Evidences of Some Unusual Behaviours of 2-Aminothiazol and 2-Aminobenzothiazol in Reactions with Formaldehyde and Glyoxal

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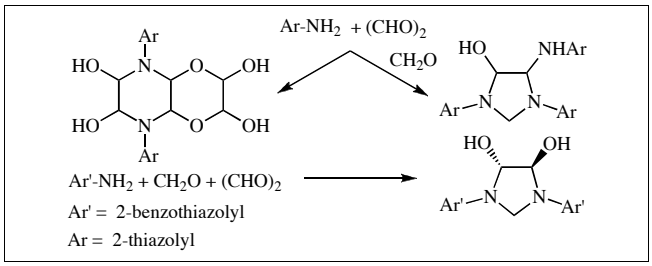

In contrast to the previously reported acid-catalyzed reaction of 2-aminothiazole with aqueous formaldehyde in water at 0-5 °C which afforded *N,N'*-bis(2-thiazolyl)methanediamine (**4**), 5,5'-methylenebis(2-aminothiazole) (**5**) is obtained as the unique product under reflux conditions. Reaction of 2-aminobenzothiazole with aqueous formaldehyde in acetonitrile at 0-5 °C or under reflux conditions produces (2-benzothiazolylamino)methanol (**6**) or *N,N'*-bis(2-benzothiazolyl)methanediamine (**7**), respectively. Heating monoamine **6** in acetonitrile remarkably yields the symmetric diamine **7**. While cyclocondensation of 2-aminothiazole with aqueous glyoxal in acetonitrile gives 3,4,8,9-tetrahydroxy-7,10-bis(2-thiazolyl)-2,5-dioxa-7,10-diazabicyclo[4.4.0]decane (**8**), reaction of 2-aminobenzothiazole with glyoxal fails to produce similar results; In the presence of aqueous formaldehyde, although the former reaction leads to the formation of 4-hydroxy-5-(thiazolylamino)-1,3-bis(2-thiazolyl)imidazolidine (**9**), utilization of 2-aminobenzothiazole gives 4,5-dihydroxy-1,3-bis(2-benzothiazolyl)imidazolidine (**10**). Condensation of either **6** or **7** with aqueous glyoxal affords compound **10**. Details of the reactions will be discussed in this presentation.

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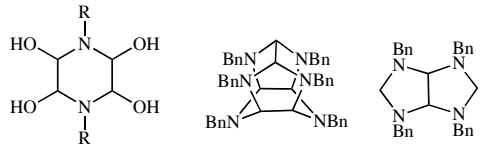
INTRODUCTION

Reaction of amines (RNH_2) and amides ($RCONH_2$) with glyoxal and formaldehyde gives a wide variety of products depending upon the nature of R and, in certain cases, upon the reaction conditions [1-16]. In 1967, Currie and co-workers reported the base-catalyzed reaction of formamide or methane sulphonamide with glyoxal leading to the corresponding 2,3,5,6-tetra-hydroxypiperazines (**1**) [6-7]. Twentythree years later, Nielsen and co-workers reported the facile condensation of glyoxal with benzylamine to produce caged ring system to which they assigned the semisystematic name hexabenzylhexaazaisowurtzitane (**2**) [2,10]. In another report, the three-component cyclocondensation reaction of benzylamine with aqueous glyoxal and aqueous formaldehyde was explained to produce 2,4,6,8-tetrabenzyl-2,4,6,8-tetraazabicyclo-[3.3.0]octane (**3**) as a polyazapolycyclic compound (Figure I) [2]. In the present work, we have found new evidences in reaction of either 2-aminothiazole or 2-aminobenzothiazole with aqueous formaldehyde and glyoxal. Moreover, one-pot three-component reactions of 2-aminothiazole and 2-aminobenzothiazole with formaldehyde and glyoxal were also investigated.



1: R= -CHO , $-SO_2CH_3$ **2** **3**

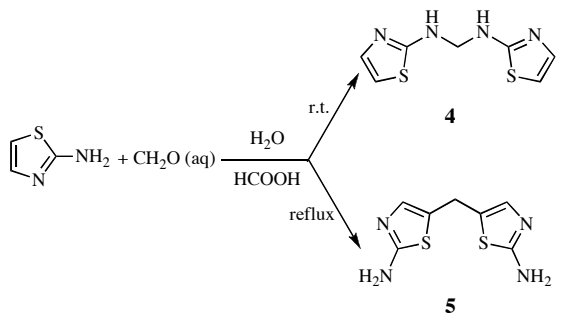
Figure I

RESULTS AND DISCUSSION

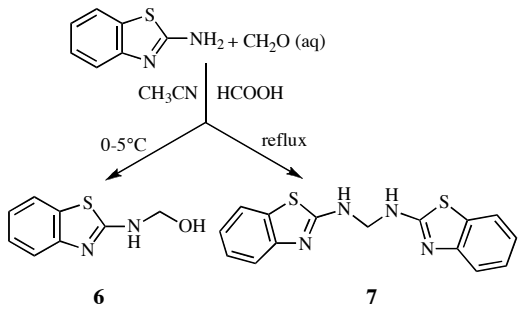
In contrast to the previously reported acid-catalyzed reaction of 2-aminothiazole with aqueous formaldehyde in water solvent at 0-5 °C affording *N,N'*-bis(2-thiazolyl)methanediamine (**4**) [17], 5,5'-methylenebis(2-aminothiazole) (**5**) is obtained as the unique product under reflux conditions (Scheme I). We assigned the structure of **5** based on the following observations. It gave the correct elemental analysis for $C_7H_8N_4S_2$. The ^1H NMR spectrum showed CH_2, CH and NH_2 protons as singlet signals at δ 3.88, 6.67 and 6.75 ppm, respectively.

Treatment of 2-aminobenzothiazol with aqueous formaldehyde in acetonitrile at 0-5 °C or at reflux conditions led to the formation of (2-benzothiazolylamino)methanol (**6**) or *N,N'*-bis(2-benzothiazolyl)methanediamine (**7**), respectively (Scheme II). The symmetric diamine **7** was also obtained when the monoamine **6** was refluxed in acetonitrile in the presence of aqueous formic acid and free 2-aminobenzothiazole. It seemed likely that the latter has arisen from the condensation of the free amine with monoamine **6**. Since our attempt to obtain the similar asymmetric diamine in the presence of either aniline or 2-aminopyridine failed and the symmetric diamine **7** was formed, therefore, this proposal was ruled out and we concluded that the operation of an internal process in the conversion of **6** to **7** was inevitable.

Scheme I

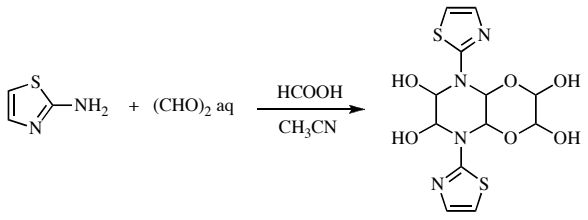


Scheme II



In another experiment, the formic acid-catalyzed reaction of 2-aminothiazole with aqueous glyoxal was examined in acetonitrile at room temperature. The reaction produced a white precipitate in 85% yield of which, on the basis of the following observations, the structure was assigned as 3,4,8,9-tetrahydroxy-7,10-bis(2-thiazolyl)-2,5-dioxa-7,10-diazabicyclo[4.4.0]-decane (**8**), a polyazapolyoxapolycyclic compound (Scheme III). Using methanol as solvent leads to relatively low yield.

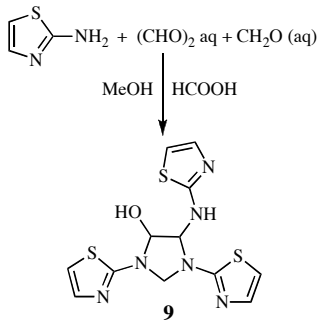
Scheme III



It gave the correct elemental analysis for $C_{12}H_{14}N_4O_6S_2$. The IR spectrum showed a sharp stretch for OH at 3427 cm^{-1} and lacked NH and CO absorptions. The ^1H NMR spectrum contained two AB quartet patterns at δ 5.29 and 6.84 ppm (J = 4.9 Hz) and at δ 5.53 and 6.63 ppm (J = 4.7 Hz) corresponding to two chemically different CH-OH moieties, as expected. Bridgehead CH protons appeared as a sharp singlet at δ 5.30 ppm. In the ^1H NMR spectrum of the deuterium exchanged sample, two signals corresponding to the OH protons disappeared and the peripheral CH protons appeared as two singlet signals at δ 5.29 and 5.51 ppm.

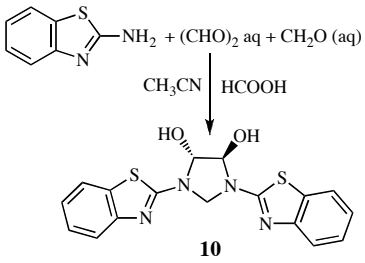
The reaction of 2-aminobenzothiazole with aqueous glyoxal in acetonitrile at room temperature produced an unstable fast equilibrating solid. It was not possible to purify the products and the molecular structures could not therefore be elucidated. 2-Hydroxy-5-(thiazolylamino)-1,3-bis(2-thiazolyl)imidazolidine (**9**) was obtained in 66% yield when 2-aminothiazole reacted with aqueous glyoxal in the presence of aqueous formaldehyde in methanol at room temperature (Scheme IV). In the aliphatic region, ^1H NMR spectrum of **9** showed three AB quartet patterns arising from CH-NH (δ 5.59 and 8.40 ppm, J = 7.2 Hz), CH-OH (δ 5.32 and 6.98 ppm, J = 7.4 Hz) and CH_2 (δ 5.07 and 5.12 ppm, J = 5.0 Hz) protons. Upon addition of D_2O into NMR tube, the signals of OH and NH disappeared and the signals of methine moieties collapsed into two sharp singlets. The remaining protons of the molecule corresponding to CH_2 and aromatic portion showed four well-resolved AB quartet patterns. It gave the correct elemental analysis for $C_{12}H_{12}N_6OS_3$. Mass spectrum revealed the molecular ion peak at m/z 352. The intense peak at m/z 212 ascribed to the *N,N'*-bis(2-thiazolyl)methanediamine cation radical further confirmed the proposed structure for compound **9**. The coupling constant ($^3J_{HH}$) of –CH-CH- fragment in **9** was very small (ca. 0 Hz), consistent with a dihedral angle close to 90° as given by the Karplus relationships. Stereochemistry determination of the five-membered ring based on dihedral angle derived by the Karplus relationships is unlikely.

Scheme IV



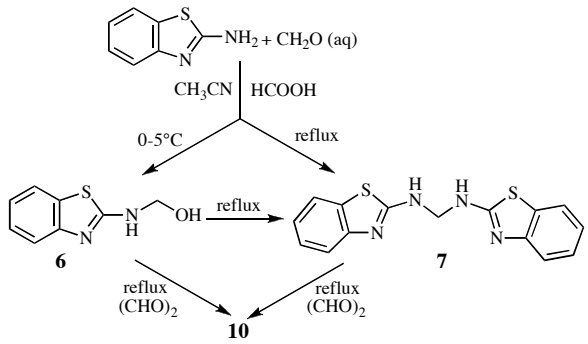
On the other hand, acid-catalyzed one-pot three-component reaction of 2-aminobenzothiazole, aqueous glyoxal and aqueous formaldehyde was also examined at reflux conditions in acetonitrile. Based on the spectroscopic analyses, the structure of product was determined as *trans*-4,5-dihydroxy-1,3-bis(2-benzothiazolyl)imidazolidine (**10**) (Scheme V). The ^{1}H NMR spectrum showed CH-OH fragment as an AB quartet pattern at δ 5.37 and 7.00 ppm (J = 7.35 Hz). Upon addition of D_2O into NMR tube, the signal of OH disappeared and the signal of CH collapsed into a singlet. The CH_2 protons revealed as a sharp singlet at δ 5.30 ppm in agreement with a *trans* stereochemistry. Whereas, they would appear as an AB spin system if the hydroxyl groups were *cis* to each other. The IR spectrum showed OH absorption at 3220 cm^{-1} and lacked NH and CO absorptions. Mass spectrum showed the molecular ion peak at m/z 370. It gave the correct elemental analysis for $C_{17}H_{14}N_4O_2S_2$. It should be noted that we have recently described the synthesis of *trans*-4,5-dihydroxy-1,3-bis(2-pyrimidinyl)imidazolidine through the reaction of *N,N'*-bis(2-pyrimidinyl)methanediamine and glyoxal in acetonitrile [18].

Scheme V



It might be inferred that 2-aminothiazole and 2-aminobenzothiazole exhibit different behaviors in reaction with formaldehyde and glyoxal if one compares their basicities. While the former seems a better nucleophile, the latter with more extended π-conjugated system is not strong enough to replace the OH group under reaction conditions. Finally, reaction of either **6** or **7** with aqueous glyoxal in refluxing acetonitrile in the presence of formic acid produced compound **10**. Scheme VI concisely represents the formation of **6** and **7**, and their subsequent heating either alone or in the presence of glyoxal in acetonitrile solvent.

Scheme VI



EXPERIMENTAL

All commercially available chemicals and reagents were used without further purification. Melting points were determined with an Electrothermal model 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu 4300 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a Bruker DRX-500 AVANCE spectrometer. Chemical shifts (δ) are reported in ppm and referenced to the NMR solvent. Mass analyses of the products were conducted with a HP (Agilent technologies) 5937 Mass Selective Detector. Elemental analyses were carried out with a Thermo Finnigan (FLASH 1112 SERIES EA) CHNS-O analyzer.

5,5'-Methylenebis(2-aminothiazole) (5). A mixture of 2-aminothiazole (0.5 g, 5 mmol), formaldehyde (0.2 g of 37% aqueous solution, 2.5 mmol) and formic acid (0.02 g of 98% aqueous solution, 0.44 mmol) in water (10 mL) was heated under reflux for 12 hours. It was then cooled to 5 °C and precipitate was collected by filtration, washed with cold water and dried. Recrystallization from water gave pale yellow crystals of (**5**) in yield 55%, mp 210-212 °C; ir (potassium bromide): 3436 and 3321 (NH_2), 3049, 2900, 1614, 1514, 1298, 1207, 1055 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 3.88 (s, 2H, CH_2), 6.67 (s, 2H, 4-H, 4'-H), 6.75 (s, 4H, NH_2); ^{1}H nmr (DMSO-d_6 + D_2O): δ 3.87 (s, 2H, CH_2), 6.67 (s, 2H, 4-H, 4'-H); ^{13}C nmr (DMSO-d_6): δ 25.20 (CH_2), 125.45 (2 x CH), 136.04 (2 x C), 168.86 (2 x C); ms (relative intensity %): m/z 212 (M^+, 87), 195 (9), 170 (14), 152 (100), 113 (23). *Anal.* Calcd. for $C_7H_8N_4S_2$: C, 39.62; H, 3.77; N, 26.41; S, 30.18. Found: C, 39.59; H, 3.86; N, 26.11; S, 30.33.

(2-Benzothiazolylamino)methanol (6). Formaldehyde (0.48 g of 37% aqueous solution, 6 mmol) and formic acid (0.02 g of 98% aqueous solution, 0.44 mmol) were slowly added to a stirring solution of 2-aminothiazole (0.6 g, 6 mmol) in acetonitrile (15 mL) at room temperature. After stirring for 16 hours, it was cooled to 5 °C and the white precipitate was

collected by filtration, washed with cold acetonitrile and dried. Recrystallization from acetonitrile gave white crystals of (**6**) in yield 95%, mp 157-159 °C; ir (potassium bromide): 3288, 3159, 3035, 2920, 1596, 1541, 1446, 1384, 1286, 1211, 1064 cm^{-1}; ^1H nmr (DMSO-d_6): δ 4.80 (dd, 2H, *CH_2*, *J* = 6.1, 6.7 Hz), 5.79 (t, 1H, *OH*, *J* = 6.7 Hz), 7.03-7.71 (m, 4H, benzothiazole protons), 8.56 (t, 1H, *NH*, *J* = 6.1 Hz); ^1H nmr (DMSO-d_6 + D_2O): δ 4.78 (s, 2H, *CH_2*), 7.03-7.70 (m, 4H, benzothiazole protons); ^{13}C nmr (DMSO-d_6): δ 68.31 (CH_2), 119.18 (CH), 121.81 (CH), 122.00 (CH), 126.38 (CH), 131.27 (C), 153.19 (C), 166.98 (C); ms (relative intensity %): m/z 180 (M^+, 87), 162 (14), 150 (100), 135 (21), 123 (83), 108 (25), 96 (63). *Anal.* Calcd. for $C_8H_8N_2OS$: C, 53.33; H, 4.44; N, 15.55; S, 17.77. Found: C, 53.14; H, 4.48; N, 15.70; S, 17.82.

***N,N'*-Bis(2-benzothiazolyl)methanediamine (7).** Formaldehyde (0.24 g of 37% aqueous solution, 3 mmol) and formic acid (0.02 g of 98% aqueous solution, 0.44 mmol) were slowly added to a solution of 2-aminothiazole (0.6 g, 6 mmol) in acetonitrile (10 mL). The solution was heated under reflux for 16 hours. It was then cooled to 5 °C and the white precipitate was filtered, washed with cold acetonitrile and dried. Recrystallization from DMSO-H_2O (1:1) gave white crystals of (**7**) in yield 75%, mp 208-210 °C; ir (potassium bromide): 3320 (NH), 3101, 2977, 1608, 1573, 1456, 1380, 1276, 1130, 1020 cm^{-1}; ^1H nmr (DMSO-d_6): δ 5.03 (t, 2H, *CH_2*, *J* = 5.5 Hz), 7.04-7.71 (m, 8H, benzothiazole protons), 8.86 (t, 2H, *NH*, *J* = 5.5 Hz); ^1H nmr (DMSO-d_6 + D_2O): δ 5.00 (s, 2H, *CH_2*), 7.05-7.70 (m, 8H, benzothiazole protons); ^{13}C nmr (DMSO-d_6): δ 52.93 (CH_2), 119.20 (2 x CH), 121.95 (2 x CH), 122.16 (2 x CH), 126.46 (2 x CH), 131.46 (2 x C), 152.96 (2 x C), 166.57 (2 x C); ms (relative intensity %): m/z 312 (M^+, 11), 162 (61), 150 (100), 135 (52), 108 (25). *Anal.* Calcd for $C_{15}H_{12}N_4S_2$: C, 57.69; H, 3.84; N, 17.94; S, 20.51. Found: C, 57.45; H, 3.75; N, 18.04; S, 20.74.

3,4,8,9-Tetrahydroxy-7,10-bis(2-thiazolyl)-2,5-dioxa-7,10-diazabicyclo[4.4.0]decane (8). To a stirring solution of 2-aminothiazole (0.5 g, 5 mmol) and formic acid (0.02 g of 98% aqueous solution, 0.44 mmol) in acetonitrile (10 mL), was added glyoxal (1.09 g of 40% aqueous solution, 7.5 mmol). After stirring for 45 hours at room temperature, the white solid that formed was collected by filtration, washed with cold acetonitrile and air dried to give (**8**) in yield 85%, mp 149-151 °C (decomp.); ir (potassium bromide): 3427 (OH), 3100, 2979, 1517, 1463, 1373, 1064, 1043 cm^{-1}; ^1H nmr (DMSO-d_6): δ 5.29 (d, 2H, 2 x -N-*CH*-OH, *J* = 4.9 Hz,), 5.30 (s, 2H, 2 x -O-*CH*-N-), 5.53 (d, 2H, 2 x -O-*CH*-OH, *J* = 4.7 Hz), 6.63 (d, 2H, 2 x -O-CH-*OH*, *J* = 4.7 Hz), 6.84 (d, 2H, 2 x -N-CH-*OH*, *J* = 4.9 Hz,), 6.92 and 7.23 (AB, 4H, thiazole protons, *J* = 3.5 Hz); ^1H nmr (DMSO-d_6 + D_2O): δ 5.29 (s, 2H, 2 x -N-*CH*-OH), 5.30 (s, 2H, 2 x -O-*CH*-N-), 5.51 (s, 2H, 2 x -O-*CH*-OH), 6.91 and 7.21 (AB, 4H, thiazole protons, *J* = 3.5 Hz); ^{13}C nmr (DMSO-d_6): δ 90.06 (2 x CH), 94.98 (2 x CH), 101.57 (2 x CH), 110.05 (2 x CH), 139.35 (2 x CH), 168.59 (2 x C). *Anal.* Calcd. for $C_{12}H_{14}N_4O_6S_2$: C, 38.50; H, 3.74; N, 14.97; S, 17.11. Found: C, 38.21; H, 3.77; N, 14.75; S, 17.21.

4-Hydroxy-5-(thiazolylamino)-1,3-bis(2-thiazolyl)imidazolidine (9). Glyoxal (0.23 g of 40% aqueous solution, 1.6 mmol), formaldehyde (0.13 g of 37% aqueous solution, 1.6 mmol) and formic acid (0.02 g of 98% aqueous solution, 0.44 mmol) were slowly added to a stirring solution of 2-aminothiazole (0.5 g, 5 mmol) in methanol (4 mL) at room temperature. After stirring for 45 hours, the solution was cooled to 5 °C and the white solid that formed was collected by filtration, washed with cold methanol and air dried to give (**9**) in yield 66%, mp 163-165 °C; ir (potassium bromide): 3300, 3182, 3053, 2923, 1508, 1382, 1236, 1093 cm^{-1}; ^1H nmr (DMSO-d_6): δ 5.07 and 5.12 (AB, 2H, *CH_2*, *J* = 5.0 Hz), 5.32 (d, 1H, -*CH*-OH, *J* = 7.4 Hz), 5.59 (d, 1H, -*CH*-NH, *J* = 7.2 Hz), 6.76-7.28 (3AB, 6H, thiazole protons, *J* = 3.6, 3.5, 3.9 Hz), 6.98 (d, 1H, -CH-*OH*, *J* = 7.4 Hz), 8.40 (d, 1H, -CH-*NH_2*, *J* = 7.2 Hz); ^1H nmr (DMSO-d_6 + D_2O): δ 5.07 and 5.12 (AB, 2H, *CH_2*, *J* = 5.1 Hz), 5.31 (s, 1H, -*CH*-OH), 5.57 (s, 1H, -*CH*-NH), 6.76-7.27 (3AB, 6H, thiazole protons, *J* = 3.6, 3.5, 3.8 Hz); ^{13}C nmr (DMSO-d_6): δ 65.95 (CH_2), 77.84 (CH), 88.09 (CH), 108.71 (CH), 110.39 (2 x CH), 139.5 (CH), 140.16 (CH), 140.31 (CH), 165.22 (C), 165.28 (C), 167.33 (C); ms (relative intensity %): m/z 352 (M^+, 3), 334 (2), 222 (16), 212 (33), 113 (100), 100 (88), 85 (63). *Anal.* Calcd. for $C_{12}H_{12}N_6OS_3$: C, 40.91; H, 3.41; N, 23.86; S, 27.27. Found: C, 40.75; H, 3.51; N, 24.05; S, 27.37.

***trans*-4,5-Dihydroxy-1,3-bis(2-benzothiazolyl)imidazolidine (10).** A mixture of glyoxal (0.14 g of 40% aqueous solution, 1.0 mmol), formaldehyde (0.08 g of 37% aqueous solution, 1.0 mmol), formic acid (0.01 g of 98% aqueous solution, 0.22 mmol) and 2-aminobenzothiazole (0.3 g, 2 mmol) in acetonitrile (10 mL) was refluxed for 16 hours. It was then cooled to 5 °C and the white crystals were filtered, washed with cold acetonitrile and dried. Recrystallization from DMSO-H_2O (1:1) gave white crystals of (**10**) in yield 80%, mp 200-202 °C; ir (potassium bromide): 3220 (OH), 3114, 2921, 1598, 1530, 1448, 1380, 1276, 1134, 1041 cm^{-1}; ^1H nmr (DMSO-d_6): δ 5.30 (s, 2H, *CH_2*), 5.37 (d, 2H, 2 x -*CH*-OH, *J* = 7.35 Hz), 7.0 (d, 2H, 2 x *OH*, *J* = 7.35 Hz), 7.17-7.90 (m, 8H, benzothiazole protons); ^1H nmr (DMSO-d_6 + D_2O): δ 5.30 (s, 2H, *CH_2*), 5.36 (s, 2H, 2 x -*CH*-OH), 7.17-7.85 (m, 8H, benzothiazole protons); ^{13}C nmr (DMSO-d_6): δ 65.47 (CH_2), 89.38 (2 x CH), 120.16 (2 x CH), 122.44 (2 x CH), 123.02 (2 x CH), 127.03 (2 x CH), 131.49 (2 x C), 152.58 (2 x C), 163.36 (2 x C); ms (relative intensity %): m/z 370 (M^+, 2), 368 (4), 312 (9.5), 162 (74), 150 (100), 135 (64), 123 (24), 108 (35). *Anal.* Calcd. for $C_{17}H_{14}N_4O_2S_2$: C, 55.13; H, 3.78; N, 15.13; S, 17.29. Found: C, 55.0; H, 3.61; N, 15.20; S, 17.21.

Dimerization of 6. A suspension of (**6**) (0.5 g, 2.8 mmol) and formic acid (0.01 g of 98% aqueous solution, 0.22 mmol) in acetonitrile (25 mL) was refluxed for 16 hours. It was then cooled to 5 °C and the white precipitate was collected by filtration, washed with cold acetonitrile and dried to give a white precipitate (85%), which was identical with (**7**) based on melting point and NMR.

Reaction of 6 with glyoxal. A mixture of (**6**) (0.4 g, 2.2 mmol), glyoxal (0.15 g of 40% aqueous solution, 1.1 mmol) and formic acid (0.01 g of 98% aqueous solution, 0.22 mmol) in acetonitrile (20 mL) was refluxed for 20 hours. It was then cooled to 5 °C and the white precipitate was collected by filtration, washed with cold acetonitrile and dried to give a white precipitate (65%), which was identical with (**10**) based on melting point and NMR.

Reaction of 7 with glyoxal. A mixture of (**7**) (0.4 g, 1.3 mmol), glyoxal (0.18 g of 40% aqueous solution, 1.3 mmol) and formic acid (0.01 g of 98% aqueous solution, 0.22 mmol) in acetonitrile (40 mL) was refluxed for 16 hours. It was then cooled to 5 °C and the white precipitate was collected by filtration, washed with cold acetonitrile and dried to give a white precipitate (71%), which was identical with (**10**) based on melting point and NMR.

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REFERENCES

[1] S. L. Vail, C. M. Moran, H. B. Moore and R. M. H. Kullman, *J. Org. Chem.,* **27**, 2071 (1962).

[2] A. T. Nielsen, R. A. Nissan, A. P. Chafin, R. D. Gilardi and C. F. George, *J. Org. Chem.,* **57**, 6756 (1992).

[3] S. M. F. Farnia, A. Kakanejadifard and D. Soudbar, *Tetrahedron,* **53**, 2557 (1997).

[4] S. M. F. Farnia, A. Kakanejadifard and D. Soudbar, *J. Org. Chem.*, **50**, 2368 (1985).

[5] A. Alexakis, J. P. Tranchier, N. Lensen and P. Mangeney, *J. Am. Chem. Soc*., **117**, 10767 (1995).

[6] A. C. Currie, A. H. Dinwoodie, G. Fort and J. M. C. Thompson, *J. Chem. Soc. C*,, 491 (1967).

[7] A. H. Dinwoodie, J. A. Gibson and J. B. Parker, *J. Chem. Soc. C,* 496 (1967).

[8] L. Randaccio, E. Zangrando, M. H. Gei and A.G. Giumanini, *J. Prakt. Chem* ., **329**, 187 (1987).

[9] A. T. Nielsen, R. L. Atkins, J. Dipol and D. W. Moore, *J. Org. Chem.*, **39**, 1349 (1974).

[10] M. Chaykovsky, W. M. Koppes, T. P. Russell, R. Gilardi, C. George and J. L. Flippen-Anderson, *J. Org. Chem.,* **57**, 4295 (1992).

[11] R. L. Willer, D. W. Moore and D. J. Vanderah, *J. Org. Chem.,* **50**, 2365 (1985).

[12] D. S. Black, D. C. Craig, O. Giitsidis, R. W. Read, A. Salek and M. A. Sefton, *J. Org. Chem.,* **54**, 4771 (1989).

[13] A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall and M. Unverzagt, *Tetrahedron,* **55**, 14523 (1999).

[14] J. M. Kliegman and R. K. Barnes, *J. Org. Chem.,* **35**, 3140 (1970).

[15] S. Balasubramanian, *Inorg. Chem.,* **26**, 553 (1987).

[16] J. Barluenga, A. M. Bayon, P. Campos, G. Asensio, E. Gonzalez-Nunez and Y. Molina, *J. Chem. Soc., Prekin Trans. 1*, 1631 (1988).

[17] B. Skowronska-Serafinowa, *Roczniki Chem.,* **29**, 932 (1955).

[18] M. Ghandi, F. Salimi and A. Olyaei, *J. Heterocyclic Chem*., **43,** 791 (2006).