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Synthesis of 9-chloro-4-ethyl carboxylate-5-imino-3-thiomethyl benzothiazolo[2,3-c]-1,2,4-triazole

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INTRODUCTION

A survey of literature reveals that very little work has been carried out on the synthesis of pyrimidine condensed with benzothiazole system. Nair Mohan D. et al.^[1] synthesized pyrimido [2,1-b]benzothiazole by cyclisation of which in turns obtained by refluxing 2-amino benzothiazoles with diethyl ethoxy methylene malonate. These derivatives were found to have antiviral activity. The benzothiazolo derivatives^[1-23] are well known to possess various pharmacological properties. On other hand some of the derivatives of 1,4-benzodiazepines^[24-25] are psychotropic agents possessing weak analgesic activity. Synthesis of some thiazolotriazepines has been reported,^[26-27] which were found to possess CNS depressant activity psycho sedative and tranquilizing properties. A survey of literature made it evident that very little work has been carried out for the preparation of fused benzothiazolo-1,2,4-triazepine^[28,29] systems. The reported methods for the synthesis of such compounds are tedious, time consuming and require uncommon starting material. In view of this, recently our group reported^[30] synthesis of fused benzothiazolo triazepine system.

RESULT AND DISCUSSION

In present work we report one pot synthesis of 9-chloro-4-ethylcarboxylate-5-imino-3-thiomethyl benzothiazolo[2,3-c]-1,2,4-triazepine. The parent com-

pound was prepared by the reaction of 6-chloro-2-hydrazino benzothiazole with ethyl 2-cyano-3,3-bisthiomethyl acrylate in presence of dimethyl formamide and catalytic amount of anhydrous potassium carbonate. The required starting compound 6-chloro-2-hydrazino benzothiazole was prepared by heating 2-amino-6-chloro benzothiazole with 80% hydrazine hydrate in presence of ethylene glycol. The structure of this compound was assigned on the basis of analytical and spectral data i.e. IR, NMR and Mass spectral data.

EXPERIMENTAL

All melting points were determined in capillary tube and uncorrected. IR spectra were recorded in KBr pellets on a Bomen, MB 104 FT infrared spectrophotometer. The ¹H-NMR were obtained on a FT Gemino 60 (60MHz) spectrophotometer with tetramethyl silane as an internal standard. Mass spectra were recorded on a FTVG-7070H mass spectrophotometer using EI technique of 70ev. Microanalysis was performed on a Heracus CHN-O rapid analyser. All the reactions were monitored by thin layer chromatography carried out on 0.2 mm silica gel-Gplate using iodine vapors for detection.

2-Amino-6-chlorobenzothiazole

A mixture of P-chloro aniline(12.7gm)and acetic acid 20-30 ml and potassium thiocyanate(32gm)was taken in two necked round bottom flask. In another

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conical flask bromine in acetic acid(20ml)was taken. Temperature of both reaction mixtures was maintained at 0-5^oc by keeping in ice bath. Then bromine mixture was added drop by drop with constant stirring for 2-3 hours. The flask was kept for overnight. 30ml of acetic acid in 100ml water was added with stirring for half an hour. The mixture was transferred in 500ml beaker and neutralized by adding ammonia by maintaining temperature 0-5^oC. The separated product was filtered and recrystallised from DMF ethanol mixture.

m.p.192^oC, Found; C,45.62; H,2.70; N,15.20. C₇H₅N₂SCl Requires; C,45.65 H,2.72; N,15.22.

6-Chloro-2 Hydrazino Benzothiazole

2-Amino-6-chloro benzothiazole(1.92gm,0.001-mole), 4.5ml of hydrazine hydrate in 5-10ml of ethylene glycol was taken in a round bottom flask.2ml

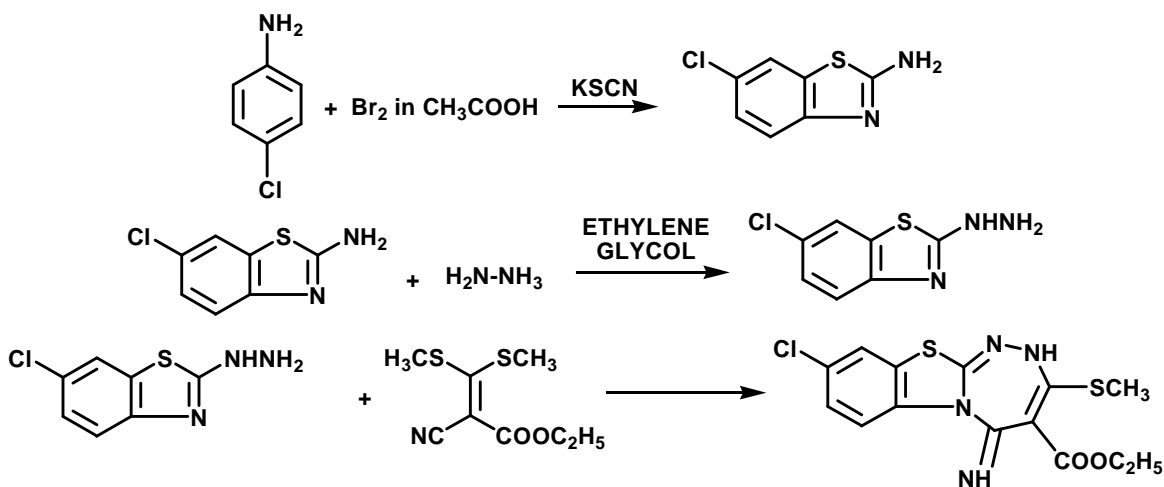
of concentration HCl was added with constant stirring. The reaction mixture was refluxed on oil bath for 2 hours maintaining temperature and poured in ice cold water. The separated solid product was filtered, washed with water and recrystallised by ethanol.

m.p.268^oC , Found; C,42.20; H,2.99; N,21.08. C₃H₆N₃SCl Requires; C,42.21; H,3.01.; N,21.10.1.99gm (0.01mole) Of 6-chloro-2-hydrazino benzothiazole and 2.21gm(o.01mole) of ethyl - 2-cyano-3,3-bisthiomethyl thioacrylate

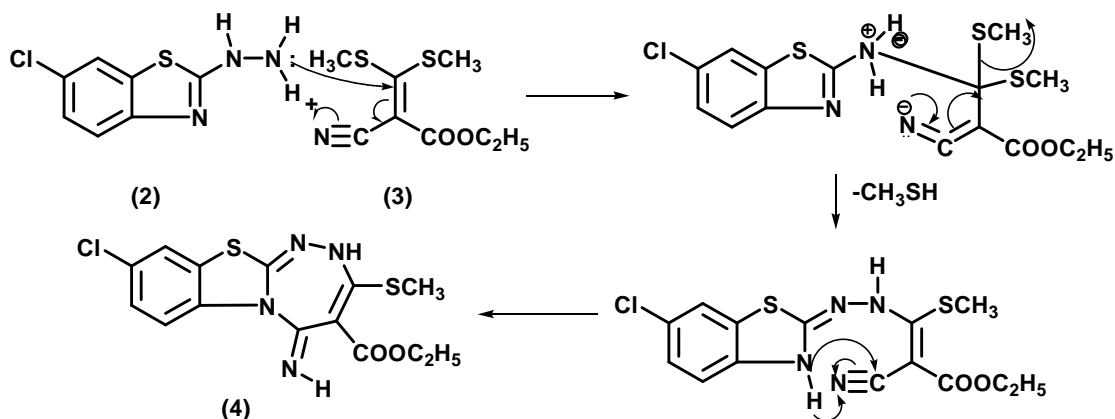
9-chloro-4-ethyl carboxylate-5-imino-3-thiomethyl benzothiazolo[2,3-c]-1,2,4-triazepine

A mixture of m.p.156^oC, IR(cm-1,KBr) 3398cm-1 (NH), 3323cm-1 (=NH imino group), 1701cm-1 (c=o), 1257cm-1(C-O)stretch). Found; C,47.85; H,3.96; N,15.93. C₁₄H₁₄N₄O₂S₂Cl Requires; C,47.86; H,3.98; N,15.95.

Scheme :



Mechanism :



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