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**Research Article**

**Theme-** *New horizons in chemical sciences.*

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**Simple, Efficient and One-Pot Synthesis of Different Tetra Cyclic Heterocycles Pyrazolo Imino Pyrimido Pyrazole.**

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**ABSTRACT**

A series of novel pyrazolo-imino-pyrimido pyrazole derivatives has been reported by the condensation of 2,6-diimino-4,8 bis (methylthio) -2,6 dihydro-1H-pyrimido[1,2-a] pyrimidine-3-carbonitrile with hydrazine/substituted phenyl hydrazine/substituted hydrazine benzothiazole using potassium carbonate in DMF under reflux condition to afford 2N-7N-disubstituted-3,8-diamino-4,9-dimino-pyrazolo-[3,4-d]-pyrimido-[1,2-b]-1H-pyrimido-[4,5-c]-pyrazole. The product formation was confirmed from TLC taken on silica gel F254 plates. Further the compounds were characterized by spectral analysis (FT-IR, <sup>1</sup>H NMR and elemental analysis).

**KEYWORDS**

Addition elimination reaction, pyrimido pyrimidine. Substituted hydrazine, Pyrazolo Pyrazole.

## 1. INTRODUCTION

Multicomponent condensation reaction (RCM) have recently been discovered to be an efficient and powerful tool in modern synthetic organic chemistry allowing the formation of fused and poly fused compounds in one pot transformation. Synthetic methodologies for the synthesis of novel fused pyrazolo pyrazole nucleus have better interest in pharmaceutical and biological activity, particularly in cancer research. The pyrazole compounds are the important class of nitrogen containing heterocyclic compounds in pharmaceuticals and agriculture industries [1-5]. In the last few years researchers have been highly interested in the chemistry of heterocyclic derivatives with their expected biological activity[6-8]. Earlier of this fused pyrimido benzothiazole possessing three to four rings[9-11] have been reported, which exhibit the activities like Anti-inflammatory[12], antiallergic[13], antitumor[14] and antiparakinsonism[15] some pyrimidine derivatives showed antihypertensive, antipyretics, analgesics[16] activity. Few pyrimidine derivatives are pesticides[17], herbicides and plant growth regulators[17].Herein, we have synthesized different tetra cyclic fused heterocycle contains Pyrazoloimino pyrimido pyrazole in one step using 2,6-diimino-4,8 bis (methylthio) -2,6 dihydro-1H-pyrimido[1,2-a] pyrimidine-3-carbonitrile with hydrazine substituted phenyl hydrazine and substituted hydrazine benzothiazole using potassium carbonate in DMF as a solvent under reflux condition.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Melting points were determined in open capillary tubes and are uncorrected. The silica gel F<sub>254</sub> plates were used for thin layer chromatography (TLC); the spots were examined under UV light and then developed in an iodine vapor. Column chromatography was performed with silica gel (BDH 100-200 mesh). Solvents were purified according to standard procedures. The spectra were recorded as follows: IR, KBr pellets, a Perkin-Elmer RX1 FT-IR spectrophotometer; <sup>1</sup>H NMR, CDCl<sub>3</sub>, 200 MHz, a Varian Gemini 200 instrument. Elemental analysis was performed on a Heraeus CHN-O rapid analyzer.

### 2.2. Methods

#### *2N-7N-disubstituted-3,8-diamino-4,9-dimino-pyrazolo-[3,4-d]-pyrimido-[1,2-b]-1h-pyrimido-[4,5-c]-pyrazole(3a-3h)*

A mixture of 2, 6-diimino-4,8 bis (methylthio) -2,6 dihydro-1H –pyrimido[1,2-a] pyrimidine-3-carbonitrile1 ( 1 mmol) and hydrazine 2, substituted hydrazine benzothiazole 3 and substituted phenyl hydrazine 4( 2mmol), DMF (10 mL) and anhydrous potassium carbonate (10 mg) were heated under reflux for 6 hr. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature, washed with water (3 x 10 mL) and extracted with ethyl acetate (3 x 10 mL). The extract was concentrated and the residue was subjected to column chromatography (silica gel, hexane-ethyl acetate) to obtain pure solid compounds.

### 2.3. Spectral Studies

(3a) *2N-7N-3, 8-diamino-4, 9-diimino-pyrazolo [3, 4-d] pyrimido [1,2-b]1H-pyrimido[4,5-c] pyrazole*

Yield 70-72%; mp150- 152°C, IR: 3418, 3330, 1678 cm<sup>-1</sup>; <sup>1</sup>H NMR: δ4.5 (s, 4H), 5.0 (s, 3H), 9.10(s,1H), 9.18 (s,1H), ESI-MS: *m/z*271 Anal. Calcd for C<sub>21</sub>H<sub>17</sub>N<sub>11</sub>: C, 39.80; H, 3.39; N, 56.80; Found: C, 39.85; H, 3.34; N, 56.80.

(3b) *2N-7N-di-(phenyl)-3,8-diamino-4,9-diimino-pyrazolo [3,4-d]pyrimido[1,2-b]1H-pyrimido [4, 5-c]pyrazole*

Yield 67-69%; mp178- 180°C, IR: 3418, 3330, 1678 cm<sup>-1</sup>; <sup>1</sup>H NMR: δ4.5 (s, 4H), 5.0 (s,1H),7.3(S,10H),9.10(s,1H), 9.18 (s,1H), ESI-MS: *m/z* 423 [M<sup>+</sup>],282,125,Anal. Calcd for C<sub>21</sub>H<sub>17</sub>N<sub>11</sub>: C, 59.58; H-4.10; N,-36.38; Found: C, 59.50.; H-4.10; N, 36.42

(3d) *2N-7N-di-(2,4-dinitro-phenyl)-3,8-diamino-4,9-diimino-pyrazolo [3,4-d]pyrimido[1,2-b]1H-pyrimido[4, 5-c]pyrazole*

IR 3423, 3312cm<sup>-1</sup>.<sup>1</sup>H-NMR δ5.0 (s, 4H), 5.5 (s 1H) 7.3-7.5 (m, 6H), 9.14 (s, 1H), 9.20(s,1H). MS *m/z*603 (M<sup>+</sup>). Anal. Calcd forC-41.80; H-2.17; N-34.82.C<sub>21</sub>H<sub>13</sub>N<sub>15</sub> O<sub>8</sub> Found C-41.85; H-2.12; N-34.84; O-21.19.Mol. Formula C<sub>21</sub>H<sub>13</sub>N<sub>15</sub> O<sub>8</sub>.Mol. Wt. 603.

(3e) *2N-7N-di(benzothiazolyl)- 3,8-diamino-4,9-diimino pyrazolo[3,4-d] Pyrimido[1,2-b]1H-pyrimido[4, 5-c]pyrazole*

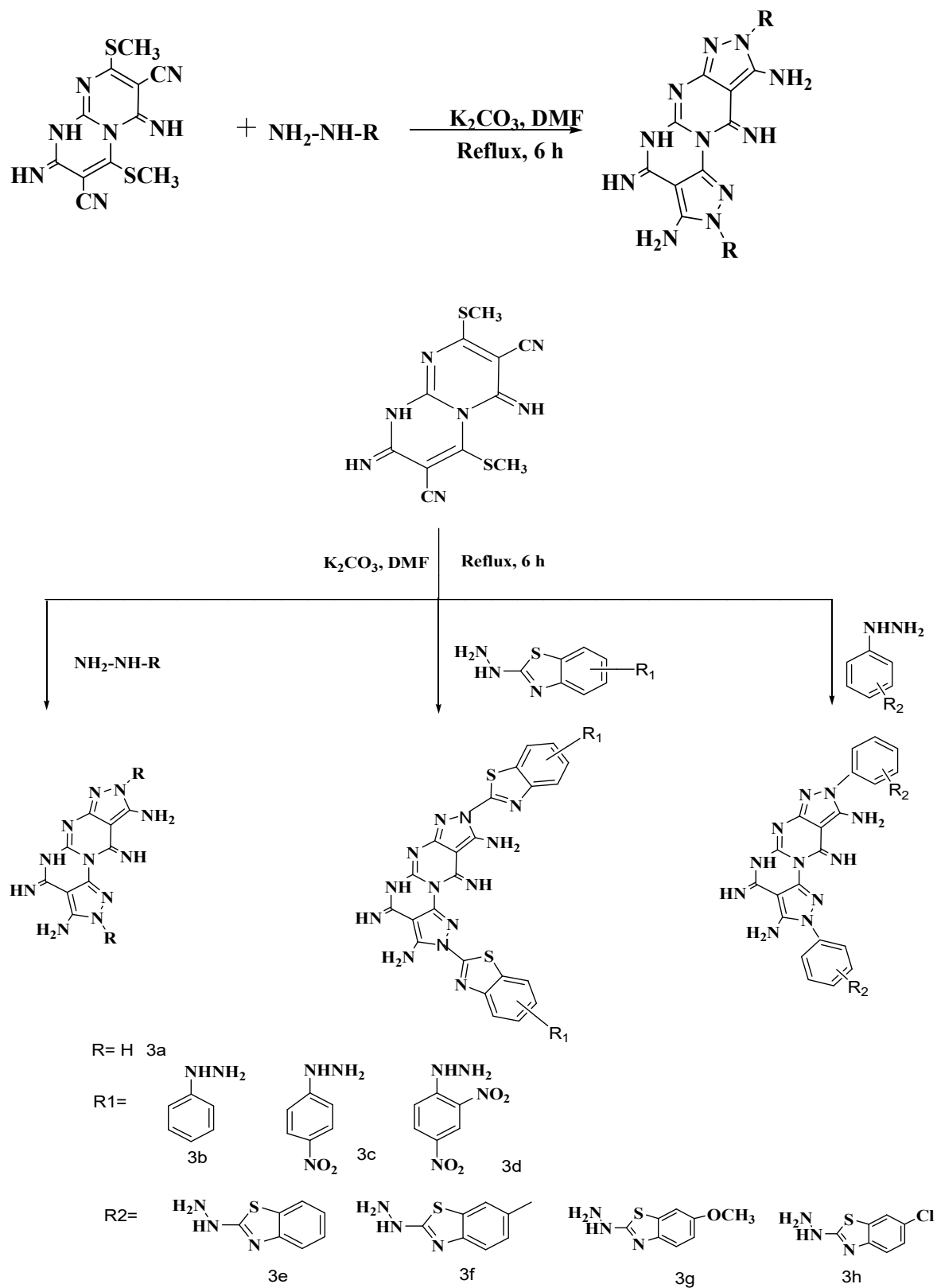
IR 3442, 3334 cm<sup>-1</sup>.<sup>1</sup>H-NMR δ9.04 (s, 1H), 9.12(s, 1H), 4.20 (s, 4H), 5.0 (s 1H), 7.4-7.8 (m, 8H), .MS *m/z*537 (M<sup>+</sup>). Anal. Calcd for C-51.39; H-2.81; N-33.87; S-11.93C<sub>23</sub>H<sub>15</sub>N<sub>13</sub> S<sub>2</sub>.FoundC-51.40; H, 2.88; N-33.80; S-11.93. Mol. Formula C<sub>23</sub>H<sub>15</sub>N<sub>13</sub> S<sub>2</sub>, Mol. Wt.537.

(3h) *2N-7N-di-(6'-chlro-benzothiazolyl)-3,8-diamino-4,9-diiminopyrazolo[3,4-d]pyrimido[1,2-b]1H-pyrimido[4, 5-c]pyrazole*

IR 3422 , 3323cm<sup>-1</sup>. <sup>1</sup>H-NMR δ4.27 (s, 4H), 4.90 (s 1H), 7.0-7.2 (m, 6H), 9.10(s, 1H), 9.18(s, 1H).MS *m/z*605 (M<sup>+</sup>), 607 (M<sup>+</sup>). Anal.Calcd forC-45.55; H-2.16; Cl-11.69; N-30.02; S-10.57 .C<sub>23</sub>H<sub>13</sub>N<sub>13</sub>S<sub>2</sub>Cl<sub>2</sub>.Found C-45.55; H-2.16; Cl-11.69; N-30.02; S-10.57Mol. Formuld,C<sub>23</sub>H<sub>13</sub>N<sub>13</sub>S<sub>2</sub>Cl<sub>2</sub>, .Mol. Wt. 605.

### 3. RESULTS AND DISCUSSION

The fused tetra cyclic heterocyclic compounds 3 was prepared by the reaction of 2,6-diimino-4,8 bis (methylthio) -2,6 dihydro-1H -pyrimido[1,2-a] pyrimidine-3-carbonitrile 1 and hydrazine 2 substituted hydrazine benzothiazole (3) and substituted phenyl hydrazine (4) in the presence of a catalytic amount of potassium bicarbonate in DMF under reflux conditions. The optimized molar ratio of these substrates is 1:2. Scheme 1.



**Scheme 1.** Synthesis of pyrazolo-imino-pyrimido pyrazole derivatives.

**Table 1.** Aryl/heteryl Pyrazolo iminopyrimido pyrimidine physical data.

Entry	Product No	Mol. Formula	Yield %	M. P. (°C)
<b>1</b>	3a	C <sub>9</sub> H <sub>9</sub> N <sub>11</sub>	70-72	<b>150-152</b>
<b>2</b>	3b	C <sub>21</sub> H <sub>17</sub> N <sub>11</sub>	67-69	<b>178-180</b>
<b>3</b>	3c	C <sub>21</sub> H <sub>15</sub> N <sub>13</sub> O <sub>4</sub>	65-70	<b>173-175</b>
<b>4</b>	3d	C <sub>21</sub> H <sub>13</sub> N <sub>15</sub> O <sub>8</sub>	77-80	<b>190-193</b>
<b>5</b>	3e	C <sub>23</sub> H <sub>15</sub> N <sub>13</sub> S <sub>2</sub>	67-69	<b>153-155</b>
<b>6</b>	3f	C <sub>25</sub> H <sub>19</sub> N <sub>13</sub> S <sub>2</sub>	69-75	<b>145-148</b>
<b>7</b>	3g	C <sub>25</sub> H <sub>19</sub> N <sub>13</sub> S <sub>2</sub> O <sub>2</sub>	73-75	<b>163-165</b>
<b>8</b>	<b>3h</b>	<b>C<sub>23</sub>H<sub>15</sub>N<sub>13</sub> S<sub>2</sub> Cl<sub>2</sub></b>	<b>81-85</b>	<b>117-119</b>

#### 4. CONCLUSION

A new different 2N-7N-disubstituted-3,8-diamino-4,9-dimino-pyrazolo-[3,4-d]-pyrimido-[1,2-b]-1h-pyrimido-[4,5-c]-pyrazole are synthesized by using simple and efficient way by one pot synthesis.

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