

## Synthesis of 2-Aryl-4-arylaZO-2-thiazolin-5-ones and their Reaction with Aromatic Amines

A. Mohamed Khalil,<sup>A,B</sup> Ibrahim I. Abd El-Gawad<sup>A,B</sup> and Hesien M. Hassan<sup>A</sup>

<sup>A</sup> Chemistry Department, Al-Mansoura Faculty of Science,  
Al-Mansoura University, A.R.E. (Egypt).

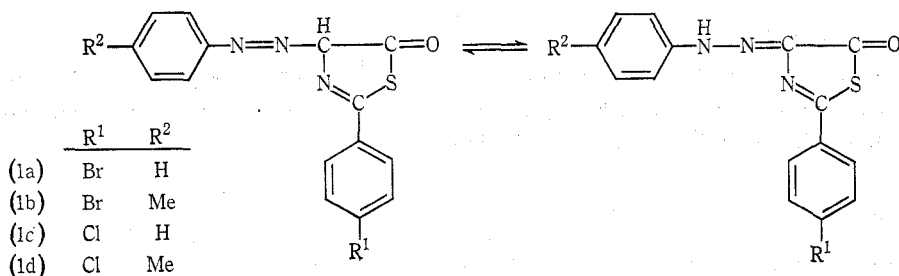
<sup>B</sup> Present address: Department of Chemistry, Faculty of Science,  
King Abdulaziz University, P.O. Box 1540, Jeddah, Saudi Arabia.

### Abstract

2-Aryl-4-arylaZO-2-thiazolin-5-ones are prepared by a coupling reaction between thioaroylglycine and the appropriate diazonium salt. Their heterocyclic ring is readily opened by the action of primary aromatic amines in acetic acid containing a catalytic amount of sodium acetate with the formation of 1,5,*N*<sub>2</sub>-triaryl-1*H*-1,2,4-triazole-3-carboxamides.

Although many substituted thiazolones and their reactions with a variety of reagents have been described in the literature,<sup>1-5</sup> the 2-aryl-4-arylaZO-2-thiazolin-5-ones have not been reported.

In this investigation the 2-aryl-4-arylaZO-2-thiazolin-5-ones (1a-d) were prepared, similarly to the corresponding 2-aryl-4-arylaZO-2-oxazolin-5-ones,<sup>6</sup> by a coupling reaction between thioaroylglycine and the appropriate diazonium salt in cold acetic anhydride containing freshly fused sodium acetate.



The structures (1a-d) were established by analytical results and by i.r. measurements which showed stretching frequencies at 1700 cm<sup>-1</sup> characteristic for the carbonyl group of the thiazolone ring and at 3300 cm<sup>-1</sup> characteristic for an NH group. The i.r. spectra do not reveal any N=N band around 1540 cm<sup>-1</sup>, which suggests that the hydrazone structure rather than the alternative azo structure predominates.

<sup>1</sup> Rath, P. C., Tripathy, P. B., and Rout, M. K., *J. Indian Chem. Soc.*, 1964, **41**, 107.

<sup>2</sup> Filler, R., and Rao, Y. S., *J. Org. Chem.*, 1962, **27**, 3730.

<sup>3</sup> Knott, E. B., U.S. Pat. 2,743,273 (Apr. 1956).

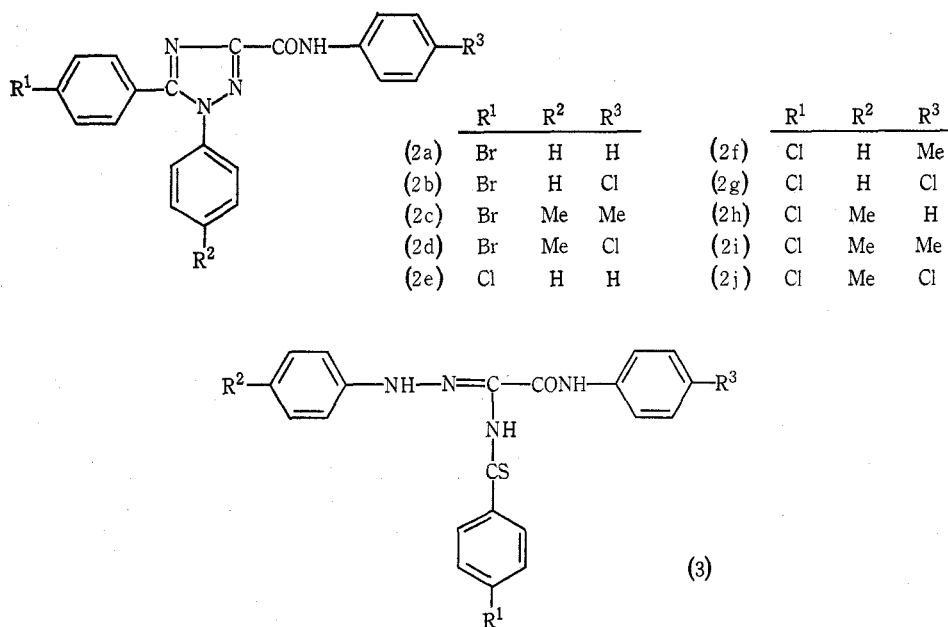
<sup>4</sup> Johnson, T. B., and Nicolet, B. H., *J. Am. Chem. Soc.*, 1912, **34**, 1048.

<sup>5</sup> Khalil, A. M., Abd El-Gawad, I. I., and Hammouda, M., *Aust. J. Chem.*, 1974, **27**, 2035.

<sup>6</sup> Khalil, A. M., Abd El-Gawad, I. I., and Hassan, H. M., *Aust. J. Chem.*, 1974, **27**, 2509.

In continuation of the previous study,<sup>5-8</sup> the present communication reports the reaction of 2-aryl-4-arylaazo-2-thiazolin-5-ones (1a-d) with primary aromatic amines in acetic acid solution and in the presence of freshly fused sodium acetate. An evolution of hydrogen sulphide was observed and the corresponding 1,5,*N*<sub>x</sub>-triaryl-1*H*-1,2,4-triazole-3-carboxamides (2a-j) were obtained.

The identity of compounds (2a-j) was established by comparison with authentic samples prepared by reaction of 2-aryl-4-arylaazo-2-oxazolin-5-ones with the appropriate amine in acetic acid containing freshly fused sodium acetate.<sup>6,9</sup>



Attempts to isolate the possible intermediates of type (3) by treatment of 2-aryl-4-arylaazo-2-thiazolin-5-ones with amines in ethanol were unsuccessful; only the corresponding 1,2,4-triazoles (2a-j) were obtained.

## Experimental

Analytical data were determined by the Microanalytical Unit, Cairo University. Infrared spectra were recorded on a SP 1000 Pye-Unicam spectrophotometer. All the melting points are uncorrected.

### 2-Aryl-4-arylaazo-2-thiazolin-5-ones (1a-d)

To a stirred solution of thioaroylglycine (0.1 mol) in acetic anhydride (30 ml) containing freshly fused sodium acetate (1 g) in an ice-salt bath was added slowly a diazonium solution. Stirring was then continued for 15 min at 0°C. The stirred mixture was then allowed to attain room temperature.

The crude product was almost completely precipitated within 1 h. It was filtered, dried by suction and recrystallized from acetone to give 2-aryl-4-arylaazo-2-thiazolin-5-ones (1a-d) (Table 1).

<sup>7</sup> Islam, A. M., Khalil, A. M., and Abd El-Gawad, I. I., *Aust. J. Chem.*, 1973, **26**, 827.

<sup>8</sup> Islam, A. M., Khalil, A. M., and El-Houseni, M. S., *Aust. J. Chem.*, 1973, **26**, 1701.

<sup>9</sup> Khalil, A. M., and Abd El-Gawad, I. I., unpublished data.

*1,5,N<sub>2</sub>-Triaryl-1H-1,2,4-triazole-3-carboxamides (2a-j)*

A mixture of the 2-aryl-4-arylo-2-thiazolin-5-one (1a-d) (0.01 mol) and the appropriate primary aromatic amine (0.01 mol) in acetic acid (50 ml) containing freshly fused sodium acetate (1.5 g) was heated under reflux for 2 h. The mixture was cooled, and the crude product was collected by suction filtration. Recrystallization from ethanol gave the substituted amides (2a-j) as white crystals (Table 2).

Table 1. 2-Aryl-4-arylo-2-thiazolin-5-ones (1a-d)

Com- pound	Colour	M.p. (°C)	Yield (%)	Molecular formula	Found (%)			Calc. (%)		
					C	H	N	C	H	N
(1a)	orange	152	82	C <sub>15</sub> H <sub>10</sub> BrN <sub>3</sub> OS	52.0	2.5	12.2	52.0	2.8	12.2
(1b)	orange	158	85	C <sub>16</sub> H <sub>12</sub> BrN <sub>3</sub> OS	51.2	3.1	11.1	51.3	3.2	11.2
(1c)	yellow	165	80	C <sub>15</sub> H <sub>10</sub> ClN <sub>3</sub> OS	56.9	3.0	13.2	56.9	3.2	13.3
(1d)	yellow	155	82	C <sub>16</sub> H <sub>12</sub> ClN <sub>3</sub> OS	58.1	3.5	12.6	58.2	3.6	12.7

Table 2. 1,5,N<sub>2</sub>-Triaryl-1H-1,2,4-triazole-3-carboxamides

Com- pound	M.p. (°C)	Yield (%)	Molecular formula	Found (%)			Calc. (%)		
				C	H	N	C	H	N
(2a)	205	85	C <sub>21</sub> H <sub>14</sub> BrN <sub>4</sub> O	60.4	3.3	13.2	60.4	3.6	13.4
(2b)	192	75	C <sub>21</sub> H <sub>14</sub> BrClN <sub>4</sub> O	55.2	3.0	12.0	55.6	3.1	12.1
(2c)	170	92	C <sub>23</sub> H <sub>19</sub> BrN <sub>4</sub> O	61.4	4.0	12.3	61.8	4.3	12.5
(2d) <sup>a</sup>	185	85	C <sub>22</sub> H <sub>16</sub> BrClN <sub>4</sub> O	54.6	3.4	11.5	54.6	3.3	11.6

<sup>a</sup> Complete details for the remaining compounds (2e-j) have been published.<sup>6</sup>

The melting points of the above products (2a-j) were undepressed on admixture with authentic samples prepared by the reaction of 2-aryl-4-arylo-2-oxazolin-5-ones with the appropriate amine in acetic acid containing fused sodium acetate.<sup>6,9</sup>

The attempted preparation of arylcarboxamides of  $\alpha$ -arylthiocarboxamido- $\alpha$ -arylhydrazonoacetic acid (3) by heating under reflux a mixture of 2-aryl-4-arylo-2-thiazolin-5-ones (1a-d) (0.01 mol in each case) and in primary aromatic amines (0.01 mol), in ethanol (30 ml) for 2 h, was unsuccessful. The products were identified as (2a-j), with correct elementary analyses, m.p. and m.m.p.

Manuscript received 17 November 1975