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RESEARCH ARTICLE

SYNTHESIS OF 1-(4-PYRIDINE) IMINO-5-SUBSTITUTED DITHIOBIURETS

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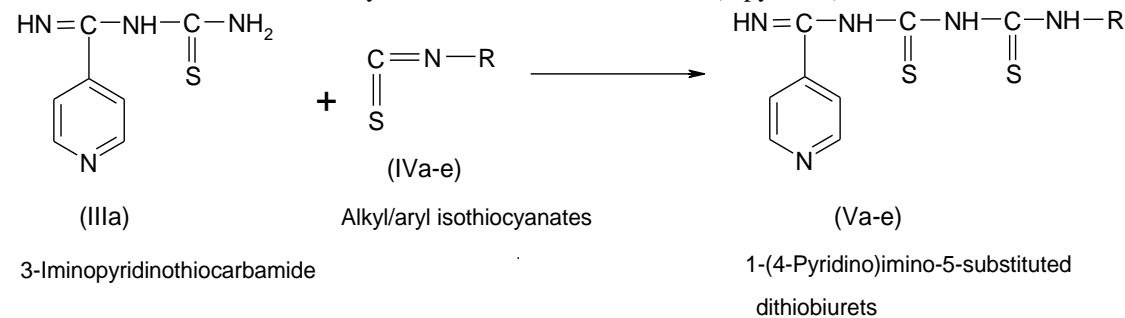
Abstract

Recently in this laboratory, a direct, suitable and simple method for the synthesis of 1-(4-pyridine)imino-5-substituted dithiobiurets (**Va-e**) was developed. A novel series of 1-(4-pyridine)imino-5-substituted dithiobiurets (**Va-e**) was synthesized by the interacting 3-(4-pyridine)iminothiocarbamide (**IIIa**) with various isothiocyanates (**IVa-e**) in acetone-ethanol medium on water bath. The reaction mixture was filtered in hot conditions, after distillation of excess solvent, brown coloured crystals were obtained, recrystallised from ethanol. The structure of the synthesized compounds was justified on the basis of chemical characteristics, elemental and spectral analysis.

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Introduction:-

Thiocarbamido, dithiobiureto and triazino nucleus containing drugs possess an important applications and significances in medicinal, pharmaceutical, industrial, agricultural and biochemical sciences¹⁻⁹. The important reactions of amino compounds have been briefly investigate by Pandey¹⁰, Pathe¹¹⁻¹³, Berad¹⁴, Aprajit¹⁵, Tayade¹⁶, Deohate¹⁷, Kodape¹⁸ and Bhagwatkar¹⁹ for the synthesis of several 5, 6 and 7 membered nitrogen, nitrogen and sulphur containing heterocycles with several references to 1,2,4-triazoles, 1,3,5-thiadiazolidines, 1,3,5-dithiazines, 1,3,5-thiadiazines and s-triazines. These molecules possess various medicinal, agricultural, industrial and biochemical applications and importance, hence the present research scheme was designed to describe somewhat suitable and direct method for a synthesis of the novel series of 1-(4-pyridine)imino-5-substituted dithiobiurets.



Where, R = - phenyl, -methyl, -ethyl, -t-butyl, -p-chlorophenyl.

Scheme I

Materials and method:-

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 (Indian make) except allylthiourea Lancaster (Germany make). Alkyl/Aryl isothiocyanates have been prepared by known literature methods¹⁶.

Experiment No. 1:-

Synthesis of 1-(4-pyridine)imino-5-phenyldithiobiuret (Va):

1-(4-Pyridine)imino-5-phenyldithiobiuret (Va) was synthesized by refluxing the mixture of 3-(4-pyridine)iminothiocarbamide **III(a)** with phenyl isothiocyanate (IVa) in 1:1 molar proportion in acetone-ethanol medium for 4 hours on water bath, dark brown coloured crystals were separated out, they were filtered and dried at room condition and recrystallised from ethanol. Yield 85%, m. p. 180⁰C.

Experiment No. 2:-

Synthesis of 1-(4-pyridine)imino-5-methyldithiobiuret (Vb):

1-(4-Pyridine)imino-5-methyldithiobiuret(Vb) was synthesized by refluxing the mixture of 3-(4-pyridine)iminothiocarbamide (**IIIa**) with methyl isothiocyanate (IVb) in 1:1 molar proportion in acetone-ethanol medium for 4 hours on water bath. Dark brown coloured crystals were obtained they were filtered, dried and recrystallised from ethanol, yield 87%, m. p. 168⁰C.

Experiment No. 3:-

Synthesis of 1-(4-pyridine)imino-5-ethylthiobiuret (Vc):

1-(4-Pyridine)imino-5-ethylthiobiuret (Vc) was synthesized by refluxing the mixture of 3-(4-pyridine)iminothiocarbamide (**IIIa**) with ethyl isothiocyanate (IVc) in 1:1 molar proportion in acetone-ethanol medium for 4 hours on water bath. Dark Brown coloured crystals were obtained they were filtered, dried and recrystallised from ethanol, yield 86%, m. p. 175⁰C.

Experiment No. 4:-

Synthesis of 1-(4-pyridine)imino-5-t-butyldithiobiuret (Vd):

1-(4-Pyridine)imino-5-t-butyldithiobiuret (Vd) was synthesized by refluxing the mixture of 3-(4-pyridine)iminothiocarbamide (**IIIa**) with t-butyl isothiocyanate (IVd) in 1:1 molar proportion in acetone-ethanol medium for 4 hours on water bath. Brown coloured crystals were obtained they were filtered, dried and recrystallised from ethanol, yield 80%, m. p. 210⁰C.

Experiment No. 5:-

Synthesis of 1-(4-pyridine)imino-5-p-chlorophenyldithiobiuret (Ve):

1-(4-Pyridine)imino-5-p-chlorophenyldithiobiuret (Ve) was synthesized by refluxing the mixture of 3-(4-pyridine)iminothiocarbamide (**IIIa**) with p-chlorophenyl isothiocyanate (IVe) in 1:1 molar proportion in acetone-ethanol medium for 4 hours on water bath. Brown coloured crystals were obtained they were filtered, dried and recrystallised from ethanol, yield 82%, m. p. 189⁰C.

Result and Discussion:-

A) Synthesis of 1-(4-pyridine)imino-5-phenyldithiobiuret (Va)

1-(4-Pyridine)imino-5-phenyldithiobiuret (Va) was synthesized by refluxing the mixture of 3-(4-pyridine)iminothiocarbamide **III(a)** with phenyl isothiocyanate (IVa) in 1:1 molar proportion in acetone-ethanol medium for 4 hours on water bath, dark brown coloured crystals were separated out, they were filtered and dried at room condition and recrystallised from ethanol. Yield 85%, m. p. 180⁰C.

Properties of (Va):-

- 1) It was dark brown crystalline solid having m. p. 180⁰C.
- 2) It gave positive test for nitrogen and sulphur elements.
- 3) It was desulphurized by alkaline plumbite solution.
- 4) It was soluble in DMSO, dioxane, ethanol, acetone while insoluble in benzene.
- 5) It formed picrate having m. p. 167⁰ C.
- 6) **Elemental Analysis:** The result of elemental analysis are given in **Table No. III-1**.

Table No. III-1

Sr. No.	Elements	Found	Calculated
1	Carbon	43.03	44.94
2	Hydrogen	3.91	4.86
3	Nitrogen	26.21	26.21
4	Sulphur	23.04	23.97

- 7) From the analytical data the molecular formula was found to be C₁₀H₁₃N₅S₂.
- 8) **IR Spectrum:** IR spectrum of compound (Va) was carried out in KBr-pellets. The important absorptions are correlated as follows and are depicted in **Table No. III-2**

Table No. III-2

Sr. No.	Absorption Observed (cm ⁻¹)	Assignment	Absorption expected (cm ⁻¹)
1	3303.17	C-H (Ar) stretching	3500-3000 ²⁰
2	1611.14	C = NH (imino group)	1989-1471 ²¹
3	1090.32	C=S stretching	1200-1050 ²²
4	1668.22	N-H stretching	1789-1471 ²³
5	1400.19	C=S stretching	1380-1050 ²³
6	1240.31	C-N stretching	1340-1250 ²⁴

- 9) **PMR Spectrum:** PMR Spectrum²⁴ of a compound (Va) was carried out in DMSO-d₆ and CDCl₃. This spectrum distinctly displayed the signals due to Ar-H/ pyridino protons at δ5.0894-8.9878 ppm, =NH protons δ1.2426-1.3100 ppm and -NH protons at δ 2.5560-2.6004 ppm.

B) Synthesis of 1-(4-pyridine)imino-5-methyldithiobiuret (Vb)

1-(4-Pyridine)imino-5-methyldithiobiuret (Vb) was synthesized by refluxing the mixture of 3-(4-pyridine)iminothiocarbamide **III(a)** with methyl isothiocyanate (IVb) in 1:1 molar proportion in acetone-ethanol medium for 4 hours on water bath, dark brown coloured crystals were separated out, they were filtered and dried at room condition and recrystallised from ethanol. Yield 87%, m. p. 168⁰C.

Properties of (Vb):-

- 1) It was dark brown crystalline solid having m. p. 168⁰C.
- 2) It gave positive test for nitrogen and sulphur elements.
- 3) It was desulphurized by alkaline plumbite solution.
- 4) It was soluble in DMSO, dioxane, ethanol, acetone while insoluble in benzene.
- 5) It formed picrate having m. p. 145⁰ C.
- 6) **Elemental Analysis:** The result of elemental analysis are given in **Table No. III-3**.

Table No. III-3

Sr. No.	Elements	Found	Calculated
1	Carbon	41.01	42.68
2	Hydrogen	3.89	4.34
3	Nitrogen	27.66	27.66
4	Sulphur	24.78	25.29

- 10) From the analytical data the molecular formula was found to be $C_9H_{11}N_5S_2$.
- 11) **IR Spectrum:** IR spectrum of compound (**Vb**) was carried out in KBr-pellets. The important absorptions are correlated as follows and are depicted in **Table No. III-4**.

Table No. III-4

Sr. No.	Absorption Observed (cm^{-1})	Assignment	Absorption expected (cm^{-1})
1	3390	N-H stretching	3500-3000 ²⁰
2	1609	C=NH (imino group)	1989-1471 ²¹
3	1051	C=S stretching	1200-1050 ²²
4	1416	C=S stretching	1380-1050 ²³
5	1265	C-N stretching	1340-1250 ²⁴

- 12) **PMR Spectrum:** PMR Spectrum²⁴ of a compound (**Vb**) was carried out in DMSO- d_6 and $CDCl_3$. This spectrum distinctly displayed the signals due to Ar-H/ pyridino protons at δ 7.0309-9.7581 ppm, -NH protons at δ 2.5439-2.5524 ppm and - CH_3 protons δ 1.0049-1.3938 ppm.

Similarly, 1-(4-pyridine)imino-5-ethyldithiobiuret (**Vc**), 1-(4-pyridine) imino-5-t-butyldithiobiuret (**Vd**) and 1-(4-pyridine)imino-5-p-chlorophenyl dithiobiuret (**Ve**) were synthesized by the interactions of ethylisothiocyanate (**IVc**), t-butylisothiocyanate (**IVd**) and p-chlorophenylisothiocyanate (**IVe**) with 3-(4-pyridine)iminothiocarbamide **III(a)** acetone-ethanol medium respectively by above mentioned method. (**Table No. III-5**)

Table No. III-5

Sr. No.	Expt. No.	1-(4-Pyridine)imino-5-substituted dithiobiuret	Yield (%)	M. P. ($^{\circ}C$)
1	3	-----ethyl-----	86	175
2	4	-----t-butyl-----	80	210
3	5	-----p-Cl-phenyl--	82	189

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