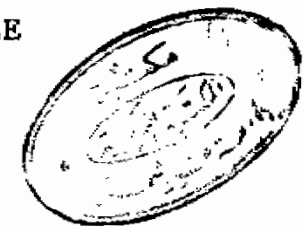
REACTIONS WITH
2-AMINO-3, 5-DICYANOPYRIDINES

A THESIS

In Partial Fulfilment of the Requirement

of

MASTER OF SCIENCE DEGREE



By

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Faculty of Science

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1984

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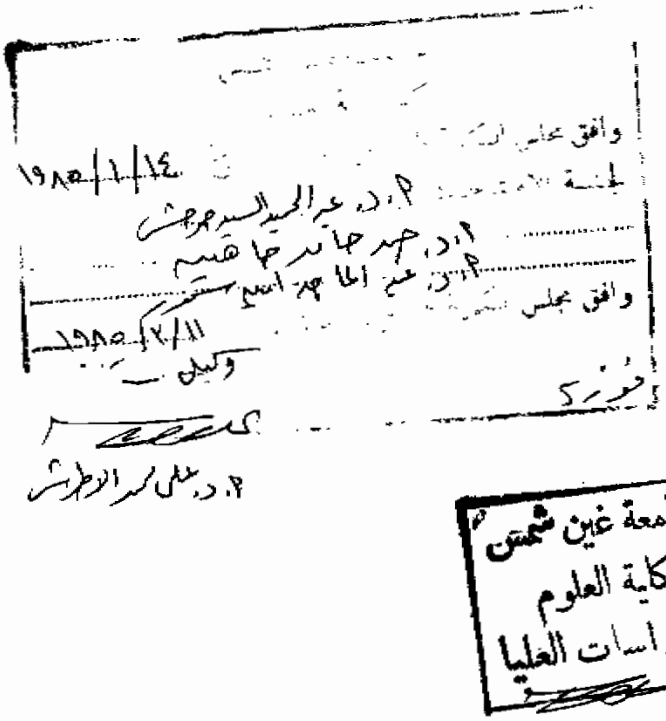

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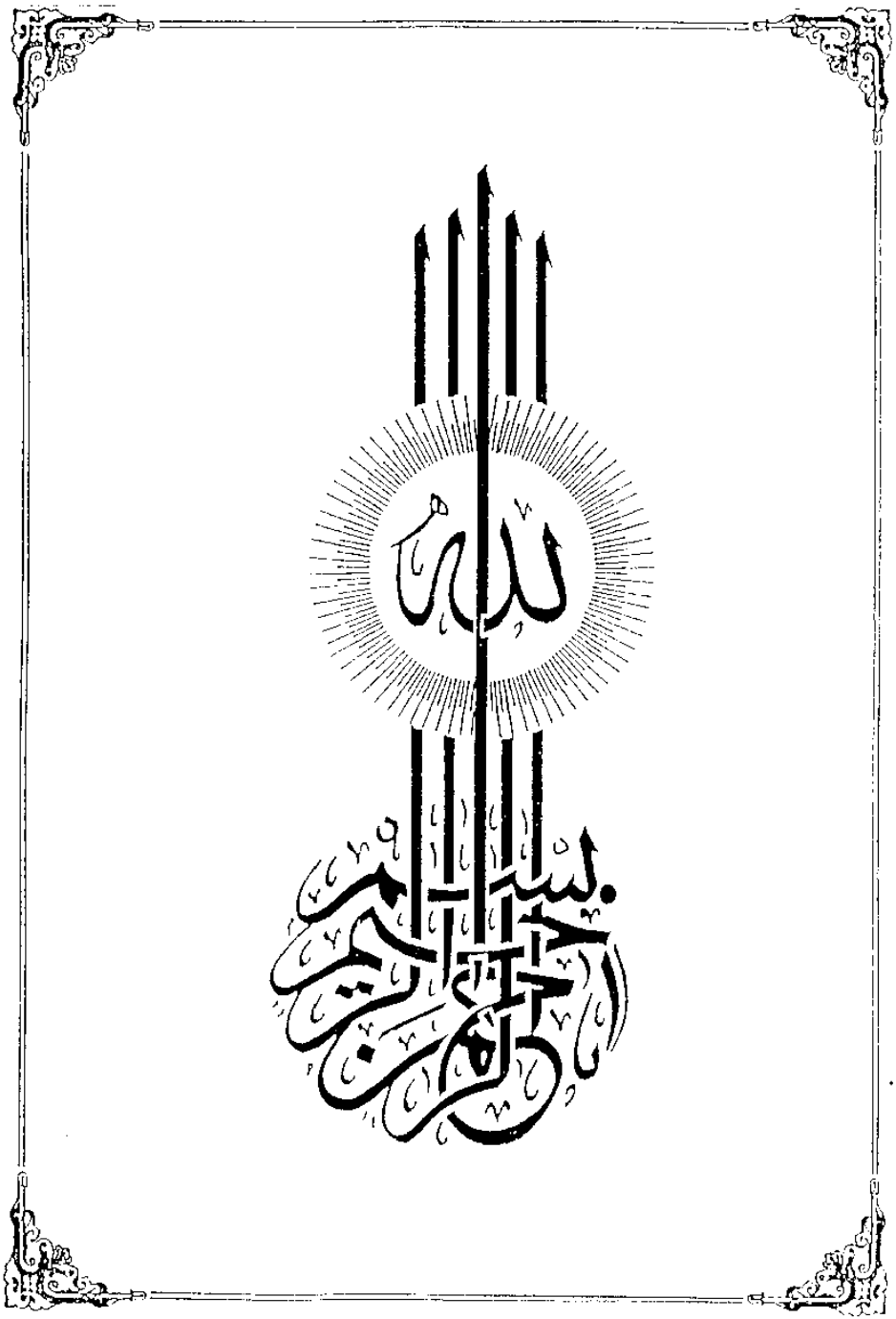

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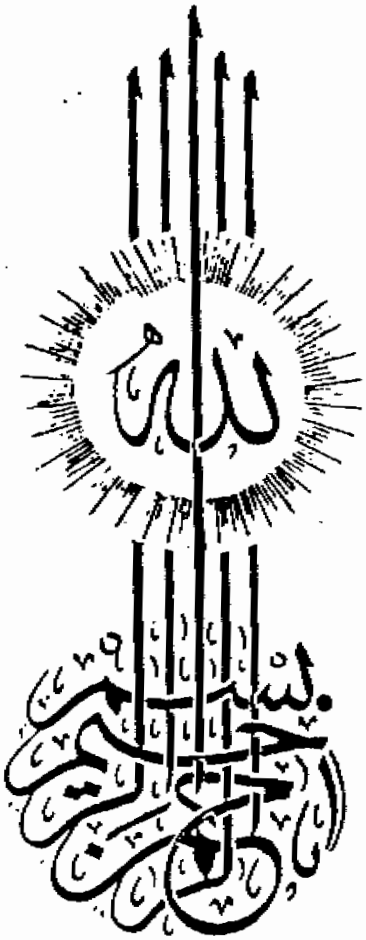

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REACTIONS WITH

2-AMINO-3, 5-DICYANOPYRIDINES

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TO MY FATHER

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N O T E

Besides the work carried out in this thesis, the candidate has attended post-graduate courses for one year in organic chemistry including the following topics:

1- Physico-organic chemistry.

2- Infrared, U.V., N.M.R. and Mass spectroscopy of organic molecules.

3- Free Radical reactions.

4- Quantum Mechanics.

5- Phosphorous compounds.

6- Polymer Chemistry.

7- Aromaticity.

8- Oxidation -Reduction Reactions of organic compounds.

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V I T A E

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SUMMARY OF THE ORIGINAL WORK

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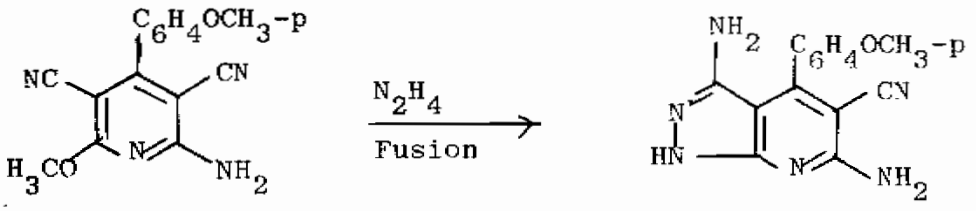
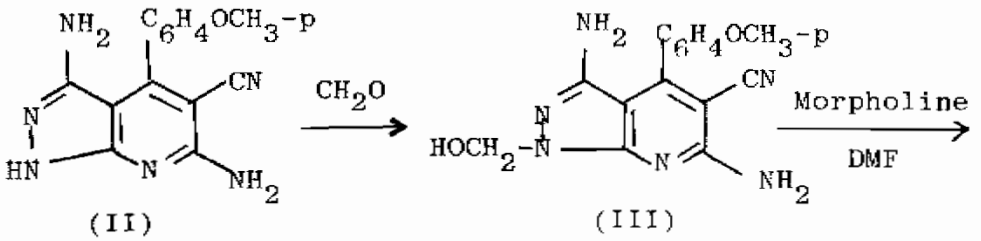
SUMMARY OF THE ORIGINAL WORK

Fusion of 2-amino-4-(p-anisyl)-5-cyano-6- methoxy-nicotinonitrile (I) with hydrazine hydrate afforded 3,6-diamino-4-(p-anisyl)-5-cyano-pyrazolo[3,4-b] pyridine (II).

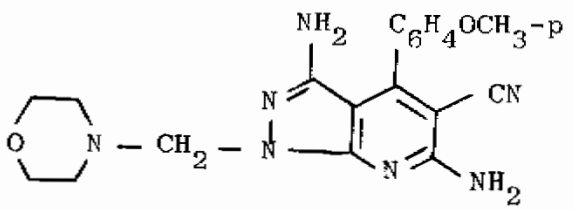


(I) (II)

Treatment of II with formaldehyde afforded 1-hydroxymethyl-3,6-diamino-4-(p-anisyl)-5-cyano-pyrazolo [3,4-b] pyridine (III). Heating III with morpholine in DMF gave Mannich base (IV).



(II) (III)



(IV)

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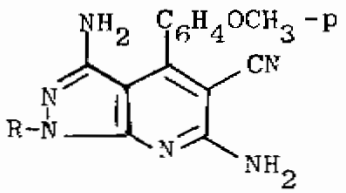
The reaction of 3,6-diamino-4-(p-anisyl)-5-cyano pyrazolo [3,4-b]pyridine (II) with dimethyl sulfate and ethyl bromoacetate led to the formation of N-alkylated products, 1-methyl-3,6-diamino-4-(p-anisyl)-5-cyanopyrazolo [3,4-b] pyridine (Va) and 3,6-diamino-4-(p-anisyl) -5-cyano-pyrazolo [3,4-b] pryidine-1-acetic acid ethyl ester (Vb), respectively. Vb on treatment with hydrazine hydrate or p-toluidine gave the corresponding hydrazide Vc and p-toluidide Vd, respectively.



(V)

a, R = CH_3

b, R = $CH_2COOC_2H_5$

c, R = $CH_2CONHNH_2$

d, R = $CH_2CONHC_6H_4CH_3$-p

The condensation of Vc with aromatic aldehydes namely benzaldehyde and p-chlorobenzaldehyde gave 3,6-diamino-4-(p-anisyl)-5-cyano-pyrazolo[3,4-b] pyridine-1-acetic acid benzylidenehydrazide (VIa) and 3,6-diamino-4-(p-anisyl)-5-cyano-pyrazolo [3,4-b] pyridine-1-acetic acid p-chlorobenzylidinehydrazide (VIb), respectively.

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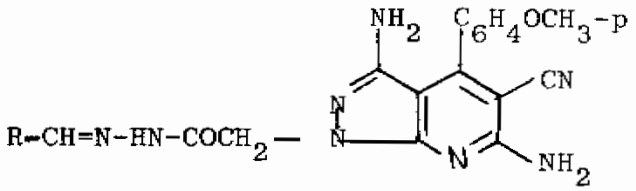
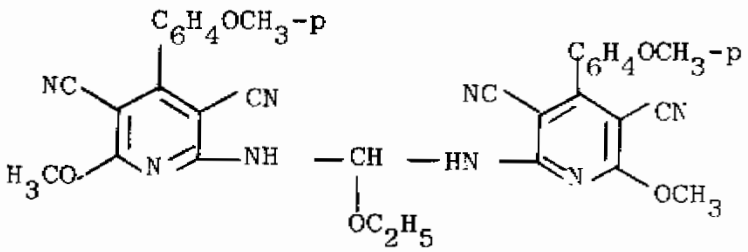


(VI)

a, R = C_6H_5

b, R = C_6H_4Cl-p

The reaction of triethylorthoformate with I or Vc led to the formation of bis- [2-imino-4-(p-anisyl) -5-cyano-6-methoxy-nictotinonitrile]ethoxymethane (VII) and 1- [(2'-methylene-4'-acetyl-5'-ethoxy)- Δ^{2}- 1,3,4 -oxadiazoline]-3-acetamido-6-amino-4-(p-anisyl)-5-cyano-pyrazolo [3,4-b] pyridine (VIII), respectively.



(VII)

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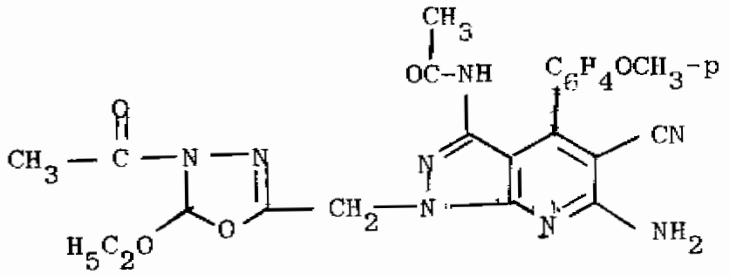
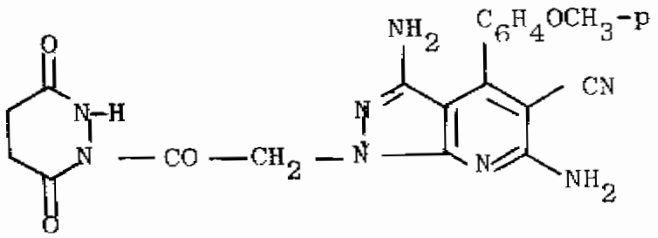


(VIII)

The action of succinic anhydride on Vc in glacial acetic acid was also undertaken, where IX was obtained .



IX

The reaction of 2-amino-4-(p-anisyl)-5-cyano-6-methoxy-nicotinonitrile (I) or 3,6-diamino-4-(p-anisyl)-5-cyano-pyrazolo [3,4-b] pyridine (II) with ethyl cyanoacetate in the presence of sodamide gave 4-amino-5-(p-anisyl)-3,6-dicyano-1,2-dihydro-7-methoxy-1, 8-naphthyridin-2-one (X) and XI, respectively.

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