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SYNTHESIS OF 2, 5-DISUBSTITUTEDAMINO-2-THIO-1, 3, 5-THIADIAZOLES

D.T.Tayade[1*], S.P. Ingole[1], S.A. Waghmare[2]

[1]Department of Chemistry, Government Vidarbha Institute of Science and Humanities, Amravati 444606.
[2]Department of Chemistry, Ghulam Nabi Azad Arts, Comm. & Science College, Barshitakli, Dist. Akola 444401.

Abstract:
A novel series of 2,5-disubstitutedamino-2-thio-1,3,5-thiadiazoles ***(Xa-g)*** *was synthesized by the oxidative cyclisation of 1-substitued-thioamido-5-formamidinosubstituedthioamido-2-imino-4-thiabiurates* ***(VIIa-g)*** *in ethanol using iodine as oxidizing agent. The products were isolated characterised and justified on the basis of elemental analysis, chemical characteristics, and spectral studies.*

Keywords*:1-substitued-thioamido-5-formamidinosubstituedthioamido-2-imino -4-thiabiurates and chloroform, microwave.*

Corresponding author:
D.T.Tayade,
Department of Chemistry,
Government Vidarbha Institute of Science and Humanities,
Amravati 444606.
Email:- *skdtayade@gmail.com*

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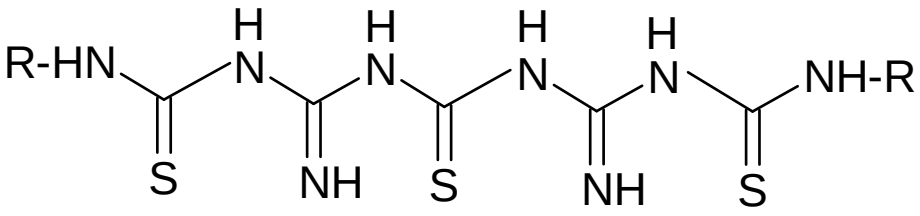
INTRODUCTION:

Thiadiazoles and triazoles nucleus containing compounds possesses their own identity and importance in pharmaceutical, medicinal, agricultural, industrial, biochemical and biotechnological fields[1-7]. The compounds having thiadiazoles and triazoles as a parent nucleus are widely used in pharmaceutical, medicinal and biological sciences8-9. It was noticed that these drugs possesses antidiabetic10, herbicidal[11], amoebicidal[12] and antibacterial[13-14] properties. Recently in this laboratory the oxidative cyclisation of some cyanoamidinothiocarbamides, diformamidino-thiocarbamides, substituted N-glucosides and thioglucosides were carried out. Oxidative cyclisation for the synthesis of 1,3,4-thiadiazoles, 1,3,4-thiadiazolines and 1,2,4-triazoles have been studied by various researchers[15-25].

As a part of research work presently been undertaken in this laboratory in the synthesis of heteroacycles and heterocycles, it was thought interesting to investigate the cyclisation of 1-substituedthioamido-5-formamidino-substitutedthioamido-2-imino-4-thiabiurates **(VIIa-g)** with liquid ethanol medium to obtain a novel series of 2,5-disubstitutedamino-2-thio-1,3,5-thiadiazoles **(Xa-g)** respectively which are hither to unknown. The present work describes suitable, convenient and somewhat direct method for the synthesis of **(Xa-g)** are reaction depicted in **(Scheme-1)** .



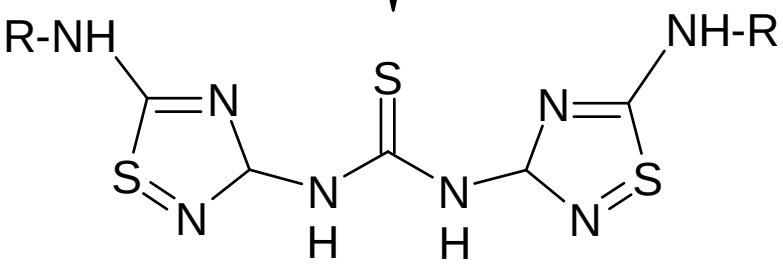
(VIIa-g)

1-Substitutedthioamido-5-formamidinosubstituted thioamido-2-imino-4-thiobiurates

oxidative cyclisation

Iodine,

ethanol



(Xa-g)

2,5-Disubstitutedamino-2-thio-1,3,5-thiadiazoles

Scheme-1

EXPERIMENTAL:

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. Data for ^{1}H are recorded as follows: δ chemical shift (ppm), multiplicity (s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (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.

RESULT AND DISCUSSION:

General procedure for the Synthesis of 2,5-diethylamino-2-thio-1,3,5-thiadiazole

A paste of 1-ethylthioamido-5-formamidinoethylthioamido-2-imino -4-thiabiurate **(VIIa)** was prepared in ethanol. To it iodine in ethanol was added with constant stirring. Initially the colour of iodine was disappear the addition was continued till colour of iodine persisted to the reaction mixture. The reaction mixture was allowed to stand for 8 hours, it afforded lemon yellow product. It was crystallised from aqueous ethanol, yield 76%, m.p. 198^{0}C.

1) 2,5-diethylamino-2-thio-1,3,5-thiadiazole

Lemon yellow solid, Molecular formula $C_9H_{14}N_8S_1$. Yield 95%, m.p. 204˚C, Elemental analysis: [(Found) C: 56.15, H: 04.50, N: 21.05, S: 7.02 (Calculated) C: 57.14, H: 05.76, N: 21.05, S: 08.02]. **IR:** 3405.50 (N-H Streching), 2858.10, (C-H Streching), 1689.20, (N=C-N Streching), 1591.40, (C=C Streching), 1477.60, (N-C=S stretching), 1197.60, (C-N stretching), **H^1 NMR**: –NH proton at δ 3.2297-3.2477 ppm, =NH proton at δ 2.6543 ppm, –CH proton at δ 2.1465 ppm and CH_3 protons at δ 1.3306-1.7039 ppm.

2) 2,5-diphenylamino-2-thio-1,3,5-thiadiazole (Xc)

Faint yellow solid, Molecular formula $C_{17}H_{16}N_8S_3$.Yield 95%, m.p. 204˚C, Elemental analysis: [(Found) C: 46.21, H: 02.50, N: 26.29, S: 21.02 (Calculated) C: 47.88, H: 03.28, N: 26.29, S: 22.53]. **IR:** 3405.50 (N-H Streching), 2858.10, (C-H Streching), 1689.20, (N=C-N Streching), 1591.40, (C=C Streching), 1477.60, (N-C=S stretching), 1197.60, (C-N stretching), **H^1 NMR**: -NH protons at δ 4.5711, -NH (imino) protons at δ 2.0124, ppm, -CH_3 protons at δ 1.2471.

3)1-Methylthiocarbamido-5-formamidinomethylthiocarbamido-2-imino-4-thiobiurate (VIIc)

Crystalline faint Yellow solid, Molecular formula $C_7H_{14}N_8S_3$, Yield 95%, m.p.204˚C. Elemental analysis [(Found) C: 27.00, H: 04.00, N: 36.60, S: 30.24 (Calculated) C: 27.45, H: 04.57, N: 36.60, S: 31.37]. **IR:** 3324.70 (N-H Streching), 2984.10, (C-H Streching), 1754.20, (N=C-N Streching), 1568.40, (C=C Streching), 1504.60, (N-C=S stretching), 1201.60, (C-N stretching), **H^1 NMR**-NH protons at δ 4.5711, -NH (imino) protons at δ 2.0124, ppm, -CH_3 protons at δ 1.2471.

4)**1-(p-chlorophenyl)thiocarbamido-5-formamidino(p-chlorophenyl)thio carbamido-2-imino-4-thiobiurate (VIId)**

Crystalline faint yellow solid, Molecular formula $C_{17}H_{16}N_8S_3$. Yield 95%, m.p. 204˚C. Elemental analysis, [(Found) C: 43.84, H: 03.24, N: 24.40, S: 19.85, Cl: 06.35 (Calculated) C: 44.15, H: 03.46, N: 24.24, S: 20.77, Cl: 07.35]. **IR:** 3321.50 (N-H Streching), 2758.10, (C-H Streching), 1598.20, (N=C-N Streching), 1554.40, (C=C Streching), 1447.60, (N-C=S stretching), 1141.60, (C-N stretching), **H^{1}NMR**:- Ar-H protons at δ 88451-6.1452 ppm, -NH protons at δ 3.8511, -NH (imino) protons at δ 1.2224 ppm.

5) 1-o-Tolylthiocarbamido-5-formamidino (o-tolyl)thiocarbamido-2-imino-4- thiobiurate (VIIe)

Crystalline faint yellow solid molecular formula $C_{19}H_{22}N_8S_3$, Yield 95%, m.p. 204˚C. Elemental analysis, [(Found) C: 48.40, H: 3.47, N: 24.45, S: 21.90 (Calculated) C: 49.78, H: 03.05, N: 24.45, S: 20.96] **IR:** 3248.50 (N-H Streching), 2741.10, (C-H Streching), 1659.20, (N=C-N Streching), 1421.40, (C=C Streching), 1321.60, (N-C=S stretching), 1019.60, (C-N stretching), **H^1 NMR**: Ar-H protons at δ 8.4021-6.2212 ppm, -NH protons at δ 3.4111, -NH (imino) protons at δ 2.6124 ppm.

6) 1-(m-Tolyl)thiocarbamido-5-formamidino(m-tolyl)thiocarbamido-2-imino-4-thiobiurate (VIIf)

Crystalline faint, yellow solid, molecular formula $C_{19}H_{22}N_8S_3$ yield 95%, m.p. 204˚C. Elemental analysis, [(Found) C: 48.88, H: 2.90, N: 24.45, S: 20.20 (Calculated) C: 49.78, H: 03.05, N: 24.45, S: 20.96] **IR:** 3364.50 (N-H Streching), 2698.10, (C-H Streching), 1584.20, (N=C-N Streching), 1568.20, (C=C Streching), 1547.60, (N-C=S stretching), 1024.60, (C-N stretching), **H^1 NMR**: Ar-H protons at δ 7.7451-6.1412 ppm, -NH protons at δ 3.2411, -NH (imino) protons at δ 1.2224, ppm.

7) 1-(p-Tolyl) thiocarbamido-5-formamidino(p-tolyl)thiocarbami -do-2-imino-4-thiobiurate (VIIg)

Crystalline faint yellow solid, molecular formula $C_{19}H_{22}N_8S_3$, Yield 95%, m.p. 204˚C. Elemental analysis, [(Found) C: 47.78, H: 2.54, N: 23.75, S: 19.58 (Calculated) C: 49.78, H: 03.05, N: 24.45, S: 20.96]. **IR:** 3207.50 (N-H Streching), 2721, (C-H Streching), 1704, (N=C-N Streching), 1605.00, (C=C Streching), 1501.60, (N-C=S stretching), 1098.60, (C-N stretching), **H^1 NMR**: Ar-H protons at δ 7.2421-6.4012 ppm, -NH_2 protons at δ 4.4211, -NH protons at δ 2.6124 ppm.

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