



شبكة المعلومات الجامعية

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ





شبكة المعلومات الجامعية



شبكة المعلومات الجامعية

التوثيق الالكتروني والميكرو فيلم

جامعة عين شمس

التوثيق الالكتروني والميكروفيلم



نقسم بالله العظيم أن المادة التي تم توثيقها وتسجيلها
علي هذه الأفلام قد اعدت دون أية تغيرات



يجب أن

تحفظ هذه الأفلام بعيداً عن الغبار

في درجة حرارة من 15 – 20 مئوية ورطوبة نسبية من 20-40 %

To be kept away from dust in dry cool place of
15 – 25c and relative humidity 20-40 %



شبكة المعلومات الجامعية



بعض الوثائق الأصلية تالفة



شبكة المعلومات الجامعية



بالرسالة صفحات

لم ترد بالأصل

B 1.142

**UTILITY OF ENAMINONITRILES IN ORGANIC
SYNTHESIS, NEW ROUTES TO ARYL
SUBSTITUTED AZOLES.**

A Thesis Submitted

By

Farid Mohammed Sayed Mohammed Ahmed

B.Sc. (2003, very good)

As Partial Fulfillment Of The Requirement For The
Degree of M. Sc. In Organic Chemistry.

Department of Chemistry

Faculty of Science

El Minia University

Egypt

2006

ABSTRACT

Name: **Farid Mohammed Sayed Mohammed Ahmed**

Title of the M. Sc. Thesis:

**UTILITY OF ENAMINONITRILES IN ORGANIC SYNTHESIS ,NEW
ROUTES TO ARYL SUBSTITUTED AZOLES.**

Degree. (M. Sc.) thesis, Faculty Of Science, El Minia University. (2006)

This work has been carried out to investigate the possible utility of **enaminonitriles and 2-arylhydrazononitriles** and to define the synthetic potential of the latter hydrazones especially as a source of **aminopyrazoles and aminotriazoles**.

Supervisors:

Prof. Dr. Mohamed Hilmy Elnagdi .

Prof. Dr. Kamal Usef Sadek .

Prof. Dr.

Chairman of the Chemistry Department
Faculty of Science, El Minia University.

Acknowledgements

I would like to express my sincere gratitude to professor **Dr. Mohammed H. Elnagdi**, for his invaluable advice, encouragement, and for always being ready for discussion through my work, he was always there when needed, and try to show me that I am capable of doing more than I think I can do. He has proven himself to be a real hardworking person who deserves everybody's appreciation.

My deepest thanks to professor Dr. **Kamal U. Sadek**, I would like to thank him profusely for all the times he stood by me, for all he taught to me, and for sharing the benefit of him life experiences, and finally in preparing this thesis. They were my role model in everything they did.

Finally thanks are also due **Dean** of faculty of Science **Professor Dr. Ezzat Mahmoud Fadelallah**, **Chairman** of department of chemistry, and the college of El Minia university. Faculty of Science, Chemistry Department, which is sure behind this success.

CONTENTES

ENGLISH SUMMARY

1- INTRODUCTION

Chemistry of carbo- functionally Substituted hydrazones

1.1.Introduction	1
1.2.Synthetic Approaches	2
1.2.1. Condensation of Functional Aldehydes and Ketones with Hydrazones	2
1.2.2.Coupling active Methylenes with Aromatic and Hetero aromatic diazonium salts.	3
1.3.Structural Investigation.	9
1.4.Chemical Reactivity	11
1.4.1.Introduction	11
1.4.2. Reactivity toward electrophilic reagents.	11
1.4.2.1.Reaction with carbon electrophiles.	11
1.4.2.2.Reaction with nitrogen electrophiles.	18
1.4.2.3.Reaction with halogen electrophiles.	20
1.4.3.Reactivity toward nucleophilic reagents.	23
1.4.3.1.Introduction	23
1.4.3.2.Reaction with carbon nucleophiles.	23
1.4.3.3.Reaction with nitrogen nucleophiles.	28

2-SPECIAL WORK 35

UTILITY OF ENAMINONITRILES IN ORGANIC SYNTHESIS , NEW ROUTES TO ARYL SUBSTITUTED AZOLES.

2.1.INTRODUCTION.	35
2.2.RESULTS AND DISCUSSION	36
2.3.EXPERIMENTAL.	43

REFERENCES 52

FIGURES OF TYPICAL SPECTROSCOPIC CHARTS 65

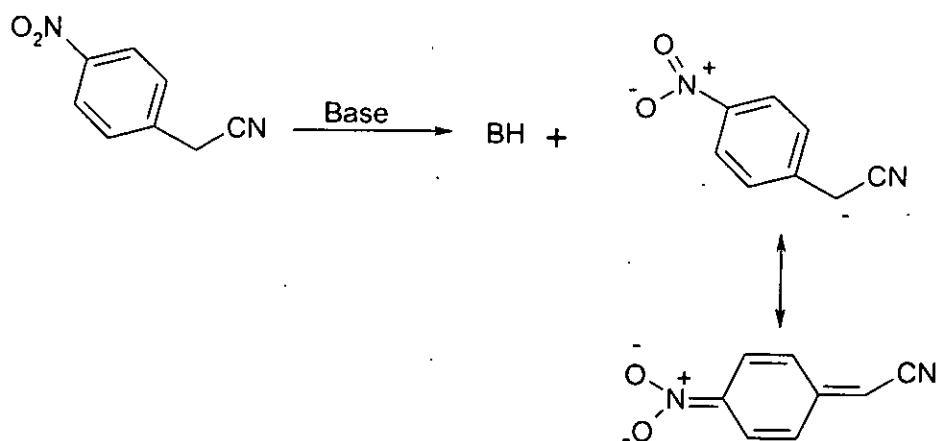
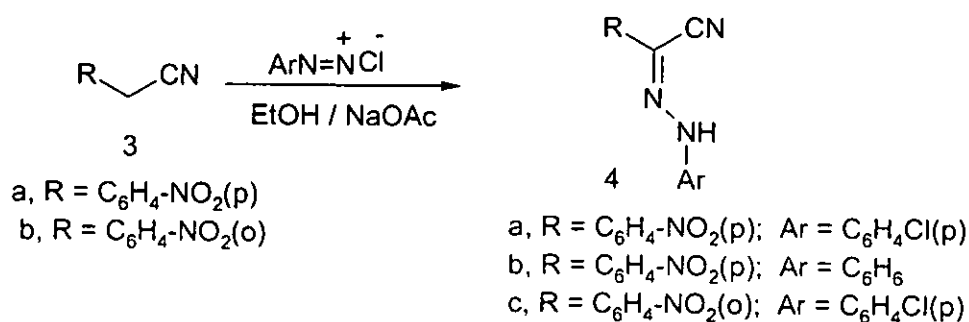
ARABIC SUMMARY 105

ENGLISH SUMMARY

ENGLISH SUMMARY

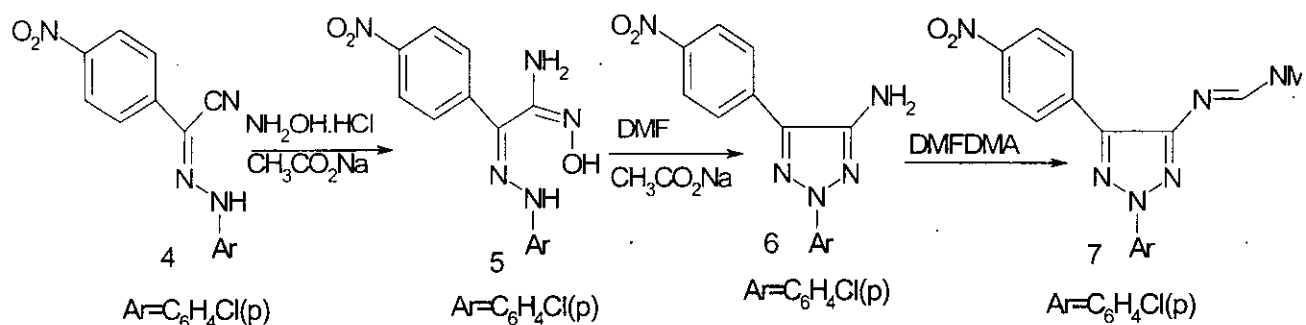
UTILITY OF ENAMINONITRILES IN ORGANIC SYNTHESIS, NEW ROUTES TO ARYL SUBSTITUTED AZOLES.

Coupling of P- or O-nitrobenzylcyanide(**3a,b**) with aromatic-diazonium salts yield (**4a-c**).[Scheme1]



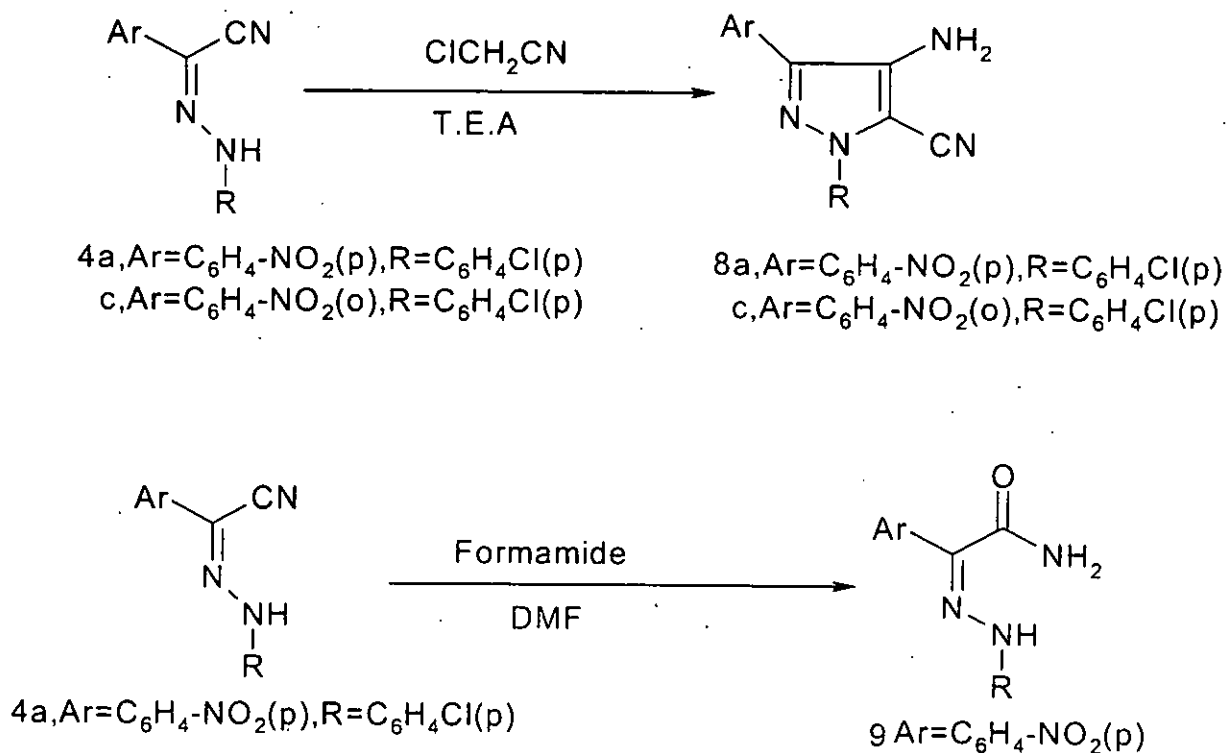
Scheme 1

The reaction of arylhydrazone (**4a,d**) with hydroxylamine hydrochloride in acetic acid (or ethanol) in the presence of anhydrous sodium acetate yields amidoxime (**5**); structure of which was established based on the presence of protons for aminoxime moiety at δ 6.06, 5.6 ppm respectively. Also, IR revealed the absence of a signal for cyano group indicating involvement of the latter in the reaction, aminoximes (**5**) smoothly cyclized into 2-substituted -5-p-nitrophenyl-1,2,3-triazole-4-amine (**6**) up on refluxing in DMF in the presence of anhydrous sodium acetate, to our knowledge this is first reported synthesis of 2-substituted 1,2,3-triazole-4-amines as reported synthetic approaches to these compound leads only to 1-substituted-1,2,3-triazoleamine. Condensing, the formed triazole(**6**) with dimethylformalidedimethylAcetal (DMFDMA) results in the formation of enamine (**7**) [Scheme 2].



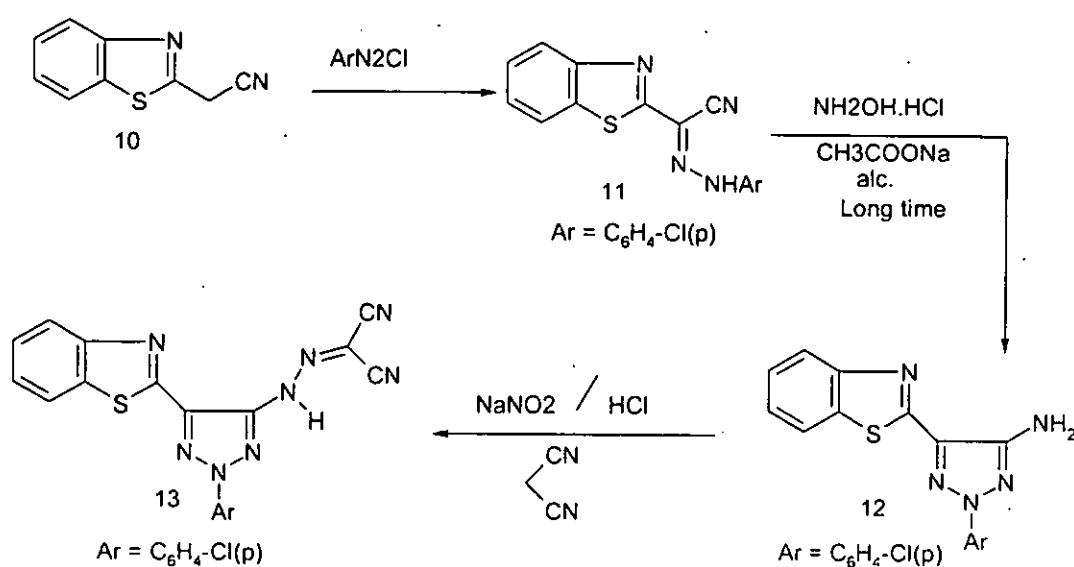
Scheme 2

Refluxing (**4a,c**) with chloroacetonitrile, in triethylamine enabled synthesis of targeted molecules (**8a,c**) in good yields. Cyano group in compound (**4a**) could be hydrolysed by refluxing (**4a**) with formamide in dimethylformamide (DMF) yielding The amide (**9**). [Scheme 3]



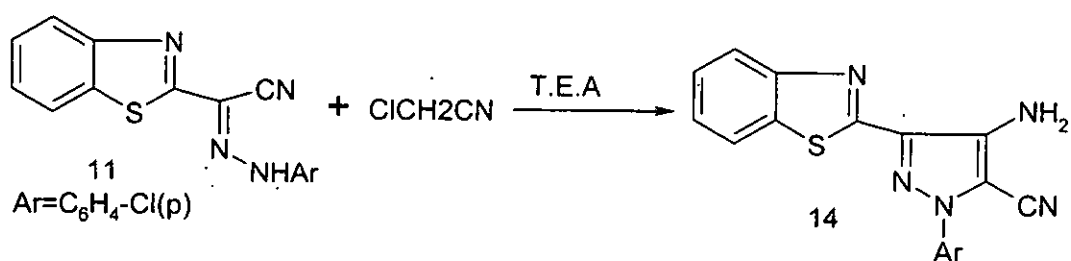
Scheme 3

Cyanomethylbenzthiazole(10) coupled readily with aromaticdiazonium salts to yield(11),which reacted with Hydroxylamine hydrochloride in alchool and anhydrous sodium acetate for long time yielding 4-amino-1,2,3-triazole (12), aminotriazole product coupled with malononitrile yielding (13) [c.f.Scheme 4].



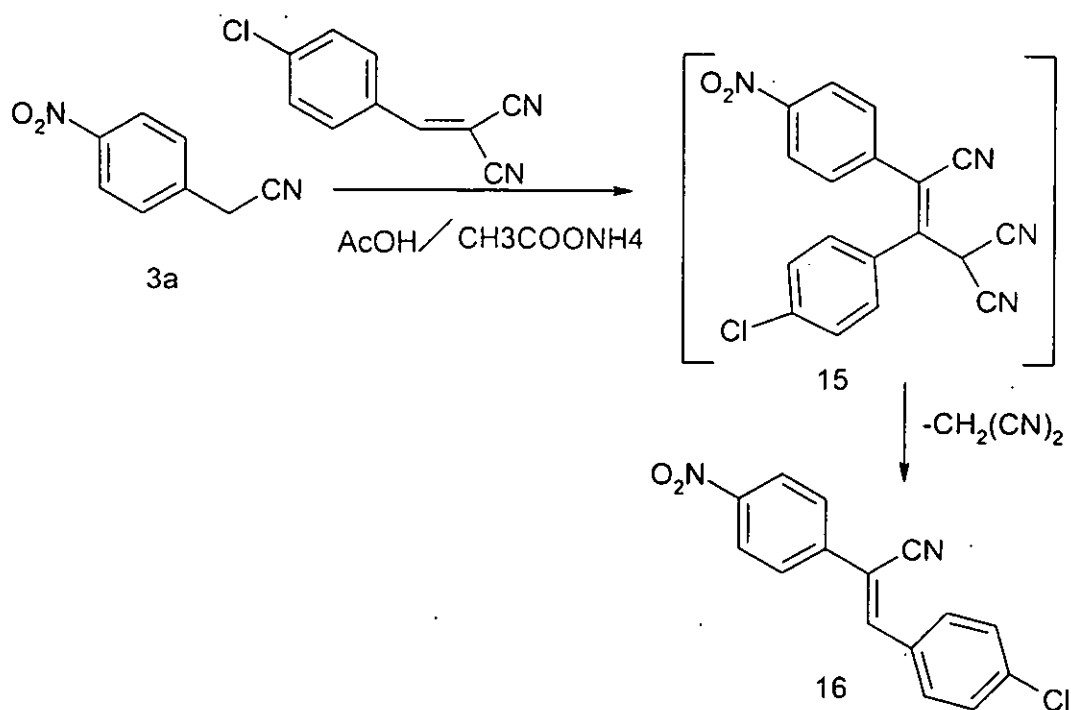
Scheme 4

The reaction of (11) with chloroacetonitriles in triethylamine yield aminopyrazole (14) in good yield [c.f. Scheme 5].



Scheme 5

p-Nitrobenzylcyanide (**3a**) reacted readily with p-chlorobenzylidenemalononitrile in acetic acid and amm. acetate yielding (**16**) via intermediate (**15**) [c.f. Scheme 6].



Scheme 6