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Green synthesis of 2-substitutedimino-4-amino-6-methyl formamidino-1,3,5-thiadiazines

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ABSTRACT

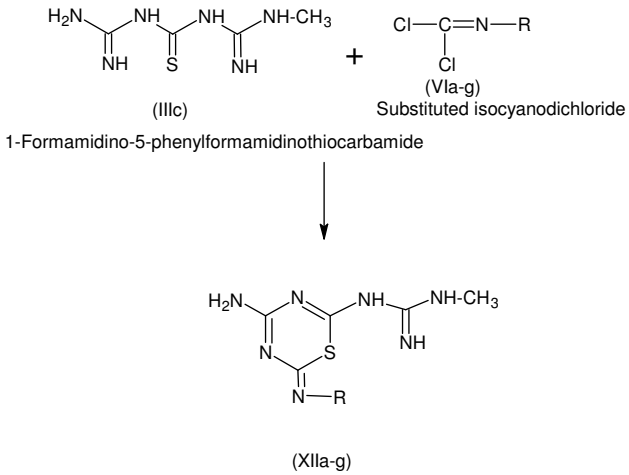
"Non-conventional" synthetic method has shown broad applications as a very efficient way to accelerate the course of many organic reactions, producing high yields, higher selectivity and lower quantities of side products consequently easier work-up and purification of the products. One-pot two-component condensation of 1-formamidino-5-methylformamidonothicarbamide (llla) with various isocyanodichlo- rides (Xla-g) were carried out in presence of lemon juice as a biocatalyst respectively to synthesize a novel series of 2-substitutedimino-4-amino-6-methylformamidino-1,3,5-thiadiazines (Xlla-g) which are heither to unknown. The structures were confirmed by conventional chemical characterization, elemental analysis and spectral studies.

Keywords: Lemon Juice, various isocyanodichlorides, 1-formamidino-5-methylformamidonothicarbamide.

1. INTRODUCTION

In recent years the chemical research has been focused on the eco friendly, environmentally, benign process to reduce the impact of environmental pollution. Green Chemistry [1-4] is placed in the frontier areas in this regard which involves the design, development and implementation of the performance criterion. So the 'greening' of conventional reactions is done to meet the ever increasing demands of selectivity in modern synthesis [5]. Microwave and sonochemical methods of synthesis use non classical forms of energy to modify the time duration and product yield by avoiding the undesired side products [6,7]. Microwave heating and sonochemical methods have emerged as a powerful energy and time saving techniques to promote a variety of chemical reactions [8-12]. These reaction methods, under solvent-free conditions are eco-friendly by reducing pollution and offer low cost, facile, safe and reproducible experimental procedures[13]. Therefore by using lemon juice as a biocatalyst [14-15] technique has gained popularity in past decade as a powerful tool for rapid, economic and efficient synthesis of variety of compounds.

Literature survey reveals example of specific reactions, which do not occur under conventional conditional heating, but could be possible by lemon juice with good product yields. The present work describes suitable, convenient and somewhat direct method for the synthesis of 2-substitutedimino-4-amino-6-phenylformamidino-1,3,5-thiadiazines depicted below,



Scheme - 1: 2-substitutedimino-4-amino-6-methylformamidino-1,3,5-thiadiazines.

2. MATERIALS AND METHODS

All reagents were purchased from commercial suppliers and used without further purification. Dry methanol and diethyl ether were purchased from Aldrich and were used as such. All

reactions were run in oven-dried round bottom flask or vial containing a teflon-coated stir bar and sealed with septum. Analytical thin layer chromatography was carried out on silica pre-coated glass plates (Silica gel 60 F254, 0.25 mm thickness) and visualized with UV light at 254 nm. ^{1}H NMR spectra were recorded on Bruker 400-MHz Ultrashield Advance II 400 model (400 and 100 MHz, respectively) at ambient temperature with $CDCl_3$ or DMSO-d6 as solvents. $CDCl_3$ (δ 7.26 ppm), DMSO-d6 (δ 2.50 ppm) or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS.

2.1. General procedure for the Synthesis of 2-ethylimino-4-amino-6-methylformamidino-1,3,5-thiadiazine (Xlla)

A mixture of 1-formamidino-5-formamidonothiocarbamide (0.1M) (IIIa), ethylisocyanodichloride (0.2M) (Xla) freshly extracted lemon juice (20 ml) was taken in round bottom flask. It was tightly sealed and the reaction mixtures were kept in sun light for 50 hours. Then the reaction mixture was poured on ice cubes with vigorous stirring, iveroy crystals were obtained these were washed several times with water. Recrystalised from ethanol. Yield 96%, melting point 245^{0}C.

3. RESULTS AND DISCUSSION

3.1. Properties of (XI)

It is brown colour crystalline solid having melting point 210^{0}C. It gave positive test for nitrogen and sulphur. It was desulphurized by alkaline plumbite solution which clearly indicate the presence of C=S group. It was soluble in water, ethanol, DMSO-d_6 while insoluble in carbon tetrachloride, chloroform, benzene, petroleum ether. It formed picrate having melting point 180^{0}C.

3.2. Elemental analysis

[C: 67.37% (found), 37.00% (calculated)], [H: 04.23% (found), 05.89% (calculated)], [N: 43.17% (found), 43.17% (calculated], [S: 13.14% (found), 14.09% (calculated)].

3.3. IR Spectrum

The IR spectrum was carried out in KBr-pellets The important absorptions are correlated as (cm^{-1}) : 3280.29 N–H stretching, 2850.64 C-H stretching, 1658.78 N=C-N stretching, 1083.99 C-N stretching, 731.02 monosubstituted benzene

3.4. NMR Spectrum

The NMR spectrum was carried out in DMSO-d_6 and $CDCl_3$ This spectrum distinctly displayed the signals due to Ar-H protons at δ 7.2234-6.0495 ppm, -NH proton at δ 3.2437-3.1482 ppm, -CH_2 protons at δ 2.487-2.2963 ppm, -CH_3 protons at δ 1.1137 ppm.

Similarly, 2-phenylimino-4-amino-6-methylformamidino-1,3,5-thia diazine (Xllb), 2-methylimino-4-amino-6-methylformamidino-1,3,5 -thiadi- azine (Xllc), 2-p-chlorophenylimino-4-amino-6-methylformamidino-1,3,5-thiadiazine (Xlld), 2-o-tolylimino-4-amino-6-methylformamidino -1,3,5-thiadiazine (Xlle), 2-m-tolylimino-4-amino-6-methylformamidino-1,3,5-thiadiazine (Xllf) and 2-p-tolylimino-4-amino-6-methylformamidino-1,3,5-thiadiazine (Xllg) were synthesized by the interaction of 1-formamidino-3-methylformamidinothiocarbamide (0.1M) (IIIc) with methylisocyanodichlo ride, (0.2M) (XIc), p-chlorophenylisocyanodichloride (0.2M) (XId), o-tolyl isocyanodichloride (0.2M) (XIe) m-tolylisocyanodichloride (XIf) and p-tolyl isocyanodichloride (XIg) lemon juice respectively and enlisted in table 1.

Table - 1: Study of other synthesized 1,3,5-thiazines

2-Substitutedimino-4-amino-6-methylformamidino-1,3,5-thiadiazine	Juice	Yield %	M. P.
2-methylimino----thiadiazine	Lemon	94	205
2-phenylimino--thiadiazine	Lemon	90	216
2-p-chlorophenylimino--thiadiazine	Lemon	93	209
2-o-tolylimino------thiadiazine	Lemon	97	222
2-m-tolylimino----thiadiazine	Lemon	97	196
2-p-tolylimino-----thiadiazine	Lemon	97	164

4. CONCLUSION

The Spectral analysis confirms the synthesized compound (IIIc). A variety of such a 1,3,5-thiadizines can be synthesized using the same method. This method is convenient and less time consumable and synthesized thiadizines are applicable for various biological activities.

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