

## Synthesis of 1-Substituted-2-Formamidino-4-Amino-6-Thio-1,3,5-Triazines

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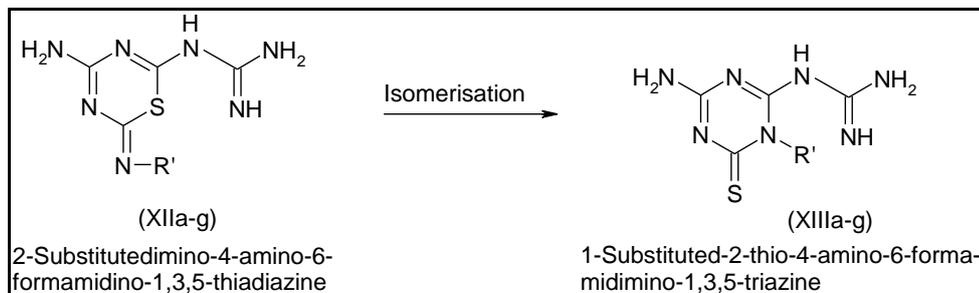
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**Abstract :** Recently in this laboratory 1-substituted-2-formamidino-4-amino-6-thio-1,3,5-triazines (**XIIIa-g**) were synthesised by isomerisation of 2-substituted imino-4-amino-6-formamidino-1,3,5-thiadiazines (**XIIa-g**) successfully by refluxing with 10% aqueous ethanolic sodium bicarbonate medium. The structure of all the synthesized compounds was justified on the basis of chemical characteristics, elemental analysis and spectral studies.

**Keywords:** Triazines, synthesis, 1-Substituted-2-Formamidino-4-Amino-6-Thio-1,3,5-Triazines.

### Introduction

The 1,3,5-triazine nucleus containing compounds having huge importance in human life due to their varieties of applications in medicinal, industrial pharmaceutical and agricultural fields<sup>1-6</sup>. These 1,3,5-triazines have their own identity and importance in medicinal<sup>7</sup>, pharmaceutical<sup>8</sup>, agricultural<sup>9</sup> and industrial<sup>10</sup> fields few of them possesses antidiabetic<sup>11-12</sup>, anti-tumor<sup>13-16</sup>, anti-inflammatory<sup>17</sup>, anti-depressant<sup>18</sup>, hypoglycaemic<sup>19</sup> activities. They are also used as herbicidal<sup>20-26</sup>, fungicidal<sup>27-29</sup>, insecticidal<sup>30</sup>, anti-corrosive<sup>31</sup>, antimicrobial<sup>32</sup> and anti-convulsant<sup>33</sup> properties. Hence it was thought interesting to carry out the isomerisation of 2-substituted guanidino-4-substituted imine-6-substituted imino-1,3,5-thiadiazines (**XIIa-g**) into 1-substituted-2-substituted guanidino-4-substituted imine-6-thio-1,3,5-triazines (**XIIIa-g**) in the presence of 10% ethanolic sodium bicarbonate medium. The tentative reaction for the formation of product is depicted below (**Scheme-I**).



(Scheme-I)

## General remarks

All reagents were purchased from commercial suppliers and used without further purification. Dry methanol and diethyl ether were purchased from Aldrich and were used as such. All reactions were run in oven-dried round bottom flask or vial containing a teflon-coated stir bar and sealed with septum. Analytical thin layer chromatography was carried out on silica pre-coated glass plates (Silica gel 60 F254, 0.25 mm thickness) and visualized with UV light at 254 nm. <sup>1</sup>H NMR spectra were recorded on Bruker 400-MHz Ultrashield Advance II 400 model (400 and 100 MHz, respectively) at ambient temperature with CDCl<sub>3</sub> or DMSO-d<sub>6</sub> as solvents. Data for <sup>1</sup>H are recorded as follows: δ chemical shift (ppm), multiplicity (s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. Spectra were referenced internally to the residual proton resonance in CDCl<sub>3</sub> (δ 7.26 ppm), DMSO-d<sub>6</sub> (δ 2.50 ppm) or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS.

## Result and Discussion

### General procedure for the Synthesis of 1-phenyl-2-formamidino-4-amino-6-thio-1,3,5-triazine (XIIIa)

2-Phenylimino-4-amino-6-formamidino-1,3,5-thiadiazine(XIIa) was suspended in 10% ethanolic sodium bicarbonate solution and refluxed for half an hour on water bath. During heating the reactant went into the solvent. After distillation of excess solvent milky white crystals were isolated and recrystallised from glacial acetic acid to obtain (XIIIa), Yield 78%, m.p. 185<sup>o</sup>C.

### 1-p-Chlorophenyl-2-formamidino-4-amino-6-thio-1,3,5-triazine (XIIIa)

It is crystalline faint yellow solid, Recrystlised from aqueous ethanol, yield 78%, m.p. 185<sup>o</sup>C. It gave satisfactory elemental analysis, [(Found) C: 44.84, H: 03.60, N: 36.37, S: 10.50, (Calculated) C: 45.32, H: 04.61, N: 36.37, S: 11.55]. The molecular formula was found to be C<sub>10</sub>H<sub>10</sub>N<sub>7</sub>S. **PMR Spectrum:**-Ar-H protons at δ 7.5610-6.4175 ppm, -NH<sub>2</sub> protons at δ 3.0241, -NH protons at δ 2.0147 ppm, -CH<sub>3</sub> protons at δ 1.0214 ppm.

### 1-Ethyl-2-formamidino-4-amino-6-thio-1,3,5-triazine (XIIIb)

It is crystalline white solid, Recrystlised from aqueous ethanol, Yield 95%, m.p. 185<sup>o</sup>C. It gave satisfactory elemental analysis, [(Found) C: 29.34, H: 04.02, N: 48.20, S: 15.20 (Calculated) C: 51.82, H: 04.98, N: 32.55, S: 10.63]. The molecular formula was found to be C<sub>5</sub>H<sub>9</sub>N<sub>7</sub>S. **PMR Spectrum:**- -NH<sub>2</sub> protons at δ 3.9878, -NH protons at δ 2.6561 ppm, -CH<sub>3</sub> protons at δ 1.0471.

### 1-Methyl-2-formamidino-4-amino-6-thio-1,3,5-triazine (XIIIc)

It is crystalline faint yellow solid, Recrystlised from aqueous ethanol, Yield 95%, m.p. 204<sup>o</sup>C. It gave satisfactory elemental analysis, [(Found) C: 29.34, H: 04.02, N: 48.20, S: 15.20 (Calculated) C: 30.15, H: 04.57, N: 49.24, S: 16.08]. The molecular formula was found to be C<sub>5</sub>H<sub>9</sub>N<sub>7</sub>S. **PMR Spectrum:**- -NH<sub>2</sub> protons at δ 4.3211, -NH protons at δ 2.5461, ppm, -CH<sub>3</sub> protons at δ 1.2171.

### 1-p-Chlorophenyl-2-formamidino-4-amino-6-thio-1,3,5-triazine (XIIIId)

It is crystalline faint yellow solid, Recrystlised from aqueous ethanol, yield 95%, m.p. 204<sup>o</sup>C. It gave satisfactory elemental analysis, [(Found) C: 42.84, H: 03.24, N: 35.37, S: 10.50, Cl: 06.01 (Calculated) C: 43.32, H: 03.61, N: 35.37, S: 11.55, Cl: 06.13]. The molecular formula was found to be C<sub>10</sub>H<sub>10</sub>N<sub>7</sub>S. **PMR Spectrum:**-Ar-H protons at δ 8.7051-6.4052 ppm, -NH<sub>2</sub> protons at δ 3.9565, -NH protons at δ 2.3424 ppm, -CH<sub>3</sub> protons at δ 1.5421 ppm.

### 1-o-Tolyl -2-formamidino-4-amino-6-thio-1,3,5-triazine (XIIIe)

It is crystalline faint yellow solid, Recrystlised from aqueous ethanol, yield 95%, m.p. 204<sup>o</sup>C. It gave satisfactory elemental analysis, [(Found) C: 47.40, H: 03.47, N: 35.63, S: 10.63 (Calculated) C: 48.00, H: 04.72, N: 35.63, S: 11.63]. The molecular formula was found to be C<sub>11</sub>H<sub>13</sub>N<sub>7</sub>S. **PMR Spectrum:** Ar-H protons at δ 8.5021-6.5212 ppm, -NH<sub>2</sub> protons at δ 3.4271, -NH protons at δ 2.5724 ppm, -CH<sub>3</sub> protons at δ 1.0224 ppm.

**1-m-Tolyl -2-formamidino-4-amino-6-thio-1,3,5-triazine (XIII f)**

It is crystalline faint yellow solid, Recrystlised from aqueous ethanol, yield 95%, m.p. 204°C. It gave satisfactory elemental analysis, [(Found) C: 47.00, H: 03.90, N: 35.64, S: 10.10 (Calculated) C: 48.00, H: 04.72, N: 35.63, S: 11.63]. The molecular formula was found to be C<sub>11</sub>H<sub>13</sub>N<sub>7</sub>S. **PMR Spectrum:**-Ar-H protons at  $\delta$  7.8451-6.1012 ppm, -NH<sub>2</sub> protons at  $\delta$  4.2411, -NH protons at  $\delta$  1.5724, ppm, -CH<sub>3</sub> protons at  $\delta$  1.0224 ppm.

**1-p-Tolyl-2-formamidino-4-amino-6-thio-1,3,5-triazine (XIII g)**

It is crystalline faint yellow solid, Recrystlised from aqueous ethanol, yield 95%, m.p. 204°C. It gave satisfactory elemental analysis, [(Found) C: 47.01, H: 3.70, N: 35.63, S: 10.58 (Calculated) C: 48.00, H: 04.72, N: 35.63, S: 11.63]. The molecular formula was found to be C<sub>11</sub>H<sub>13</sub>N<sub>7</sub>S. **PMR Spectrum:**-Ar-H protons at  $\delta$  7.2421-6.6512 ppm, -NH<sub>2</sub> protons at  $\delta$  4.2111, -NH protons at  $\delta$  2.4524 ppm, -CH<sub>3</sub> protons at  $\delta$  1.1424 ppm.

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