*ejpmr, 2016,3(2), 333-339*

SJIF Impact Factor 2.026

**EUROPEAN JOURNAL OF PHARMACEUTICAL AND MEDICAL RESEARCH**

www.ejpmr.com

Research Article

ISSN 3294-3211

EJPMR

# SYNTHESIS OF 3-SUBSTITUTEDIMINO-5-(4-PYRIDINEIMINO) -AMINO-1,2,4-DITHIAZOLES

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**Article Received on 17/12/2015** **Article Revised on 08/01/2016** **Article Accepted on 29/01/2016**

**ABSTRACT**

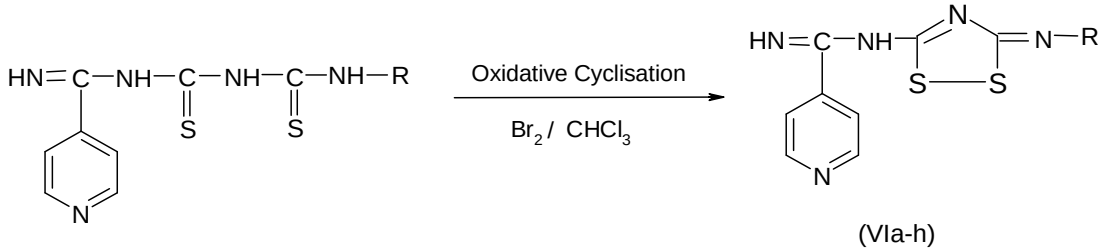
A novel series of 3-substitutedimino-5-(4-pyridineimino)amino-1,2,4-dithiazoles **(VIa-h)** was synthesized by the oxidative cyclisation of 1-(4-pyridineimino)-5-substituteddithiobiurets **(Va-h)** in chloroform medium by making use of liquid bromine as oxidizing agent. The products which were isolated in these reactions were characterized and justified on the basis of elemental analysis, chemical characteristics and spectral data.

**KEYWORDS:** Bromine, chloroform, 1-(4-pyridineimino)-5-substituteddithiobiurets, etc.

## INTRODUCTION

Dithiazolo, thiadiazolo and triazolo nucleus containing multifarious molecules possesses their own identity and importance in pharmaceutical, medicinal, agricultural, industrial, biochemical and biotechnological fields.[1-6] The compounds having dithiazolo and triazolo moiety as a parent nucleus are widely used in pharmaceutical, medicinal and biological sciences[7-8]. It was noticed that these drugs possesses anti-diabeticp[9], herbicidal[10], amoebicidal[11] and antibacterial[12-13] properties. Recently in this laboratory the oxidative cyclisation of some cyanoamidinothiocarbamides, diformamidinothiocarbamides, substituted N-glucosides and thioglucosides were carried out by Waghmare[14], Panpalia[15], Bhagwatkar[16] and Raghuwanshi[17] to isolate 1,2,4-thiadiazoles. Oxidative cyclisation for the synthesis of 1,3,4-thiadiazoles, 1,3,4-thiadiazolines and 1,2,4-triazoles have been studied by various researchers[18-24].

As a part of research work presently been undertaken in this laboratory in the synthesis of heteroacycles and heterocycles, it was thought interesting to investigate the cyclisation of 1-(4-pyridineimino)-5-substituted dithiobiurets **(Va-h)** with liquid chloroform medium to obtain a novel series of 3-substitutedimino-5-(4-pyridineimino)amino-1,2,4-dithiazoles **(VIa-h)** respectively which are hither to unknown. The present work describes suitable, convenient and somewhat direct method for the synthesis of **(VIa-h).**




(Va-h)

1-Substituted-5-iminopyridinedithiobirets

(VIa-h)

3-Substitutedimino-5-(4-pyridineimino)

amino-1,2,4-dithiazoles

Where, R = – phenyl, – methyl, – ethyl, – t-butyl, – p-chlorophenyl, – p-tolyl, – o-tolyl, – m-tolyl,

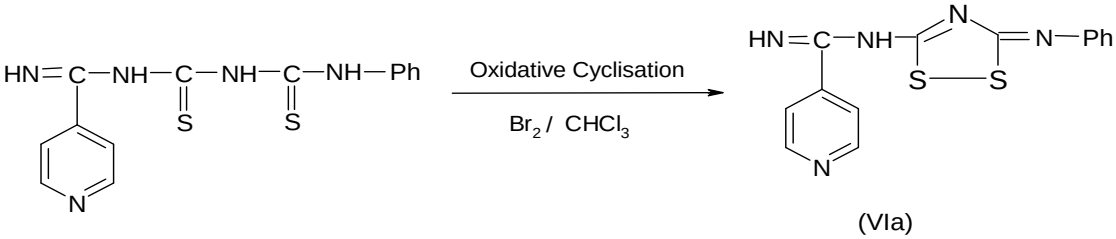
**Scheme-III**

## RESULT AND DISCUSSION

### A) Synthesis of 3-phenylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole (VIa)

3-Phenylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole **(VIa)** was synthesized by the oxidative cyclisation of 1-(4-pyridineimino)-5-phenyl-dithiobiuret **(Va)** with liquid bromine in presence of chloroform. A paste of 1-(4-pyridineimino)-5-phenyldithiobiuret **(Va)** was prepared in chloroform. To it liquid bromine in chloroform was added with constant stirring. Initially the colour of bromine disappear the addition was continued till the colour of bromine persisted to the reaction mixture. The reaction mixture was allowed to stand for 8 hours, it afforded dark yellow coloured product. It was recrystallized from ethanol, yield 78%, m.p. 204$^0$C. The probable reaction for the formation of **(VIa)** is depicted below,

**REACTION**




(Va)

1-Phenyl-5-iminopyridinedithiobirets

(VIa)

3-Phenylimino-5-(4-pyridineimino) amino-1,2,4-dithiazoles

**Properties of (VIa)**

1) It was dark yellow crystalline solid having m.p. 204$^0$C.
2) It gave positive test for nitrogen and sulphur.
3) It was soluble in acetone, chloroform, carbontetrachloride while insoluble in water and petroleum ether.
4) It formed picrate having m.p. 170$^0$C.
5) Desulphurization was not observed when warm with silver nitrate, sodium plumbite solution indicating sulphur is blocked.[26-27]
6) Elemental analysis: The result of elemental analysis is given in Table No.IV-1

**Table No. IV-1**

| Element | Found (%) | Calculated (%) |
|---|---|---|
| Carbon | 52.76 | 53.67 |
| Hydrogen | 2.88 | 3.51 |
| Nitrogen | 22.35 | 22.36 |
| Sulphur | 19.93 | 20.44 |

7) From the analytical data, the molecular formula was found to be $C_{14}H_{11}N_5S_2$.
8) **IR Spectrum:** The IR spectrum of compound **(VIa)** was carried out in KBr pellets and is reproduce on **IR Plate No. DTT-14**. The IR spectrum clearly indicated the important absorption bands can be correlated in **Table No. IV-2** as follows,

**Table No. IV-2**

| Sr.No. | Absorption ($cm^{-1}$) | Assignment Observed | Absorption Expected ($cm^{-1}$) |
|---|---|---|---|
| 1. | 3366.0 | N-H Stretching | 3450-3300[19,26] |
| 2. | 3173.0 | Ar-CH stretching | 3150-3000[27] |
| 3. | 1613.0 | C = NH (imino grouping) | 1789-1471[28,29] |
| 4. | 1465.2 | C = N stretching (Ring) | 1600-1430[30] |
| 5. | 1246.5 | C-N stretching | 1340-1250[31] |
| 6. | 734.9 | Monosubstituted Benzene | 750-700 |

9) **PMR Spectrum:** The PMR spectrum of compound **(VIa)** was carried out in DMSO-$d_6$ and $CDCl_3$ and reproduce on **PMR Plate No. DTT-14**. This spectrum distinctly displayed the signals due to pyridino/Ar-H protons at δ 5.5661-9.0653 ppm, =NH proton at δ 1.2396-1.3028 ppm and -NH protons at δ 2.5566 ppm.

10) **XRD Analysis:** The XRD Analysis of the compound No. **(Va)** was carried out, during the analysis the start position is 02 Th which shows reading from 5.0084 and the end position 02 Th is 79.9784 It take 25.1973 sec. For complete analysis the analysis of this compound was carried out at 25$^0$C. Copper is used as anode material. The peak list obtained during analysis is

shown in **Table No.IV-3** and the spectral analysis is given in **XRD Plate No. MSL-7.** The measurements conditions are as depicted below,

**Measurement Conditions**
(Bookmark 1)

| | |
|---|---|
| Dataset Name | MSL-7 |
| File name | C:\X'Pert Data\DEC2014\MSL-7.xrdml |
| Comment | Configuration=Flat Sample Stage, Owner=jagtar, Creation date=6/11/2007 3:57:00 PM<br><br>Goniometer=PW3050/60 (Theta/Theta); Minimum step size 2Theta:0.001; Minimum step size Omega:0.001 Sample stage=PW3071/xx Bracke Diffractometer system=XPERT-PRO Measurement program=PU, Owner=jagtar, Creation date=4/15/2008 1:52:59 PM |
| Measurement Date / Time | 12/22/2014 11:07:34 AM |
| Operator | Panjab University |
| Raw Data Origin | XRD measurement (*.XRDML) |
| Scan Axis | Gonio |
| Start Position [°2Th.] | 20.0084 |
| End Position [°2Th.] | 79.9844 |
| Step Size [°2Th.] | 0.0170 |
| Scan Step Time [s] | 30.3609 |
| Scan Type | Continuous |
| PSD Mode | Scanning |
| PSD Length [°2Th.] | 2.12 |
| Offset [°2Th.] | 0.0000 |
| Divergence Slit Type | Fixed |
| Divergence Slit Size [°] | 0.8709 |
| Specimen Length [mm] | 10.00 |
| Measurement Temperature [°C] | 25.00 |
| Anode Material | Cu |
| K-Alpha1 [Å] | 1.54060 |
| K-Alpha2 [Å] | 1.54443 |
| K-Beta [Å] | 1.39225 |
| K-A2 / K-A1 Ratio | 0.50000 |
| Generator Settings | 40 mA, 45 kV |
| Diffractometer Type | 0000000011023505 |
| Diffractometer Number | 0 |
| Goniometer Radius [mm] | 240.00 |
| Dist. Focus-Diverg. Slit [mm] | 100.00 |
| Incident Beam Monochromator | No |
| Spinning | No |

**Main Graphics, Analyze View**
(Bookmark 2)

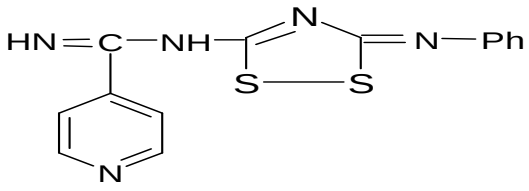
**Peak List**
(Bookmark 3)

**Table No.IV-3**

| Pos. [°2Th.] | FWHM [°2Th.] | d-spacing [Å] | Rel. Int. [%] | Area [cts*°2Th.] |
|---|---|---|---|---|
| 20.1337 | 0.1338 | 4.41047 | 68.23 | 73.57 |
| 20.3484 | 0.1171 | 4.36441 | 64.91 | 61.24 |
| 21.6353 | 0.1004 | 4.10763 | 100.00 | 80.87 |
| 21.8494 | 0.1004 | 4.06787 | 92.43 | 74.75 |
| 23.1881 | 0.1004 | 3.83596 | 39.04 | 31.58 |
| 24.3999 | 0.1004 | 3.64812 | 95.91 | 77.57 |
| 25.1057 | 0.1338 | 3.54715 | 28.23 | 30.44 |
| 26.5320 | 0.1673 | 3.35961 | 57.54 | 77.56 |
| 26.7613 | 0.1506 | 3.33134 | 74.81 | 90.75 |
| 28.5963 | 0.1224 | 3.11903 | 90.19 | 120.23 |
| 28.7339 | 0.1004 | 3.10698 | 75.51 | 61.06 |
| 29.9368 | 0.1840 | 2.98482 | 60.75 | 90.07 |
| 30.6035 | 0.2676 | 2.92129 | 29.40 | 63.40 |
| 31.7596 | 0.1171 | 2.81755 | 23.08 | 21.77 |
| 32.7534 | 0.1338 | 2.73429 | 72.08 | 77.72 |
| 33.6068 | 0.2676 | 2.66678 | 20.23 | 43.62 |
| 34.5795 | 0.1673 | 2.59397 | 49.46 | 66.67 |
| 36.1408 | 0.2007 | 2.48541 | 17.81 | 28.81 |
| 37.2383 | 0.2007 | 2.41464 | 13.97 | 22.60 |
| 39.3142 | 0.5353 | 2.29179 | 6.13 | 26.44 |
| 40.4819 | 0.1506 | 2.22834 | 34.95 | 42.39 |
| 42.6981 | 0.2007 | 2.11767 | 9.47 | 15.31 |
| 44.0841 | 0.2007 | 2.05426 | 10.48 | 16.95 |
| 48.3439 | 0.4684 | 1.88274 | 6.32 | 23.84 |
| 50.9143 | 0.1171 | 1.79356 | 27.91 | 26.34 |
| 51.6872 | 0.2676 | 1.76855 | 11.18 | 24.11 |
| 52.2621 | 0.2007 | 1.75044 | 11.80 | 19.08 |
| 54.6865 | 0.2676 | 1.67843 | 9.45 | 20.37 |
| 56.9999 | 0.2676 | 1.61568 | 4.19 | 9.05 |

| | | | | |
|---|---|---|---|---|
| 60.6507 | 0.2342 | 1.52688 | 10.93 | 20.63 |
| 63.5554 | 0.2676 | 1.46392 | 5.82 | 12.55 |
| 66.1608 | 0.6691 | 1.41245 | 4.67 | 25.20 |
| 68.5663 | 0.4684 | 1.36865 | 4.23 | 15.98 |
| 73.9786 | 0.4896 | 1.28028 | 2.33 | 12.40 |

From the above properties and spectral analysis of the compound **(VIa)** was assigned the structure as 3-phenylimino-5-(4-pyridineimino) amino-1,2,4-dithiazole **(VIa).**



(VIa)

3-Phenylimino-5-(4-pyridineimino)

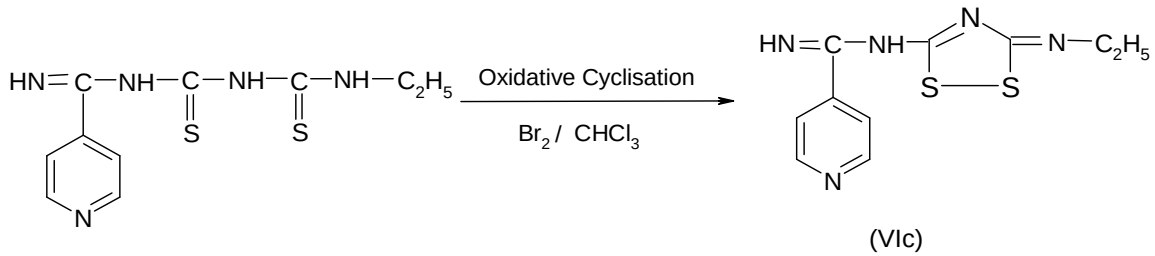
amino-1,2,4-dithiazoles

**B) Synthesis of 3-ethylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole (VIc)**

3-Ethylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole **(VIc)** was synthesized by the oxidative cyclisation of 1-(4-pyridineimino)-5-ethyl- dithiobiuret **(Vc)** with liquid bromine in presence of chloroform. A paste of 1-(4-pyridineimino)-5-ethyldithiobiuret **(Vc)** was prepared in chloroform. To it liquid bromine in chloroform was added with constant stirring. Initially the colour of bromine disappear the addition was continued till the colour of bromine persisted to the reaction mixture. The reaction mixture was allowed to stand for 8 hours, it afforded dark brown coloured product. It was crystallized from ethanol, yield 85%, m.p. 198$^0$C.

The probable reaction and mechanism for the formation of **(VIc)** is depicted below,

**REACTION**




(Vc)

1-Ethyl-5-iminopyridinedithiobirets

(VIc)

3-Ethylimino-5-(4-pyridineimino)

amino-1,2,4-dithiazoles

**Properties of (Xc)**

**1)** It was brown crystalline solid having m.p. 198$^0$C.

**2)** It gave positive test for nitrogen and sulphur.

**3)** It was soluble in acetone, chloroform, carbontetrachloride while insoluble in water and petroleum ether.

**4)** It formed picrate having m.p. 149$^0$C.

**5)** Desulphurization was not observed when warm with silver nitrate, sodium plumbite solution indicating sulphur is blocked[25-26].

**6) Elemental analysis:** The result of elemental analysis is given in **Table No. IV-3**

**Table No. IV-3**

| Element | Found (%) | Calculated (%) |
|---|---|---|
| Carbon | 44.54 | 45.28 |
| Hydrogen | 3.32 | 4.15 |
| Nitrogen | 26.41 | 26.41 |
| Sulphur | 23.65 | 24.15 |

**7)** From the analytical data, the molecular formula was found to be $C_{10}H_{11}N_5S_2$.

**8) IR Spectrum:** The IR spectrum of compound **(VIc)** was carried out in KBr pellets and is reproduced on **IR Plate No. DDT-16** The IR spectrum clearly indicated the important absorption bands can be correlated in **Table No. IV-4** as follows,

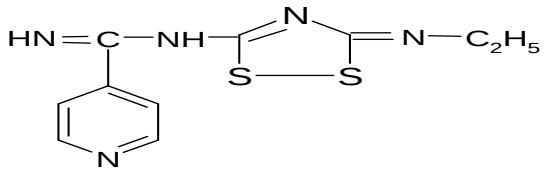
**9)**

**Table No. IV-4**

| Sr.No. | Absorption ($cm^{-1}$) | Assignment Observed | Absorption Expected ($cm^{-1}$) |
|---|---|---|---|
| 1. | 3334.11 | N-H Stretching | 3450-3300[20,26] |
| 2. | 3151.11 | Ar-CH Stretching | 3100-3000 |
| 3. | 2923.24 | Ar C=C Stretching | 2950-2750[19] |
| 4. | 1639.5 | C=N Stretching | 1700-1400[20] |
| 5. | 1074.21 | C-N Stretching | 1200-1000[20] |
| 6. | 670.26 | C-S Stretching | 800-600[21] |

**10) PMR Spectrum:** The PMR spectrum of compound **(VIc)** was carried out in DMSO-$d_6$ and $CDCl_3$ and reproduce on **PMR Plate No. DTT-16**. This spectrum distinctly displayed the signals due to pyridine/Ar–H protons at δ 7.0855-8.0751 ppm, –NH protons at δ 4.7897 ppm, =NH protons at δ 2.5571 ppm and =CH proton at δ 2.1202 ppm.

From the above properties and spectral analysis of the compound **(VIc)** was assigned the structure as 3-ethylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole.



(VIc)

3-Ethylimino-5-(4-pyridineimino)
amino-1,2,4-dithiazoles

Similarly, 1-(4-pyridineimino)-5-methyldithiobiuret **(Vb),** 1-(4-pyridine imino)-5-t-butyldithiobiuret **(Vd),** 1-(4-pyridineimino)-5-p-chlorophenyldithio- biuret **(Ve),** 1-(4-pyridineimino)-5-p-tolyldithiobiuret **(Vf),** 1-(4-pyridineimino) -5-o-tolyl- dithiobiuret **(Vg)** and 1-(4-pyridineimino)-5-m-tolyldithiobiuret **(Vh)** were successfully oxidatively cyclised with bromine in chloroform medium to isolate 3-methylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole **(VI b)**, 3-t-butylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole **(VI d),** 3-p-chloro- phenylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole **(VIe)**, 3-p-tolylimino-5-(4-pyridineimino)- amino-1,2,4-dithiazole **(VI f)**, 3-o-tolylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole **(VIg)** and 3-m-tolylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole **(VI h)** respectively by the above mentioned method in **Table No. IV-5.**

**Table No. IV-5**

| Sr.No. | 1-(4-Pyridineimino)-5-substituteddithiobiurets | 3-Substitutedimino-5-(4-pyridineimino) amino-1,2,4-dithiazole | Yield (%) | M.P. ($^0$C) |
|---|---|---|---|---|
| 1. | ---methyl------- | 3-Methyl-------- | 84 | 210 |
| 2. | ---t-butyl------- | 3-t-Butyl-------- | 74 | 187 |
| 3. | --p-Cl-phenyl-- | 3-p-Cl-phenyl-- | 72 | 175 |
| 4. | ---p-tolyl------- | 3-p-Tolyl-------- | 78 | 157 |
| 5. | ---o-tolyl------- | 3-o-Tolyl-------- | 76 | 163 |
| 6. | ---m-tolyl------- | 3-m-Tolyl------- | 75 | 161 |

## MATERIALS AND METHOD

The melting points of all the synthesized compounds were recorded using hot paraffin bath and are uncorrected. The carbon and hydrogen analysis was carried out on Carlo-Ebra-1106 analyser, nitrogen estimation was carried out on Colman-N-analyser-29. IR spectra were recorded on Perkin-Elmer spectrometer in the range 4000-400 $cm^{-1}$ in KBr pellets. PMR spectra were recorded on Bruker AC-300F spectrometer with TMS as internal standard using $CDCl_3$ and DMSO-$d_6$ as solvent. The purity of the compounds was checked on Silica Gel-G plates by TLC with layer thickness of 0.3 mm. All chemicals used were of AR grade (Indian make) except allylthiourea Lancaster (Germany make). Alkyl/Aryl isothiocynates have been prepared by known literature methods.[25]

**Experiment No.-1**

**Synthesis of 3-phenylimino-5-(4-pyridineimino) amino-1,2,4-dithiazole (VIa)**

3-Phenylimino-5-(4-pyridineimino) amino-1,2,4-dithiazole **(VIa)** was synthesized by the oxidative cyclisation of 1-(4-pyridineimino)-5-phenyl-dithiobiuret **(Va)** with liquid bromine in presence of chloroform. A paste of 1-(4-pyridineimino)-5-phenyldithiobiuret **(Va)** was prepared in chloroform. To it liquid bromine in chloroform was added with constant stirring. Initially the colour of bromine disappear the addition was continued till the colour of bromine persisted to the reaction mixture. The reaction mixture was allowed to stand for 8 hours, it afforded dark yellow colour product. It was recrystallized from ethanol, yield 78%, m.p. 204$^0$C.

**Experiment No.-2**

**Synthesis of 3-methylimino-5-(4-pyridineimino) amino-1,2,4-dithiazole (VIb)**

3-Methylimino-5-(4-pyridineimino) amino-1,2,4-dithiazole, **(VIb)** was synthesized by the oxidative cyclisation of 1-(4-pyridineimino)-5-methyl- dithiobiuret **(Vb),** with liquid bromine in presence of chloroform. A paste of 1-(4-pyridineimino)-5-methyldithiobiuret **(Vb)** was prepared in chloroform. To it liquid bromine in chloroform was added with constant stirring. Initially the colour of bromine disappear the addition was continued till the colour of bromine persisted to the reaction mixture. The reaction mixture was allowed to stand for 8 hours, it afforded dark brown colour product. It was crystallized from ethanol, yield 84%, m.p. 210$^0$C.

**Experiment No.-3**

**Synthesis of 3-ethylimino-5-(4-pyridineimino) amino-1,2,4-dithiazole (VIc)**

3-Ethylimino-5-(4-pyridineimino) amino-1,2,4-dithiazole **(VIc)** was synthesized by the oxidative cyclisation of 1-(4-pyridineimino)-5-ethyl- dithiobiuret **(Vc)** with liquid bromine in presence of chloroform. A paste of 1-(4-pyridineimino)-5-ethyldithiobiuret **(Vc)** was prepared in chloroform. To it liquid bromine in chloroform was added with constant stirring. Initially the colour of bromine disappear the addition was continued till the colour of bromine persisted to the reaction mixture. The reaction mixture was allowed to stand for 8 hours, it afforded dark brown colour product. It was crystallized from ethanol, yield 85%, m.p. 198$^0$C.

**Experiment No.-4**

**Synthesis of 3-t-butylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole (VId):**

3-t-Butylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole **(VId)** was synthesized by the oxidative cyclisation of 1-(4-pyridineimino)-5-t-butyl-dithiobiuret **(Vd)** with liquid bromine in presence of chloroform. A paste of 1-(4-pyridineimino)-5-t-butyldithiobiuret **(Vd)** was prepared in chloroform. To it liquid bromine in chloroform was added with constant stirring. Initially the colour of bromine disappear the addition was continued till the colour of bromine persisted to the reaction mixture. The reaction mixture was allowed to stand for 8 hours, it afforded dark brown colour product. It was crystallized from ethanol, yield 74%, m.p. 187$^0$C.

**Experiment No.-5**

**Synthesis of 3-p-chlorophenylimino-5-(4-pyridineimino) amino-1,2,4-dithiazole (VIe):**

3-p-Chlorophenylimino-5-(4-pyridineimino) amino-1,2,4-dithiazole **(VIe)** was synthesized by the oxidative cyclisation of 1-(4-pyridineimino)-5-p-chlorophenyldithiobiuret **(Ve),** with liquid bromine in presence of chloroform. A paste of 1-(4-pyridineimino)-5-p-chlorophenyldithiobiuret **(Ve),** was prepared in chloroform. To it liquid bromine in chloroform was added with constant stirring. Initially the colour of bromine disappear the addition was continued till the colour of bromine persisted to the reaction mixture. The reaction mixture was allowed to stand for 8 hours, it afforded dark brown coloured product. It was crystallized from ethanol, yield 72%, m.p. 175$^0$C.

**Experiment No.-6**

**Synthesis of 3-p-tolylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole (VIf)**

3-p-Tolylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole **(VIf)** was synthesized by the oxidative cyclisation of 1-(4-pyridineimino)-5-p-tolyldithiobiuret **(Vf),** with liquid bromine in presence of chloroform. A paste of 1-(4-pyridineimino)-5-p-tolyldithiobiuret **(Vf),** was prepared in chloroform. To it liquid bromine in chloroform was added with constant stirring. Initially the colour of bromine disappear the addition was continued till the colour of bromine persisted to the reaction mixture. The reaction mixture was allowed to stand for 8 hours, it afforded dark brown colour product. It was crystallized from ethanol, yield 78%, m.p. 157$^0$C.

**Experiment No.-7**

**Synthesis of 3-o-tolylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole (VIg)**

3-o-Tolylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole **(VIg)** was synthesized by the oxidative cyclisation of 1-(4-pyridineimino)-5-o-tolyldithiobiuret **(Vg),** with liquid bromine in presence of chloroform. A paste of 1-(4-pyridineimino)-5-o-tolyldithiobiuret **(Vg),** was prepared in chloroform. To it liquid bromine in chloroform was added with constant stirring. Initially the colour of bromine disappear the addition was continued till the colour of bromine persisted to the reaction mixture. The reaction mixture was allowed to stand for 8 hours, it afforded dark brown colour product. It was crystallized from ethanol, yield 76%, m.p. 163$^0$C.

**Experiment No.-8**

**Synthesis of 3-m-tolylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole (VIh):**

3-m-Tolylimino-5-(4-pyridineimino)amino-1,2,4-dithiazole **(VIh)** was synthesized by the oxidative cyclisation of 1-(4-pyridineimino)-5-m-tolyldithiobiuret **(Vh),** with liquid bromine in presence of chloroform. A paste of 1-(4-pyridineimino)-5-m-tolyldithiobiuret **(Vh),** was prepared in chloroform. To it liquid bromine in chloroform was added with constant stirring. Initially the colour of bromine disappear the addition was continued till the colour of bromine persisted to the reaction mixture. The reaction mixture was allowed to stand for 8 hours, it afforded dark brown coloured product. It was crystallized from ethanol, yield 75%, m.p. 161$^0$C.

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