Research Article

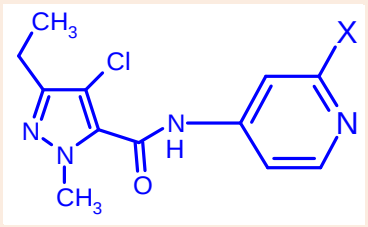
# Synthesis of Novel Pyrazole Amide Derivatives Containing a Pyridine Moiety

Pramod Kumar Sahu*, Ajeet Singh Tomar, Samson Waghmare and Bhupesh S Samant

Godrej Agrovet Ltd., R& D Department , Pirojshanagar , Vikhroli (E), Mumbai - 400079, India

**Abstract**

Title molecules have been synthesized by chlorination of 1-Methyl-3-ethyl-4-chloro-Pyrazole-5-Carboxylic acid [i] to it's acid chloride[ii] and followed by condensation with 2-methoxy-4-amino pyridine and 2-chloro-4-amino pyridine [iii]. The above product[iv] has pesticidal activity.



**Keywords:** Pyrazole carboxylic acid , Chloro and Methoxy Amino Pyridine, Acid chloride, Carboxamide , Pesticidal activity

***Correspondence**
Pramod Kumar Sahu
Email: pramodkr.sahu@godrejagrovet.com

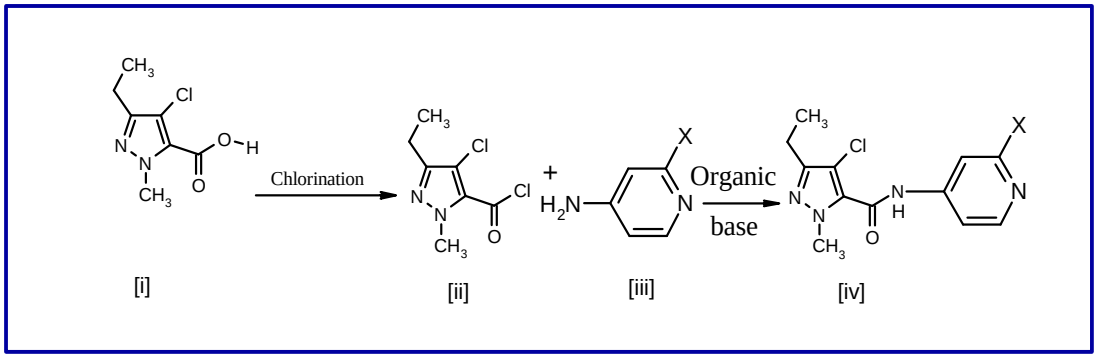
## Introduction

Pyrazole and substituted pyridine or combine of both derivative compounds have attracted great interest in agrochemical field. Heterocycles bearing a pyrazole and substituted pyridine 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 multiple applications in medicine and agriculture field. Pyrazole derivatives were present in numerous herbicides [1] , fungicides [2], insecticides [3] , pesticides [4] and dyestuffs [5] .

In order to discover novel active compounds for use in agriculture, we thought to combine the active structures of substituted pyridine and pyrazole to design and synthesize a class of novel pyrazole carboxamide derivatives. The synthetic route is shown in **Scheme 1**. The compounds have been characterized by IR, NMR and LCMS analysis.

## Chemical Reaction:

**(Scheme 1)**




X → $OCH_3$ ( iv-a) and Cl ( iv-b)

## Experimental:

### *Materials and Reagents:*

Thionyl chloride ( Sd Fine), Diemthylformamide (DMF) (Sd Fine), Ethylene dichloride (Sd Fine) , Tri ethyl amine ( Alkyl Amine Chemicals Ltd.) , N-Methyl-3-ethyl-4-chloro pyrazole-5-carboxylic acid ( Commercial grade) , 2-Methoxy-4-amino pyridine , 2-Chloro-4-amino pyridine (Commercial grade) has been used in the reaction.

### *Method:*

**Step 01: Preparation of N-Methyl-3-ethyl pyrazole-5-carboxy acid chloride**

Ethane dichloride (EDC) (75 ml) was charged in to 250 ml round bottom flask fitted with mechanical stirrer, condenser outlet was connected to 20 % caustic solution. Added N-methyl-3-ethyl-4-chloro pyrazole-5-carboxylic acid ( i ) (0.125 gm-mole) followed by catalytic amount of N,N-dimethyl formamide. Thionyl chloride (0.375 gm-mole) was added to the reaction mass under stirring in 2 hrs at temperature 75.0 $^{O}$C. After addition of thionyl chloride reaction was continued for 3.0 hrs and excess thionyl chloride was distilled under vacuum. The product N-methyl-3-ethyl-4-chloro pyrazole-5-carboxylic acid chloride (ii) was isolated having purity >95% and used for next step.

**Step 02: Preparation of 4-chloro-3-ethyl-1-methyl-N-[2-methoxy-Pyridyl]1H pyrazole-5-carboxamide**

Ethane dichloride (EDC) (250 ml) , 2-methoxy -4- amino pyridine ( 0.125 gm mol) [iii] and tri ethyl amine (TEA) (0.155 gm-mole) was added to 250 ml round bottom flask fitted with mechanical stirrer and condenser. The above reaction mass was cooled to 5.0 $^{O}$C. The acid chloride ( ii ) from step:01 was added in 2.0 hrs by maintaining reaction mass temperature 5.0 to 15.0 $^{O}$C .Further reaction was continued for 6 hrs at temp. 15.0 to 20.0 $^{O}$C. At the end, reaction mass was filtered and from mother liquor EDC was distilled under vacuum and bottom residue was cooled to 0 $^{O}$C and product [iv] was isolated by filtration and crystallized from Methanol. Purity of the product >97.0%, having over all yield is 65.0%.

Similarly 4-chloro-3-ethyl-1-methyl-N-[2-Chloro-Pyridyl]1H pyrazole-5-carboxamide has been prepared in above method by reacting 2-chloro-4-amino pyridine (iii) with (ii) . Purity of the product is > 95.0%, having over all yield 53.0%.

## 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 (iv-a) has been characterized by IR and $H^1$ NMR and LCMS. The final product is light yellow color solid having melting point 110 - 112 $^{O}$C 4-chloro-3-ethyl-1-methyl-N-[2-methoxy-pyridyl]1H pyrazole-5-carboxamide ( iv-a) and 4-chloro-3-ethyl-1-methyl-N-[2-chloro-pyridyl]1H pyrazole-5-carboxamide (iv-b) is liquid syrup with light brown color, and instrumental analysis not done.

***Molecular formula:*** $C_{13}H_{15}ClN_4O_2$ (iv-a)

***Table 01: NMR Data***
1.249 – 1.287 ( t, 3H) ; 2.64 – 2.7 ( q, 2H) ; 3.95 ( s, 3H) ; 4.17 (s , 3H) ; 7.074 – 7.128 ( m, 2H) ; 8.11- 8.127 (d, 1H) ; 8.5 (s, 1H)

***Table 02: IR Data ( $cm^{-1}$)***
3452 ( -NH), 1730 ( -C=O) , 1511 ( - CNH) ,1335 ( - C-N)

***Table : 03 LCMC Data***
( m+1) → 295.34

***Molecular formula*:** $C_{12}H_{12}Cl_2N_4O$ ( iv-b) Syrup light brown liquid

## Conclusions:

We have synthesized the compound 4-chloro-3-ethyl-1-methyl-N-[2-Methoxy and chloro pyridyl]1Hpyrazole-5-carboxamide[iv-].Confirmed the structure by instrumental analysis: $H^1$NMR, IR and LCMS for compound ( iv-a) where X→ $OCH_3$ . This product has unique combination of pyrazole and pyridine ring having pesticidal effects.

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