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The preparation and displacement reactions of 3-amino-5,6-bismethylthio-1,2,4-triazine (**3**) are described.

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We have been interested in the synthesis of 5,6-disubstituted-1,2,4-triazines for some time and wish to report the following observations concerning such preparations. Compound **1** (**2**) was treated with phosphorus pentasulfide in pyridine and **2** was isolated as described in the Experimental. The ir and uv spectra of **2** indicated introduction of the thioamide moiety. Without further purification, **2** was dissolved in aqueous base and stirred with an excess of methyl iodide affording compound **3**. The pmr of **3** revealed the presence of two nonequivalent methyl resonances at δ 2.5 and 2.55. Further confirmation of the structure assigned to **3** was obtained from the mass spectrum where M^+ peak was observed at m/e 188 and $M^+ \cdot CH_3$ at m/e 173. In addition, **3** was treated with an excess of acetic anhydride producing **4** which was characterized by means of spectral data (See Experimental). This data is consistent with sulfur-oxygen exchange at C-5 and bromine displacement by sulfur at C-6. Precedent for such behavior has been reported previously (**3**); however, this is the first example for the 1,2,4-triazine ring system.

Preliminary experiments designed to test the possibility of sequential displacement of the methylthio groups produced the following results. Compound **3** and alcoholic ammonia afforded **5**. The presence of a resonance at δ 2.45 in the pmr spectrum of **5** suggested the retention of one methylthio group. However, the spectral data was inadequate in determining if substitution had occurred at C-5 or C-6. Analogy with similar systems (**4**) strongly sug-

gests that displacement occurred at C-5. We found no reaction conditions which would bring about displacement of the remaining methylthio group. These reactions are summarized in Scheme I.

EXPERIMENTAL (5)

3-Amino-1,2,4-triazine-5,6-(1*H*,4*H*)dithione (**2**).

Phosphorus pentasulfide (8.0 g., 0.036 mole) was dissolved in hot pyridine (150 ml.). After solution was complete, **1** (2.5 g., 0.013 mole) was added slowly and the suspension heated under reflux for 3 hours. The mixture was cooled to room temperature and the solid collected. This solid was suspended in boiling water (250 ml.) whereupon it dissolved forming a deep red solution. Cooling at 5° overnight afforded a crop of red plates (0.85 g., 41%), m.p. < 300°; ir (potassium bromide): 3375, 1650, 1105, 750. The compound was not purified beyond this point.

3-Amino-5,6-bismethylthio-1,2,4-triazine (**3**).

Compound **2** (1.0 g., 0.006 mole) was dissolved in aqueous potassium hydroxide (0.5*M*) and excess methyl iodide was added. The two phase system was vigorously stirred at room temperature for 30 minutes. The precipitate that formed was collected and recrystallized from toluene (0.91 g., 77%), m.p. 158°; ir (potassium bromide): 3400, 3200, 2915, 1665, 1300, 1250, 935; nmr (DMSO-*d*₆): 2.5 (s, 3, SCH₃), 2.55 (s, 3, SCH₃), 7.0 (s, 2, NH₂); ms (RA): m/e 188 (100), 173 (35).

Anal. Calcd. for C₅H₈N₄S₂: C, 31.90; H, 4.28; N, 29.76. Found: C, 31.87; H, 4.32; N, 29.68.

3-Acetylamino-5,6-bismethylthio-1,2,4-triazine (**4**).

Compound **3** (0.27 g., 0.001 mole) was dissolved in acetic anhydride (15 ml.). The solution was stirred at room temperature and after a few minutes, white plates began to form. Stirring was continued for 30 minutes and the precipitate collected. Recrystallization from 2-propanol afforded analytically pure material (0.13 g., 55%), m.p. 213°; ir (potassium bromide): 3220, 3090, 1702; nmr (DMSO-*d*₆): 2.2 (s, 3, COCH₃), 2.6 (s, 3, SCH₃), 2.67 (s, 3, SCH₃); ms (RA): m/e 230 (81).

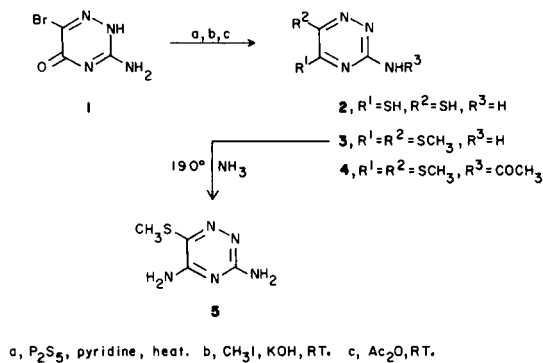
Anal. Calcd. for C₇H₁₀N₄OS₂: C, 36.51; H, 4.38; N, 24.33. Found: C, 36.75; H, 4.29; N, 24.59.

3,5-Diamino-6-methylthio-1,2,4-triazine (**5**).

Compound **3** (0.5 g., 0.003 mole) was suspended in a saturated solution of ammonia and isopropanol (25 ml.) and was heated at 190° for 20 hours. The yellow solution that resulted was concentrated to dryness under reduced pressure. Recrystallization from isopropanol afforded **5** (0.34; 72%), m.p. 212°; ir (potassium bromide): 3420, 1622, 1330; nmr (DMSO-*d*₆): 2.45 (s, 3, SCH₃), 6.07 (s, 2, NH₂), 6.88 (s, 2, NH₂); ms (RA): m/e 157 (63).

Anal. Calcd. for C₄H₇N₅S: C, 30.56; H, 4.49; N, 44.55. Found: C, 30.78; H, 4.61; N, 44.64.

Scheme I



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(1) Undergraduate Research Participant

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(5) All reagents were employed as received from Aldrich Inc. Ir spectra were obtained on a Beckman Aculab-2. Pmr spectra were obtained on a Perkin-Elmer R12. Ultraviolet spectra were obtained on a Perkin-Elmer 200. Mass spectra were obtained on a Perkin-Elmer RMU-6. Microanalyses were performed by Instranal Labs Inc., East Greenwich, New York, and Galbraith Labs Inc., Knoxville, Tennessee.