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شبكة المعلومات الجامعية

التوثيق الالكتروني والميكروفيلم

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التوثيق الالكتروني والميكروفيلم

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بالرسالة صفحات لم ترد بالاصل

THESIS
On

New trends in the synthesis of Heterocyclic Compounds through Unsaturated nitriles

by

Emad Hilmy El-Gawish
B.Sc. (Chemistry), 1987

for
The Partial fulfilment of the Degree of Master of Science (Chemistry)

supervised by

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"Nothing from me except with help of ALLAH".

NOTES

Beside the work carried out in this thesis, the candidate Emad Hilmy Ali Mohamed has pursued post graduate studies for the partial fulfilment of the M.Sc. degree in the following topics:

1- Natural products.

2- Organic synthesis.

3- Stereochemistry.

4- Advanced physical organic chemistry.

5- New organic reactions.

6- Theoretical organic chemistry.

7- Special course

8- Statistics.

He has also passed successfully an examination in the above mentioned topics.

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Head of chemistry Department.

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Summary

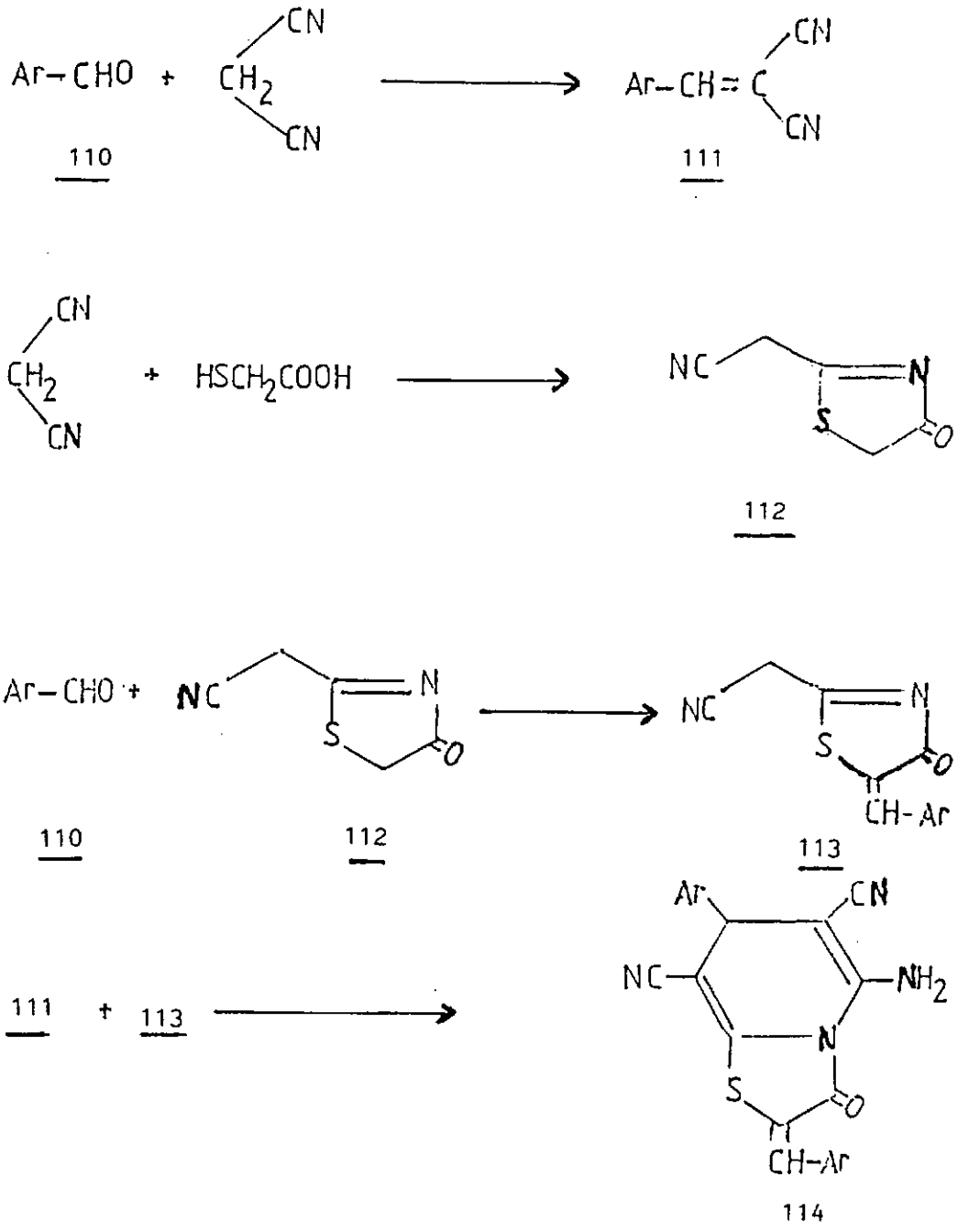
of the Original Work

PART I

SYNTHESIS THROUGH REACTIONS OF NUCLEOPHILES WITH ACRYLONITRILES; A DIRECT ONE-POT SYNTHESIS OF THIAZOLOPYRIDINES

In conjuction with our previous studies for the synthesis of heterocyclic compounds via multi-componant one-flask reactions. It has been found that the ternary condensation of aldehyde (110_{a-n}), malononitrile and thioglycolic acid in a 2:2:1 molar ratio in ethanol and in the presence of piperidine as a basic catalyst afforded (114_{a-n})(cf. Scheme 1).

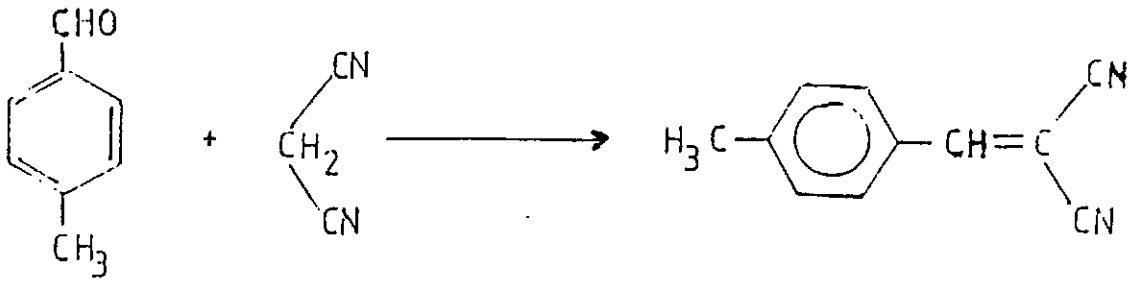
In order to investigate the possible utility of this one-pot method to prepare polyfunctionally thiazolopyridines having two different aryl moieties, we succeeded in preparing thiazolopyridines (115_{a-h}) by using one mole of p-tolualdehyde and one mole of aryl aldehyde insteadof the two molos of aldehyde, malononitriles two moles and two moles of thioglycolic acid under the previous conditions (cf. Scheme 2).



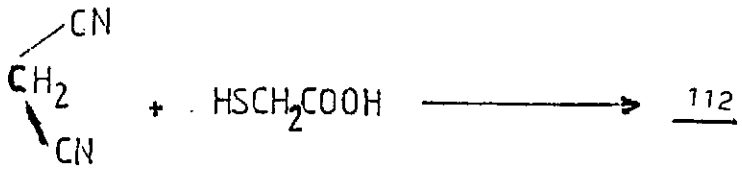
114	Ar
a	3-Pyridyl
b	2-Thienyl
c	2-Furyl
d	1-Naphthyl
e	2-Methoxyphenyl
f	2-Chlorophenyl
g	4-Nitrophenyl

114	Ar
h	4-Methoxyphenyl
i	4-Chlorophenyl
j	C_6H_4-CH_3-p
k	Phenyl
l	2,4-Dimethoxyphenyl
m	2,5-Dimethoxyphenyl
n	3,4-Dimethoxyphenyl

Scheme 1

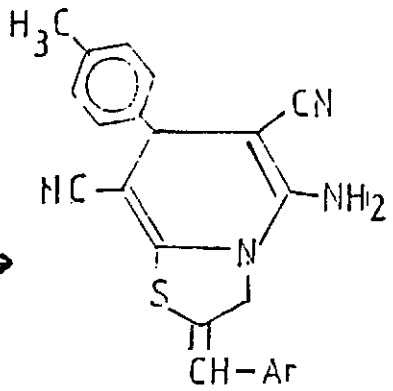


111



112

110 + 112 ⟶ 113



111 + 113 ⟶

115

115	Ar
a	3-Pyridyl
b	Phenyl
c	2-Chlorophenyl
d	2-Methoxyphenyl
e	2-Furyl
f	1-Naphthyl
g	4-Methoxyphenyl
h	2,5-Dimethoxyphenyl

Scheme 2

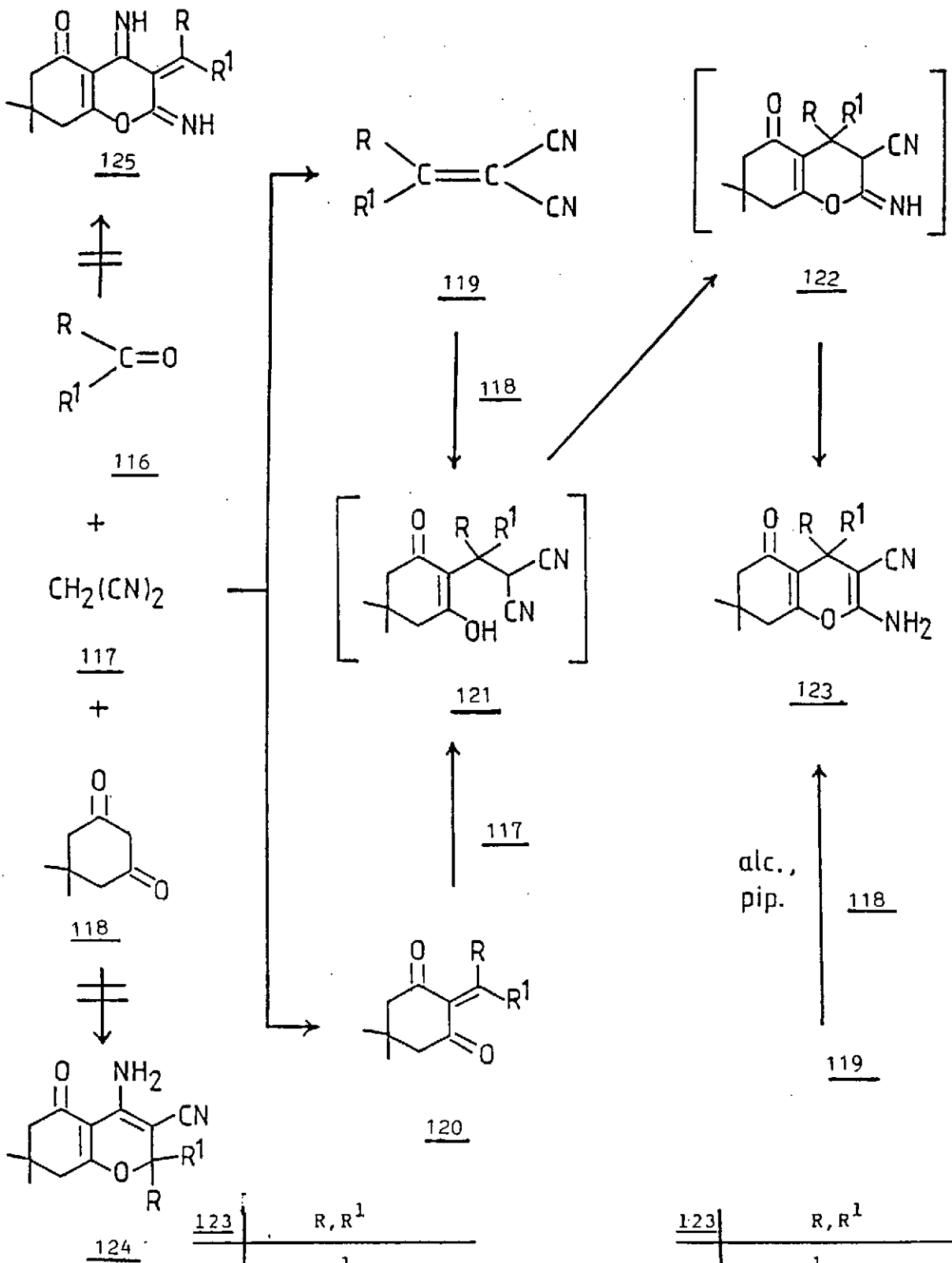
PART II

SYNTHESIS OF HETEROCYCLES THROUGH REACTIONS OF NUCLEOPHILES WITH ACRYLONITRILES, SYNTHESIS OF SOME NEW FUNCTIONALIZED BENZO[b]PYRANS AND INDENO[1,2-b]PYRANS OF POTENTIAL BIOLOGICAL ACTIVITY

In conjuction with the previous work. It has been found that stirring an equimolar ratio of aldehyde or ketone (116_{a-k}), malononitrile (117) and 5,5-dimethyl-1,3-cyclohexanedione (118) and a catalytic amount of piperidine in ethanol at room temperature gaves a solid product whose structure was as assumed to (123)(cf. Scheme 3). Two isomeric structures 124 and 125 seemed possible for the reaction product were ruled out based on its spectral data (cf. Experimental).

The ternary condensation of isatin (126), malononitrile (117) and 5,5-dimethyl-1,3-cyclohexanedione (118) in ethanolic/pipridine solution afforded (127)(cf. Scheme 4).

1,3-indandione (129) reacts with malononitrile (117) and the carbonyl compounds (116_{a-h}) under the same previous conditions afforded the corresponding-2H-pyran moeity in (130_{a-h})(cf. Scheme 5).



123	R, R^1
a	R=H, R^1=4-Br-C_6H_4
b	R=H, R^1=2-Chlorophenyl
c	R=H, R^1=2-Methoxyphenyl
d	R=H, R^1=3,4-Dimethoxyphenyl
e	R=H, R^1=1-Naphthyl
f	R=H, R^1=Isopropyl

123	R, R^1
g	R=H, R^1=Pentyl
h	R=H, R^1=2-Thienyl
i	R=H, R^1=2-Furyl
j	R=CH_3, R^1=4-Nitrophenyl
k	R=CH_3, R^1=2-Hydroxyphenyl

Scheme 3