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SYNTHESIS OF 1-SUBSTITUTED-2-SUBSTITUTEDGUANIDINO-4-SUBSTITUTEDIMINE-6-THIO-1,3,5-TRIAZINES

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Abstract:

*2-Substitutedguanidino-4-substitutedimine-6-substitutedimino-1,3,5-thia-diazines **(VIIIa-r)** were successfully isomerised into 1-substituted-2-sub-stitutedguanidino-4-substitutedimine-6-thio-1,3,5-triazines or 1-methyl-3-(1-substituted-4-{[(E)-substitutedmethylidene]amino}-6-thioxo-1,6-dihydro-1,3,5-triazin-2-yl)guanidines **(IXa-r)** 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 analysis.*

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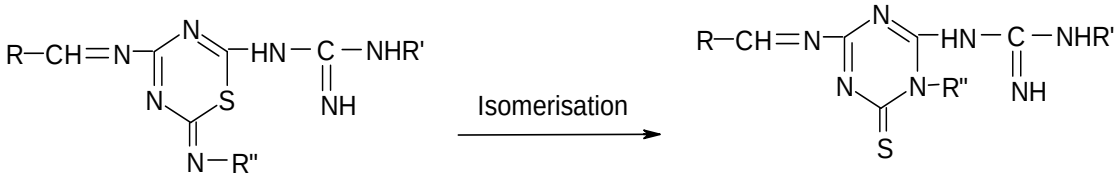
INTRODUCTION:

The 1,3,5-triazine nucleus containing compounds have gained immense importance in human life due to their varieties of applications in medicinal, industrial pharmaceutical and agricultural fields[1-5]. These 1,3,5-triazines have their own identity and importance in medicinal[6], pharmaceutical[7], agricultural[8] and industrial[9] fields. Some S-triazines possesses antidiabetic[10-11], anti-tumor[12-15], anti-inflammatory[16], anti-depresent[17], hypoglycaemic[18] activities. They are also used as herbicidal[19-25], fungicidal[26-28], insecticidal[29], anti-corrosive, antimicrobial, anti-convulsant and anti-oxidant properties.

Hence it was thought interesting to carry out the isomerisation of 2-substitutedguanidino-4-substitutedimine-6-substitutedimino-1,3,5-thiadiazines **(VIIIa-r)** into 1-substituted-2-substituted guanidino-4-substitutedimine-6-thio-1,3,5-triazines **(IXa-r)** in the presence of 10% ethanolic sodium bicarbonate medium. The tentative reaction for the formation of product is depicted below.



(VIIIa-r)

2-Substitutedguanidino-4-substitutedimine-6-substitutedimino-1,3,5-thiadiazine

OR

1-Substituted-3-[(2Z)-2-(substitutedimino)-4-{[(E)-substituted-methylidene]amino}2H-1,3,5-thiadiazin-6-yl]guanidine

(IXa-r)

1-Substituted-2-substitutedguanidino-4-substitutedimine-6-thio-1,3,5-triazine

O

1-Methyl-3-(1-substituted-4-{[(E)-substitutedmethylidene]-amino}-6-thioxo-5,6-dihydro-1,3,5-triazin-2-yl]guanidine

Where R, R' = -methyl, -ethyl, -phenyl, -3-nitrobenzene, -4nitrobenzene, -p-dimethylaniline.

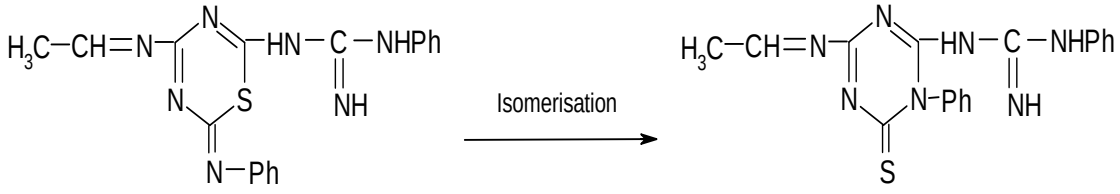
R" = -ethyl, -phenyl, p-chlorophenyl.

Reaction Scheme-1

EXPERIMENTAL:

Synthesis of 1-phenyl-2-phenylguanidino-4-methylimine-6-thio-1,3,5-triazine (IXa):

2-Phenylguanidino-4-methylimino-6-phenylimino-1,3,5-thiadiazine **(VIIIa)** was suspended in 5% 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 colour crystals were isolated. It was recrystallised from glacial acetic acid to obtain **(IXa)**, yield 78%, m.p. 125^{0}C. The probable reaction mechanism for the formation of **(IXa)** may be as depicted below **(Scheme-2).**



(VIIIa)

2-Phenylguanidino-4-methylimine-6-phenylimino-1,3,5-thiadiazine

(IXa)

1-Phenyl-2-phenylguanidino-4-methylimine-6-thio-1,3,5-triazine

Reaction Scheme-2

RESULTS & DISCUSION:

Properties of (IXa):

1) It was milky white crystalline solid having m.p.125^{0}C.
2) It gave positive test for nitrogen and sulphur.
3) It was desulphurized when boiled with alkaline plumbite solution.
4) It was soluble in benzene, acetic acid, DMF, dioxane and DMSO.
5) It gave positive test for imino group.
6) Elemental analysis:
   The result of elemental analysis is given in **following table-1**

Elements	Found (%)	Calculated (%)
Carbon	49.89	51.82
Hydrogen	3.92	4.98
Nitrogen	31.55	32.55
Sulphur	10.28	10.63

7) From the analytical data the molecular formula was found to be $C_{13}H_{15}N_7S_1$.
8) **IR Spectrum of compound:**

IR spectrum of compound was carried out in KBr pellets and the important absorptions are correlated as follows and are depicted as **fallowing table-2.**

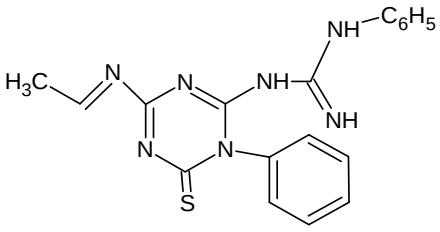
Absorption observed in(cm^{-1})	Assignment	Absorption Expected in (cm^{-1})
3389.6	NH stretching[30]	3500-3300
1635.6	C=N stretching ring	1600-1430
109026	C-N stretching[32]	1200-1000
1254.24	C=S stretching[33]	1500-1200
669.28	Monosubstituted benzene [34]	800-600
1509.14	Ar C=C Stretch	1600-1475

9) PMR-Spectrum:

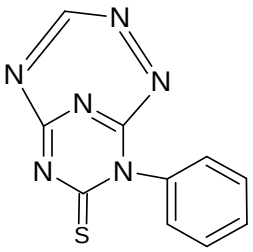
The PMR spectrum of compound was carried out in $CDCl_3$ and DMSO-d_6**.** This spectrum distinctly displayed the signals due to Ar-protons at δ 6.6098-8.4552 ppm, NH protons at δ 3.4693-3.4861 ppm, -CH proton at δ 2.5412-2.5499 ppm and –CH_3 protons at δ 1.2433-1.3867 ppm

10) **Mass spectrum**:-

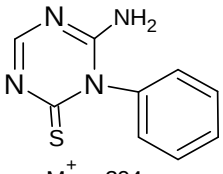
The Mass analysis of the compound was carried out and the fragmentation occurs during the analysis is given in **Mass Scheme-I.**



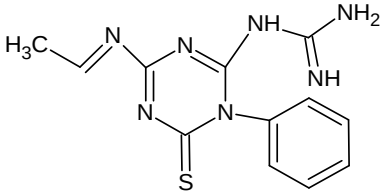
PVR 9 (363)



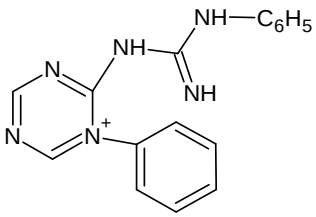
M+1 = 243



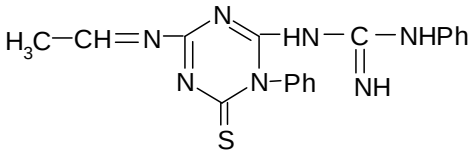
M^+ = 204



M^+1 = 288



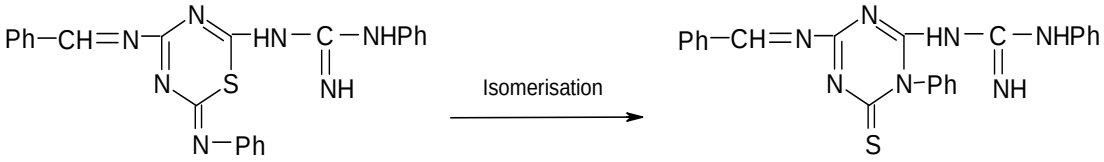
From the above properties and spectral analysis of the compound **(IXa)** was assigned the structure as 1-phenyl-2-phenylguanidino-4-methylimine-6-thio-1,3,5-triazine **(IXa)**



(IXa)

1-Phenyl-2-phenylguanidino-4-methylimine-6-thio-1,3,5-triazine

Synthesis of 1-phenyl-2-phenylguanidino-4-phenylimine-6-thio-1,3,5-triazine (IXc):
2-Phenylguanidino-4-phenylimino-6-phenylimino-1,3,5-thiadiazine**(VIIIc)** was suspended in 5% 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 colour crystals were isolated. It was recrystallised from glacial acetic acid to obtain **(IXc)**, yield 66%, m.p. 131^{0}C. The probable reaction of the formation of **(IXc)** may be as depicted below **(Scheme-VI).**



(VIIIc)

2-Phenylguanidino-4-phenylimine-6-phenylimino-1,3,5-thiadiazine

(IXc)

1-Phenyl-2-phenylguanidino-4-phenylimine-6-thio-1,3,5-triazine

Reaction Scheme-3

Properties of (IXc):
1) It was milky white crystalline solid having m.p.131^{0}C.
2) It gave positive test for nitrogen and sulphur.
3) It was desulphurized when boiled with alkaline plumbite solution.
4) It was soluble in benzene, acetic acid, dioxane, DMF and DMSO.
5) Elemental analysis:
The result of elemental analysis is given in **following table-3**

Elements	Found (%)	Calculated (%)
Carbon	63.95	64.94
Hydrogen	3.55	4.47
Nitrogen	23.05	23.05
Sulphur	6.51	7.52

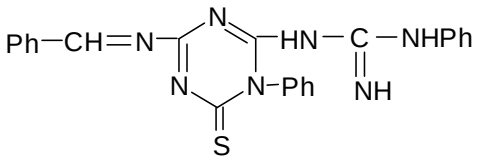
7) From the analytical data the molecular formula was found to be $C_{23}H_{19}N_7S_1$.
8) IR Spectrum of compound:
IR spectrum of compound was carried out in KBr pellets and the important absorptions are correlated as follows and are depicted in **following table-4**

Absorption observed in cm^{-1}	Assignment	Absorption Expected in cm^{-1}
3389.8	NH stretching[30]	3500-3300
1636.7	N-C=N grouping showing hexocyclic ring[31]	1660-1500
1553.26	C=N stretching ring	1600-1430
1092.3	C-N stretching[32]	1200-1000
1405.19	C=S stretching[33]	1500-1200
668.29	Monosubstituted benzene [34]	800-600
1510.16	Ar C=C stretching	1600-1475

9) PMR-Spectrum:

The PMR spectrum of compound was carried out in CDCl3 and DMSO-d6 and reproduced on **PMR Plate No. PVR-10.** This spectrum distinctly displayed the signals due to Ar-protons at δ 6.1380-7.9602 ppm, NH proton at δ 5.5986 ppm, =NH proton at δ 3.6594 ppm and -CH proton at δ 2.3946-2.5937 ppm.

From the above properties and spectral analysis of the compound **(IXc)** was assigned the structure as 1-phenyl-2-phenylguanidino-4-phenylimine-6-thio-1,3,5-triazine **(IXc).**



(IXc)

1-Phenyl-2-phenylguanidino-4-phenylimine-6-thio-1,3,5-triazine

Similarly, the other 2-phenylguanidino-4-ethylimino-6-phenylimino-1,3,5-thiadiazine **(VIIIb),** 2-phenylguanidino-4-(3-nitro)phenylimine-6-phenylimino-1,3,5-thiadiazine **(VIIId),** 2-phenylguanidino-4-(4-nitro)phenyl-imine-6-phenylimino-1,3,5-thiadiazine**(VIIIe)**, 2-phenylguanidino-4-(3-p-di-methyl)-phenylimine-6-phenylimino-1,3,5-thiadiazine**(VIIIf),** 2-phenyl-guanidino-4-methylimino-6-ethylimino-1,3,5-thiadiazine**(VIIIg),** 2-phenyl-guanidino-4-ethylimino-6-ethylimino-1,3,5-thiadiazine **(VIIIh),** 2-phenyl-guanidino-4-phenylimino-6-ethylimino-1,3,5-thiadiazine **(VIIIi),** 2-phenyl-guanidino-4-(3-nitro)phenylimine-6-ethylimino-1,3,5-thiadiazine **(VIIIj),** 2-phenylguanidino-4-(4-nitro)phenylimine-6-ethylimino-1,3,5-thiadiazine **(VIIIk),** 2-phenylguanidino-4-(3-p-dimethyl)phenylimine-6-ethylimino-1,3,5-thiadiazine **(VIIIl),** 2-phenylguanidino-4-methylimino-6-(p-Cl)phenylimino-1,3,5-thiadi-azine **(VIIIm),** 2-phenylguanidino-4-ethylimino-6-(p-Cl)phenylimino-1,3,5-thiadiazine **(VIIIn),** 2-phenylguanidino-4-phenylimino-6-(p-Cl)phenylimino -1,3,5-thiadiazine **(VIIIo),** 2-phenylguanidino-4-(3-nitro)phenylimine-6-(p-Cl)-phenylimino-1,3,5-thiadiazine **(VIIIp),** 2-phenylguanidino-4-(4-nitro) phenyl-imine-6-(p-Cl)phenylimino -1,3,5-thiadiazine **(VIIIq)** and 2-phenyl guanidino-4-(3-p-dimethyl)phenylimine-6-(p-Cl)phenylimino-1,3,5-thiadiazine **(VIIIr)** were isomerises to 1-phenyl-2-phenylguanidino-4-ethylimine-6-thio-1,3,5-triazine **(IXb),** 1-phenyl-2-phenylguanidino-4-(3-nitro)phenylimine-6-thio-1,3,5-triazine **(IXd),** 1-phenyl-2-phenylguanidino-4-(4-nitro)phenylimine-6-thio-1,3,5-triazine **(IXe),** 1-phenyl-2-phenylguanidino-4-(p-dimethyl) phenylimine-6-thio-1,3,5-triazine **(IXf),** 1-ethyl-2-phenylguanidino-4-methylimine-6-thio-1,3,5-triazine **(IXg),** 1-ethyl-2-phenylguanidino-4-ethylimine-6-thio-1,3,5-triazine **(IXh),** 1-ethyl-2-phenylguanidino-4-phenylimine-6-thio-1,3,5-triazine **(IXi)**1-ethyl-2-phenylguanidino-4-(3-nitro)phenylimine-6-thio-1,3,5-triazine **(IXj),** 1-ethyl-2-phenylguanidino-4-(4-nitro)phenylimine-6-thio-1,3,5-triazine **(IXk),** 1-ethyl-2-phenylguanidino-4-(p-dimethyl)phenylimine-6-thio-1,3,5-triazine **(IX l),** 1-p-chlorophenyl-2-phenylguanidino-4-methylimine-6-thio-1,3,5-triazine**(IXm),** 1-p-chlorophenyl-2-phenylguanidino-4-ethylimine-6-thio-1,3,5-triazine **(IXn),** 1-p-chlorophenyl-2-phenylguanidino-4-phenylimine-6-thio-1,3,5-triazine **(IXo),** 1-p-chlorophenyl-2-phenylguanidino-4-(3-nitro)phenylimine-6-thio-1,3,5-tri-azine **(IXp),** 1-p-chlorophenyl-2-phenylguanidino-4-(4-nitro)phenylimine-6-thio-1,3,5-triazine **(IXq)** and 1-p-chlorophenyl-2-phenyl guanidino-4-(p-di-methyl)phenylimine-6-thio-1,3,5-triazine **(IXr)** respectively by above mentioned method and described in **Experiment No. 1-18** and enlisted in **following table-5.**

Sr.No.	2-**Substituted** guanidine -4-**substituted**imino-1,3,5-thiadiazines **(VIIIa-r)**	1-**Substituted**-2-**substituted**guanidino-4-**substituted**imine-6-thio-1,3,5-triazines **(IXa-r)**	**Yield (%)**	**m.p. (^{0}C)**
1	2-phenylguanidino-4-ethylimino-6-phenylimino-1,3,5-thiadiazine**(VIIIb)**	1-phenyl-2-phenylguanidino-4-ethylimine-6-thio-1,3,5-triazine **(IXb)**	74	115
2	2-phenylguanidino-4-(3-nitro)phenylimine-6-phenylimino -1,3,5-thiadiazine **(VIIId)**	1-phenyl-2-phenylguanidino-4-(3-nitro)phenylimine-6-thio-1,3,5-triazine **(IXd)**	78	119
3	2-phenylguanidino-4-(4-nitro)phenylimine-6-phenylimino-1,3,5-thiadiazine**(VIIIe)**	1-phenyl-2-phenylguanidino-4-(4-nitro)phenylimine-6-thio-1,3,5-triazine **(IXe)**	73	130
4	2-phenylguanidino-4-(3-p-dimethyl)- phenylimine-6-phenylimino-1,3,5-thiadiazine**(VIIIf)**	1-phenyl-2-phenylguanidino-4-(p-dimethyl) phenyl imine-6-thio-1,3,5-triazine **(IXf)**	68	123
5	2-phenylguanidino-4-methylimino-6-ethylimino-1,3,5-thiadiazine**(VIIIg)**	1-ethyl-2-phenylguanidino-4-methylimine-6-thio-1,3,5-triazine **(IXg)**	70	127
6	2-phenylguanidino-4-ethylimino-6-ethylimino-1,3,5-thiadiazine **(VIIIh)**	1-ethyl-2-phenylguanidino-4-ethylimine-6-thio-1,3,5-triazine **(IXh)**	73	124
7	2-phenylguanidino-4-phenylimino-6-ethylimino-1,3,5-thiadiazine **(VIIIi)**	1-ethyl-2-phenylguanidino-4-phenylimine-6-thio-1,3,5-triazine **(IXi)**	75	116
8	2-phenylguanidino-4-(3-nitro)phenylimine-6-ethylimino-1,3,5-thiadiazine **(VIIIj)**	1-ethyl-2-phenylguanidino-4-(3-nitro)phenylimine-6-thio-1,3,5-triazine **(IXj)**	68	113
9	2-phenylguanidino-4-(4-nitro)phenylimine-6-ethylimino-1,3,5-thiadiazine **(VIIIk)**	1-ethyl-2-phenylguanidino-4-(4-nitro)phenylimine-6-thio-1,3,5-triazine **(IXk)**	72	117
10	2-phenyl guanidino-4-(3-p-dimethyl)phenylimine-6-ethylimino-1,3,5-thiadiazine **(VIII l)**	1-ethyl-2-phenylguanidino-4-(p-dimethyl)phenylimine-6-thio-1,3,5-triazine **(IX l)**	69	129
11	2-phenylguanidino-4-methylimino-6-(p-Cl)phenylimino-1,3,5-thiadiazine **(VIIIm)**	1-p-chlorophenyl-2-phenylguanidino-4-methylimine-6-thio-1,3,5-triazine **(IXm)**	64	145

12	2-phenylguanidino-4-ethylimino-6-(p-Cl)phenylimino-1,3,5-thiadiazine **(VIIIn)**	1-p-chlorophenyl-2-phenylguanidino-4-ethylimine-6-thio-1,3,5-triazine **(IXn)**	66	127
13	2-phenylguanidino-4-phenylimino-6-(p-Cl)phenylimino -1,3,5-thiadiazine **(VIIIo)**	1-p-chlorophenyl-2-phenylguanidino-4-phenylimine-6-thio-1,3,5-triazine **(IXo)**	70	125
14	2-phenylguanidino-4-(3-nitro)phenylimine-6-(p-Cl)phenylimino -1,3,5-thiadiazine **(VIIIp)**	1-p-chlorophenyl-2-phenylguanidino-4-(3-nitro) phenylimine-6-thio-1,3,5-triazine **(IXp)**	64	135
15	2-phenylguanidino-4-(4-nitro) phenylimine-6-(p-Cl)phenylimino -1,3,5-thiadiazine **(VIIIq)**	1-p-chlorophenyl-2-phenylguanidino-4-(4-nitro)phenylimine-6-thio-1,3,5-triazine **(IXq)**	68	128
16	2-phenyl guanidino-4-(3-p-dimethyl)phenylimine-6-(p-Cl)phenylimino-1,3,5-thiadiazine **(VIIIr)**	1-p-chlorophenyl-2-phenyl guanidino-4-(p-dimethyl)phenylimine-6-thio-1,3,5-triazine **(IX r)**	75	119

CONCLUSION:

Data obtained by the chemical tests, elemental analysis & spectral characterization strongly supports the target molecules.

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