SYNTHESIS AND CHARACTERIZATION OF SOME N-SUBSTITUTEDFORMAMIDINO-N'-PHENYLIMINOTHIOCARBAMIDE SERIES

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Abstract : A series of N-substitutedformamidino-N'-substitutediminothiocarbamides (IIIa-f) was successfully synthesized by the interactions of cyanoformadinosubstitutedimines (Ia-f) with phenylthiourea (II) in the presence of hydrochloric acid in 50% ethanol-acetone medium. The products were isolated, characterized and justified on the basis of conventional elemental analysis, chemical characteristics and spectral studies**.**

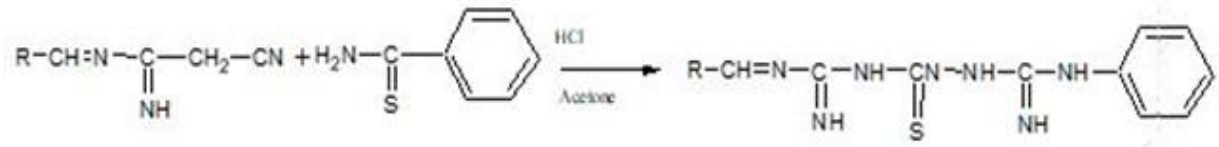
Index Terms **- substitutedformamidine, substitutediminothiocarbamides, cyanoformadinosubstitutedimine, phenylthiourea etc.**

I. INTRODUCTION

As evident from the structure of cyanoformadinosubstitutedimines, it was observed that there are =NH, -CN and C=N important reactive sites for the reactions in this molecule. Formamidino and iminothiocarbamido nucleus containing hetroacycles possesses their own identity and importance in medicinal, pharmaceutical, biological, industrial and agricultural sciences.

As a wider programme of this laboratory in the synthesis of nitrogen, nitrogen and sulphur containing hetroacycles, the interactions of cyanoguanidine with various thioureas had been investigated in sufficient details in various reaction conditions. As cyanoformamidinosubstitutedimine **(Ia-f)** have cynamide like structure and as a part of research work presently been undertaken in this laboratory in the synthesis of nitrogen, nitrogen and sulphur containing heteroacycles.

It was thought interesting to explore the interaction of cyanoformamidinosubstitutedimine **(Ia-f)** with phenylthiourea **(II)** in presence of hydrochloric acid in 50% ethanol-acetone medium to obtained a novel series of N-substitutedformamidino-N'-substitutediminothiocarbamides **(IIIa-f).** This work describes somewhat suitable, cheaper and more practical utility.



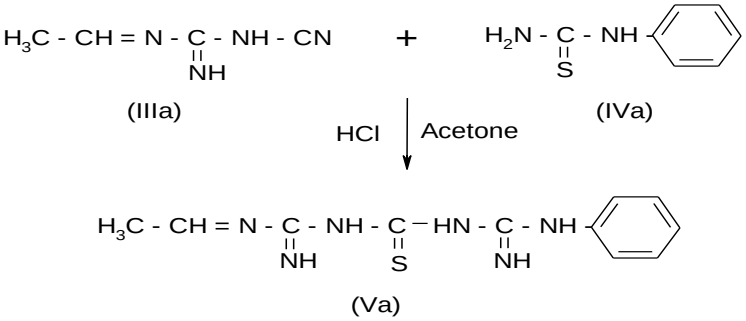
II. EXPERIMENTAL

N-substitutedformamidino-N'-phenyliminothiocarbamide **(IIIa)** was synthesized by refluxing the cyanoformamidino-1-substitutedimine **(Ia-e)** (0.1M) with phenylthiourea **(II)** (0.1M) and hydrochloric acid (2ml) in 50% ethanol-acetone medium on water bath for 2 hours. During refluxtion first clear solution was obtained which turned yellowish in colour it was filtered in hot conditions and after the distillation of excess of solvent, yellow needle shaped crystal was isolated out, which on basification with dilute ammonium hydroxide afforded a product it was recrystallized from ethanol. Yield 83%, melting point 176^0C..

III. RESULT AND DISCUSSION

Synthesis of N-methylformamidino-N'-phenyliminothiocarbamide(IIIa):

N-Methylformamidino-N'-phenyliminothiocarbamide (**IIIa**) was synthesized by refluxing the cyanoformamidino-1-methylimine (**Ia**) with phenylthiourea (**II**) and hydrochloric acid in 50% ethanol-acetone medium on water bath for 2 hours. During refluxtion first clear solution was obtained which turned yellowish in colour it was filtered in hot conditions and after the distillation of excess of solvent, yellow needle shaped crystal was isolated out, which on basification with dilute ammonium hydroxide afforded a product it was recrystallized from ethanol. Yield 83%, melting point 1760C. The probable reaction and mechanism for the formation of (**IIIb**) is depicted below,



Properties of (IIIa):

1) It is dark yellow crystalline solid having melting point 1760C.
2) It gave positive test for nitrogen and sulphur.
3) It was desulphurised by alkaline plumbite solution which clearly indicate the presence of C=S group.
4) It gave positive test for imino group.
5) It formed picrate having melting point 1430C.
6) From the analytical data the molecular formula was found to be $C_{11}H_{14}N_6S_1$
7) Elemental Analysis: The result of elemental analysis is given in Table No. 1

Table No. 1

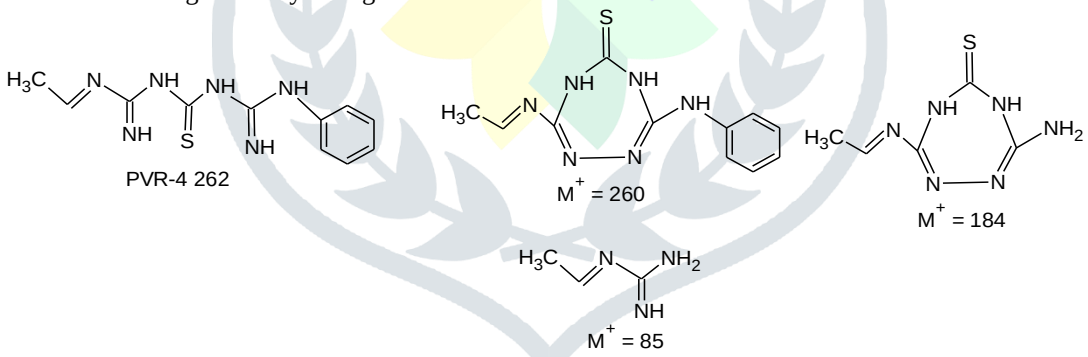
Sr. No.	Elements	Found (%)	Calculated(%)
1.	Carbon	49.9358	50.3816
2.	Hydrogen	05.14	05.3435
3.	Nitrogen	31.5952	32.0610
4.	Sulphur	12.2137	12.2137

8) IR spectrum: The IR spectrum of compound (IIIa) was carried out in KBr-pellets and is reproduced on IR Plate No-PVR-IIIa. The important absorption are correlated as follows and are depicted in Table No. 2

Table No. 2

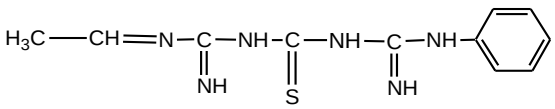
Sr. No.	Absorption Observed (cm^{-1})	Assignment	Absorption[3] (cm^{-1})
1.	3285.0	NH stretching	3500-3000
2.	1607.0	N-C=N grouping showing Hexocyclic ring	1660-1520
3.	1555.24	C = N stretching (Ring)	1790-1470
4.	1607.0	C=N stretching	1750-1405[1-5]
5.	1199.1	-C=S stretching	1600-1100
6.	1092.0	-N-C=S stretching	1200-1050

9) **PMR spectrum:** The PMR spectrum of compound was carried out in $CDCl_3$ and DMSO-d_6 and reproduced on **PMR Plate No. PVR-IIIa**. This spectrum distinctly displayed the signals due to Ar-H protons at δ 8.2053-6.6618 ppm, NH protons at δ 4.2573-3.9266 ppm, =NH protons at δ 3.1976-3.1793 ppm, =CH proton at δ 2.6138 ppm and -CH_3 protons at δ 1.4456-1.2922 ppm.
10) **Mass spectrum**:- The Mass analysis of the compound was carried out and reproduced on **Mass Plate No. PVR-IIIa**. The fragmentation occurs during the analysis is given in **Mass Scheme-I.**



Mass Scheme-I

From the above chemical characteristics, elemental and spectral analysis the compound **(IIIa)** was assigned the structure as N-Methylformamidino-N'-phenyliminothiocarbamide.



(Va)

Similarly, cyanoformamidino-1-ethylimine **(IIb),** cyanoformamidino-1-phenylimine **(IIc),** cyanoformamidino-1-(3-nitrophenyl)imine **(IId),** cyanoformamidino-1-(4-nitrophenyl)imine **(IIe),** cyanoformamidino-1-(p-dimethylamine-phenyl)imine **(IIf)** were interacted with phenylthiourea **(II)** respectively by the above mentioned method to isolate N-**Substituted**-formamidino-N'-phenyl- iminothiocarbamide**(Vb-e)** in **Experiment No. 2 to 6** and enlisted in **Table No.3**

Table No. 3

Sr. No.	Expt. No.	N-Substitutedformamidino-N'-phenyliminothiocarbamide (IIIa-f)	Yield (%)	M.P. ^{0}C
1.	**2**	..... **ethyl**…….	80	122
2.	**3**	..... **phenyl**…….	83	267
3.	**4**	.....**3-nitro phenyl** …….	86	138
4.	**5**	.....**4-nitro phenyl** …….	77	108
5.	**6**	……**p-dimethyl phenyl**…….	89	137

REFERENCES

[1] Tayade, DT. and Waghmare SA.2016. Design, synthesis and characterization of novel series of 1,2,4-dithiazole based chalcones, Journal of Chemical and Pharmaceutical Research, 8(5):934-937.

[2] Tayade, DT. and Waghmare SA.2016. Design, Design, synthesis, characterization and anti-microbial screening of some novel 2,4-dithiobiueret based chalcones, Der Pharma Chemica, 8(8):78-81.

[3] Manna, P. and Singh, R. et al. 2005. Synthesis, antifungal, antitumor and anti-inflammatory activities of some new 5-substituted arylimino-3-(2,4-diethoxyarylimino)-1,2,4-dithiazolidines, Indian Journal of Chemistry, 44(B), 1880-1886.

[4] Wanjari, AK. and Pund, DA. et al. 2012. Synthesis and Antimicrobial Activities of N-(7-SubstitutedthioCarbamidoquinoline-4-Yl)-N, N-Diethyl-Pentane-1, 4-Diamine, 1(1), 1-5.

[5] Mishra R and Tomer, I. et al.2012. Synthesis and antimicrobial evaluation of some novel thiazole derivatives, Pelagia Research Library, 3(3), 361-366.

[6] Kumawat, M. and Talesara, G. 2013. Synthesis of ethoxyphthalimido derivatized thiadizole assembled imidazolidinone and chloroazetidinone systems from common intermediate Schiff's bases and evaluation of their antibacterial activity, Journal of Applicable Chemistry, 2 (4): 754-764.

[7] Franco, E., Torres, E., Mendiola, M. and Sevilla, M. 2000. Synthesis, spectroscopic and voltammetry studies of copper (II) complexes with open chain, cyclic and a new macrocyclic thiosemicarbazones. Polyhedron, 19, 441-451.

[8] Mounika, K., Anupama, B., Pragathi, J. and Gyanakumari, C. 2010. Synthesis, characterization and biological activity of a Schiff base derived from 3-ethoxy salicylaldehyde and 2-amino benzoic acid and its transition metal complexes. Journal of Scientometric Research, 2, 513-524.

[9] Ducki, S. Forrest, R. Hadfield, J. Kendall, A. Lawrence, N. McGownA. T. Rennison D. 1998. Potent antimitotic and cell growth inhibitory properties of substituted chalcones. Bioorg. Med. Chem. Lett. 8, 1051-1056.

[10] Sliverstein, RM. Bassler, GC.,Morill TC. **1991.** *"Spectroscopic Identification of Organic Compounds*", *John Wiley and Sons, Inc., New York*, 5th Ed., 108.