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## Synthesis of 1-substituted-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-substitutedguanidino-3-yl)-1,2-dihydro-s-triazine

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### ABSTRACT

Novel series of 1-substituted-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-substituted-guanidino-3-yl)-1,2-dihydro-s-triazine (**4a(i) to 4f(ii)**) has been obtained by the isomerisation of 2-(1-substitutedguanidino-3-yl)-4-(3-phenylthiocarbamido-1-yl)-6-substitutedimino-1,3,5-thiadiazine (**3a(i) to 3f(ii)**) in presence of ethanolic sodium bicarbonate solution, which have been obtained by basification of their hydrochlorides (**2a(i) to 2f(ii)**) which are synthesized by the interaction of 1-Formamidino- (N-substituted-thioamido)-5-phenyl-2-thio-4-iminobiuret (**1a-f**) and N-aryl/alkylisocyanodichlorides. The latter were prepared initially by the condensation of N-aryl/alkylisothiocyanate with N-phenylformamidinoformamidinothiocarbamide. The structure of all these compounds was established on the basis of elemental analysis, IR and PMR spectral data.

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### KEYWORDS

N-phenylformamidinoformamidinothiocarbamide;  
1,3,5-thiadiazines;  
S-triazines;  
Synthesis.

### INTRODUCTION

The heterocyclic compounds containing triazines nucleus gain immense importance in human life due to their applications in pharmaceutical, industrial, medicinal, agricultural values. s-triazines possess potential therapeutic value for several diseases. Some s-triazines acts as antibacterial<sup>[1]</sup>, antiinflammatory, antidiabetic, hypoglycemic agent and muscle relaxant. They are also used as herbicidal, sea water algicidal, insecticidal<sup>[2-4]</sup> and bacteriocidal<sup>[5-7]</sup>. Some of them have been used as chain lengthening agents in polymerization, paints, plastic and rubber. In the view of the utility of those compounds in various fields and as a part of wider programme of these research lab to provide alternative routes for the synthe-

sis of various 6-membered heterocyclic compounds. It was thought interesting to investigate the isomerisation of 1,3,5-thiadiazines to s-triazines.

### RESULT AND DISCUSSION

The parent compound 1-Formamidino-(N-phenylthioamido)-5-phenyl-2-thio-4-iminobiuret (**1a-f**) was prepared by refluxing the mixture of N-phenylformamidinoformamidinothiocarbamide (0.05mol) and phenylisothiocyanate (0.05 mol) was refluxed in carbon tetrachloride medium for 4 hr. on water bath. The compound (**1a-f**) was then further reacted with N-substitutedisocyanodichlorides in 1:1 molar proportion in carbon tetrachloride medium for

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4 hrs. During heating evolution of hydrogen chloride gas was noticed as tested with moist blue litmus paper. Cooling the reaction mixture and distilling off excess solvent needle shape crystals were isolated. These were acidic to litmus and identified as monohydrochlorides of 2-(1-phenylguanidino-3-yl)-4-(3-phenylthiocarbamido-1-yl)-6-phenylimino-1,3,5-thiadiazine (**2a(i) to 2f(iii)**). These on basification with aqueous ammonium hydroxide solution afforded free bases (**3a(i) to 3f(iii)**), which on boiling in presence of ethanolic sodium bicarbonate solution isomerize into 1-phenyl-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-phenylguanidino-3-yl)-1,2-dihydro-s-triazine (**4a(i) to 4f(iii)**).

### EXPERIMENTAL SECTION

All chemicals used were of analar grade except guanidine carbonate (Lancaster, Germany made). N-aryl/alkylisocyanodichlorides were prepared according to literature method<sup>[8]</sup>. Melting point of all synthesized compounds were determined in open capillary and uncorrected, IR spectra were recorded on Perkin-Elmer spectrometer in the range 4000-400  $\text{cm}^{-1}$  in Nujol mull as KBr pellets. PMR spectra were recorded with TMS as internal standard using  $\text{CDCl}_3$  and  $\text{DMSO}-d_6$ . TLC checked the purity of the compounds on silica gel-G plates with layer thickness of 0.3mm. All compounds gave satisfactory C, H, N and S elemental analysis.

#### Synthesis of 2-(1-phenylguanidino-3-yl)-4-(3-phenylthiocarbamido-1-yl)-6-phenylimino-1,3,5-thiadiazine (**3a(i)**)

1-Formamidino-(N-phenylthioamido)-5-phenyl-2-thio-4-iminobiotin (0.01m) (**1a**) was suspended in carbon tetrachloride medium (25ml). To this a solution of phenylisocyanodichlorides (0.01m) was added in 1:1 molar proportions. The reaction mixture was refluxed on water bath for 4 h. During heating evolution of hydrogen chloride gas was observed and tested with moist blue litmus paper. Cooling the reaction mixture and distilled off excess solvent needle shape crystals were separated out. And crystallized from aqueous ethanol. Yield 82 %; m.p.272°C and identified as of 2-(1-phenylguanidino-3-yl)-4-(3-phenylthiocarbamido-1-yl)-6-phenylimino-1,3,5-thiadiazine hy-

drochloride (**2a(i)**), which on basification with aqueous ammonium hydroxide solution afforded free base (**3a(i)**). It was recrystallised from aqueous ethanol. Yield 72% m.p.265°C. IR spectrum of compound showed  $\nu(\text{N-H})$  3396.6  $\text{cm}^{-1}$ ,  $\nu(\text{CH-Ar})$  2924.7  $\text{cm}^{-1}$ ,  $\nu(\text{C=N})$  1661.1  $\text{cm}^{-1}$ ,  $\nu(\text{C=S})$  grouping 1101.1  $\text{cm}^{-1}$ ,  $\nu(\text{C-S})$  778.2  $\text{cm}^{-1}$ . The PMR spectrum of compound showed signals due to Ar-NH protons at  $\delta$  6.16 ppm, N-H protons at  $\delta$  4.00 ppm and Ar-H protons at  $\delta$  7.22 ppm. Similarly others compounds (**2a(ii) to 2f(ii)**), (**3a(ii) to 3f(ii)**) were synthesized by above mention method.

#### Synthesis of 1-phenyl-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-phenylguanidino-3-yl)-1,2-dihydro-s-triazine (**4a(i)**)

2-(1-phenylguanidino-3-yl)-4-(3-phenylthiocarbamido-1-yl)-6-phenylimino-1,3,5-thiadiazine (**3a(i)**) was suspended in 5% aqueous ethanolic sodium bicarbonate solution and refluxed for 2 h. during heating reactant went in to solvent. Then excess solvent was distilled off, a needle shape pale yellow crystals were separated out and crystallized from glacial acetic acid. Yield 61% m.p.258°C and identified 1-phenyl-2-thio-(1H)-4-(3-phenylthiocarbamido-1-yl)-6-(1-phenylguanidino-3-yl)-1,2-dihydro-S-triazine (**4a(i)**). IR spectrum of compound showed  $\nu(\text{N-H})$  3387.3  $\text{cm}^{-1}$ ,  $\nu(\text{CH-Ar})$  3147.7  $\text{cm}^{-1}$ ,  $\nu(\text{C=N})$  1666.3  $\text{cm}^{-1}$ ,  $\nu(\text{C-N})$  1305.3  $\text{cm}^{-1}$ ,  $\nu(\text{C=S})$  grouping 1178.0  $\text{cm}^{-1}$ ,  $\nu(\text{C-S})$  746.9  $\text{cm}^{-1}$ . The PMR spectrum of com-

TABLE 1: Physical data of the compounds (**4a(i) to 4f(ii)**)

Compd.	R	R <sub>1</sub>	Yield	m.p. (°C)
4a(i)	Phenyl	Phenyl	61	258
4a(ii)	Phenyl	Ethyl	59	246
4b(i)	<i>p</i> -Chlorophenyl	Phenyl	65	249
4b(ii)	<i>p</i> -Chlorophenyl	Ethyl	69	244
4c(i)	<i>p</i> -Tolyl	Phenyl	72	262
4c(ii)	<i>p</i> -Tolyl	Ethyl	69	267
4d(i)	Ethyl	Phenyl	73	256
4d(ii)	Ethyl	Ethyl	66	231
4e(i)	Methyl	Phenyl	65	221
4e(ii)	Methyl	Ethyl	77	209
4f(i)	<i>t</i> -Butyl	Phenyl	70	219
4f(ii)	<i>t</i> -Butyl	Ethyl	71	252

\*All compounds gave satisfactory C, H, N, and S analysis.

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pound showed signals due to NH protons at  $\delta$  3.21-3.42 ppm, Ar-NH protons at  $\delta$  7.87-8.60 ppm, Ar-H protons at  $\delta$  6.8-7.2 and the signal at  $\delta$  2.51-2.53 ppm is due to moisture in DMSO- $d_6$  and  $\delta$  2.24 ppm is due to DMSO. Similarly others compounds (**4a(ii)** to **4f(ii)**) were synthesized by above mention method and enlisted in TABLE 1.

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