

Synthesis of 4-chloro-3-ethyl-1-methyl-N-[1,2,3-thiadiazole]1Hpyrazole-5-carboxamide

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Abstract- Title molecule has been synthesized by chlorination of 1-Methyl-3-ethyl-4-chloro-Pyrazole-5-Carboxylic acid [a] to its acid chloride[b] and followed by condensation with 5-Amino-1,2,3-thiadiazole[c]. The above product[d] has pesticidal activity

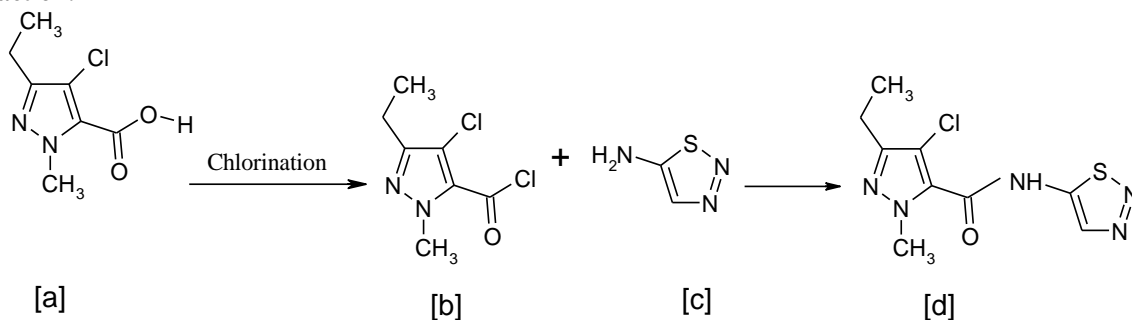
Index Terms- Pyrazole carboxylic acid , Amino thiadiazole , Carboxamide , Pesticidal activity

I. INTRODUCTION

Development of crop-protection molecules with unique modes of action is essential to combat widespread insecticide resistance. Heterocycles bearing a pyrazole or 1,2,3-thiadiazole moiety are reported to show pesticidal activity. In addition, the *N*-bridged heterocycles derived from 1-Methyl-3-ethyl-4-chloro-Pyrazole-5-Carboxylic acid have applications in

the field of medicine, agriculture and industry. 1,2,3-Thiadiazoles exhibit broad spectrum of pesticidal activities, Many pyrazole carboxamide derivatives are well known to possess a wide range of bioactivities and are often employed as fungicidal, antiviral and regulating activities for plant protection in agriculture. Some of them are employed as commercial insecticides , herbicides and fungicides. Dozens of pyrazole products are available and widely used as fungicides, antiviral agents, analgesic agents, insecticides and herbicides. In order to discover novel active compounds for use in agriculture, we sought to combine the active structures of thiadiazole and pyrazole to design and synthesize a class of novel pyrazole carboxamide derivatives. The synthetic route is shown in Scheme 1. The compounds is characterized by IR, NMR and LCMS analysis.

Chemical Reaction:



Experimental:

[A] Materials: Thionyl chloride (Sd Fine), Diethylformamide (DMF) (Sd Fine), Ethylene Dichloride (EDC) (Sd Fine) , Tri ethyl amine (Alkyl Amine Chemicals Ltd.) , N-Methyl-3-ethyl-4-chloro pyrazole-5-carboxylic acid (Commercial grade) and 5-Amino-1,2,3-thiadiazole (Commercial Grade) has been used in the reaction.

[B] Method:

Step : 01

EDC 50 ml was charged in to 100 ml RBF fitted mechanical stirrer, condenser outlet was connected to 20 % Caustic solution. Charged N-Methyl-3-ethyl-4-chloro pyrazole-5-carboxylic acid (1.0 gm-mole) followed by catalytic amount of DMF. Thionyl chloride (3.0 gm-mole) was added to the reaction mass under stirring in 4 hrs at temperature 75 °C. After addition of thionyl chloride reaction was continued for 3 hrs and excess thionyl chloride was distilled under vacuum. The product

N-Methyl-3-ethyl-4-chloro pyrazole-5-carboxylic acid chloride was isolated having purity >95% and used for next step.

Step : 02

Ethane Dichloride (EDC) 100 ml , 5-Amino-1,2,3-thiadiazole (1.0 gm mol) [c] and Tri ethyl amine (TEA) (1.1 gm-mole) was added to RBF fitted with Mechanical stirrer and condenser. The above reaction mass was cooled to 0 °C. The acid chloride (from step:01) was added in 2.0 hrs by maintaining reaction mass temp. 0 to 5.0 °C .Further reaction was continued for 3 hrs at temp. 0 to 5°C. At the end, reaction mass was filtered and from mother liquor EDC was distilled under vacuum and bottom residue was cooled to 0 °C and product [d] was isolated by filtration and crystallized from EDC. Purity of the product >95.0% having over all yield is 60.0%.

II. RESULTS AND DISCUSSION

The titled compound has been synthesized according to the procedures as given in the experimental section. The physical constants like melting point and solubility has been determined for the intermediate as well as final product. The compound has been characterized by IR and ¹H NMR and LCMS. The final product is grey color solid having melting point 176 - 178.0 °C.

III. CONCLUSIONS

We have synthesized the compound 4-chloro-3-ethyl-1-methyl-N-[1,2,3-thiadiazole]1Hpyrazole-5-carboxamide[d], confirmed the structure by instrumental analysis: NMR, FT-IR and LCMS. This product has unique combination of pyrazole and thiadiazole ring tested for its pesticidal effects.

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