

Synthesis and Reactions of Some  
6-(2-Hydroxy-1-naphthyl)-1,2,4-triazines  
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4,5-Benzocoumaran-2,3-dione condenses with semicarbazide and thiosemicarbazide at the 3-position and the products obtained were converted to the corresponding 6-(2-hydroxy-1-naphthyl)-1,2,4-triazines. Reactions of these triazines with some reagents are described.

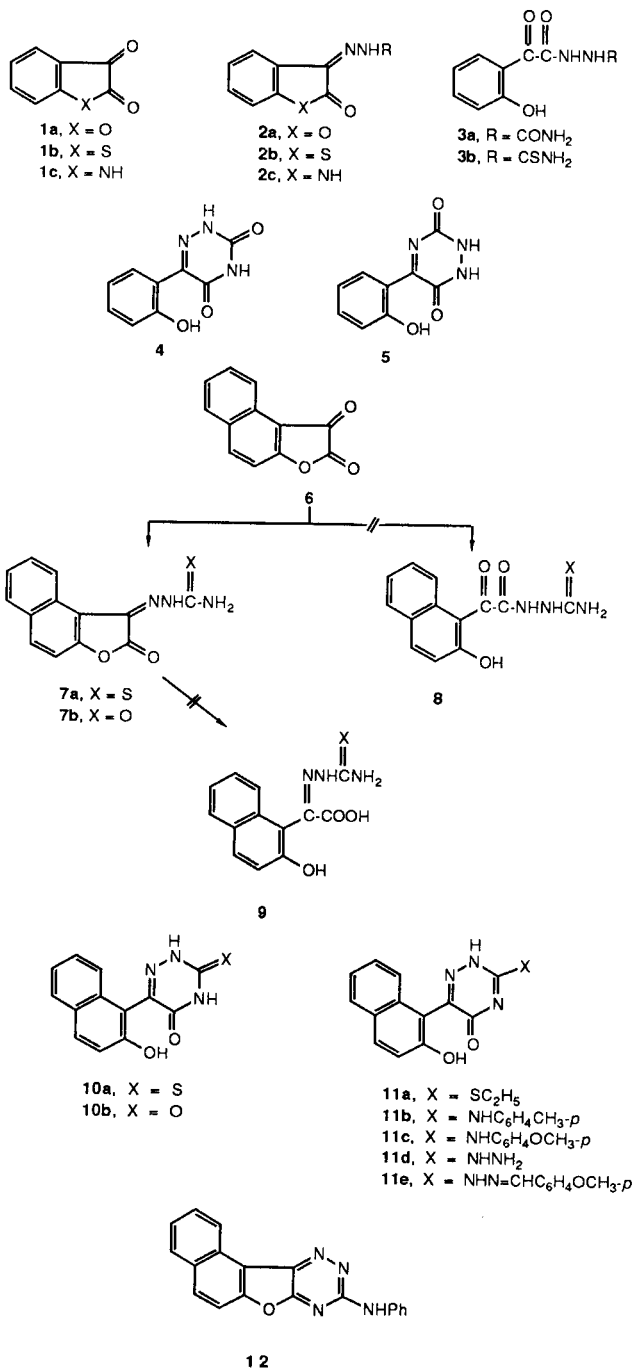
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In continuation to a previous work in the area of 1,2,4-triazines chemistry [1], our interest has now been extended to the synthesis and reactions of some new 1,2,4-triazines.

Recently, it has been shown that coumaran-2,3-dione (**1a**) reacts with semicarbazide and thiosemicarbazide to give the semicarbazone **2a** (R = CONH<sub>2</sub>) and the thiosemicarbazone **2b** (R = CSNH<sub>2</sub>) or the semicarbazide **3a** and the thiosemicarbazide **3b**. The formation of these products depends on the reaction conditions and the pH of the medium. Compounds **2a** and **3a** were converted into the two isomeric 1,2,4-triazine derivatives **4** and **5** [2].

We now have studied the behaviour of 4,5-benzocoumaran-2,3-dione (**6**) in similar condensation reactions. Thus, compound **6** was found to condense with thiosemicarbazide in boiling acetic acid to give the corresponding thiosemicarbazone **7a**. Attempts to prepare the thiosemicarbazide **8**, by performing the reaction at 50°, failed (this condition was applied to prepare the thiosemicarbazide **3b** of coumarandione [3]). Also treatment of compound **7a** with 1*N* hydrochloric acid to obtain the  $\alpha$ -ketoacid thiosemicarbazone **9** (similar to the behavior of compound **3**) was unsuccessful. This indicates that the behavior of 4,5-benzocoumaran-2,3-dione (**6**) differs markedly from that of coumarandione (**1a**), and much resembles the behavior of thianaphthenequinone (**1b**) and isatin (**1c**) which gave the hydrazones **2b** and **2c** respectively.

The thiosemicarbazone **7a** was converted into 6-(2-hydroxy-1-naphthyl)-3-thioxo-1,2,4-triazine-5-one (**10a**) in basic medium. Treatment of compound **10a** with ethyl iodide in a methanolic sodium methoxide solution afforded the 3-ethylmercapto derivative **11a**. Hydrolysis of compound **11a** yielded the 3,5-dioxo-1,2,4-triazine derivative **10b**. The latter compound **10b** was also obtained by first condensing compound **6** with semicarbazide to give the semicarbazone **7b** which was readily converted into the triazine **10b** in basic medium. On the other hand, aminolysis of compound **11a** with aromatic amines, namely, *p*-toluidine and *p*-anisidine gave the corresponding 3-aryl-amino derivatives **11b-c**. However, longer reaction time of **11a** with aniline gave the tetracyclic derivative **12**. Hydra-



zinolysis of compound **11a** gave the 3-hydrazino derivative **11d** which was condensed with anisaldehyde to give the corresponding hydrazone **11e**.

Table

Compound	Mp °C	Yield %	Formula (MW)	C	Analysis %			S
					Calcd.	Found		
<b>7a</b>	248-250 dec	51	C <sub>13</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub> S (271.29)	57.55	3.34	15.49	11.82	
				57.61	3.30	15.50	11.75	
<b>7b</b>	255	96	C <sub>13</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub> (255.23)	61.18	3.55	16.46		
				61.48	3.45	16.86		
<b>10a</b>	277-278	79	C <sub>13</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub> S (271.29)	57.55	3.34	15.49	11.82	
				57.40	3.49	15.40	11.84	
<b>10b</b>	300	80	C <sub>13</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub> (255.23)	61.18	3.55	16.46		
				60.93	3.74	16.45		
<b>11a</b>	218	91	C <sub>15</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> S (299.35)	60.18	4.38	14.04	10.71	
				59.87	4.65	13.80	10.50	
<b>11b</b>	335	70	C <sub>20</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> (344.37)	69.75	4.68	16.27		
				70.03	4.80	16.50		
<b>11c</b>	310	72	C <sub>20</sub> H <sub>16</sub> N <sub>4</sub> O <sub>3</sub> (360.37)	66.66	4.48	15.55		
				66.50	4.21	15.85		
<b>11d</b>	265	60	C <sub>13</sub> H <sub>11</sub> N <sub>5</sub> O <sub>2</sub> (269.26)	57.99	4.12	26.01		
				57.60	4.40	26.30		
<b>11e</b>	305-306	82	C <sub>21</sub> H <sub>17</sub> N <sub>5</sub> O <sub>3</sub> (387.39)	65.11	4.42	18.08		
				64.90	4.50	17.90		
<b>12</b>	335	90	C <sub>19</sub> H <sub>12</sub> N <sub>4</sub> O (312.33)	73.07	3.87	17.94		
				73.27	3.79	18.08		

## EXPERIMENTAL

All melting points are uncorrected. The ir spectra (potassium bromide) were recorded on a Unicam SP 1200 infrared spectrophotometer.

4,5-Benzocoumaran-2,3-dione (**6**).

This compound was prepared by the procedure described by Giua and De Franciscis [4], mp 181°, yield ca. 70%.

4,5-Benzocoumaran-2,3-dione-3-thiosemicarbazone (**7a**).

A hot solution of 4,5-benzocoumaran-2,3-dione (**6**) (0.05 mole) in glacial acetic acid (20 ml) was treated with thiosemicarbazide (0.05 mole). The reaction mixture was boiled under reflux for 30 minutes. After cooling, the orange yellow crystals, of **7a**, which separated were recrystallized from acetic acid (Table); ir (potassium bromide): 3490, 3350, 1756 cm<sup>-1</sup>.

6-(2-Hydroxy-1-naphthyl)-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazin-5-one (**10a**).

A solution of compound **7a** (5.5 g, 0.02 mole) in aqueous sodium hydroxide (150 ml, 1 M) was boiled under reflux for 3 hours. The reaction mixture was then cooled in ice, and acidified with 6 N hydrochloric acid (dropwise). The pale yellow precipitate of **10a** obtained was collected, washed well with water, and recrystallized from ethanol/water (Table); ir (potassium bromide): 3520-2550 (br), 1685 cm<sup>-1</sup>.

6-(2-Hydroxy-1-naphthyl)-3-ethylmercapto-2,5-dihydro-1,2,4-triazin-5-one (**11a**).

A solution of compound **10a** (27.1 g, 0.1 mole) in methanolic sodium methoxide (prepared from 2.3 g sodium metal in 50 ml of methanol), was

treated with ethyl iodide (15.6 g). The reaction mixture was boiled under reflux for 1 hour. It was then cooled and acidified with acetic acid. The pale yellow precipitate of **11a**, obtained was collected, washed with water, dried and recrystallized from ethanol (Table).

4,5-Benzocoumaran-2,3-dione 3-Semicarbazone (**7b**).

To a hot solution of compound **6** (10 g, 0.05 mole) in glacial acetic acid (20 ml) was added semicarbazide hydrochloride (5.6 g, 0.05 mole dissolved in the least amount of water). The reaction mixture was boiled under reflux for 1 hour. The pale yellow precipitate of **7b** which separated on cooling, was collected and recrystallized from acetic acid (Table); ir (potassium bromide): 3458, 3280, 3180, 3150, 1775, 1690 cm<sup>-1</sup>.

6-(2-Hydroxy-1-naphthyl)-2,3,4,5-tetrahydro-1,2,4-triazin-3,5-dione (**10b**).

(a) A solution of compound **7b** (5 g, 0.02 mole) in boiling aqueous sodium hydroxide (30 ml, 1 M) was heated under reflux for 3 hours. The reaction mixture was then cooled in ice and acidified with hydrochloric acid (6 N) and allowed to stand for 15 minutes. The pale yellow precipitate of **10b** was collected, washed with water and recrystallized from ethanol (Table); ir (potassium bromide): 3388, 3150, 3050, 1745, 1660 cm<sup>-1</sup>.

(b) To compound **11a** (1.0 g) in acetic acid (3 ml) was added concentrated hydrochloric acid (1.0 ml). The reaction mixture was boiled under reflux for 2 hours. The product, which separated after cooling was collected and recrystallized from ethanol to give compound **10b**, mp 300°, yield ca 35%, (mixed mp with the product obtained from the previous method showed no depression).

6-(2-Hydroxy-1-naphthyl)-3-arylamino-2,5-dihydro-1,2,4-triazin-5-ones (**11b,c**).

A mixture of 3-ethylmercaptotriazine **11a** (0.001 mole) and *p*-toluidine (0.001 mole) was heated at 180° for 1 hour. After cooling, the reaction mixture was triturated with ethanol and the pale yellow product **11b** was collected and recrystallized from dilute pyridine (Table); ir (potassium bromide): 3320, 3215, 3160, 1620 cm<sup>-1</sup>. Following the same procedure using *p*-anisidine instead of *p*-toluidine, compound **11c** was obtained (Table); ir (potassium bromide): 3325, 3135, 1640 cm<sup>-1</sup>.

3-Anilidonaphtho[2,1-*b*]furo[2,3-*e*]-1,2,4-triazine (**12**).

A mixture of compound **11a** (0.3 g) and aniline (0.2 ml) was heated at 180° for 3 hours. After cooling, the reaction mixture was triturated with ethanol and the product was collected and recrystallized from DMF as pale yellow crystals of **12** (Table).

6-(2-Hydroxy-1-naphthyl)-3-hydrazino-1,2,4-triazin-5-one (**11d**).

To a solution of compound **11a** (0.5 g) in isopropyl alcohol (10 ml) was added hydrazine hydrate (2 ml, 99%). The reaction mixture was boiled under reflux for 3 hours, and allowed to stand overnight at room temperature. The precipitate obtained was collected and recrystallized from DMF/ethanol as yellow crystals of **11d** (Table).

6-(2-Hydroxy-1-naphthyl)-5-oxo-1,2,4-triazin-3-ylhydrazone of *p*-Anisaldehyde (**11e**).

A mixture of the hydrazinotriazine **11d** (0.54 g) and *p*-anisaldehyde (0.2 g) in DMF (10 ml) was heated for 10 minutes. After cooling the product **11e** was collected and recrystallized from butanol into yellow crystals (Table).

## REFERENCES AND NOTES

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