

SYNTHESIS OF N'-SUBSTITUTED-N''-SUBSTITUTEDFORMAMIDINO-2-IMINO-4-  
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## ABSTRACT

The role of naturally available fruit juice in organic synthesis has attracted the interest of chemist, particularly from the view of green chemistry. Fruit juices act as a biocatalyst in different chemical transformation. Lemon fruit juice is extensively used for condensation reactions due to their powerful and selective natural acid biocatalytic property in organic synthesis and allows mild and highly selective transformation and synthesis in facile and environmentally friendly manner. Moreover, fruits are inexpensive and easily available in the market and its juice can be extracted easily which can be used as biocatalyst in the organic transformations. Hence one-pot three-component condensation of 1,3-diformamidinothiocarbamide with various aldehydes in presence of one drop of concentrated sulphuric acid was carried out in presence of lemon juice as a biocatalyst respectively to synthesize a novel series of N'-substituted-N''-substitutedformamidino-2-imino-4-thiobiurates, which is heither to unknown.

**KEYWORDS:** thiocarbamide, various aldehyde, lemon juice.

## INTRODUCTION

Green chemistry is the utilization of set of principles that will help to reduce the use of hazardous substances during manufactured of chemical products.<sup>[1]</sup> Green chemistry aims to not only protect the environment by cleaning up but also inventing new chemical processes. It is a rapidly developing and an important area in the chemical science which is tremendous application in synthetic chemistry. Aromatic substituted aldehydes with a hydroxyl group have initially the researcher's interest because it having two attacking sites for further reaction.<sup>[2-6]</sup> The antitumor activity relationship of a series of Schiff bases derived from various substituted aromatic amines and aldehydes it has been shown that azomethines from salicylaldehydes gave the basic correlation<sup>[7-8]</sup> Schiff bases of salicylaldehydes have been shown various activities like as a plant growth regulators<sup>[9]</sup>, antimicrobial<sup>[10]</sup>, antimycotic.<sup>[11]</sup>

Schiff base  $-N=CH$ -(imine) characterized by the elucidating the mechanism of transformation and racemisation reaction in biological system.<sup>[13-14]</sup> The lone pair of electron in nitrogen  $sp^2$  hybridized in the azomethine group has extensive chemical and biological importance.<sup>[15-21]</sup> Synthesis of Schiff bases have been describes in variant condition using sulphuric acid and glacial acetic acid.<sup>[22]</sup> Schiff bases having significant

biological activities like anticancer<sup>[23]</sup>, anti-tumor<sup>[24]</sup>, anti-inflammatory<sup>[25]</sup>, insecticidal<sup>[26]</sup>, antibacterial.<sup>[27]</sup> Last decades improvement in the synthetic of procedure of metal complexes interacts with Schiff are investigated and it has also played a key role in the synthesis of metal complexes. In the field of co-ordination chemistry Schiff bases is played vital role as chelating agents.

The main objective of the research work is that to synthesize a novel series of N'-substituted-N''-substitutedformamidino-2-imino-4-thiobiurates (**Va-f**) also 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 of them. It was observed during the studies lemon juice 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. The formation of product is as depicted below.

During the work it was observed that lemon juices is the best solvent which increase the yield of product as well as curtail time span of reaction by maintaining the purity of products, the results obtained during work is depicted in **Table No. 1**.

Table No. 1

Sr. No.	Solvents	Time span in hrs.	Yield (%)
1.	Acetic acid	H <sub>2</sub> O r t 10 days	71
2.	Alum	H <sub>2</sub> O 80°C 50 min	94
3.	Benzoic acid	H <sub>2</sub> O 80°C 15 h <sup>32</sup>	80
4.	Lanthanide triflate	EtOH H <sub>2</sub> O 12 h 95	95
5.	Zirconium oxychloride	EtOH, H <sub>2</sub> O r t 3 h	93
6.	Lemon juice	H <sub>2</sub> O rt. 6 h	82
7.	Lemon juice	H <sub>2</sub> O 80°C 2 h	95

## EXPERIMENTAL

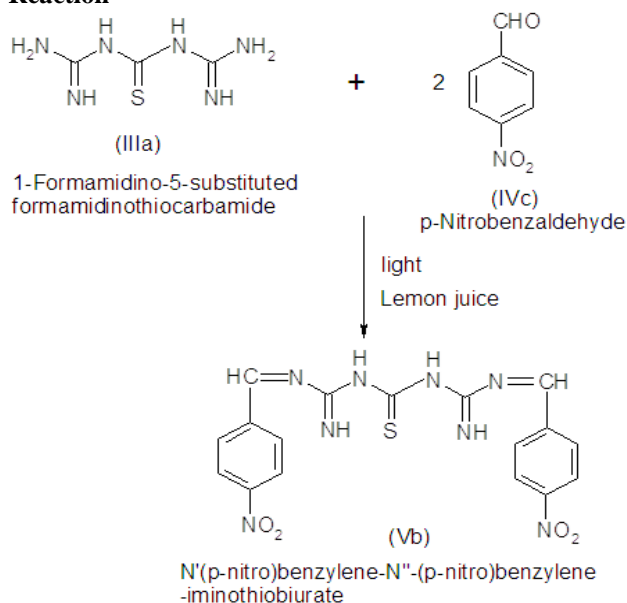
The melting point of the all synthesized compounds was recorded using hot paraffin bath. The carbon and hydrogen analysis were carried out on Carlo-Ebra1106 analyzer. Nitrogen estimation was carried out on Colman-N-analyzer-29. IR spectra were recorded on Perkin Elmer Spectrometer in range 4000-400cm<sup>-1</sup> in KBr pellets. PMR spectra were recorded on Bruker400F spectrometer with TMS as internal standard using CDCl<sub>3</sub> and DMSO-d<sub>6</sub> as solvent. The purity of compound was checked on silica Gel-G Pellets by TLC with layer thickness of 0.3mm. All chemicals used were AR-grade.

## RESULT AND DISCUSSION

### Synthesis of N-(p-nitro) benzylene-N''-(p-nitro)benzyleneformamidino-2-imino-4-thiobiurate in lemon juice (Vb)

A mixture of 1,3-diformamidinothiocarbamide (0.1M) (**IIIa**), p-nitro-benzaldehyde (0.2M) (**IVc**) and concentrated sulphuric acid (0.1 drop) and freshly extracted lemon juice (20 ml) was taken in round bottom flask. It was tightly sealed and the reaction mixture was kept in sun light for 52 hours. Then the reaction mixture was poured on ice cubes with vigorous stirring, ivory crystals were obtained; these were washed several times with water. Recrystallized from aqueous ethanol. Yield 92%, melting point 278°C.

### Reaction



## Properties

It is yellow crystalline solid having melting point 168°C. It gave positive test gave for nitrogen and sulphur. It was desulphurized by alkaline plumbite solution. It formed picrate having melting point 181°C.

## Elemental Analysis

C[(found 56.20%) calculated 57.14], H[(found 4.40%) calculated 05.76], N[(found 21.5%) calculated 21.5], S[(found 07.08%) calculated 08.02].

## IR spectrum (cm<sup>-1</sup>)

The IR spectrum was carried out in KBr-pellets: 3405.50 (N-H stretching), 2858.10 (Ar-CH stretching), 1689.20(C=S stretching), 1591.40(C=NH imino group), 1477.60(N-C=S stretching), 1197.60(C-N stretching).

## NMR Spectrum

The PMR spectrum of compound was carried out in CDCl<sub>3</sub> and DMSO-d<sub>6</sub> and reproduced on PMR. This spectrum distinctly displayed the signals due to Ar-H protons at  $\delta$ 10.1833-8.1600 ppm, -NH proton at  $\delta$  3.7679 ppm, =CH proton at  $\delta$  2.5364-2.5276 ppm.

Similarly, N-benzylene-N''-benzyleneformamidino-2-imino-4-thiobiurate (**Vc**), N-(m-nitro)benzylene-N''-(m-nitro)benzyleneformamidino-2-imino-4-thiobiurate (**Vd**) and N-methyl-N''-methylformamidino-2-imino-4-thiobiurate (**Ve**) were synthesized by the interaction of 1,3-diformamidinothiocarbamide (0.1M) (**IIIa**) with benzaldehyde, (0.2M) (**IVc**), m-nitrobenzaldehyde (0.2M) (**IVd**) and aldehyde (0.2M) (**IVe**) and sulphuric acid (0.1 drop) lemon juice, respectively and enlisted in **Table-II**.

Table-II

Sr. No.	N-substituted-N''-substitutedformami- dino- 2-imino-4-thiobiurate	Juice	Yield %	M. P.
1	N-benzylene-N''-benzylene -----	Lemon	94	272
2	N-(m-nitro)benzylene-N''-(m-nitro) -----	Lemon	93	275
3	N-methyl-N''methyl-----	Lemon	97	222

## REFERENCES

- Cimerman Z. Miljanic S. and Galic N., *Croatica Chemica Acta*, 2000; 73: 81-95.
- Pfeiffer P. Breith E. Llibbe E. and Tsumaki T., *Justus Liebigs., Ann. Chem.*, 1993; 84: 503.
- Hunter L. and Marriott J.A., *J. Chem. Soc.*, 1937; 2000.
- Sacconi L. Ciampolini M. Maggio F. and Cavasini F.P., *J. Am. Chem. Soc.*, 1962; 84: 3246.
- Holm R.H. and Swaminathan K., *Inorg. Chem.*, 1962; 1: 599.
- Perryand G.C. and Thornton D.A., *J. Inorg. Nue. Chem.*, 1972; 34: 3357.
- Hodnett E.M. and Dunn W.J., *J. Med. Chem.*, 1970; 13: 768.
- Hodnett E.M. and Mooney P.D., *J. Med. Chem.*, 1970; 13: 786.
- Alt G.H. (Monsanto Co.), US. 1980, 4.226.615; *Chem. Abstr.*, 1981; 94: 26155.
- Hamada Y. Takeuchi I. Ita Y. Matsui S. and Ita T., *Yakugaku Zassli*, 1981; 101: 633; *Chem. Abstr.*, 1981; 95: 181559.
- Ismail M., *Indian J. Pharm. Sci.*, 1986; 45: 121; *Chem. Abstr.*, 1987; 107: 175589.
- Palet P.R. Thaker B.T. and Zele S., *Indian, J. Chem.*, 1999; 38A: 563.
- Lau K.Y. Mayr A. and Cheung K.K., *Inorg. Chem. Acta*, 1999; 285: 223.
- Shawal, A.S. Harb N.M.S. and Badahdah K.O., *J. Heterocyclic Chem.*, 1985; 22: 1397.
- Patal S 1970 *The chemistry of carbon nitrogen double bond* (New York: Interscience Publishers Inc.) Bob De Clercq and Francis V 2002 *J. Molecular Catal- ysis A: Chemical.*, 180: 67.
- Aurea E, Maria da G N, Vanilde G, Joseph M and Astréa G J 1999 *Braz. Chem. Soc.* 10: 60.
- Kuzmin V E, Lozitsky V P, Kamalov G L, Lozitskaya R N, Zheltvay A I, Fedtchouk A S and Kryzhanovsky D N 2000 *Acta Biochemical Polonica.*, 47: 867
- Holm R H, Everett G W and Chakraborty A 1966 *Prog. Inorg. Chem.*, 7: 83.
- Yamada S 1966, 1967 *Coord. Chem. Rev.* 1 415; (b) Yamada S 1967 *Coord. Chem. Rev.* 2: 82 12. Dey K J 1974 *Scient. Ind. Res.*, 33: 76
- Gheorghe R and Mioara A 2001 *Bulletin of the Chemists and Technologists of Macedonia*, 20: 131.
- Santosh K, Niranjana M S, Chaluvaram K C, Jamakhandi C M and Dayanand K 2010 *Journal of Current Pharma- ceutical Research*, 1: 39.
- F.D. Popp, *J. Org. Chem.*, 1961; 26: 1566.
- D. Kong, X. Zhang, Q. Zhu, J. Xie, X. Zhou, *Zhongguo Yaowu Huaxue Zazhi*, 1998; 8(4): 245.
- D. J. Hadjipavlou-litina, A. A. Geronikaki, *Drug Des. Discov.*, 1996; 15: 199.
- S. S. Murthy, A. Kaur, B. Sreenivasalu, R.N. Sarma, *Indian J. Exp. Biol.*, 1998; 36: 724.
- K.N. Venugopala, V.A. Jayashree, *Indian J. Pharm. Sci.*, 2008; 70: 88.