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The Rearrangement of 2-Benzothiazolylthioacetyl Hydrazide in Synthesis of s-Triazolo[3, 4-b]benzothiazole-3-thiol

Yan ZHANG, Ren Zhong QIAO, Chao Feng DAI, Peng Fei XU, Zi Yi ZHANG*

National Laboratory of Applied Organic Chemistry,
Department of Chemistry, Lanzhou University, Lanzhou 730000

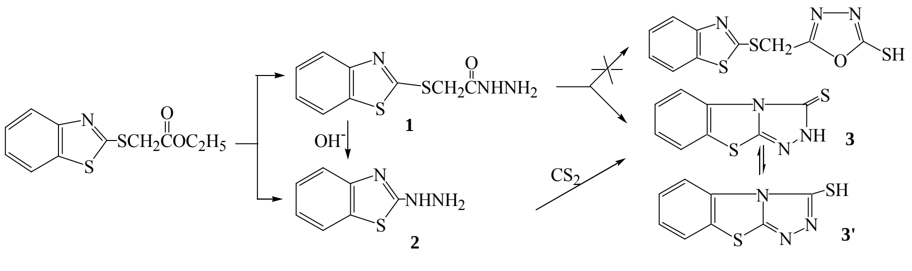
Abstract: The rearrangement reaction of 2-benzothiazolylthioacetyl hydrazide **1** with potassium hydroxide and carbon disulfide in ethanol to produce s-triazolo[3, 4-b]benzothiazole-3-thiol **3** was described. **3** also can be obtained from 2-benzothiazolylhydazine **2** and the two methods for getting **3** were compared. Mannich reaction of compounds **3** was reported too.

Keywords: Rearrangement, s-triazolo[3, 4-b]benzothiazole-3-thiol, Mannich reaction.

2/3-Substituted-benzothiazoles and their derivatives have attracted much attention of chemists and pharmacologists because of their broad spectrum biological activities and use as photographic materials[1-3]. 2-Benzothiazolylthioacetyl hydrazide **1** as a rather active compound, generally when it reacted with CS_2 in ethanol solution of KOH, should cyclize to give 5-substituted-1, 3, 4-oxadiazol-2-thiol[4]. Unexpectedly, we did not get the desired compounds, but s-triazolo[3, 4-b]benzothiazole-3-thiol **3** was isolated. This is due to the rearrangement reaction of hydrazide. In order to identify this result, we handled 2-benzothiazolyhydrazine **2** in the same condition for obtaining **3**. Other method of synthesis **3** had been discussed before[6-7]. Reynolds[7] pointed out that it might have a double-bonded sulfur in **3** rather than a mercapto group as in **3′** (**Scheme 1**).

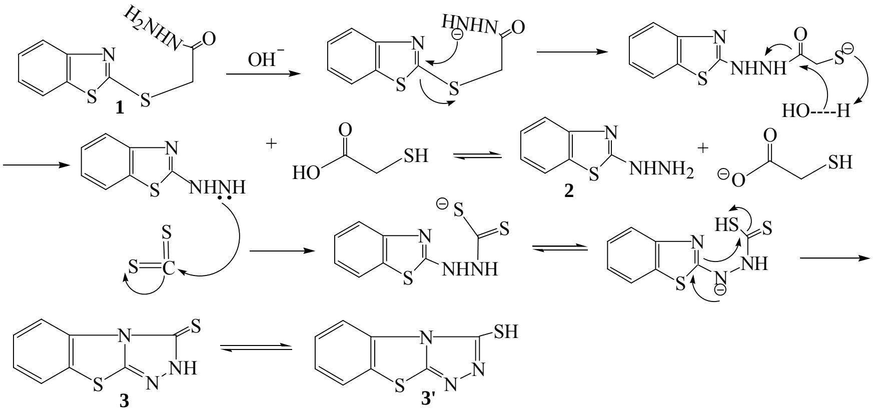
Compound **3**: pale yellow microcrystals, mp 252~254°C (255°C[6a]); ^{1}H NMR (DMSO-d_6, δ ppm): 14.23 (s, 1H, NH), 8.94~8.92 (m, 1H, ArH), 8.11~7.99 (m, 1H, ArH), 7.61~7.47 (m, 2H, ArH).

Scheme 1 Preparation of s-triazolo[3, 4-b]benzothiazole-3-thiol **3**



In this reaction we could find white needle crystal appeared and odd odor released shortly after **1** was dissolved completely in the ethanol solution of potassium hydroxide. The precipitate was separated and assigned to be 2-benzothiazolylhydrazine **2** by melting point and standard IR spectra data. From this fact, we proposed treating hydrazine **2** with CS_2 and KOH also could form compound **3**. Above all, we could think that there is intramolecular addition- elimination reaction occurred about 2-benzothiazolylthioacetyl hydrazide **1** to form 2-benzothiazolylhydrazine **2** in the presence of KOH at heating. Hydrazine **2** reacted with KOH and CS_2 further to convert s-triazolo[3, 4-b]benzothiazole-3-thiol **3**. The reaction mechanism was proposed as follows (**Scheme 2**).

Scheme 2 Mechanism of rearrangement reaction



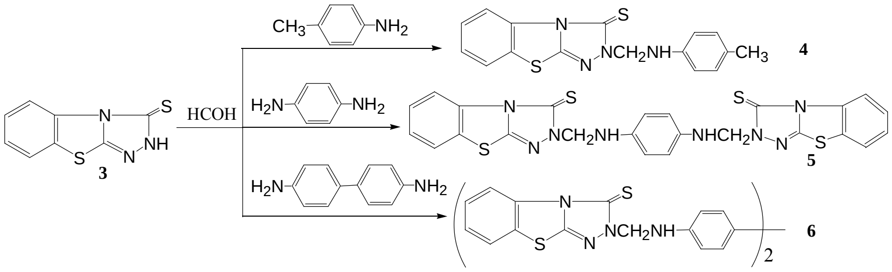
As we known, 1, 2, 4-triazolo[3, 4-b]benzothiazole-3-thiol **3** and their derivatives are extensively applied in agrochemistry[8]. 3-substituted and 3-thiolsubstituted derivatives of **3** have been studied[9]. But there is seldom report on the synthesis of derivatives at 2- position of **3**. We were interested in this work because the derivatives in 2-position may possess potential biological activity and be used as fungicide agents. Generally, Mannich reaction is a good method to form biologically active compounds[10]. We performed Mannich and double Mannich reaction with 1, 2, 4-triazolo[3, 4-b]benzo thiazole-3-thiol **3** to get 2-*p*-toludinomethyl-3-thion-1, 2, 4-triazolo[3, 4-b]benzothiazole **4,** *N, N′*-bis(2-methyleno-1, 2, 4-triazolo[3, 4-b]benzothiazole-3-thione)-phenylenedia mine **5** and *N, N′*-bis(2-methyleno-1, 2, 4-triazolo[3, 4-b]benzothiazole-3-thione)-diami nobiphenyl **6**. In order to finish Mannich reaction, a suspension of **3** in cold ethanol containing 1.5 equivalent formaldehyde was stirred for 0.5 h, then appropriate *p*-toludine, phenylenediamine or benzidine was added and the mixture was stirred for 8 h in room temperature until needle substrate **3** disappeared to afford **4~6** (**Scheme 3**).

Compound **4**: pale yellow needles, mp 142~143°C; ^{1}H NMR (DMSO-d_6, δppm): 8.96~8.85 (m, 1H, Ar-H), 8.10~7.98 (m, 1H, Ar-H), 7.60~7.46 (m, 2H, Ar-H), 6.86 (s, 4H, Ar-H), 5.54 (s, 2H, CH_2), 4.74 (s, 1H, NH), 2.11 (s, 3H, CH_3).

Compound **5**: pale yellow granules, mp 260~262°C; ^{1}H NMR (DMSO-d_6, δppm): 8.90~8.66 (m, 2H, Ar-H), 7.97~7.78 (m, 2H, Ar-H), 7.57~7.30 (m, 4H, Ar-H), 6.76 (s, 4H, Ar-H), 5.49 (s, 4H, $2CH_2$), 4.61 (b, 2H, 2NH).

Compound **5**: white powder, mp 256~257°C; ^{1}H NMR (DMSO-d_6, δppm): 8.97~8.85 (m, 2H, Ar-H), 8.10~7.98 (m, 2H, Ar-H), 7.58~7.49 (m, 4H, Ar-H), 7.31 (d, J=8.2Hz, 4H, Ar-H), 6.94 (d, J=8.2Hz, 4H, Ar-H), 5.60 (s, 4H, 2CH_2), 4.91 (br, 2H, 2NH).

Scheme 3 Preparation of Mannich bases **4-6**



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