

Synthesis, Mercuration and Reactions of 1,3-Benzoxazin -4-One Derivatives

A THESIS

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Requirements of
M.Sc. Degree in Chemistry

Presented By
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To



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وَعَلَّمَكَ مَا لَمْ تَكُن تَعْلَمُ

وَكَانَ فَضْلُ اللَّهِ عَلَيْكَ عَظِيمًا

صَدَقَ اللَّهُ الْعَظِيمُ

سورة النساء آية ١١٣

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Dedication

To yours . . . The greatest heart in
the universe .

To yours . . . Who blessed me and
whose pleasings I
retain .
I dedicate my thesis.

TO MY FAMILY



Ain Shams University

Faculty of Women

For Arts, Science and Education

Chemistry Department

Post Graduate Studies For M.Sc. Student

In organic Chemistry

This is to certify that : **Osama Lotfy Ali Hassan** has attended passed successfully the following postgraduate courses as partial fulfillment for the Degree of Master of Science .

- 1- Spectroscopy .
- 2- Heterocyclic compounds .
- 3- Natural products and biochemistry .
- 4- Organometallic .
- 5- Pericyclic reactions and organic reaction mechanism .
- 6- Photochemistry .
- 7- Chemical kinetics .
- 8- Quantum chemistry .
- 9- Thermodynamics .
- 10- Instrumental analysis .
- 11- German Language course .

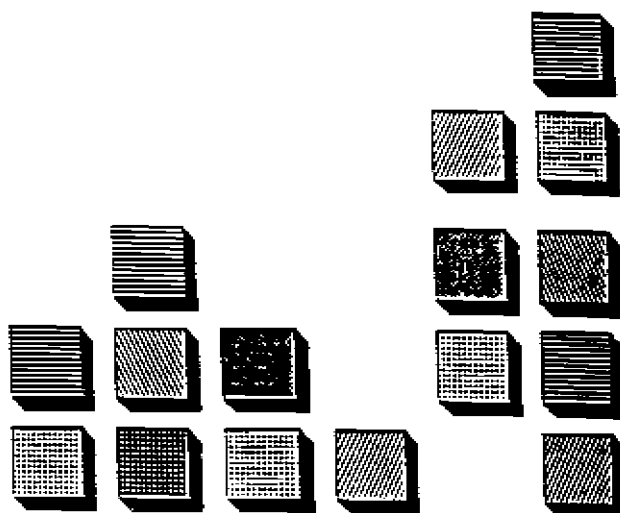
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SUMMARY



SYNTHESIS, MERCURATION
AND REACTIONS OF
1,3-BENZOXAZIN-4-ONE DERIVATIVES

This thesis is interested in the synthesis of some 2-styryl-(4H)-1,3-Benzoxazin-4-one derivatives and mercuration of some of the obtained compounds and other similar compounds which may have same biological activity .

The first part is interested in the synthesis of different derivatives via interaction of salicylamide with aromatic aldehydes namely, m-chlorobenzaldehyde and o-bromobenzaldehyde in the presence of acetic anhydride .

The mechanisms of these reactions firstly involving acetylation of phenolic(OH) of salicylamide followed by nucleophilic attack by lone pair of nitrogen atom yield the intermediate (145) which in the presence of acetic anhydride yields the corresponding carbanion which in turn attacks the aromatic aldehyde furnished compounds (146 a, 146b), 2-(m-chlorostyryl)-(4H)-1,3-benzoxazin-4-one and 2-(o-bromostyryl)-(4H)-1,3 - benzoxazin -4-one .

study the behaviour of 2-substituted styryl-(4H)-1,3-benzoxazin-4-ones (146) towards hydrazines, hydroxylamine and benzylamine.

The reaction of (146b) with benzylamine in boiling ethanol gave 2-(β -(2-bromophenyl)- β -benzylamino)vinyl-(4H)-1,3-benzoxazin-4-one (147b) via 1,4 addition without ring opening contrary to the behavior of 3,1-benzoxazinones and chromones .

The reaction of (146a,b) too with hydrazine hydrate give 2-(β -aryl- β -hydrazino)ethylidene-(3H)-1,3-benzoxazine-4-ones (148 a,b) via 1,4 addition .

The compound (146b) was allowed to react with phenylhydrazine in boiling ethanol. Yielded 2-(β -(2-bromophenyl)- β -phenylhydrazino) ethylidene-(3H)-1,3-benzoxazin-4-one (150) via 1,4-addition.

But the aim of study the behavior of compound (146b) towards hydroxylamine hydrochloride to know more precise information about the mode of addition. Thus, reaction of (146b) with hydroxylamine hydrochloride yielded 2-(β -(2-bromophenyl)- β -hydroxylamino) ethylidene-1,3-benzoxazin-4-one (151).

On the other hand cyclo addition reaction of 2-styryl-1,3-benzoxazin-4-ones undergo cyclo addition reaction under Diels-Alder conditions to give the corresponding Diels-Alder adducts.

The second part is interested in the mercuration of some 2-styryl-(4H)-1,3-benzoxazin-4-ones derivatives by using mercurating agent such as mercuric acetate.

Mercuric acetate reacts with all of: 2-(β -(m-nitrophenyl) styryl-(4H)-1,3-benzoxazin-4-one in methyl alcohol under reflux to give (153) (mercury bis.), 2-(β -(p-chlorophenyl) -(4H)-1,3-benzoxazin-4-one under the same conditions reacts with mercuric acetate to give mercurated product (154) (monomercurated product) via addition reaction, 2-(β -(p-dimethylaminophenyl) styryl-(4H)-1,3-benzoxazin-4-one to yield two products (156) and (157). The reaction seems to proceed via C-C(Ar) bond cleavage and 1,2 addition to the double bond, and 2-(β -(m,p,m-trimethoxyphenyl) styryl-(4H)-1,3-benzoxazin-4-one gives rise to substituted oxirane (155). The reaction may proceed via mercuration by 1,2-addition followed by demercuration then cyclization.

Finally mercurated reactions for all of :-

2-(β -(O-bromophenyl)- β -hydrazino) ethylidene-(3H)-1,3-benzoxazin-4-one, 2-(β -(O-bromophenol)- β -phenylhydrazino) ethylidene-(3H)-