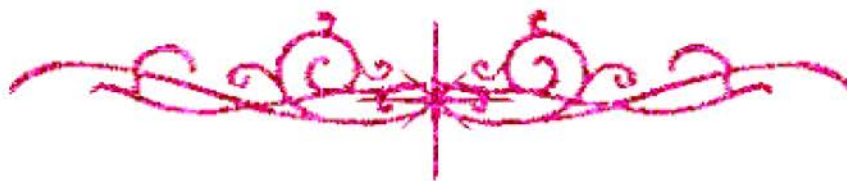


بسم الله الرحمن الرحيم





شبكة المعلومات الجامعية التوثيق الالكتروني والميكروفيلم



جامعة عين شمس

التوثيق الإلكتروني والميكروفيلم

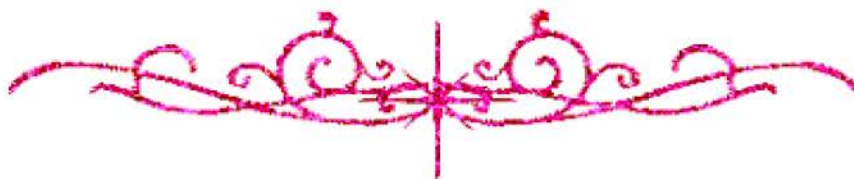
قسم

نقسم بالله العظيم أن المادة التي تم توثيقها وتسجيلها
علي هذه الأقراص المدمجة قد أعدت دون أية تغيرات



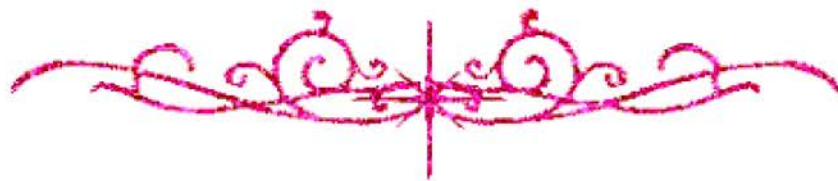
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تحفظ هذه الأقراص المدمجة بعيدا عن الغبار



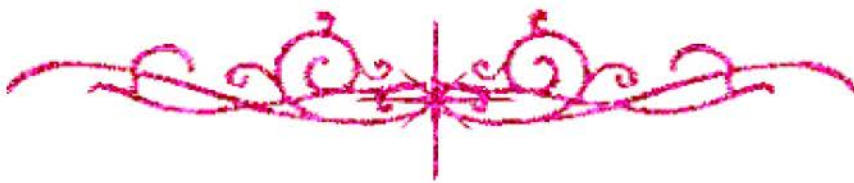


بالرسالة صفحات
لم ترد بالأصل





بعض الوثائق الأصلية تالفة



B 11014

**SYNTHESIS OF COMPOUNDS WITH
EXPECTED BIOLOGICAL ACTIVITY FROM
BENZOXAZOLES AND HORMONES**

Thesis

Submitted By

Mervat Mahmoud Abd El-Halim Hasan
M.Sc. 1995

For

The Degree of Ph.D.
In Organic Chemistry

Department of Chemistry
Faculty of Science
Cairo University

2002

APPROVAL SHEET FOR SUBMISSION

Title of [Ph.D.] Thesis: Synthesis of Compounds with Expected
Biological Activity from Benzoxazoles and
Hormones

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ABSTRACT

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Title of Thesis: Synthesis of Compounds with Expected Biological Activity
from Benzoxazoles and Hormones.

Degree: (Ph.D.) Thesis, in Organic Chemistry

This work has been carried out to investigate the reactivity of 2-benzoxazol-2-ylethannitrile (4) toward various chemical reagents to produce new heterocyclic ring attached or fused with benzoxazole moiety. Also, the reactivity of the aminopyrazole derivative (9) toward as variety of chemical reagent was studied. The work also has been carried out to investigate the reactivity of the steroidal hormones toward some alkyl hydrazinecarbdithioate derivatives to gives the corresponding hydrazones which react readily with the appropriate hydrazonoyl halide to give the corresponding steroidal azines.

Keywords:

Benzoxazolyl-2-acetcarbonitrile, Hydrazonoyl halides, pyrazolo[5,1-c]triazines, 2,3-Dihydro-1,3,4-thiadiazoles and Hormone.

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ACKNOWLEDGMENT

First of all, I would like to extend due praise and thanks to ALLAH that this work has been completed.

The author wishes to express her deepest gratitude to **Prof. Dr. Abdou Osman Abd El-Hamid**, Professor of Organic Chemistry, Faculty of Science, Cairo University, for suggesting the work, continuous help, valuable discussion, sincere guidance, precious advices, for his support through whole work and valuable criticism as well.

Thanks also are due to **Prof. Dr. S. H. Doss**, National Research Center, Dokki, Cairo, for his continuous help and support.

Deep thanks and gratitude refers also to **Prof. Dr. Victorin Beshara Baghos**, Professor of Organic Chemistry, Faculty of Science, Cairo University, for her advice and valuable help.

The author thanks the National Research Centre for financial support and facilities provided during this work.

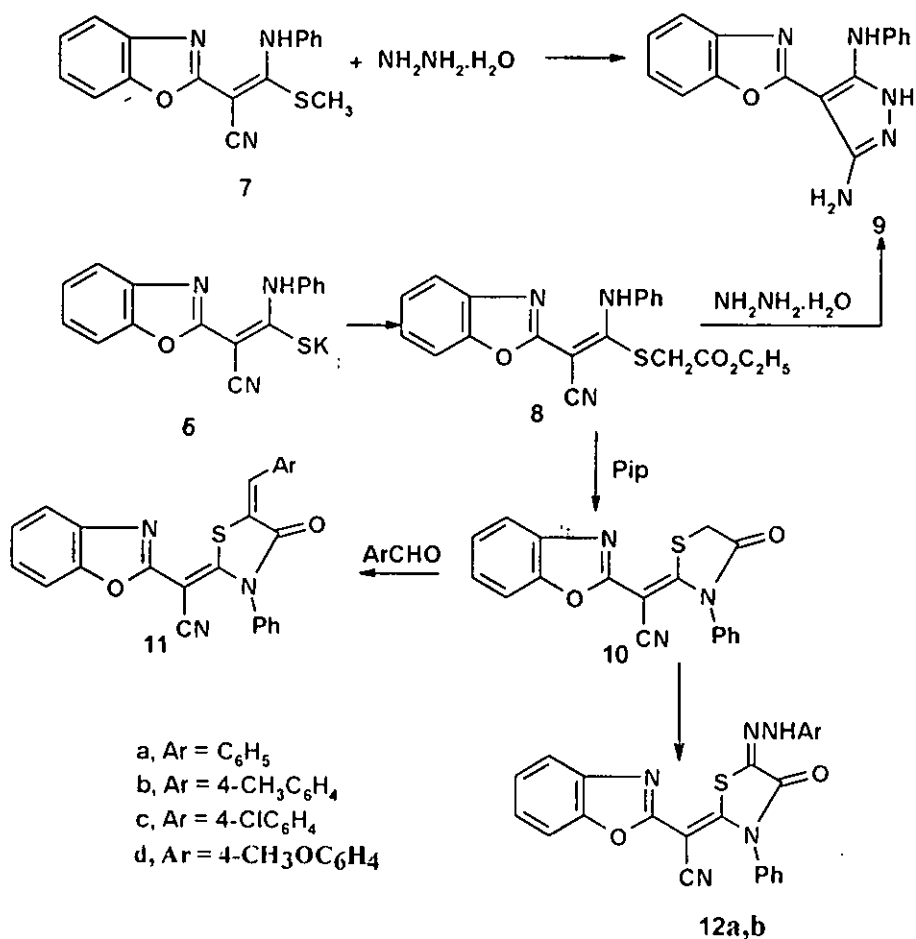
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ENGLISH SUMMARY

SUMMARY

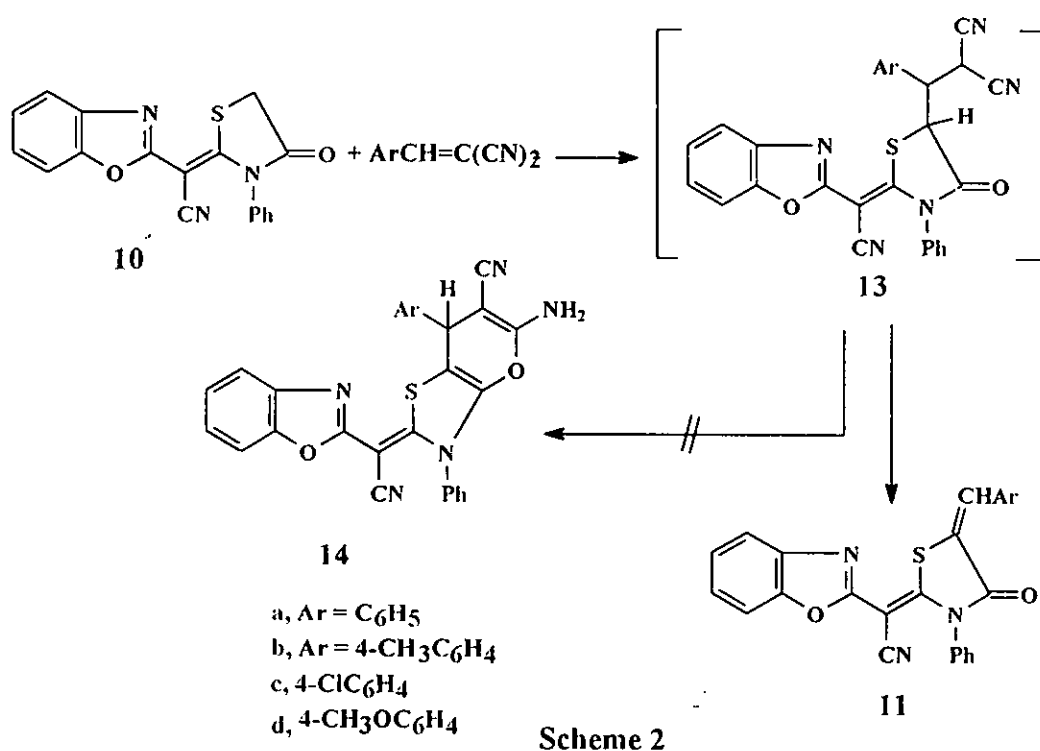
Thioanilide-2-benzoxazol-2-yl-3-(phenylamino)-3-thioxopropane-nitrile (**6**) reacts with ethyl chloroacetate in *N,N*-dimethylformamide containing potassium hydroxide to give the thioester **8**. Structure of **8** was confirmed on the basis of elemental analysis, spectral data and chemical transformation. Thus compound **8** reacts with either hydrazine hydrate or refluxed in ethanolic piperidine solution to give aminopyrazole **9** and thiazolone **10**, respectively (cf. Scheme 1).



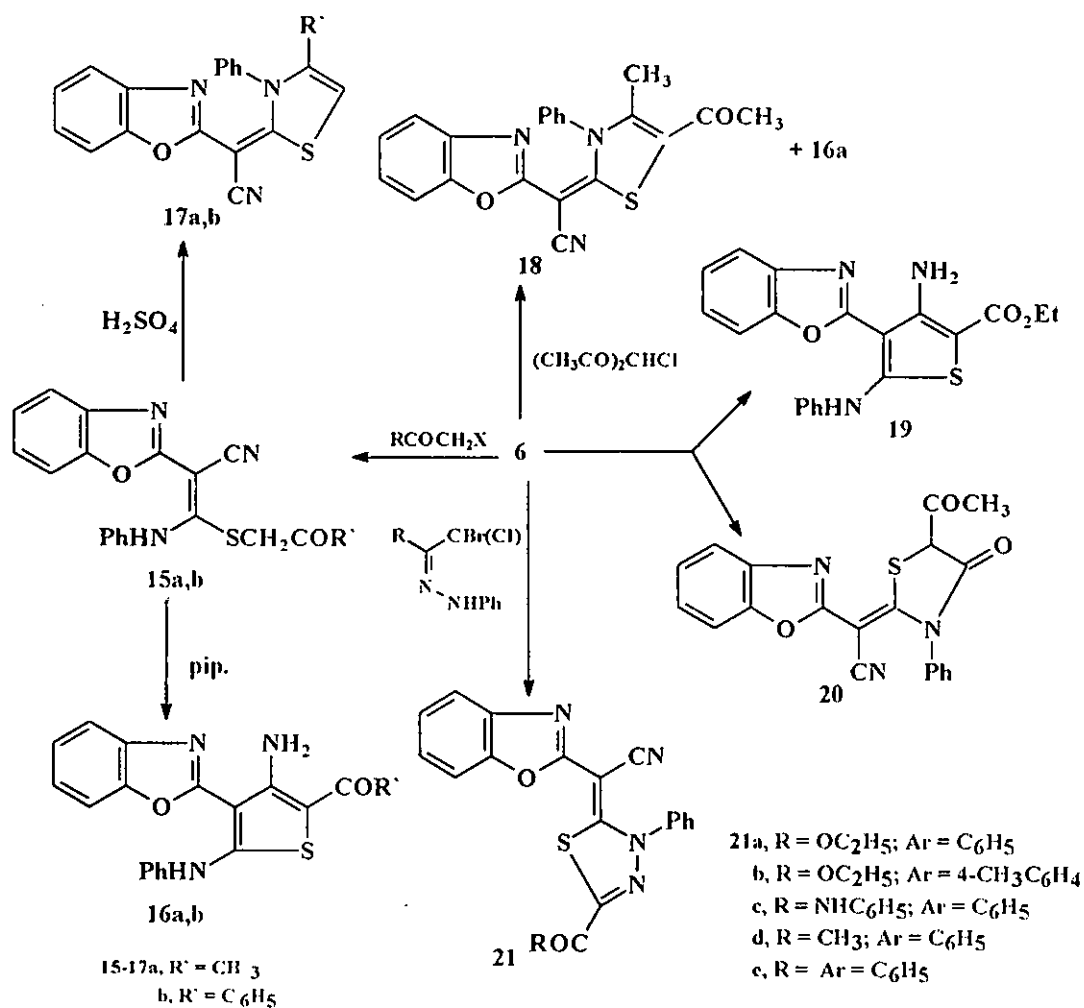
Scheme 1

Compound **10** reacted with the appropriate aromatic aldehyde, or arenediazonium chloride to give 2-benzoxazol-2-yl-2-[4-oxo-3-phenyl-5-(arylmethylene)(1,3-thiazolidin-2-ylidene)ethanenitrile (**11a-d**) and hydrazones **12a,b** (Scheme 1).

In contrast **10** reacted with substituted α -cyanocinnamonnitriles to give the product identical in all respects (mp., mixed mp., and spectral) with **11a-d**. The reaction mechanism was studied (cf. Scheme 2).



Also, **6** reacted with appropriate α -haloketone, α -haloester or hydrazonoyl halides in ethanolic potassium hydroxide to give thiophene, thiazole and 2,3-dihydro-1,3,4- thiadiazoline derivatives, respectively (cf. Scheme 3). Compound (2E)-2-benzoxazol-2-yl-3-(2-oxopropylthio)-3-(phenylamino) prop-2-enenitrile (**15a**) and (2E)-2-benzoxazol-2-yl-3-(2-oxo-2-phenylethylthio)-3-(phenylamino)prop-2-enenitrile (**15b**) can be cyclized to give thiophene derivatives **16a**, **16b** or thiazoles **17a**, **17b** depending on the reaction condition (cf. Scheme 3).

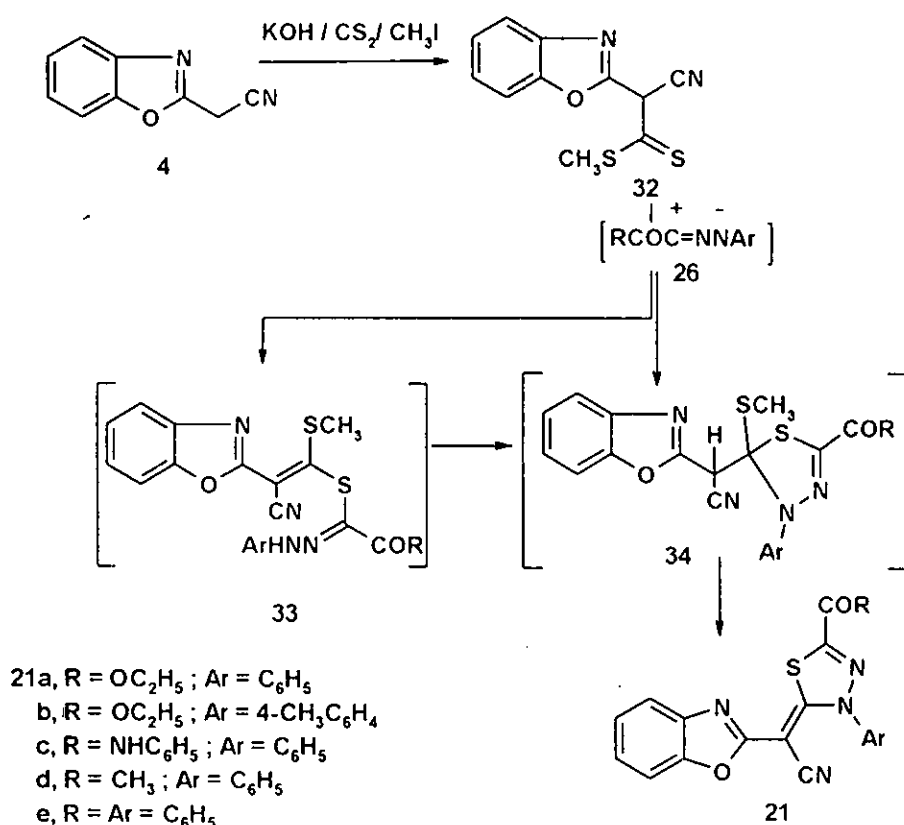


Scheme 3

Also, 6 reacted with the appropriate 3-chloropentan-2,4-dione or ethyl 2-chloro-3-oxobutanoate to give thiophene 16a and thiazole 18 or thiophene 19 and thiazole 20 respectively (cf. Scheme 3).

Thioanilide 6 reacted with the appropriate hydrazonoyl halides to give 2,3-dihydro-1,3,4-thiadiazole derivatives 21a-e. Thiadiazole 21 was elucidated on the basis of analysis, spectral data and alternative method of synthesis. (cf. Scheme 3).

An unequivocal support for structure **21**, came from reaction of the appropriate hydrazoneyl halides **25a-e** with 2-benzoxazol-2-yl-3-methylthio-3-thioxopropanenitrile **32** (which was prepared from 2-benzoxazole-2-yl-ethanenitrile **4** with carbon disulfide in N,N-dimethylformamide containing potassium hydroxide followed by addition of iodomethane) in presence of triethylamine gave product identical in all respects (mp., mixed mp. and spectra with **21** (cf. Scheme 4).



Scheme 4

3-Amino-4-benzoxazol-2-yl pyrazol-5-yl)phenylamine (**9**) reacted with the appropriate pentane-2,4-dione, ethyl 3-oxobutanoate, diethyl malonate, 1-cyano-2-substituted acrylonitrile, aromatic aldehydes, and ethyl 1-cyanocinnamate to give pyrazolo[1,5-a]pyrimidine derivative **35-40** (cf., Scheme 5). All structures were confirmed on the basis of