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Eco-friendly benign synthesis of cyanoformamidino substituted-imines

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ABSTRACT

*A novel series of cyanoformamidino substituted imines **(IIIa-f)** was synthesized by the interactions of cyanoguanidine **(I)** with various aldehydes **(IIa-f)** in acetone, ethanol and ethanol-acetone medium at various reaction conditions, for creating a new green route for the synthesis of cyanoformamidino substituted imines **(IIIa-f)** which increase the yield of product as well as maintain purity. At the same time it was also considered to maintain green chemistry parameters by decreasing time duration of the reaction mentioned in the literature. The synthesized compounds were recrystallised and their structure were justified and established on the basis of elemental analysis, chemical characteristics and spectral studies.*

Keywords: cyanoformamidino substituted imines; cyanoguanidine; cyanoformamidino substituted imines; Green synthesis etc.

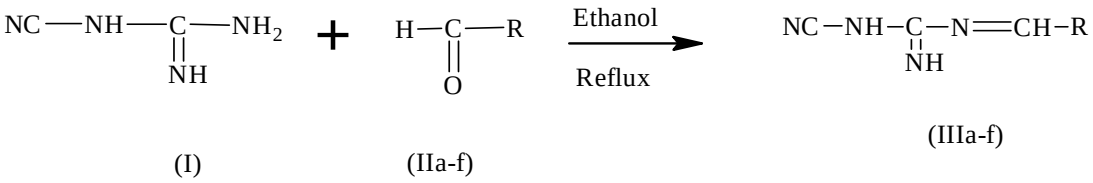
INTRODUCTION

Structural organic chemistry of cynoguanidine is an important organic compound for its pharmaceutical, medicinal, biological, industrial and agricultural application[1-6]. Cynoguanidine is a bifunctional molecule. It has basic form amidino group at position 3 and cyno/nitrilo group at position-1. Therefore this molecule is expected to produce varieties of certain interesting heteroacycles and heterocycles containing nitrogen and nitrogen and sulphur, through its reactive basic amino group and cyano group. As evident from the structure of cynoguanidine, it is quite likely that cynoguanidine which is basic formamidino group react with various aldehyde to produce related cyanoformamidino substituted imine (III). This reaction is akin to the reaction of parent guanidine and isothiocyanates[7]. Cyanoguanidine also have cyanamide like structure. Interaction of cyanamide with various thioureas had been investigated in sufficient details[8-11]. These entire compounds possess agricultural, industrial, pharmaceutical and medicinal significances and applications[12-13].

Thiadiazoles, thiadiazines and dithiazines by exploring the synthetic applications of –amino, -cyano and -halo groups. They also successfully studied their antimicrobial, antifungal and physiochemical parameters. Taking all these facts into consideration this reaction scheme was designed. During designing this, it was also planned to develop a new route for the synthesis of cyanoformamidino substituted imines **(IIIa-f)** by the interactions of cyanoguanidine **(I)** with various aldehydes **(IIa-f)** in presence of sulphuric acid in acetone, ethanol, ethanol-acetone mediums at various percentage composition and ratio.

The main objective of the research work is to synthesize a novel series cyanoformamidino substituted imines **(IIIa-f)** and also to investigate and set up a new reaction condition which reduces the time span of such reactions and at the same time it was also thought to increase yield of product by maintaining the purity.

It was observed during the study, that the 60% ethanol-acetone solvent was the best solvent which curtails the time span and also maintains green chemistry parameters. This work is useful to incoming researcher in organic chemistry and medicinal as well as pharmaceutical sciences. The formation of product is as depicted below,



(I) (IIa-f) (IIIa-f)

Where, R- ethyl, phenyl, substituted phenyl

The literature survey reveals that the reaction was carried out in ethanol medium, but we carried out this reaction in various solvents at various reaction conditions and observed that the reaction time span was changed and improvement of the percentage of yield of product was noted and the green chemistry parameters were also maintains in table No. 1.1

Table No. 1.1

Solvents	Time span in Hrs	Yield (%)
Acetone	06	47
Ethanol*	01	58
Benzene	08	28
Carban tetrachloride	12	32
Ethanol-Acetone(40%)	01	62
Ethanol-Acetone(50%)	0.5	78
Ethanol-Acetone(60%)	**0.2**	**92**
Ethanol-Acetone(70%)	01	74
Ethanol-Acetone(80%)	01	64
Ethanol-Acetone(90%)	01	62

MATERIALS AND METHODS

Synthesis of cyanoformamidino-1-methylimine (IIIa):
Cyanoformamidino-1-methylimine **(IIIa)** was synthesized by refluxing cyanoguanidine **(I)** (0.1 M) with acetaldehyde **(IIa)** (0.1 M) and concentrated sulphuric acid (0.2 ml) in 60% ethanol-acetone (10ml) medium on water bath for 20 minutes. In hot conditions it was poured on ice cubes white crystals were obtained, which were collected by filtration. Recrystallized from ethanol and dried at room conditions. Yield 92%, m.p. 170 ^{0}C.

Similarly, cyanoformami-dino-1-ethylimine **(IIIb),** cyanoformamidino-1-(3-nitrophenyl)imine **(III d),** cyanoformamidino-1-(4-nitrophenyl)imine **(IIIe)** and cyanoformamidino-1-(p-dimethylaminephenyl)imine **(III_f)** were prepared by the interactions of cyanoguanidine **(I)** with acetaldehyde **(IIa),** propionoaldehyde **(IIb),** benzaldehyde **(IIc),** 3-nitrobenzaldehyde **(IId)** 4-nitrobenzaldehyde **(IIe)** and 4-dimethylaminebenzaldehyde **(IIf)** respectively by the above mentioned method and results enlisted in table No. 1.2,

Table No.1.2

Cyanoformamidino **substituted** imines **(IIIa-f)**	**Yield (%)**	**M.P. ^{0}C**
..... methyl …….	92	170
.....ethyl…….	82	176
.....phenyl…….	87	215
.....3-nitro phenyl …….	90	110
.....4-nitro phenyl …….	81	115
……**p-dimethyl phenyl**……..	87	130

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.

RESULTS AND DISCUSSION

1) **Elemental analysis**: Elemental analysis of compound **IIIa** and **IIIc** are as fallows in table 1.3,

Table No.1.3

Elements	IIIa		IIIc	
	Found	Calculated	Found	Calculated
Carbon	42.9204	43.6363	61.9760	62.7907
Hydrogen	05.2354	05.4545	04.5248	04.6511
Nitrogen	50.2620	50.9090	32.1198	32.5581

2) **IR spectrum**: IR spectrum of compound **(IIIa and IIIc)** was carried out in KBr-pellets. The important absorption are correlated as follows and are depicted in table No.1.4,

Table No.1.4

Assignment	Absorption Observed (cm^{-1})	
	IIIa $C_4H_6N_4$	IIIc $C_9H_8N_4$
NH stretching	3382.6	3383.0
C≡N stretching	2207.7	2751.70
C=NH (imino grouping)	1641.3	2208.0
C-N stretching	1096.3	1575.0

3) PMR spectrum:- The PMR spectrum of compound was carried out in $CDCl_3$ and DMSO-d_6 and reproduced on **PMR.** This spectrum distinctly displayed the signals shown in table no.-1.5,

Table No.1.5

Signal due to	Chemical shift (δ) in ppm	
	IIIa	IIIc
NH	4.0419-4.1285	3.5549
imino =NH	3.1794-3.8834	2.874-3.251
=CH proton	2.3659-2.5700	2.5586
$-CH_3$	1.2399-1.3238	1.452

CONCLUSION

The elemental data, IR spectra, PMR spectra and Mass spectra in the above research work supports the synthesis of target molecules (IIIa-f). This is a very convenient method for the synthesis of Cyanoformamidino substituted-Imines, which fallows all the parameters of green synthesis. Cyanoformamidino substituted-Imines which are a very important class of intermediate can be synthesised by such a cheaper and eco-friendly method.

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