

**SYNTHESIS OF SOME NEW 2-(4-NITROANILINO)-4-(4-CARBOXYANILINO)-6-(SUBSTITUTED THIOUREIDO)-1,3,5-TRIAZINES**

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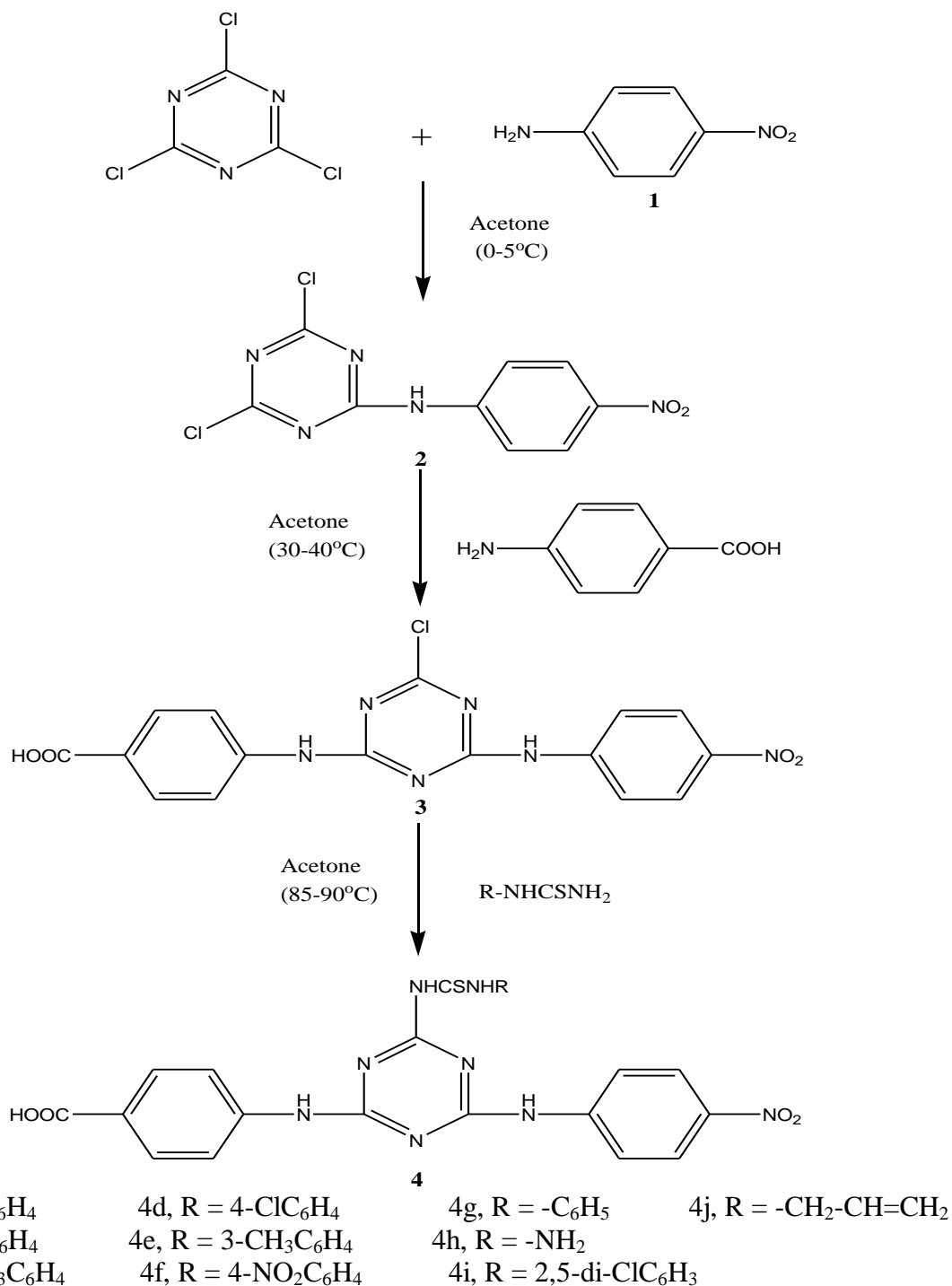
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**Abstract:** Some new 2-(4-nitroanilino)-4-(4-carboxyanilino)-6-(substituted thioureido)-1,3,5-triazines have been prepared by reacting 2,4,6-trichloro-1,3,5-triazine with nucleophilic reagents, 4-nitroaniline, 4-carboxyaniline and different substituted thioureas to give the title compounds. The structure of these compounds has been confirmed by IR, <sup>1</sup>H NMR spectra data and elemental analysis.

**Introduction:-** 1,3,5-triazines are a class of compounds well known for a long time and still continue the subject of various considerable fields.<sup>1</sup> Nitrogen ring compounds are biologically relevant as model nucleobases due to their H-acceptor abilities<sup>2</sup> and their role in bioactivity.<sup>3</sup> Triazine derivatives are commonly used as agriculture herbicides, fungicides,<sup>4</sup> pharmaceutical products, as effective corrosion inhibitor for mild steel,<sup>5</sup> as fluorescent brighteners agents and as light stabilizer in polymer (polymer photostabilizers).

Many of the unique chemical and physical properties of the triazine compounds arise from the interaction of the carbon atoms with the electron withdrawing nitrogen atoms within the aromatic ring.<sup>6</sup> While the structure reactivity relationship of nitro aromatics have been extensively studied, more recently the electrostatic interaction of anions with electron-deficient arenes and heteroarenes has gained interest.<sup>7,8</sup> In continuation of our work on heterocyclic compounds<sup>9</sup> we have now synthesized some new 1,3,5-triazine derivatives.

**Experimental:-** Purity of all the new synthesized compounds was checked on silica gel G plates using iodine vapour as the detecting agent. Melting points were determined in open capillary tubes using Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded on a SHIMADZU 8400 FT-IR spectrophotometer in KBr pellets. <sup>1</sup>H NMR spectra (chemical shift in  $\delta$  ppm) were recorded at 89.99 MHz using BRUKER AVANCE II 400 apparatus with TMS as an internal standard.



Scheme 1

### 2-(4-nitroanilino)-4,6-dichloro-1,3,5-triazine (2)

A solution of 4-nitroaniline (13.8g, 0.1 mol) in acetone (100 ml.) was added with constant stirring to a cooled solution (0-5°C) of 2,4,6-trichloro-1,3,5-triazine (18.4g, 0.1 mol) in acetone (100ml.). The solution was kept alkaline during the reaction by the addition of NaOH (4g, 0.1 mol) with constant stirring. The reaction mixture was stirred for 3 hrs and then poured into the

crushed ice and acidified with dilute HCl. The resulting solid was washed with acetone, dried and recrystallized from ethanol.

### 2-(4-nitroanilino)-4-(4-carboxyanilino)-6-chloro-1,3,5-triazine (3)

2-(4-nitroanilino)-4,6-dichloro-1,3,5-triazine (2.86g, 0.1m mol) dissolved in acetone (100ml) was added to 4-carboxyaniline (1.37g 0.1m mol) in acetone (100ml) slowly with constant stirring followed by the addition of NaOH (0.4g, 0.1m mol) in ice water (50ml). The reaction mixture was stirred for 3 hrs at 30-40°C, then poured on crushed ice and acidified with dilute HCl. The resulting solid was washed with acetone, dried and recrystallized from ethanol.

### 2-(4-nitroanilino)-4-(4-carboxyanilino)-6-(substituted thioureido)-1,3,5-triazine (4)

To a solution of 2-(4-nitroanilino)-4-(4-carboxyanilino)-6-chloro-1,3,5-triazine (3.86g, 0.1m mol) dissolved in acetone (10ml) was added to 4-fluorophenyl thiourea (1.55g 0.1m mol) in acetone (10ml) slowly with constant stirring followed by the addition of NaOH (0.1m mol) in ice water (10ml). The mixture was refluxed at 85-90°C for 2 hrs, then poured on crushed ice and acidified with dilute HCl. The resulting solid was washed with acetone, dried and recrystallized from ethanol.

### Results and Discussion:-

Formation of compound 2 was confirmed by IR spectra in which it shows the presence of peak at  $3155\text{ cm}^{-1}$  (>NH group) and  $^1\text{H}$  NMR spectrum, which showed a broad singlet at  $\delta$  9.84 ppm.

The IR spectrum of compound 3 shows peak at  $3150\text{ cm}^{-1}$  (broad band for >NH) and its  $^1\text{H}$  NMR shows peak at  $\delta$  9.7 (a singlet for two >NH protons).

Compound 4a shows peaks at 3130 (>NH, broad), 3060 (>NHCSNH<) and 1115 (CS)  $\text{cm}^{-1}$  in IR spectrum.  $^1\text{H}$  NMR show peaks at 9.0-10.5 (brs, two, >NH), 4.4 (>NHCSNH<) and  $\delta$  6.0-8.0 ppm for aromatic protons.

**Table 1: Physical and analytical data of the compounds**

Compounds	M. P (°C)	Yield %	Mol. Formula	Elemental Analysis			
				N %		S%	
				Found	Calc.	Found	Calc.
4a	204	68	C <sub>23</sub> H <sub>17</sub> N <sub>8</sub> O <sub>4</sub> SF	21.48	21.53	6.12	6.15
4b	185	70	C <sub>23</sub> H <sub>17</sub> N <sub>8</sub> O <sub>4</sub> SF	21.50	21.53	6.13	6.15
4c	212	65	C <sub>24</sub> H <sub>17</sub> N <sub>8</sub> O <sub>4</sub> SF <sub>3</sub>	19.61	19.64	5.58	5.61
4d	180	72	C <sub>23</sub> H <sub>17</sub> N <sub>8</sub> O <sub>4</sub> SCl	20.84	20.87	5.92	5.96
4e	170	60	C <sub>24</sub> H <sub>20</sub> N <sub>8</sub> O <sub>4</sub> S	21.65	21.70	6.17	6.20
4f	187	55	C <sub>23</sub> H <sub>17</sub> N <sub>9</sub> O <sub>6</sub> S	23.02	23.03	5.83	5.85
4g	168	70	C <sub>23</sub> H <sub>18</sub> N <sub>8</sub> O <sub>4</sub> S	22.27	22.31	6.33	6.37
4h	190	62	C <sub>17</sub> H <sub>15</sub> N <sub>9</sub> O <sub>4</sub> S	28.55	28.57	7.23	7.25
4i	177	50	C <sub>23</sub> H <sub>16</sub> N <sub>8</sub> O <sub>4</sub> SCl <sub>2</sub>	19.63	19.61	5.62	5.60
4j	160	57	C <sub>20</sub> H <sub>18</sub> N <sub>8</sub> O <sub>4</sub> S	24.02	24.03	6.85	6.86

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Received on December 2, 2013.