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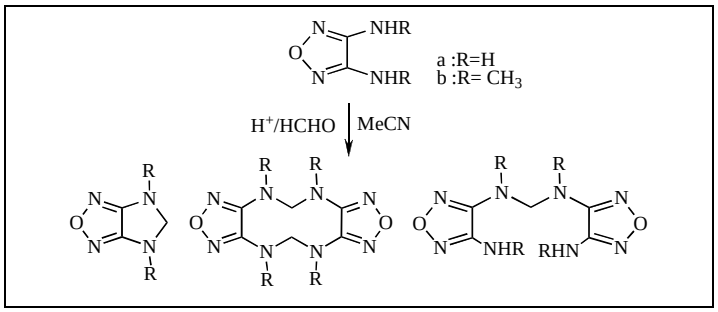

The compounds 5,6-dihydro-4*H*-imidazo[4,5-*c*][1,2,5]oxadiazole (**3a**, R=H), 4,6,10,12-tetramethyl-5,6,11,12-tetrahydro-4*H*,10*H*-bis(1,2,5)oxadiazolo[3,4-*d*:3',4'-*I*][1,3,6,8]tetraazecine (**4b**, R=CH_3), N^3,$N^{3'}$-methylenebis-3,4-diamino-1,2,5-oxadiazole (**5a**, R=H) and N^3,$N^{3'}$-methylenebis(*N*,*N*'-dimethyl-3,4-diamino-1,2,5-oxadiazolee) (**5b**, R=CH_3) were synthesized from the reaction of formaldehyde with 3,4-diamino–1,2,5-oxadiazole and *N*,*N*'-3,4-dimethylamino-1,2,5-oxadiazole in an acetonitrile.

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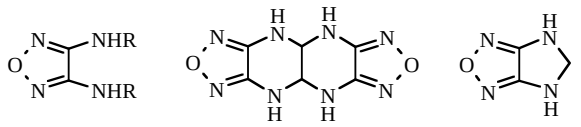
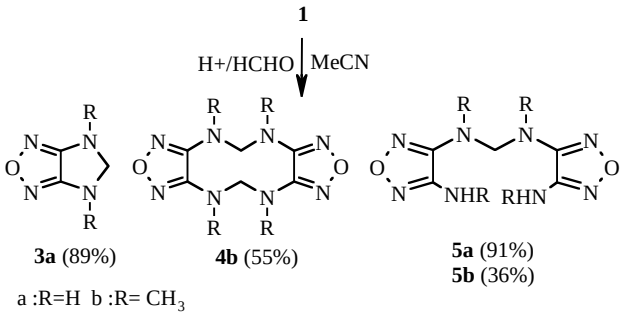
3,4-Diamino-1,2,5-oxadiazole derivatives (**1**) have been used for the preparation of the small ring high nitrogen heterocycles which are known as important starting materials for energetic compounds [1-5]. As reported by Willer and co-workers, the reaction of **1a** with glyoxal leads to compound **2** [6]. Their attempt to obtain the desired product **3** from the reaction of **1a** with formaldehyde failed and instead resulted in polymer formation. In order to synthesize compound **3**, the reaction of 3,4-diamino–1,2,5-oxadiazole (**1a**) and 3,4-dimethylamino-1,2,5-oxadiazole (**1b**) with formaldehyde was studied.



1 **2** **3**

RESULTS AND DISCUSSION

The compound 5,6-dihydro-4*H*-imidazo[4,5-*c*][1,2,5]-oxadizole (**3a**) was prepared in a very facile manner by condensation of **1a** with formaldehyde in acetonitrile at 0 ºC. An acid catalyst (formic acid, 0.1 molar % of **1a**) was required. We attempted to synthesize **3b** from the reaction of **1b** with formaldehyde under a similar condition. But the elemental analysis, mass spectra and NMR data of the product are in agreement with 4,6,10,12-tetramethyl-5,6,11,12-tetrahydro-4*H*,10*H*-bis(1,2,5)oxadiazolo[3,4-*d*:3',4'-*I*][1,3,6,8]tetraazecine (**4b**) structure. The reactions are rapid and nearly complete within a few hours. The reactions were sensitive to the concentration of formaldehyde in the reaction mixture. When formaldehyde was added to the reaction mixture, at once, it results polymeric products. But, best yields of cyclic compounds (**3a** and **4b**) were obtained by the addition of formaldehyde over a 2 h period.



3a (89%) **4b** (55%) **5a** (91%) **5b** (36%)

a :R=H b :R= CH_3

However, the reaction mixture of formaldehyde with **1a** and **1b**, at –8 ºC, resulted in the formation of precipitate N^3,$N^{3'}$-methylenebis(-3,4-diamino-1,2,5-oxadiazole) (**5a**) and N^3,$N^{3'}$-methylenebis(*N*,*N*'-dimethyl-3,4-diamin-1,2,5-oxadiazole) (**5b**), respectively. Best yields were obtained by the addition of the formaldehyde in one portion to the reaction mixture. The reactions were fast and completed within 2 hours at –8 ºC in the acetonitrile solvent. Furthermore, addition of formaldehyde to a solution of **5** did not result in **4** and a polymeric product was obtained. The yield appears to be independent of the carboxylic acid catalyst used. The reactions were completed at

temperatures less than zero and so, at temperatures higher than 10 °C, the reactions led to the formation of a polymer. The structures of final product depend on the concentration of formaldehyde in the reaction mixture. Thus, the dropwise addition of formaldehyde to the reaction mixture forces the results to yield cyclic products, while its abrupt addition led to **5**. Compounds **3a** and **4b** are stable in the acidic solution, but **5a** and **5b** are unstable and undergoes slow decomposition even at room temperature.

EXPERIMENTAL

All chemical reagents were obtained from Merck or Fluka and were used without further purification. Melting points were determined with an Electrothermal 9200 apparatus and are uncorrected. Infrared spectrum was recorded on a Shimadzu 4300 spectrometer. The nmr spectrum was recorded on a Brucker DRX-500 AVANCE spectrometer. Mass data was obtained on a FISONS TRIO 1000 GC-Mass instrument. Elemental analyses were carried out using a C,H,N,O Rapid-Heraeus apparatus.

5,6-Dihydro-4*H*-imidazo[4,5-*c*][1,2,5]oxadizole (3a) and 4,6,-10,12-tetramethyl-5,6,11,12-tetrahydro-4*H*,10*H*-bis(1,2,5)-oxadiazolo[3,4-*d*:3',4'-*I*][1,3,6,8]tetraazecine (4b). During a 2-h period, formaldehyde (4.00 g of 37% aqueous solution, 50 mmol) was added dropwise to a stirring solution of 3,4-diamino-1,2,5-oxadiazole (5.00 g, 50 mmol) [4] and formic acid (0.25 g, of 98% aqueous solution, 5.5 mmol) in MeCN (350 ml) while keeping the temperature below 0°C. The mixture was stirred for one additional hour and then 350 ml of distilled water was added to the solution. The reaction mixture was concentrated and the solid product was collected by filtration. Overall yield of crude product is 5.0 g (89% yields). Recrystallization from DMF-H_2O gave white crystals of **3a**, mp 224-226 °C. IR(KBr): 3334(NH), 1660(C=N), 1251(C-N). ^{1}H-NMR (DMSO-d_6, 25 °C) ppm: 7.08(bs, 2H, NH), 4.58(s, 2H, CH_2). Upon addition of D_2O to NMR sample, the NH signals disappeared.^{13}C-NMR (DMSO-d_6, 25 °C) ppm: 148.61(C_{ipso}), 88.63(CH_2). The EI-MS, *m/z*: 112(M^+). *Anal.* Calc. for $C_3H_4N_4O$: C, 32.14; H, 3.57; N, 50; found: C, 32.11; H, 3.59; N, 50.08.

Condensation of 3,4-dimethylamino-1,2,5-oxadiazole with formaldehyde under similar condition leads to **4b**; Yield 3.90 g (55% yield), mp 141.7-142 °C. IR(KBr): 2984(CH_2), 2912(CH_3), 1568, 1600(C=N), 1244, 1120, 1084(C-N). ^{1}H-NMR (Acetone–d_6 25 °C) ppm: 4.65 (s, 4H, CH_2), 2.98(s, 12H, CH_3). ^{13}C-NMR (Acetone-d_6, 25 °C) ppm: 152.64(C_{ipso}), 85.85(CH_2), and 35.36 (CH_3). The EI-MS, *m/z*: 280 (M^+). *Anal.* Calc. for $C_{10}H_{16}N_8O_2$ calculated: C, 42.86; H, 5.71; N, 40; found: C, 42.83; H, 5.72; N, 40.07.

Synthesis of N^3,$N^{3'}$-methylenebis[3,4-diamino-1,2,5-oxadiazole] (5a) and N^3,$N^{3'}$-methylenebis[*N*,*N*'-dimethyl-3,4-diamino-1,2,5-oxadiazole] (5b). To a stirring solution of 3,4-diamino-1,2,5-oxadiazole (0.58 g, 5 mmol) and formic acid (0.05 g of 98% aqueous solution, 1.1 mmol) in MeCN (30 ml) at –8 °C, formaldehyde (0.2 g of 37% aqueous solution, 2.5 mmol) was added in one step. The reaction mixture was stirred for 2 h and then 30 ml of distilled water was added to the solution. After 30 minutes, solvent was removed under reduced pressure to yield a white precipitate, 0.48 g (91% yield). Recrystallization from DMF-H_2O gave crystals of **5a**, mp 248-249 °C. IR(KBr): 3500(NH_2), 3290(NH) 1651, 1590(C=N), 1302-1078(C-N). ^{1}H-NMR (Acetone-d_6, 25 °C) ppm: 6.12(bs, 2H, NH), 5.36 (s, 4H, NH_2), 4.78-4.80 (t, 2H, J=6.56Hz, CH_2). Upon addition of D_2O to NMR sample, the NH and NH_2 signals disappeared and CH_2 signal collapsed into one signal. ^{13}C–NMR (Acetone–d_6, 25 °C) ppm: 149.34(C_{ipso}), 53.89(CH_2). The EI-ms, m/ z: 212(M^+), 211(M-1), 210(M-2). *Anal.* Calc.for for $C_5H_8N_8O_2$ calculated: C, 28.30; H, 3.77; N, 52.83; found: C, 28.27; H, 3.78; N, 52.84.

The reaction of 3,4-dimethylamino-1,2,5-oxadiazole with formaldehyde under similar condition of **5a**, leads to **5b**. Yield: 36%; mp 193-194.5 °C. IR(KBr): 3376(NH), 2900-2988(CH_2, CH_3), 1603, 1564(C=N), 1241, 1222, 1097(C-N). ^{1}H-NMR (Acetone-d_6, 25 °C) ppm: 5.38 (bs, 2H, NH), 4.68 (s, 2H, CH_2), 2.99 (s, 6H, CH_3), 2.91-2.92 (d, 6H, J=5 Hz, CH_3). Upon addition of D_2O to NMR sample, the NH signal disappeared and CH_3 signal collapsed in to a singlet. ^{13}C-NMR (Acetone-d_6, 25 °C) ppm: 152.96 (C_{ipso}), 152.78(C_{ipso}), 68.60(CH_2), 36.54(CH_3), and 30.98 (CH_3). The EI-MS, *m/z*: 268(M^+), 266(M-2). *Anal.* Calc. for $C_9H_{16}N_8O_2$ calculated: C, 40.30; H, 5.97; N, 41.79; found: C, 40.29; H, 5.94; N, 41.80.

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