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Synthesis and Reactivity of 2-Imino-3-(6-Methyl-1, 3-Benzothiazol-2-Yl)-1, 3-Thiazolidin-4-One

T. M. Bhagat
P.G, Department of Chemistry, G. S. Gawande College, Umarkhed, Dist-Yeotmal, Maharashtra, India

ABSTRACT

4-thiazolidinone has been prepared by the series of reactions. We have synthesized 2-amino-6-methyl benzothiazole from p-toluidine (1) which is then treated with chloro acetyl chloride to form 2-chloro-N-(6-methyl-1,3-benzothiazol-2-yl) acetamide (2). Compound (2) on thiocynation and refluxation with DMF, 2-imino-3-(6-methyl-1,3-benzothiazol-2-yl)-1,3-thiazolidin-4-one is obtained as product(4). This 4-thiazoidinone compound (4) treated with benzaldehyde, 4-methoxy benzaldehyde, 4-chloro benzaldehyde, 2-nitro benzaldehyde and 4-dimethyl amino benzaldehyde in presence of acetic acid and sodium acetate to form corresponding 5-substituted product (5a-5h). The newly synthesized compounds are characterized by spectral analysis.

Keywords : Benzothiazole, Thiazolidinone

I. INTRODUCTION

A survey of literature reveals that large work has been carried out on the synthesis of 4-thiazolidinone and known to exhibits various biological activities as antitubercular[1], antiallergic[2]. 4-thiazolidinone compound are reported to possess different biological activities, such as antimicrobial, anti-inflammatory, antiviral, antiparasitic and antituberculosis[3-9].

4-thiazolidinones are good pharmacological properties[10] and known to exhibits antitubercular[11], antibacterial[12], anticonvulsant[13], antifungal activity[14]. Large work has been carried out on 4-thiazolidinone but very less information is available about 3 and 5-substituted 4-thiazolidinone

The starting compound were prepared by the reaction of 2-amino-6-methyl benzothiazole and chloro acetyl chloride to form 2-chloro-*N*-(6-methyl-1,3-benzothiazol-2-yl) acetamide which on treatment with potassium thiocynate and DMF, 2-imino-3-(6-methyl-1,3-benzothiazol-2-yl)-1,3-thiazolidin-4-one obtained as a product. This thiazolidinone treated with substituted aromatic aldehyde to obtained corresponding 5-substituted 4-thiazolidinone

II. EXPERIMENTAL

All the melting points were determined in open capillary tube and may be uncorrected. The purity of compound was checked by TLC on silica gel coated glass plate. Infra-red spectra were monitored in KBr palates on Bomen 104 FT infra-red spectrophotometer.

H1 NMR spectra were obtained on a Gemani 200 Mz spectrometer with tetra methyl silane as an internal standard. Elemental analysis was performed on a Heraeus CHN-O rapid analyzer

2-chloro-N-(6-methyl-1,3-benzothiazol-2-yl)acetamide (2)

2-amino 6-methyl benzothiazole (5gm, 0.01M) and100ml of dry benzene is taken in a round bottom flask. 15ml of chloro acetyl chloride added drop wise fashion maintaining temperature 0-5 ^{0}C in a reaction mixture. Then reflux the reaction mixture on water bath for 5 hours. The solvent was removed by distillation, the solid product is obtained. The completion of the reaction was monitored by TLC. The solid was recrystallized by using ethanol.

Yield: 5.3 gm,(72%) M.P: 172 °C I.R. (KBr) : 3420 cm^{-1} (Asymmetric stretching of -NH), 3320 cm^{-1} (N-H Symmetrical stretching of -NH), 3052 cm^{-1} (Ar-H stretching), 1630 cm^{-1} (-C=N stretching), 1750 cm^{-1} (-C=O stretching); PMR ($CDCl_3$) δ 2.5 (singlet, 1H, NH), δ 6.8 (singlet, 1H, Ar-H), δ 7.0-7.5 (two doublet, 2H, Ar-H) [Found : C: 49.5 %, H : 3.50%, Cl : 14.5% N : 11.0%, O : 6.5% S: 13.0 %.$C_{10}H_9ClN_2OS$ required : C: 49.90 %, H : 3.77 %, Cl : 14.73% N : 11.64%, O : 6.65% S: 13.32 %.]

2-[(6-methyl-1,3-benzothiazol-2-yl)amino]-2-oxoethyl thiocyanate 9 (3)

3.8gm (0.015M) of compound (2) and 2gm (0.02M) KSCN taken in a round bottom flask. Then 40ml dry acetone was added and refluxed on water bath for 4 hours. The resulting mixture was cooled, excess of acetone was removed by distillation & residue poured into crushed ice, thus solid residue obtained was filtered, washed with cold water, dried & recrystalised from ethanol.

Yield: 3.5 gm, (80%) M.P: 172 °C I.R. (KBr) : 3420 cm^{-1} (Asymmetric stretching of -NH), 3320 cm^{-1} (N-H Symmetrical stretching of -NH), 3052 cm^{-1} (Ar-H stretching), 1630 cm^{-1} (-C=N stretching), 1750 cm^{-1} (-C=O stretching) 2230 cm^{-1} (-C≡N stretching in cyanide) ; PMR ($CDCl_3$) δ 2.4 (singlet, 1H, NH), δ 6.8 (singlet, 1H, Ar-H), δ 7.0-7.5 (two doublet, 2H, Ar-H) [Found : C: 49.5 %, H : 3.50%, N : 15.5%, O : 6.0% S: 24.0 %.$C_{11}H_9N_3OS_2$ required : C: 50.17 %, H : 3.44 %, N : 15.96%, O : 6.08% S: 24.35 %.] .

2-imino-3-(6-methyl-1,3-benzothiazol-2-yl)-1,3-thiazolidin-4-one (4)

2.63gm (0.01M) of compound (3) in a round bottom flask was refluxed in 30ml DMF (Dimethyl Formamide) in an oil bath by maintaining temperature of 150-160 ^{0}C for 6 hours. The solvent removed by distillation under vaccume & the crude product obtained is recrystallized from ethanol. The completion of reaction was monitored by TCL.

Yield: 2.6 gm, (74%) M.P: 162 °C I.R. (KBr) : 3420 cm^{-1} (Asymmetric stretching of -NH), 3320 cm^{-1} (N-H Symmetrical stretching of -NH), 3052 cm^{-1} (Ar-H stretching), 1630 cm^{-1} (-C=N stretching), 1750 cm^{-1} (-C=O stretching) ; PMR ($CDCl_3$) δ 2.6 (singlet, 1H, NH), δ 6.8 (singlet, 1H, Ar-H), δ 7.0-7.5 (two doublet, 2H, Ar-H) [Found : C: 49.5 %, H : 3.50%, N : 15.5%, O : 6.0% S: 24.0 %.$C_{11}H_9N_3OS_2$ required : C: 50.17 %, H : 3.44 %, N : 15.96%, O : 6.08% S: 24.35 %.]

5-substituted-2-imino-3-(6-methyl-1,3-benzothiazol-2-yl)-1,3-thiazolidin-4-one (5a-5f)

1.3 gm (0.005M) of compound (4) and 0.4 gm (0.005M) of sodium acetate was taken in a 50 ml round bottom flask. Then aromatic aldehyde (a-f) & 10 ml of acetic acid was added, refluxed for 5 hours and allow to cool. This reaction mixture pours on crushed ice. Precipitate once formed. Filtered & washed with cold water & recrystallized from proper solvent.

5a. Yield: 0.8 gm, M.P: 128 °C I.R. (KBr): 3420 cm^{-1} (Asymmetric stretching of -NH), 3320 cm^{-1} (N-H Symmetrical stretching of -NH), 3052 cm^{-1} (Ar-H stretching), 1630 cm^{-1} (-C=N stretching), 1750 cm^{-1} (-C=O stretching); [Found C: 61.5 %, H : 3.5 %, N : 11.5%, O : 4.5% S: 18.0 % M.F.-$C_{18}H_{13}N_3OS_2$

required : C: 61.52 %, H : 3.73 %, N : 11.96%, O : 4.55% S: 18.25 %.]

5b. Yield: 0.6 gm, M.P: 122 °C I.R. (KBr) : 3410 cm^{-1} (Asymmetric stretching of -NH), 3325 cm^{-1} (N-H Symmetrical stretching of -NH), 3050 cm^{-1} (Ar-H stretching), 1620 cm^{-1} (-C=N stretching), 1760 cm^{-1} (-C=O stretching); [Found C: 63.5 %, H : 3.8 %, N : 11.0%, O : 4.1% S: 16.80 % M.F.-$C_{20}H_{15}N_3OS_2$ required : C: 63.64 %, H : 4.0 %, N : 11.13%, O : 4.24% S: 17.0 %.]

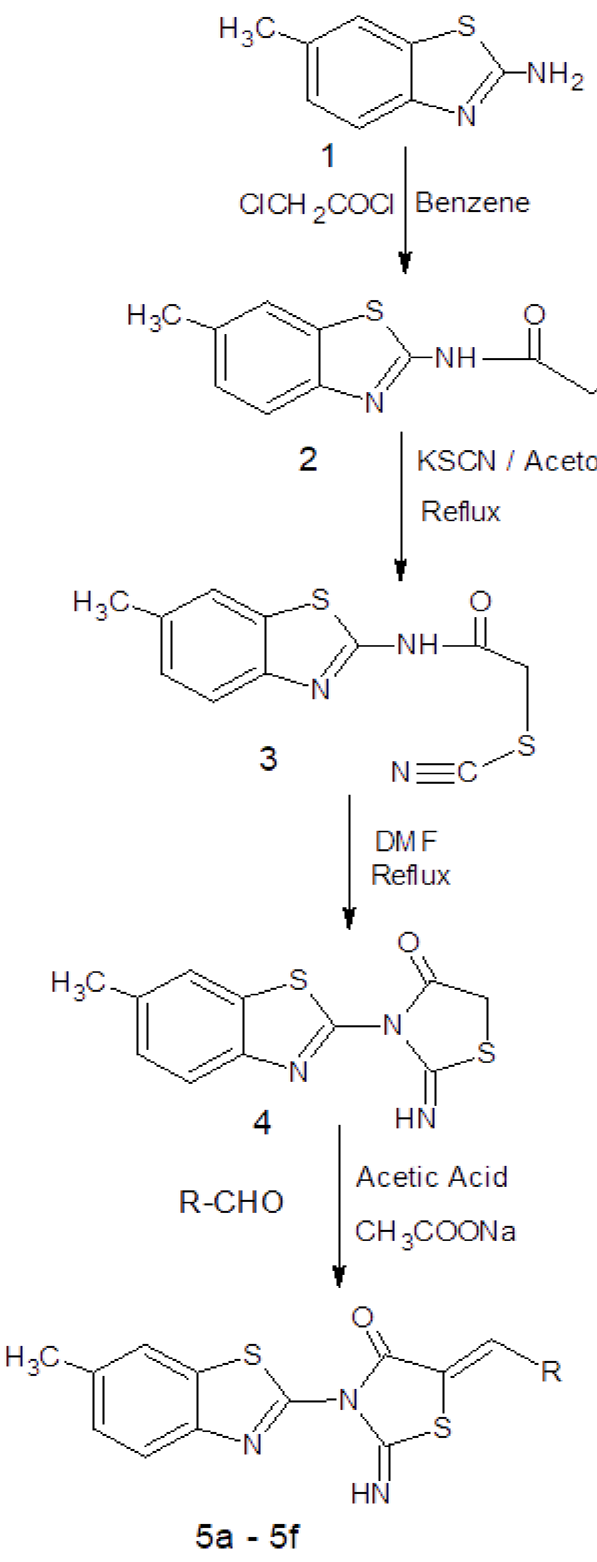
5c. Yield: 0.6 gm, M.P: 108 °C I.R. (KBr) : 3430 cm^{-1} (stretching of -NH), 3050 cm^{-1} (Ar-H stretching), 1620 cm^{-1} (-C=N stretching), 1760 cm^{-1} (-C=O stretching); [Found C: 59.7 %, H : 3.8 %, N : 11.0%, O : 8.2% S: 16.5 % M.F.-$C_{19}H_{15}N_3OS_2$ required : C: 59.82 %, H : 3.96 %, N : 11.02%, O : 8.39% S: 16.81 %.]

5d. Yield: 0.6 gm, M.P: 130 °C I.R. (KBr) : 3400 cm^{-1} (stretching of -NH), 3070 cm^{-1} (Ar-H stretching), 1620 cm^{-1} (-C=N stretching), 1720 cm^{-1} (-C=O stretching); [Found C: 55.8 %, H : 3.1 %, Cl : 9.1 %, N : 11.8%, O : 4.1% S: 16.5 %; M.F.-$C_{18}H_{12}ClN_3OS_2$ required : C: 56.02 %, H : 3.13 %, Cl : 9.19 %, N : 11.89%, O : 4.15% S: 16.62 %.]

5e. Yield: 0.7 gm, M.P: 115 °C I.R. (KBr) : 3430 cm^{-1} (stretching of -NH), 3020 cm^{-1} (Ar-H stretching), 1630 cm^{-1} (-C=N stretching), 1730 cm^{-1} (-C=O stretching); [Found C: 54.5 %, H : 3.0 %, N : 14.1%, O : 12.1% S: 16.1 %.; M.F.-$C_{18}H_{12}N_4O_3S_2$ required : C: 54.53 %, H : 3.05 %, N : 14.13%, O : 12.11% S: 16.18 %.]

5f. Yield: 0.6 gm, M.P: 125 °C I.R. (KBr) : 3440 cm^{-1} (stretching of -NH), 3050 cm^{-1} (Ar-H stretching), 1620 cm^{-1} (-C=N stretching), 1740 cm^{-1} (-C=O stretching); [Found C: 60.6 %, H : 4.5 %, N : 14.1%, O : 4.0% S: 16.2 %.; M.F.-$C_{20}H_{18}N_4OS_2$ required : C: 60.89 %, H : 4.60 %, N : 14.20%, O : 4.06% S: 16.26 %.]

Scheme



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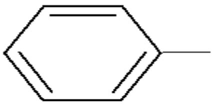

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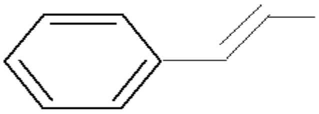

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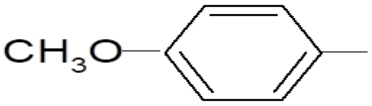

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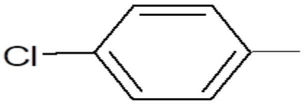

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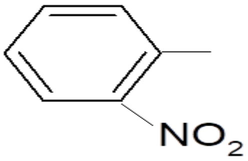

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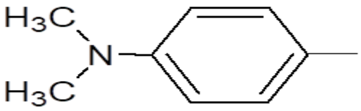

III. RESULT AND DISCUSION

The structures of these 3 and 5-substituted thiazolidinone (5a- 5f) were assigned on the basis of their elemental analysis and spectral data

2-chloro-N-(6-methyl-1,3-benzothiazol-2-yl)acetamide showed stretching absorption bands in IR spectra in the region 3320 cm^{-1} due to N-H stretching. The presence of broad singlet in their PMR spectra in the region δ 2.5 to δ 4.5 confirmed the presence of -NH proton. The signal at 1750 cm^{-1} in IR spectra indicates the presence of carbonyl group.

The I. R. spectra of Compound (3) shows absorption signal in the region 2230 cm^{-1} indicates the presence of cyano grop. While the IR spectra of compound (4) observed the absence of strong bands in the region 2230cm^{-1} due to –C-N stretching of cyano group , confirms the formation of cyclised product.

IV. REFERENCES

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