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

In connection with our studies to the synthesis of fused nitrogen-heterocycles and fused mesoionic 1,2,4-triazolium-3-thiolates 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. Taking advantage of that method, we studied the preparation of the fused mesoionic 1,3,4-oxadiazolium-2-
thiolates from \( N\)-amino-\( N,N'\)-dihyrodiazinediones.

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).

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 \( \text{CH}=\text{CH} \) 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-\( \alpha \)]phthalazinium-2-thiolate (4) was very similar to the 2-amino-2,3-dihydropthalazine-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 \( R_2\text{C}^+=\text{O} \) (m/z, 54 in 3 and 104 in 4) and corresponding \( R_2\text{CON}^+\text{R}_1 \) (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.\(^7\)

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 dicyclohexyl-carbodiimide (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 obtain the yellow needle (0.93 g, 70%).

REFERENCES AND NOTES


6. 6-Hydroxy-1,3,4-oxadiazolo[3,2-b]pyridazinium-2-thiolate (3): mp 184 °C (decomp); $^1$H NMR (DMSO-d$_6$) $\delta$ 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$_6$) $\delta$ 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).


8. 2,3-Dihydro-2-methoxythiocarbonylamino-1,4-phthalazinedione (5): mp 227 - 229 °C (decomp); $^1$H NMR (DMSO-d$_6$) $\delta$ 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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