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

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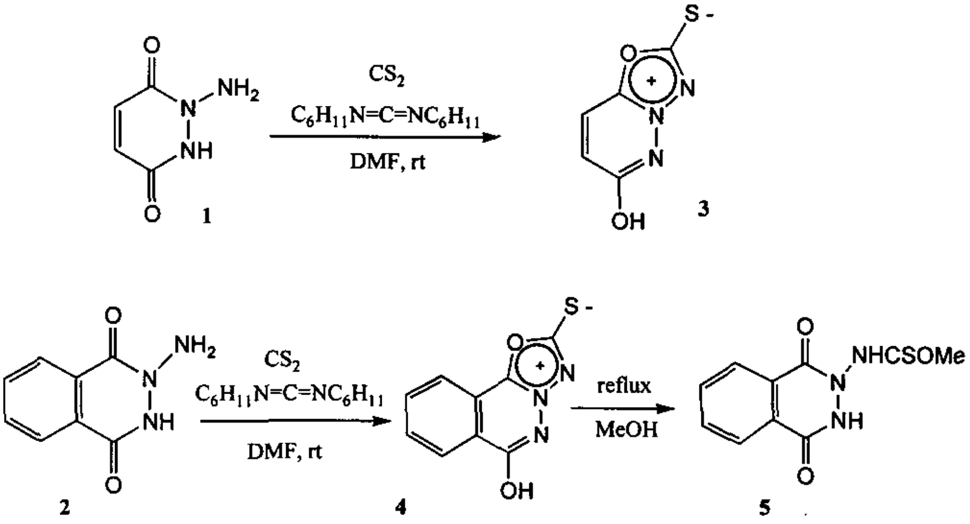
Abstract - The novel fused mesoionic 1,3,4-oxadiazolium-2-thiolates were synthesized from *N*-amino-*N,N'*-dihydrodiazinediones by treatment with carbon disulfide in the presence of 1,3-dicyclohexylcarbodiimide.

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.[1] Various types of monocyclic mesoionic 1,3,4-oxadiazolium-2-thiolates have been reported,[1] however the derivatives containing fused rings are rare.[2]

In connection with our studies to the synthesis of fused nitrogen-heterocycles[3] and fused mesoionic 1,2,4-triazolium-3-thiolates[4] 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.[5] 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**)[6] 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 cm^{-1} and 1475 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.[2] The broad band at around 3000 cm^{-1} is attributed to the enol absorption, which is in agreement with our previous work.[4] 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 ^{1}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 $R_2C^+=O$ (m/z, 54 in **3** and 104 in **4**) and corresponding $R_2CON^+R_1$ (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.[7]

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**)[8] 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_2 (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 %).

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6. 6-Hydroxy-1,3,4-oxadiazolo[3,2-*b*]pyridazinium-2-thiolate (**3**): mp 184 °C (decomp); ^{1}H NMR (DMSO-d$_6$) δ 8.40 (1H, d, J = 10 Hz), 7.55 (1H, d, J = 10 Hz); IR (KBr); 3000 cm^{-1} (br), 1470 cm^{-1}; 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); ^{1}H NMR (DMSO-d$_6$) δ 8.46 - 7.79 (4H, m, ar), 8.50 (1H, br, NH); IR (KBr); 3000 cm^{-1} (br), 1475 cm^{-1}; MS (70eV) m/z (rel. intensity); 162 (56.8), 147 (24.1), 104 (100), 77 (16.9), 60 (26.0).

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8. 2,3-Dihydro-2-methoxythiocarbonylamino-1,4-phthalazinedione (**5**); mp 227 - 229 °C (decomp); ^{1}H NMR (DMSO-d$_6$) δ 11.83 (1H, br, OH), 10.55 (1H, s, NH), 8.30 - 7.74 (4H, m, Ar); IR (KBr); 3000 cm^{-1} (br), 1480 cm^{-1}.

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