazoles, unsymmetrical azines and triazolino[4,3-*a*]pyrimidines were prepared from reaction of (2*Z*)-3-aza-2-bromo-1-naphtho[1,2-*d*]furan-2-yl-3-(phenylamino)prop-2-en-1-one (6) with each of potassium thiocyanate, potassium selenocyanate, alkyl carbodithioate, ethyl 6-methyl-2-methylthio-4-substituted 3,4-dihydropyrimidine-5-carboxylate or (ethyl 4-methyl-6-substituted 2-thione-1,3,6-trihydropyrimidine-5-carboxylate). All compounds were elucidated on the basis of elemental analysis, spectral data, and alternative synthesis method whenever possible.*

**Keywords** 1,3-dipolar cycloaddition; 1,3,4-selenadiazoles; 1,3,4-thiadiazoles; hydrazonoyl bromide; nitrilimine; triazolo[4,3-*a*]pyrimidines

## INTRODUCTION

1,3,4-Thiadiazoles have activities on many biological systems such as: antitumor,<sup>2</sup> hypoglycemic properties,<sup>3</sup> antihistamine,<sup>4</sup> and anticholinergic.<sup>5</sup> Also hydrazonoyl halides have been widely for the synthesis of heterocyclic compounds.<sup>6–10</sup> We report here the synthesis of triazolo[4,3-*a*]pyrimidines, 2,3-dihydro-1,3,4-thiadiazoles, 2,3-dihydro-1,3,4-selenadiazoles, and unsymmetrical azines.

## RESULTS AND DISCUSSION

Reaction of 2-bromo-1-naphtho[1,2-*d*]furan-2-ylethan-1-one (**2**) with dimethylsulfide in boiling ethanol under reflux afforded 1-naphtho[1,2-*d*]furan-2-yl-2-oxoethylsulfonium bromide (**3**). Structure of the latter product was established by elemental analysis, spectral data, and

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Address correspondence to Abdou O. Abdelhamid, Department of Chemistry, Faculty of Science, Cairo University, Giza 12316, Egypt. E-mail: abdou\_abdelhamid@yahoo.com

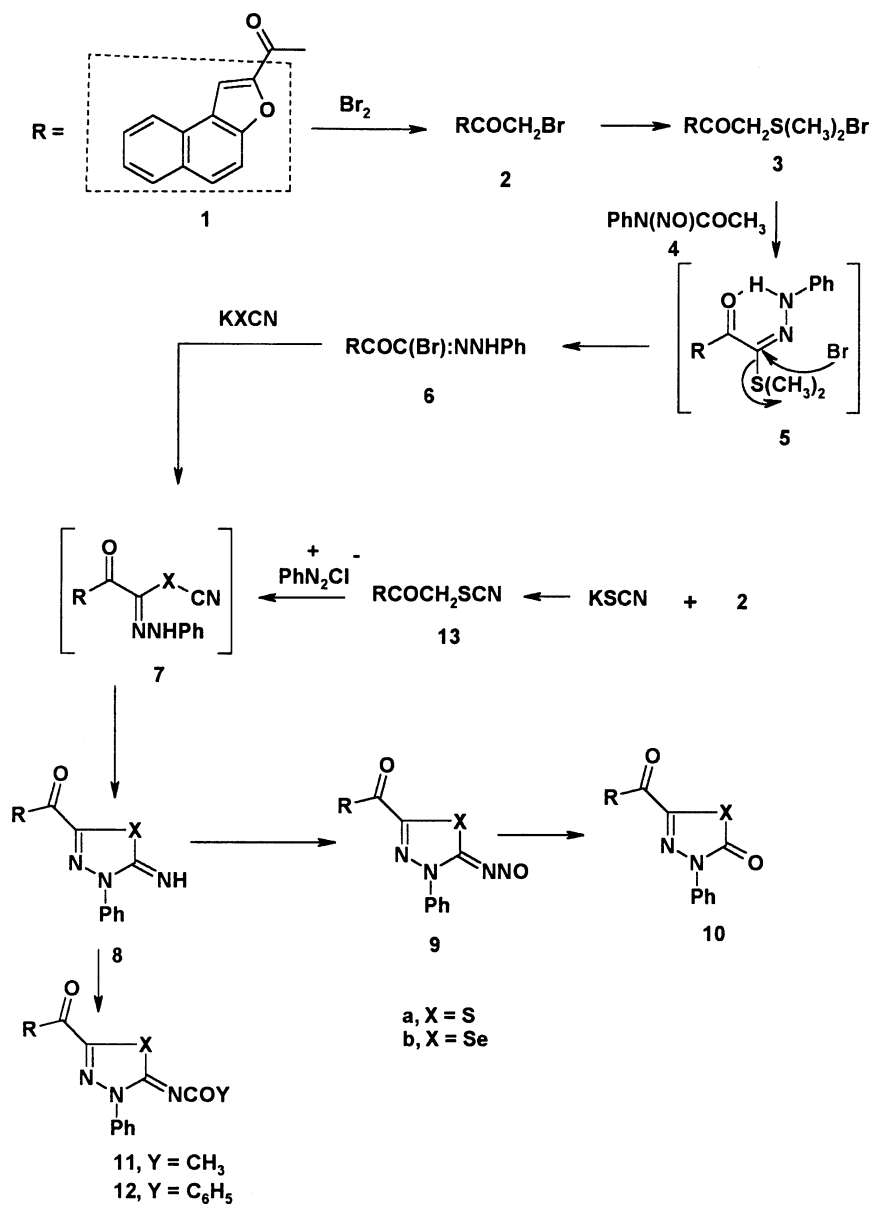
chemical transformation. Thus, treatment of **3** with N-nitroacetanilide (**4**)<sup>11</sup> in ethanol at room temperature gave (2Z)-3-aza-2-bromo-1-naphtho[1,2-*d*]furan-2-yl-3-(phenylamino)prop-2-en-1-one (**6**) (Scheme 1). Spectral data, microanalytical analysis, and chemical transformation confirmed the structure **6**. <sup>1</sup>H NMR spectrum of **6** showed signals at  $\delta$  = 6.48–7.42 (m, 10H), 7.59 (d, 1H), 7.67 (s, 1H), and 9.34 (s, br., 1H). Its IR (cm<sup>-1</sup>) spectrum revealed bands at 3241 (NH), 3049 (C–H), 1665 (CO), 1642 (C=N), and 1582 (C=C).

Treatment of hydrazoneoyl bromide **6** with potassium thiocyanate in ethanol at room temperature afforded product which gave analytical and spectral in accord with their formation as: 2-imino-3-phenyl(1,3,4-thiadiazolin-5-yl)naphtho[1,2-*d*]furan-2-ylketone (**8a**). The IR spectrum of **8** revealed the absence bands at 2156 ( $\nu$  SCN) and showed bands at 3319 (NH), 3056 (C–H), 1627 (CO conjugated). Its <sup>1</sup>HNMR spectrum showed signals at  $\delta$  = 6.46–7.42 (m, 10H), 7.59 (s, 1H), 7.69 (d, 1H) and 8.08 (s, 1H). Upon shaking with D<sub>2</sub>O a new singlet appeared at  $\delta$  = 4.55 assignable to DOH proton and multiplicity signals at  $\delta$  = 6.46–7.60 equivalent to 12 protons. Such results indicate that the reaction of **6** with potassium thiocyanate proceed through the hydrazone **7**, which cyclized readily under the reaction conditions to give **8a** (Scheme 1). Thus, benzenediazonium chloride reacted with (2-naphtho[1,2-*d*]furan-2-ylcarbonyl)thiocarbonitrile (**13**) in ethanolic sodium acetate solution at 0°C gave product identical in all respects (mp., mixed mp., and spectra) with **8a**.

Nitrosation of **8a** with sodium nitrite in acetic acid solution gave 2-(azanitrosomethylene)-3-phenyl(1,3,4-thiadiazoline-5-yl)naphtho[1,2-*d*]furan-2-ylketone (**9a**). The IR spectrum of **9a** showed no NH band, but contained common bands at 3057 (C–H), 1631.7 (CO), 1583 (C=C), and 1485 (NO). Compound **9a** decomposed to 5-(naphtho[1,2-*d*]furan-2-ylcarbonyl)-3-phenyl-1,3,4-thiadiazolin-2-one (**10a**) via boiling in xylene. The IR spectrum of **10a** revealed absorption bands at 3061 (C–H), 1691, 1633 (CO's), and 1583 (C=C) cm<sup>-1</sup>.

Acylation of **8a** with acetic anhydride or benzoyl chloride in pyridine yielded 1-aza-1-[5-(naphtho[1,2-*d*]furan-2-ylcarbonyl)-3-phenyl(1,3,4-thiadiazolin-2-yliden)]acetone (**11a**) and 2-aza-2-[5-(naphtho[1,2-*d*]furan-2-ylcarbonyl)-3-phenyl(1,3,4-thiadiazolin-2-yliden)]-1-phenylethan-1-one (**12a**), respectively. Both elemental analysis and spectral data were consistent with the assigned structure of products **11a** and **12a**. <sup>1</sup>H NMR spectrum of **11a** showed signals at  $\delta$  = 2.38 (s, 3H), 6.64–7.67 (m, 12H).

Similar, reaction of hydrazoneoyl bromide **6** with potassium selenocyanate afforded 2-imino-3-phenyl(1,3,4-selenadiazolin-5-yl)naphtho[1,2-*d*]furan-2-ylketone (**8b**). Also, compound **8b** was nitrosation and



SCHEME 1

acylation to afford 2,3-dihydro-1,3,4-selenadiazoles (**9–12**)**b**, respectively (Scheme 1).

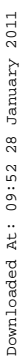
Hydrazonoyl bromide **6** was reacted with methyl phenylthiocarbamate<sup>12</sup> (**14a**) in ethanolic triethylamine solution gave 2-(azaphenylmethylene)-3-phenyl(1,3,4-thiadiazolin-5-yl)-naphtho[1,2-*d*]furan-2-ylketone (**17**) (Scheme 2). Structure **17** was confirmed on the basis of spectral data, elemental analysis, and alternative synthesis method. Thus, <sup>1</sup>H NMR spectrum of **17** showed signals at  $\delta = 6.46\text{--}7.01$  (m, ArH's). Thus, ethyl phenylthiocarbamate (**14b**) reacted with **6** in ethanolic triethylamine to give identical product in all respects (mp., mixed mp., and spectra) with **17**.

In the light of the forgoing results, the mechanism outlined in Scheme 2 seems to be the most plausible pathway for the formation of **17** from the reaction of the **6** with **14**. The reaction involves initial formation of thiohydrazonate **15**, which undergoes intermolecular cyclization as soon as it is formed to yield the intermediate **16** or via 1,3-dipolar cycloaddition of nitrilimine **18**, (which prepared in situ from **6** with triethylamine) to C=S double bond of **14**. The formation of **15** and **16** are similar to the reaction of hydrazonoyl chloride with 1-phenyl-1,4-dihydro-5-thione<sup>13</sup> and 5-phenyl-1,3,4-thiadiazole-2(3H)-thione.<sup>14</sup>

By similar route, the hydrazonoyl bromide **6** reacted with 3-{aza-[(methylthioxomethyl)amino]methylene}indoline-2-one<sup>15</sup> to give unsymmetrical azines **19** (Scheme 2).

Also, treatment of [(1E)-1-aza-phenylvinyl]amino]methylthiomethane-1-thione<sup>16</sup> **20a** with hydrazonoyl bromide **6** in ethanolic triethylamine at room temperature, gave 2-((E)-1,2-diaza-3-phenylprop-2-enylidene)-3-phenyl(1,3,4-thiadiazolin-5-yl)naphtho[1,2-*d*]furan-2-yl ketone **24a** (Scheme 3). Structure **24a** was confirmed by elemental analysis, spectral data and alternative route synthesis. <sup>1</sup>H NMR spectra of **24a** showed signals at  $\delta = 6.46\text{--}7.59$  (m, 17H) and 8.10 (s, 1H). Thus, treatment of **6** with **21a** in ethanolic triethylamine gave product identical in all respects (mp. mixed mp., and spectra) with **24a**. By the same way, compound **6** reacted with the appropriate alkyl carbodithioates<sup>17–19</sup> **20–21(b–k)** in ethanol containing triethylamine afforded 2,3-dihydro-1,3,4-thiadiazoles **24(b–k)**, respectively (Scheme 3).

Similarly, hydrazonoyl bromide **6** reacted with each of [((1E,3E)-1-aza-4-phenylbuta-1,3-dienyl)amino]methylthiomethane-1-thione<sup>20</sup> (**20l**), ({(1E)-1-aza-2-[4-(methylethyl)phenyl]vinyl}amino)methylthiomethane-1-thione<sup>20</sup> (**20m**) and [((1E)-2-(2H-benzo[3,4-*d*]1,3-dioxolan-5-yl)-1-azavinyl)amino]methylthiomethane-1-thione<sup>20</sup> (**20n**) to give unsymmetrical azines **24(l–n)**, respectively (Scheme 3).

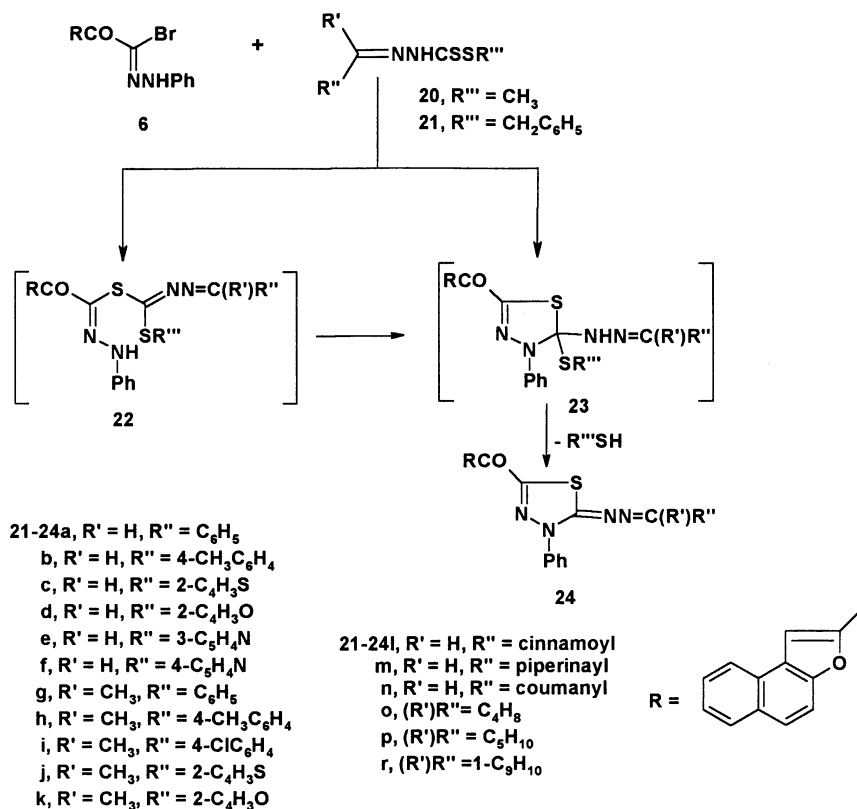


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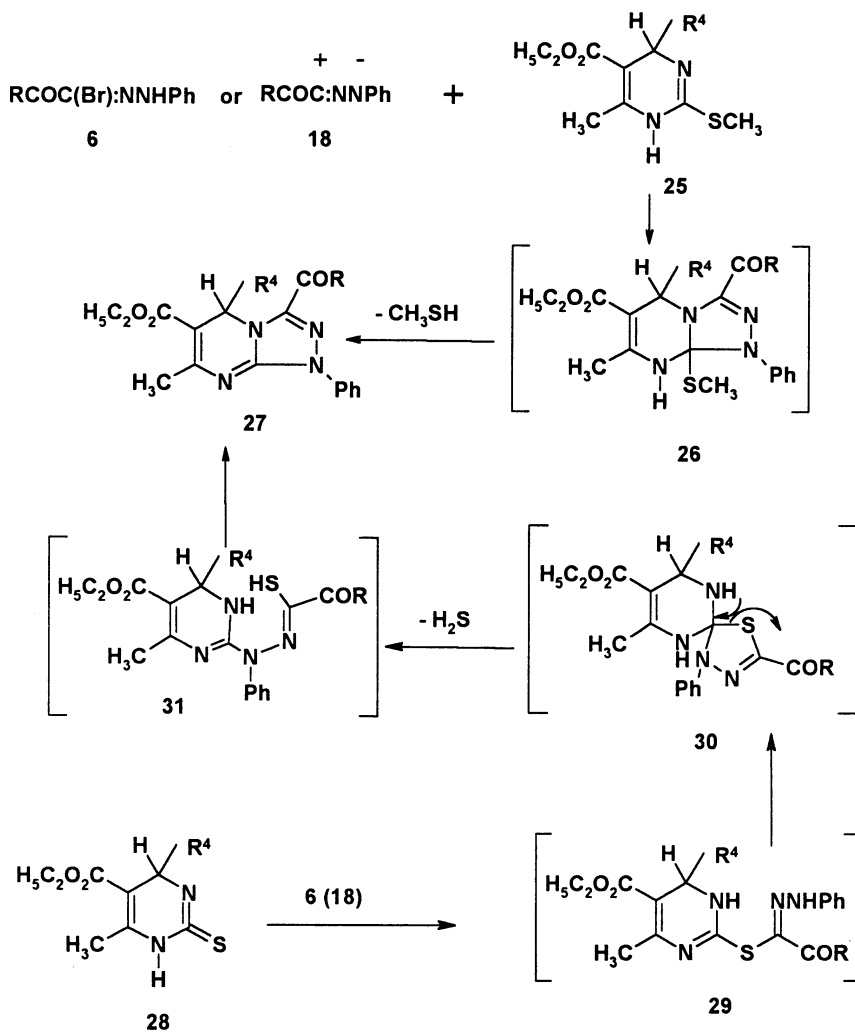


SCHEME 3

open to **31** which cyclized to yield **27** by loss hydrogen sulfide; and 2) 1,3-cycloaddition of nitrilium imide **18** to C=S double bond of **28** can give directly **30** (Scheme 4).

## 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. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> and (CD<sub>3</sub>)<sub>2</sub>SO 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.



- 25-31 a, R<sup>4</sup> = C<sub>6</sub>H<sub>5</sub>  
 b, R<sup>4</sup> = 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>  
 c, R<sup>4</sup> = 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>  
 d, R<sup>4</sup> = 4-ClC<sub>6</sub>H<sub>4</sub>  
 e, R<sup>4</sup> = 4-(CH<sub>3</sub>)<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>  
 f, R<sup>4</sup> = piperinyl

SCHEME 4



## 2-Bromo-1-naphtho[1,2-*d*]furan-2-ylethan-1-one (2)

Bromine (16g, 5 ml, 100 mmol) was added dropwise to solution of 1-naphtho[1,2-*d*]furan-2-ylethan-1-one (**1**) (21 g, 100 mmol) in a mixture of dioxane-ether (50 ml each) with stirring. The reaction mixture was poured to ice-cold water (150 ml) and the solid was collected and crystallized from ethanol to give **2** (Table I).

## 1-Naphtho[1,2-*d*]furan-2-oyldimethylsulfonium bromide (3)

A mixture of 2-Bromo-1-naphtho[1,2-*d*]furan-2-ylethan-1-one (**2**) (14.9 g, 50 mmol) and dimethylsulphide (3.1 g, 50 mmol) in ethanol was refluxed for 30 min. The reaction mixture was cooled and diluted with ether (50 ml) for complete precipitation. The crude solid was collected to give **3** (Table I).

## 3-Aza-2-bromo-1-naphtho[1,2-*d*]furan-2-yl-3-(phenylamino-2-en-1-one (6)

A mixture of sulfonium bromide **3** (17.5 g, 50 mmol) and *N*-nitroso-*N*-phenylacetamide (9.9 g, 60 mmol) in ethanol (100 ml) was stirred for 2 h. The yellow solid was collected and crystallized from ethanol to give **6** (Table I).

## Synthesis of 2-Imino-3-phenyl(1,3,4-thiadiazolin-5-yl)-naphtho[1,2-*d*]furan-2-ylketone (8a) and 2-imino-3-phenyl(1,3,4-selenadiazolin-5-yl)naphtho[1,2-*d*]furan-2-ylketone (8b)

Method A: A mixture of **6** (1.96 g, 5 mmol) and the appropriate of potassium thiocyanate (0.58 g, 6 mmol) (or potassium selenocyanate (0.86 g, 6 mmol)) in ethanol (25 ml) was stirred at room temperature for 3 h. The resulting solid was collected, washed with water, and crystallized from dioxan to give **8a** and **8b**, respectively (Tables I and II).

Method B: The appropriate benzenediazonium chloride (5 mmol), which prepared from diazotised aniline (0.46 g, 5 mmol) as usual way, was added dropwise to a cold solution of ethanol (50 ml), containing a (2-naphtho[1,2-*d*]furan-2-ylcarbonyl)thiocarbonitrile (**13**), which prepared via reaction of 2-Bromo-1-naphtho[1,2-*d*]furan-2-ylethan-1-one (**2**) with potassium thiocyanate, (1.34 g, 5 mmol) and sodium acetate (1.3 g, 10 mmol), while stirring at 0–5°C. The resulting solid was collected and crystallized from dioxan gave **8a**.

**TABLE I Characterization Data of The Newly Synthesized Compounds**

Comp. no.	Mp. °C	Yield % colour	Mol. formula mol. Wt	Analyses, calcd./found			
				C	H	N	S
<b>2</b>	120	77	C <sub>14</sub> H <sub>9</sub> BrO <sub>2</sub>	58.16	3.14		
	EtOH		289.13	58.00	3.20		
<b>3</b>	152–54	70	C <sub>16</sub> H <sub>15</sub> BrO <sub>2</sub> S	54.71	4.30		9.13
	EtOH	Pale yellow	351.26	54.90	4.20		9.00
<b>6</b>	202–204	82	C <sub>20</sub> H <sub>13</sub> N <sub>2</sub> BrO <sub>2</sub>	61.09	3.33	7.12	
	EtOH	Yellow	393.24	61.10	3.40	7.30	
<b>8a</b>	180–82	78	C <sub>21</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> S	67.91	3.53	11.13	8.63
	Dioxan	Yellow	371.42	67.71	3.68	11.21	8.51
<b>8b</b>	173–75	74	C <sub>21</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> Se	60.30	3.13	10.05	
	Dioxan	Yellowish brown	418.31	60.42	3.00	10.15	
<b>9a</b>	132–35 dec.	85	C <sub>21</sub> H <sub>12</sub> N <sub>4</sub> O <sub>3</sub> S	62.99	3.02	13.99	8.01
	Acetone	Yellowish brown	400.42	63.12	2.94	14.12	8.20
<b>9b</b>	140–42 dec.	83	C <sub>21</sub> H <sub>12</sub> N <sub>4</sub> O <sub>3</sub> Se	56.39	2.70	12.53	
	Acetone	Yellowish brown	447.31	56.76	2.97	12.35	
<b>10a</b>	258–60	77	C <sub>21</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> S	67.73	3.25	7.52	8.61
	AcOH	Orange	372.40	67.61	3.17	7.41	8.52
<b>10b</b>	226–28	72	C <sub>21</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> Se	60.16	2.88	6.68	
	AcOH	Brown	419.30	59.92	3.14	6.86	
<b>11a</b>	243–45	86	C <sub>23</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> S	66.82	3.66	10.16	7.76
	AcOH	Yellow	413.45	66.67	3.54	10.05	7.65
<b>11b</b>	203–204	78	C <sub>23</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> Se	60.01	3.28	9.13	
	AcOH	Yellow	460.35	59.22	3.22	9.17	
<b>12a</b>	266–68	64	C <sub>28</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> S	70.72	3.60	8.84	6.74
	AcOH	Pale brown	475.52	70.60	3.57	8.75	6.91
<b>12b</b>	266–68	68	C <sub>28</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> Se	64.37	3.28	8.04	
	AcOH	Pale brown	522.42	64.10	3.56	8.10	
<b>13</b>	165–67	69	C <sub>15</sub> H <sub>9</sub> NO <sub>2</sub> S	67.40	3.39	5.24	12.00
	EtOH	Yellowish brown	267.31	67.28	3.27	5.35	11.84
<b>17</b>	234–36	87	C <sub>27</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> S	72.46	3.82	9.39	7.16
	AcOH	Brownish yellow	447.52	72.62	3.74	9.27	7.04
<b>19</b>	>350	83	C <sub>29</sub> H <sub>17</sub> N <sub>5</sub> O <sub>3</sub> S	67.56	3.32	13.58	6.22
	AcOH	Orange	515.55	67.79	3.12	13.74	6.12
<b>24a</b>	252–54	89	C <sub>28</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub> S	70.87	3.82	11.81	6.76
	AcOH	Reddish orange	474.54	70.79	3.80	11.74	6.57
<b>24b</b>	250–52	84	C <sub>29</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub> S	71.29	4.13	11.47	6.56
	AcOH	Orange	488.57	70.99	4.28	11.62	6.57
<b>24c</b>	237–40	82	C <sub>26</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub>	64.98	3.36	11.66	13.34
	AcOH	Red	480.57	64.80	3.43	11.46	13.45
<b>24d</b>	248–50	78	C <sub>26</sub> H <sub>16</sub> N <sub>4</sub> O <sub>3</sub> S	67.23	3.47	12.06	6.90
	AcOH	Red	464.50	67.28	3.36	12.20	7.12
<b>24e</b>	292–94	81	C <sub>27</sub> H <sub>17</sub> N <sub>5</sub> O <sub>2</sub> S	68.20	3.60	14.73	6.74
	AcOH	Brownish red	475.53	67.98	3.87	14.62	7.12
<b>24f</b>	270–74	82	C <sub>27</sub> H <sub>17</sub> N <sub>5</sub> O <sub>2</sub> S	68.20	3.60	14.73	6.74
	AcOH	Brownish red	475.53	67.95	3.90	14.82	6.52

(Continued on next page)

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

Comp. no.	Mp. °C	Yield % Colour	Mol. formula Mol. Wt	Analyses, calcd./found			
				C	H	N	S
<b>24g</b>	260–64	84	C <sub>29</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub> S	71.29	4.13	11.47	6.56
	AcOH	Orange	488.57	71.33	4.06	11.52	6.77
<b>24h</b>	240–43	79	C <sub>30</sub> H <sub>22</sub> N <sub>4</sub> O <sub>2</sub> S	71.69	4.41	11.15	6.38
	AcOH	Orange	502.59	71.76	4.42	11.22	6.27
<b>24i</b>	260–64	76	C <sub>29</sub> H <sub>19</sub> ClN <sub>4</sub> O <sub>2</sub> S	66.60	3.66	10.71	6.13
	AcOH	Yellow	523.01	66.51	3.57	10.65	6.18
<b>24j</b>	257–60	78	C <sub>27</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub>	65.57	3.67	11.33	12.97
	AcOH	Reddish orange	494.59	65.73	3.72	11.24	12.85
<b>24k</b>	227–30	84	C <sub>27</sub> H <sub>18</sub> N <sub>4</sub> O <sub>3</sub> S	67.77	3.79	11.71	6.70
	AcOH	Red	478.53	67.53	4.02	11.91	6.80
<b>24l</b>	240–42	78	C <sub>30</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub> S	71.98	4.03	11.19	6.41
	AcOH	Red	500.58	71.76	4.16	11.22	6.32
<b>24m</b>	267–69	74	C <sub>29</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> S	67.17	3.50	10.80	6.18
	AcOH	Red	518.55	67.33	3.62	10.91	6.00
<b>24n</b>	270–72	78	C <sub>31</sub> H <sub>24</sub> N <sub>4</sub> O <sub>2</sub> S	72.07	4.68	10.85	6.21
	AcOH	Orange	516.62	71.91	4.70	10.58	6.10
<b>24o</b>	238–40	65	C <sub>26</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub> S	69.01	4.45	12.38	7.09
	AcOH	Brown	452.53	68.81	4.64	12.15	7.12
<b>24p</b>	215–18	72	C <sub>27</sub> H <sub>22</sub> N <sub>4</sub> O <sub>2</sub> S	69.51	4.75	12.01	6.86
	AcOH	Brownish red	466.56	69.68	4.78	12.21	6.68
<b>24r</b>	250–51	81	C <sub>31</sub> H <sub>22</sub> N <sub>4</sub> O <sub>2</sub> S	72.35	4.31	10.81	6.22
	AcOH	Red	514.61	72.48	4.26	10.89	6.34
<b>27a</b>	247–49	72	C <sub>34</sub> H <sub>26</sub> N <sub>4</sub> O <sub>4</sub>	73.63	4.73	10.10	11.54
	AcOH	Red	554.61	73.52	4.57	10.00	11.34
<b>27b</b>	189–90	76	C <sub>35</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub>	73.93	4.96	9.85	11.25
	EtOH	Orange	568.63	73.82	4.87	10.00	11.34
<b>27c</b>	212–14	68	C <sub>35</sub> H <sub>28</sub> N <sub>4</sub> O <sub>5</sub>	71.91	4.83	9.58	13.68
	AcOH	Orange	584.63	71.80	4.87	9.74	13.86
<b>27d</b>	244–45	64	C <sub>34</sub> H <sub>25</sub> ClN <sub>4</sub> O <sub>4</sub>	69.33	4.28	9.51	10.86
	AcOH	Orange	589.05	69.12	4.37	9.72	11.00
<b>27e</b>	226–27	71	C <sub>37</sub> H <sub>32</sub> N <sub>4</sub> O <sub>4</sub>	74.48	5.41	9.37	10.73
	AcOH	Orange	596.69	74.52	5.34	9.48	10.81
<b>27f</b>	215–17	68	C <sub>35</sub> H <sub>26</sub> N <sub>4</sub> O <sub>6</sub>	70.23	4.38	9.36	16.04
	AcOH	Orange	598.62	70.21	4.45	9.32	16.24

### Synthesis of (2-Naphtho[1,2-*d*]furan-2-ylcarbonyl)-thiocarbonitrile (**13**)

Equimolar quantities of each of 2-Bromo-1-naphtho[1,2-*d*]furan-2-ylethan-1-one (**2**) and potassium thiocyanate (50 mmol each) in ethanol (50 ml) was boiled under reflux for 30 min. The reaction mixture was poured onto ice-cold water (100 ml), the resulting solid was collected and crystallized from ethanol to give **13** (Tables I and II).

**TABLE II**  $^1\text{H}$  NMR Spectra of Some Selected Synthesized Compounds

Comp. no.	$^1\text{H}$ NMR ( $\delta$ )
<b>19</b>	6.83–8.55(m, 16H) and 8.91 (s, 1H).
<b>24b</b>	2.39 (s, 3H), 7.20–8.21 (m, 15H), 8.40 (s, 1H) and 8.64 (s, 1H).
<b>24g</b>	2.45 (s, 3H), 7.26–8.18 (m, 16H) and 8.66 (s, 1H)
<b>24h</b>	2.39 (s, 3H), 2.48 (s, 3H), 7.20–8.20 (m, 15H) and 8.66 (s, 1H).
<b>24i</b>	2.045 (s, 3H), 7.26–8.17 (m, 15H) and 8.63 (s, 1H).
<b>24j</b>	2.47 (s, 3H), 7.03–8.19 (m, 14H), 8.65 (s, 1H).
<b>24k</b>	2.39 (s, 3H), 6.48 (t, 1H), 6.88 (d, 1H), 7.26–8.17 (m, 12H) and 8.16 (s, 1H).
<b>24l</b>	5.61 (d, 1H), 6.24 (t, 1H), 6.46 (d, 2H), 6.62 (d, 1H), 7.01 (t, 2H), 7.19–7.59 (m, 12H) and 8.64 (s, 1H).
<b>24m</b>	6.00 (s, 2H), 6.84–8.32 (m, 15H) and 8.63 (s, 1H).
<b>24n</b>	1.26 (d, 6H), 2.92 (sept., 1H), 7.26–8.43 (m, 16H) and 8.64 (s, 1H).
<b>24o</b>	1.79 (t, 4H), 2.54 (quant., 4H), 7.24–8.22 (m, 11H) and 8.63 (s, 1H).
<b>24p</b>	1.68 (d, 4H), 2.43 (t, 4H), 2.68 (t, 2H), 6.46–7.59 (m, 11H) and 8.53 (s, 1H).
<b>24r</b>	1.89 (d, 2H), 2.79 (t, 2H), 2.99 (d, 2H), 6.46–7.59 (m, 15H) and 8.63 (s, 1H).
<b>27a</b>	1.24 (t, 3H), 2.50 (s, 3H), 4.09 (q, 2H) and 7.05–8.47 (m, 18H).
<b>27b</b>	1.24 (t, 3H), 2.19 (s, 3H), 2.57 (s, 3H), 4.09 (q, 2H) and 6.98–8.51 (m, 17H).
<b>27c</b>	1.24 (t, 3H), 2.59 (s, 3H), 3.66 (s, 3H), 4.09 (q, 2H) and 6.69–8.52 (m, 17H).
<b>27d</b>	1.24 (t, 3H), 2.57 (s, 3H), 4.09 (q, 2H) and 7.04–8.55 (m, 17H).
<b>27e</b>	1.08 (d, 6H), 1.21 (t, 3H), 2.58 (s, 3H), 2.71 (sept., 1H), 4.06 (q, 2H) and 7.03–8.51 (m, 17H).
<b>27f</b>	1.29 (t, 3H), 2.57 (s, 3H), 4.11 (q, 2H), 5.82 (s, 2H) and 6.59–8.45 (m, 16H).

### Synthesis of 2-(Azanitrosomethylene)-3-phenyl(1,3,4-thiadiazoline-5-yl)naphtho[1,2-*d*]furan-2-ylketone (**9a**) and 2-(azanitrosomethylene)-3-phenyl(1,3,4-selenadiazoline-5-yl)naphtho[1,2-*d*]furan-2-ylketone (**9b**)

A cold saturated solution of sodium nitrite (10 ml) was added dropwise a solution of **8a** or **8b** (1 g) in acetic acid (20 ml) in an ice bath while stirring. The reaction mixture was stirred for 30 min. The resulting

**TABLE III**  $^{13}\text{C}$  NMR Spectra of Some Selected Synthesized Compounds

Comp. no.	$^{13}\text{C}$ NMR ( $\delta$ )
<b>8a</b>	178, 163, 160, 155, 154, 152, 146, 129, 128, 126, 125, 123, 121, 115.
<b>19</b>	178, 164, 163, 161, 160, 155, 154, 147, 139, 131, 130, 129, 128, 125, 124, 123, 122, 120, 118, 115.
<b>24g</b>	181, 164, 161, 155, 154, 147, 140, 130, 129, 128, 125, 124, 123, 121, 118, 115, 111, 12.
<b>27a</b>	179, 165, 163, 160, 155, 154, 146, 142, 130, 129, 127, 126, 125, 124, 123, 121, 118, 115, 112, 60, 41, 17.

solid was collected, washed with water, and crystallized from acetone to give **9a** and **9b**, respectively (Tables I and II).

### Synthesis of 5-(Naphtho[1,2-*d*]furan-2-ylcarbonyl)-3-phenyl-1,3,4-thiadiazolin-2-one (**10a**) and 5-(naphtho[1,2-*d*]furan-2-ylcarbonyl)-3-phenyl-1,3,4-thiadiazolin-2-one (**10b**)

A solution of **9a**, **9b** (0.5 g) in xylene (20 ml) was refluxed 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 crystallized from acetic acid to give 1,3,4-thiadiazolinone **10a** and 1,3,4-selenadiazolinone **10b**, respectively (Tables I and II).

### Acylation of 1,3,4-Thiadiazoline **8a** and 1,3,4-selenadiazoline **8b**

**Acetylation.** A mixture of **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 crystallized to give the *N*-acetyl derivatives **11a** and **11b**, respectively (Tables I and II).

**Benzoylation.** **8a** or **8b** (0.5 g) and benzoyl chloride (3 ml) in pyridine (15 ml) were refluxed for 10 min, poured onto ice water (50 ml) and acidified with hydrochloric acid. The resulting product was collected and washed several time with boiling water. The resulting solid was crystallized from acetic acid to give the *N*-benzoyl derivatives **12a** and **12b**, respectively (Tables I and II).

### Synthesis of Thiadiazolines **17**, **19** and **24a–r**

Triethylamine (0.5 g (0.75 ml), 5 mmol) was added dropwise with stirring to a mixture of the appropriate alkyl carbodithioates **14a** (or **14b**), or **20a–r** (or **21a–r**) (5 mmol) and compound **6** (1.9 g, 5 mmol) in ethanol (20 ml). The resulting solid, which formed after 30 min, was collected and crystallized from acetic acid and gave the corresponding thiadiazolines **17**, **19**, and **24a–r**, respectively in a good yield (Tables I and II).

### Synthesis of 1,2,4-Triazolo[4,3-*a*]pyrimidines **27a–f**

**Method A.** An equimolar amount of each of the hydrazoneyl bromide **6**, the appropriate **25a–f** 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 to give **27a–f**, respectively (Tables I and II).

**Method B.** A mixture of the appropriate hydrazonoyl bromide **6** (5 mmol) and the appropriate pyrimidin-2-thione **28a–f** (1.68 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 to give products identical in all respects (mp., mixed mp., and spectra) with corresponding products obtained by method A.

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