

**SYNTHESIS AND CHARACTERIZATION OF FUSED MESOIONIC  
1,3,4-OXADIAZOLIUM-2-THIOLATES FROM *N*-AMINO-*N,N'*-  
DIHYDRODIAZINEDIONES**

Dong Ju Jeon,<sup>1</sup> Sung Chul Shin,<sup>2</sup> and Youn Young Lee\*

<sup>1</sup>Korea Research Institute of Chemical Technology, Taejon 305-306, Korea.

<sup>2</sup>Department of Chemistry, Gyeongsang National University, Chinju 660-701, Korea. Department of Chemistry, Seoul National University, Seoul 151-742, Korea

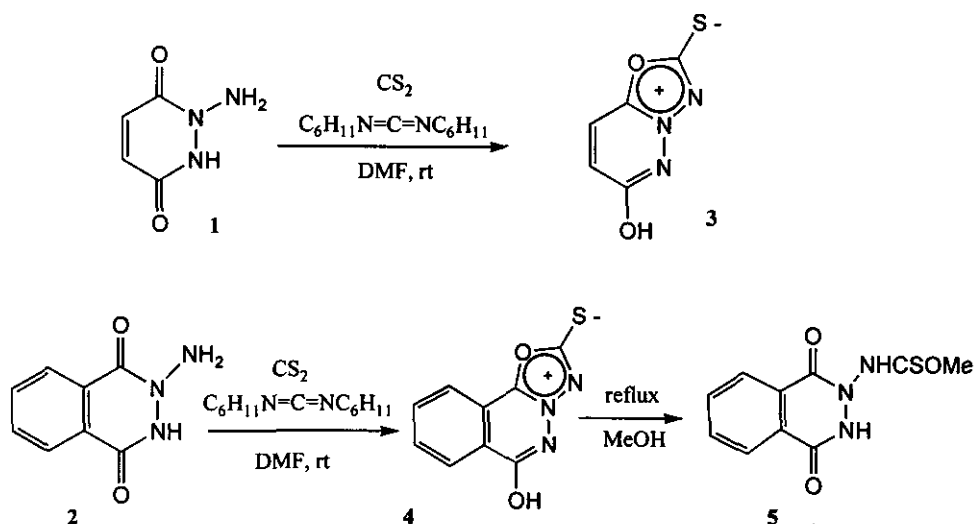
**Abstract** - The novel fused mesoionic 1,3,4-oxadiazolium-2-thiolates were synthesized from *N*-amino-*N,N'*-dihydrodiazinediones by treatment with carbon disulfide in the presence of 1,3-dicyclohexylcarbodiimide.

Mesoionic compounds have received of considerable interest in themselves due to their unique physical properties such as large dipole moment, various pharmacological activities and also providing novel synthetic routes to a large variety of heterocycles by their reactivities with various reagents.<sup>1</sup> Various types of monocyclic mesoionic 1,3,4-oxadiazolium-2-thiolates have been reported,<sup>1</sup> however the derivatives containing fused rings are rare.<sup>2</sup>

In connection with our studies to the synthesis of fused nitrogen-heterocycles<sup>3</sup> and fused mesoionic 1,2,4-triazolium-3-thiolates<sup>4</sup> from *N*-amino-*N,N'*-dihydrodiazinediones, herein we wish to report our preliminary results on the synthesis of fused mesoionic 1,3,4-oxadiazolium-2-thiolates. One of the methods for the synthesis of monocyclic mesoionic 1,3,4-oxadiazolium-2-thiolates is the reaction of *N*-aminoacylhydrazine with carbon disulfide in the presence of 1,3-dicyclohexylcarbodiimide.<sup>5</sup> Taking advantage of that method, we studied the preparation of the fused mesoionic 1,3,4-oxadiazolium-2-

thiolates from *N*-amino-*N,N'*-dihydrodiazinediones.

The reaction of *N*-aminoacylhydrazine (**1**, **2**) with carbon disulfide in the presence of 1,3-dicyclohexylcarbodiimide in DMF at 0 °C, followed by stirring at room temperature for several hours, gave the 1,3,4-oxadiazolium-2-thiolates (**3**, **4**)<sup>6</sup> in *ca.* 70 % yields (Scheme).



**Scheme**

Support for the structure of mesoionic 1,3,4-oxadiazolium-2-thiolates (**3**, **4**) was provided by their IR spectra, which showed absorptions at  $1470\text{ cm}^{-1}$  and  $1475\text{ cm}^{-1}$ , respectively, due to C=S stretching band similar in position to the C=S band shown in monocyclic 1,3,4-oxadiazolium-2-thiolates.<sup>2</sup> The broad band at around  $3000\text{ cm}^{-1}$  is attributed to the enol absorption, which is in agreement with our previous work.<sup>4</sup> 6-Hydroxy-1,3,4-oxadiazolo[3,2-*b*]pyridazinium-2-thiolate (**3**) showed two doublet signals at 8.40 and 7.55 ppm for CH=CH protons in the <sup>1</sup>H NMR, which were shifted to downfield about 1 ppm compared to those of 1-amino-1,2-dihydropyridazine-3,6-dione (**1**). Though the chemical shift of 6-hydroxy-1,3,4-oxadiazolo[2,3-*a*]phthalazinium-2-thiolate (**4**) was very similar to the 2-amino-2,3-dihydrophthalazine-1,4-dione (**2**), the splitting pattern was very different each other. The MS spectra of the compounds (**3**) and (**4**) did not show the molecular ion peaks, but the peaks of corresponding  $\text{R}_2\text{C}^+=\text{O}$  ( $m/z$ , 54 in **3** and 104 in **4**) and corresponding  $\text{R}_2\text{CON}^+\text{R}_1$  ( $m/z$ , 112 in **3** and 162 in **4**) fragments were shown, which were

well in harmony with the fragmentation patterns of monocyclic 1,3,4-oxadiazolium-2-thiolates.<sup>7</sup>

According to the spectroscopic results, the products (**3**, **4**) could be identified as 6-hydroxy-1,3,4-oxadiazolo[3,2-*b*]pyridazinium-2-thiolate and 6-hydroxy-1,3,4-oxadiazolo[2,3-*a*]phthalazinium-2-thiolate, respectively.

It has known that 1,2,4-triazolium-2-thiolates can be obtained by the reaction of mesoionic 1,3,4-oxadiazolium-2-thiolates with anilines, and the mesoionic 1,3,4-oxadiazolium-2-thiolates could be changed to mesoionic 1,3,4-thiadiazolium-2-olates by refluxing in ethanol. We have examined the reactivity and stability of **4** to aniline and alcohol. When **4** was heated with aniline at 110 °C in DMF or refluxed in ethanol, only 2,3-dihydro-1,4-phthalazinedione, degradation product, was obtained in yields of 54% or 81%, respectively. While, the thiocarbamate (**5**)<sup>8</sup> was obtained by refluxing of **4** in methanol in 27% yield (Scheme).

According to the results from our investigation of the reactivity of 6-hydroxy-1,3,4-oxadiazolo[2,3-*a*]phthalazinium-2-thiolate (**4**) and nondetectable of molecular ion peaks in mass spectra of the products **3**, **4**, it could be concluded that the fused mesoionic 1,3,4-oxadiazolium-2-thiolates (**3,4**) have the weaker stability than those of monocyclic mesoionic 1,3,4-oxadiazolium-2-thiolates.

*Typical experimental procedure for the synthesis of the fused mesoionic 1,3,4-oxadiazolium-2-thiolates (3, 4):* To a stirred suspension of **1** (1.0 g, 5.6 mmol) in dried DMF (10 ml) was added dicyclohexylcarbodiimide ( 1.0 g, 5.9 mmol ) at 0 °C. After stirring for 5 min, CS<sub>2</sub> ( 0.4 ml, 5.6 mmol ) was added slowly and the mixture was stirred for 1 h to produce the yellow solid. The solid was filtered and washed with ethyl acetate, followed by recrystallization from methanol to obtaine the yellow needle (0.93 g, 70 %).

## REFERENCES AND NOTES

1. W. D. Ollis and C. A. Ramsden, *Adv. Heterocycl. Chem.*, **1976**, *19*, 47; C. G. Newton and C. A. Ramsden, *Tetrahedron* **1982**, *38*, 2965.

2. K. T. Potts, S. K. Roy, and O. P. Jones, *J. Org. Chem.*, **1967**, *32*, 2245; K. T. Potts, S. K. Roy, S. W. Schneller, and R. M. Huseby, *J. Org. Chem.*, **1968**, *33*, 2559; P. Molina, M. Alajarin, A. Arques, R. Benzal, and H. Hernandez, *Tetrahedron Lett.*, **1983**, *24*, 3523; P. Molina, A. Arques, I. Cartagena, and M. V. Valcarcel, *Synthesis*, **1984**, 881.
3. S. C. Shin, H. C. Wang, W. Y. Lee, and Y. Y. Lee, *Bull. Kor. Chem. Soc.*, **1985**, *6*, 323; S. C. Shin and Y. Y. Lee, *Bull. Kor. Chem. Soc.*, **1988**, *9*, 359.
4. S. C. Shin, D. J. Jeon, K. A. Jang, and Y. Y. Lee, *Bull. Kor. Chem. Soc.*, **1994**, *15*, 517;
5. R. Grashey and N. Kermaris, *Tetrahedron Lett.*, **1970**, 5087; A. Y. Lazaris and A. N. Egorokin, *J. Org. Chem. USSR*, **1972**, 1569 [*Chem. Abstr.*, **1972**, *77*, 13990].
6. 6-Hydroxy-1,3,4-oxadiazolo[3,2-*b*]pyridazinium-2-thiolate (**3**): mp 184 °C (decomp); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 8.40 (1H, d, J = 10 Hz), 7.55 (1H, d, J = 10 Hz); IR (KBr); 3000 cm<sup>-1</sup> (br), 1470 cm<sup>-1</sup>; MS (70eV) m/z (rel. intensity); 112 (100), 82 (84.6), 76 (71.4), 60 (15.9), 58 (18), 54 (33.5).  
6-Hydroxy-1,3,4-oxadiazolo[2,3-*a*]phthalazinium-2-thiolate (**4**): mp 159 °C (decomp); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 8.46 - 7.79 (4H, m, ar), 8.50 (1H, br, NH); IR (KBr); 3000 cm<sup>-1</sup> (br), 1475 cm<sup>-1</sup>; MS (70eV) m/z (rel. intensity); 162 (56.8), 147 (24.1), 104 (100), 77 (16.9), 60 (26.0).
7. W. D. Ollis and C. A. Ramsden, *J. Chem. Soc., Perkin Trans. I*, **1974**, 645.
8. 2,3-Dihydro-2-methoxythiocarbonylamino-1,4-phthalazinedione (**5**): mp 227 - 229 °C (decomp); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 11.83 (1H, br, OH), 10.55 (1H, s, NH), 8.30 - 7.74 (4H, m, Ar); IR (KBr); 3000 cm<sup>-1</sup> (br), 1480 cm<sup>-1</sup>.

Received, 28th July, 1997