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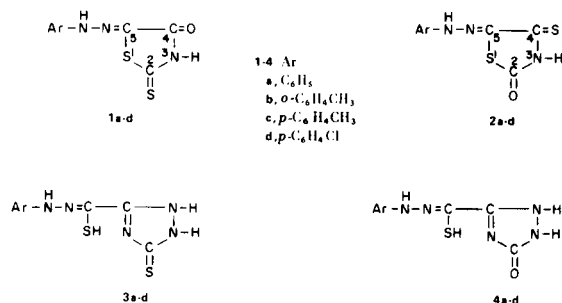
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The 5-arylhydrazone derivatives of rhodanine and isorhodanine were subjected to the action of hydrazine hydrate to afford the arylhydrazonomercaptomethyltriazolinthione and -triazolinone derivatives **3** and **4**, respectively. Treatment of **1** with benzylamine afforded thioxalic acid dibenzylamide **5**. On the other hand, treatment of **2** with the same reagent afforded the corresponding benzylamino derivatives **6**. Alkylation of **1** and **2** with ethyl bromoacetate and chloroacetamide yielded the corresponding S-alkyl derivatives **7** and **8**, respectively.

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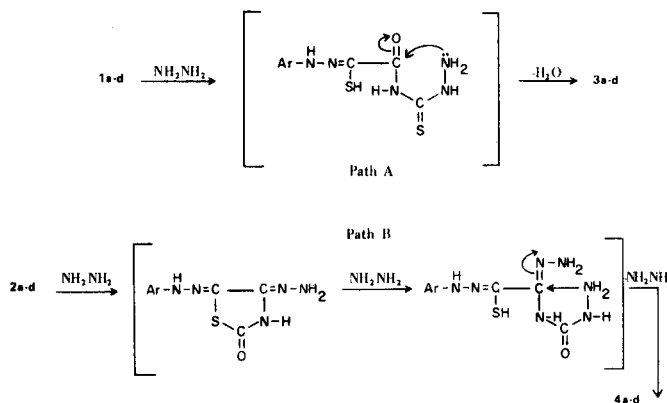
The behaviour of the thiazolidinone ring system toward a variety of nucleophilic reagents has been extensively described in the literature (2-7); reports on the behaviour of the 5-arylhydrazone derivatives of the thiazolidinone ring system remain relatively few. In continuation of our interest in the chemistry of heterocyclic imines (8-10), our studies were extended to the 5-arylhydrazone derivatives of rhodanine (11-13) and isorhodanine (14) in order to compare the effect of the presence of the arylhydrazone group on the behaviour of the thiazolidinone ring.

The 5-arylhydrazone derivatives of rhodanine (**1a-d**) and isorhodanine (**2a-d**) were subjected to the action of hydrazine hydrate at room temperature, whereby an exothermic reaction took place to afford 3-( $\alpha$ -arylhydrazono- $\alpha$ -mercapto)methyltriazolin-5-thiones (**3a-d**) and 5-ones (**4a-d**), respectively.

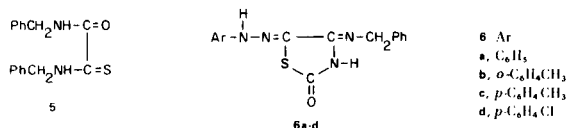


The mechanistic pathways by which **3** and **4** were obtained differ according to the point of attack of the nucleophile. Compounds **3a-d** were obtained by nucleophilic attack on the electropositive carbon of the thiocarbonyl group, effecting cleavage of the S<sub>1</sub>-C<sub>2</sub> single bond following path A. On the other hand, **4a-d** were obtained by nucleophilic attack on the thiocarbonyl center with the formation of the intermediate hydrazone, which suffers ring cleavage and recyclization following path B. Cyclization is favoured by the hydrazone group rather than the less basic arylhydrazone groups. The structures of **3** and **4** were assigned on the basis of both analytical

and spectral data. The carbonyl absorptions for **4a-d** favour a five-membered rather than a six-membered system (15). Further, an analogous reaction has been reported (16) for isorhodanine with hydrazine hydrate, affording 3-mercaptomethyl-1,2,4-triazolin-5-one.

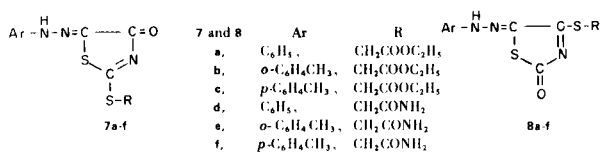


The behaviour of the thiazolidinone ring in 2,4-thiazolidindione and rhodanine, and their 5-arylidene derivatives toward the action of benzylamine has been recently reported to effect ring cleavage in 2,4-thiazolidindione (17,18), and to effect elimination of hydrogen sulphide, affording the benzylimino derivative, with rhodanine (19). This prompted us to investigate the effect of the arylhydrazone group on the stability of the thiazolidinone ring in **1** and **2**. Thus, treatment of the 5-arylhydrazone derivatives **1a-d** with benzylamine effected the arylhydrazone group removal followed by ring cleavage to afford thioxalic acid dibenzylamide (**5**). Analogous arylazo replacement by the arylimino group has been reported (20,21). On the other hand, treatment of the arylhydrazone derivatives of isorhodanine **2a-d** with benzylamine under the same condition afforded the highly coloured benzylimino derivatives **6a-d**. The structures of **5** and **6a-d** were based on spectral and analytical data.



In previous investigations (22,23) we have reported on the alkylation of the 5-arylidene derivatives of rhodanine and isorhodanine. Some of these alkyl derivatives proved to have fungicidal and bactericidal activities. (24).

Now, alkylating **1a-c** and **2a-c** with ethyl bromoacetate and/or chloroacetamide afforded the corresponding S-alkyl derivatives **7a-f** and **8a-f**, respectively. The structures for **7** and **8** were inferred from analytical and spectral data.



#### EXPERIMENTAL

Melting points are all uncorrected. Ir spectra were obtained from potassium bromide discs with a Pye-Unicam SP 1100 spectrophotometer.

Uv spectra were measured in ethanol on a Pye-Unicam SP 8000 spectrophotometer. Nmr spectra were obtained with a Varian A-60 spectrophotometer in deuteriochloroform.

Action of Hydrazine Hydrate on **1a-d** and **2a-d** to Afford **3a-d** and **4a-d**.

General procedure.

To one gram of each of **1a-d** and/or **2a-d**, was added hydrazine hydrate (2 ml., 98%), resulting in an exothermic reaction. After the reaction had subsided, the reaction mixture was diluted with water and acidified with dilute hydrochloric acid. The resulting solid product was filtered off and crystallized from acetone.

The 3-( $\alpha$ -arylhydrazono- $\alpha$ -mercapto)methyl-1,2,4-triazolin-5-ones (**3a-d**) are all pale yellow crystals and are listed in Table I. The ir spectra of **3a-d** show absorption at 3350 (arylhydrazono NH), a broad band at 3180 (ring NH) and a weak absorption at 2850  $\text{cm}^{-1}$  (SH). The uv spectra for **3a-d** show  $\lambda$  max around 360 nm (arylhydrazono, absorption).

The 3-( $\alpha$ -arylhydrazono- $\alpha$ -mercapto)methyl-1,2,4-triazolin-5-thiones (**4a-d**) are all pale yellow crystals and are listed in Table I. The ir spectra of **4a-d** show absorption at 3350 (arylhydrazono NH), a broad band at 3200-3100 (ring NH), a weak band at 2550 (SH) and strong carbonyl absorption at 1760  $\text{cm}^{-1}$  (C=O). The uv spectra of **4a-d** show  $\lambda$  max at 328 nm (arylhydrazono absorption).

Action of Benzylamine on **1a-d** to Afford Thiooxalic Acid Dibenzylamide (**5**).

A mixture of each of **1a-d** (1.0 g.) and benzylamine (1.5 ml.) was heated on a boiling water bath for 30 minutes. The reaction mixture was triturated with ethanol and the resulting solid product was crystallized from ethanol affording pale yellow crystals, m.p. 118° (yield 80%). The products obtained from each of **1a-d** proved to be the same by m.p. and

Table I  
Analytical Data for **3a-d**, **4a-d** and **6a-d**

Compound	M.p. °C	Yield %	Formula (Molecular Weight)	Analyses			Calcd. Found	
				C	H	N	S	
<b>3a</b>	225	70	$\text{C}_9\text{H}_9\text{N}_3\text{S}_2$	43.03	3.61	27.88	25.48	
			251.2	42.90	3.50	27.71	25.33	
<b>3b</b>	185	65	$\text{C}_{10}\text{H}_{11}\text{N}_3\text{S}_2$	45.28	4.18	26.41	24.13	
			265.2	45.11	3.98	26.31	24.00	
<b>3c</b>	215	70	$\text{C}_{10}\text{H}_{11}\text{N}_3\text{S}_2$	45.28	4.18	26.41	24.13	
			265.2	45.15	4.00	26.29	24.10	
<b>3d</b>	237	60	$\text{C}_9\text{H}_8\text{ClN}_3\text{S}_2$ (a)				22.40	
			285.7				22.18	
<b>4a</b>	203	80	$\text{C}_9\text{H}_9\text{N}_3\text{OS}$	45.96	3.86	29.78	13.60	
			235.2	45.81	3.69	29.69	13.51	
<b>4b</b>	220	75	$\text{C}_{10}\text{H}_{11}\text{N}_3\text{OS}$	48.19	4.45	28.10	12.84	
			249.2	48.00	4.36	27.87	12.61	
<b>4c</b>	255	75	$\text{C}_{10}\text{H}_{11}\text{N}_3\text{OS}$	48.19	4.45	28.10	12.84	
			249.2	48.00	4.31	27.91	12.68	
<b>4d</b>	212	68	$\text{C}_9\text{H}_8\text{ClN}_3\text{OS}$ (b)				11.86	
			269.7				11.66	
<b>6a</b>	210	60	$\text{C}_{16}\text{H}_{14}\text{N}_4\text{OS}$	61.93	4.55	18.06	10.31	
			310.3	61.69	4.50	17.98	10.21	
<b>6b</b>	211	65	$\text{C}_{17}\text{H}_{16}\text{N}_4\text{OS}$	62.95	4.97	17.28	9.86	
			324.3	62.77	4.71	17.00	9.73	
<b>6c</b>	155	70	$\text{C}_{17}\text{H}_{16}\text{N}_4\text{OS}$	62.95	4.97	17.28	9.86	
			324.3	62.81	4.75	17.11	9.71	
<b>6d</b>	217	68	$\text{C}_{16}\text{H}_{13}\text{ClN}_4\text{OS}$ (c)				9.28	
			344.8				9.11	

(a) Cl, Calcd.: 12.42; Found: 12.36.

(b) Cl, Calcd.: 13.16; Found: 13.01.

(c) Cl, Calcd.: 12.95; Found: 12.87.

Table II  
Analytical Data for **7a-f** and **8a-f**

Compound	M.p. °C	Yield %	Formula (Molecular Weight)	Analyses			Calcd. Found
				C	H	N	
<b>7a</b>	173	82	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> S <sub>2</sub>	48.30	4.05	13.00	19.80
			323.2	48.25	3.89	12.90	19.71
<b>7b</b>	151	70	C <sub>14</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> S <sub>2</sub>	49.85	4.48	12.46	18.97
			337.3	49.68	4.39	12.33	18.76
<b>7c</b>	180	78	C <sub>14</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> S <sub>2</sub>	49.85	4.48	12.46	18.97
			337.3	49.80	4.40	12.41	18.77
<b>7d</b>	212	68	C <sub>11</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub>	44.90	3.43	19.04	21.72
			294.2	44.66	3.31	18.71	21.66
<b>7e</b>	154	70	C <sub>12</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub>	46.76	3.92	18.18	20.76
			308.2	46.63	3.81	18.00	20.63
<b>7f</b>	183	68	C <sub>12</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub>	46.76	3.92	18.18	20.76
			308.2	46.71	3.83	18.00	20.56
<b>8a</b>	145	70	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> S <sub>2</sub>	48.30	4.05	13.00	19.80
			323.2	48.20	3.79	12.89	19.70
<b>8b</b>	113	78	C <sub>14</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> S <sub>2</sub>	49.85	4.48	12.46	18.97
			337.3	49.66	4.40	12.29	18.93
<b>8c</b>	178	82	C <sub>14</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> S <sub>2</sub>	49.85	4.48	12.46	18.97
			337.3	49.76	4.29	12.31	18.78
<b>8b</b>	192	70	C <sub>11</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub>	44.90	3.43	19.04	21.72
			294.2	44.83	3.29	18.99	21.59
<b>8e</b>	125	67	C <sub>12</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub>	46.76	3.92	18.18	20.76
			308.2	46.59	3.81	18.00	20.71
<b>8f</b>	115	72	C <sub>12</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub>	46.76	3.92	18.18	20.76
			308.2	46.72	3.86	18.11	20.69

mixed m.p.; ir: 3320 and 3280 (NH) (strong absorption), 2950 (sat. C-H) (weak absorption) and 1680 cm<sup>-1</sup> (C=O) (strong absorption); uv (ethanol): λ max 305 nm; pmr: γ 0.2 (broad, 1H, N-N), 1.4 (broad, 1H, N-H), 2.7 (S, 10H, 2C<sub>6</sub>H<sub>5</sub>), 5.15 and 5.2 (d, 2H, C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>), 5.5 and 5.55 (d, 2H, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>).

Anal. Calcd. for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>OS (284.3): C, 67.59; H, 5.67; N, 9.85; S, 11.25. Found: C, 67.50; H, 5.32; N, 9.77; S, 11.18.

Action of Benzylamine on **2a-d** to Afford 5-Arylhydrazono-4-benzylimino-2-thiazolidinones (**6a-d**).

A mixture of each of **2a-d** (1.0 g.) and benzylamine (1.5 ml.) was heated on a boiling water bath for one hour or until the odour of hydrogen sulphide ceased. The reaction mixture was triturated with ethanol and the resulting solid product was filtered off and crystallized from ethanol. Compounds **6a-d** listed in Table I are all yellow to orange in colour. The ir spectra of **6a-d** show absorption at 3380 (arylhydrazone), 3150 (ring NH), 1680 (C=O) and a weak band at 1620 cm<sup>-1</sup> (C=N). The uv spectra of **6a-d** in ethanol show λ max around 430 nm (conjugated arylhydrazone group).

5-Arylhydrazono-2-alkylmercapto-2-thiazolin-4-ones (**7a-f**) and 5-Arylhydrazono-4-alkylmercapto-2-thiazolin-2-ones (**8a-f**).

General procedure.

To a solution of each of **1a-c** (1.0 g.) in aqueous sodium carbonate (10 ml.; 10%), the appropriate alkyl halide (2.0 ml.) was added. The reaction mixture was refluxed for two hours, left over night at room temperature. The crystals that separated were filtered off and crystallized from ethanol. Compounds **7a-f** and **8a-f**, listed in Table II, are all yellow to orange in colour.

The ir spectrum of **7a** as a typical example of the mercaptoacetate ethyl esters **7a-c** shows absorption at 3320 (NH), 1720 (ester C=O), 1680 (ring carbonyl) and 1620 cm<sup>-1</sup> (C=N).

The ir spectrum of **7d** as a typical example of the mercaptoacetamides **7d-f** shows absorption at 3380 and 3320 (asym. and sym. NH<sub>2</sub>), 1690 and 1660 cm<sup>-1</sup> for ring and amide I stretchings.

The ir spectrum of **8a** as a typical example of the mercaptoacetate ethyl esters **8a-c** shows absorption at 3330 (hydrazone NH) and two carbonyl absorptions at 1740 and 1680 cm<sup>-1</sup> (ester and ring carbonyl).

The ir spectrum of the 4-mercaptoacetamido-2-thiazolin-2-ones (**8d-f**) shows absorption characteristic for NH<sub>2</sub> at 3380 and 3320 and for carbonyl absorption at 1690 and 1680 cm<sup>-1</sup> for ring and amide I band.

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