A THESIS

ENTITLED

STUDIES ON SOME ORGANOMETALLIC COMPOUNDS

Submitted By

AZZA MAHMOUD MAZZROA

(B.Sc. Major Chemistry)

In Partial Fulfillment for the Degree of

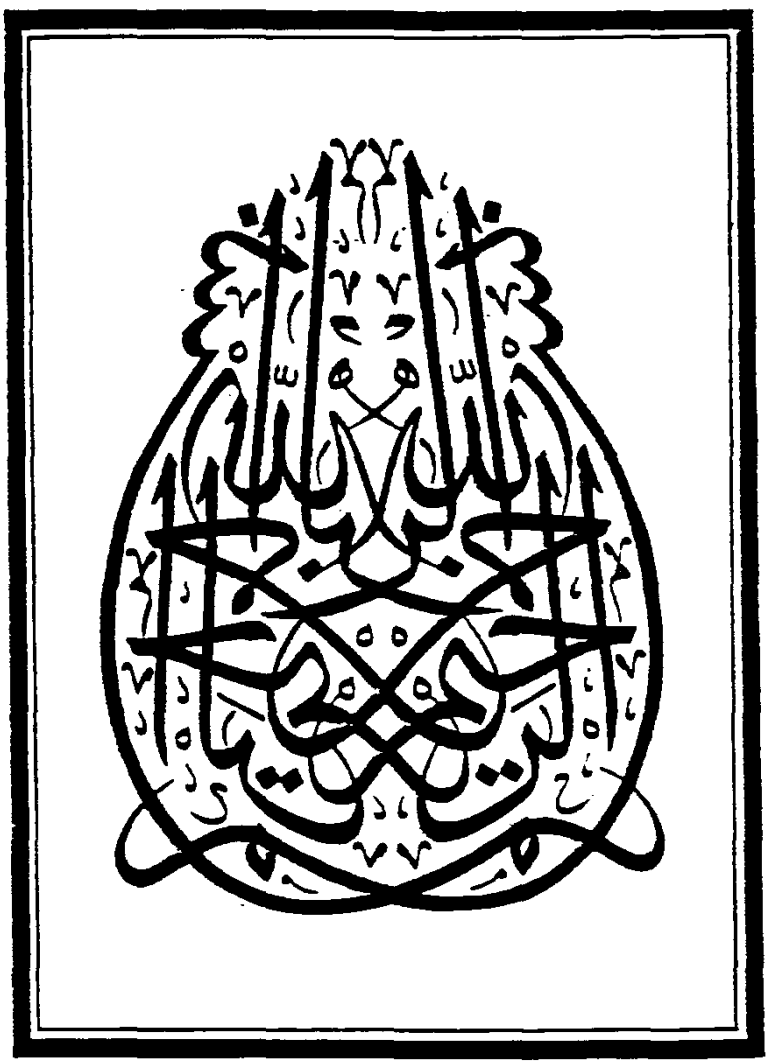
MASTER OF SCIENCE

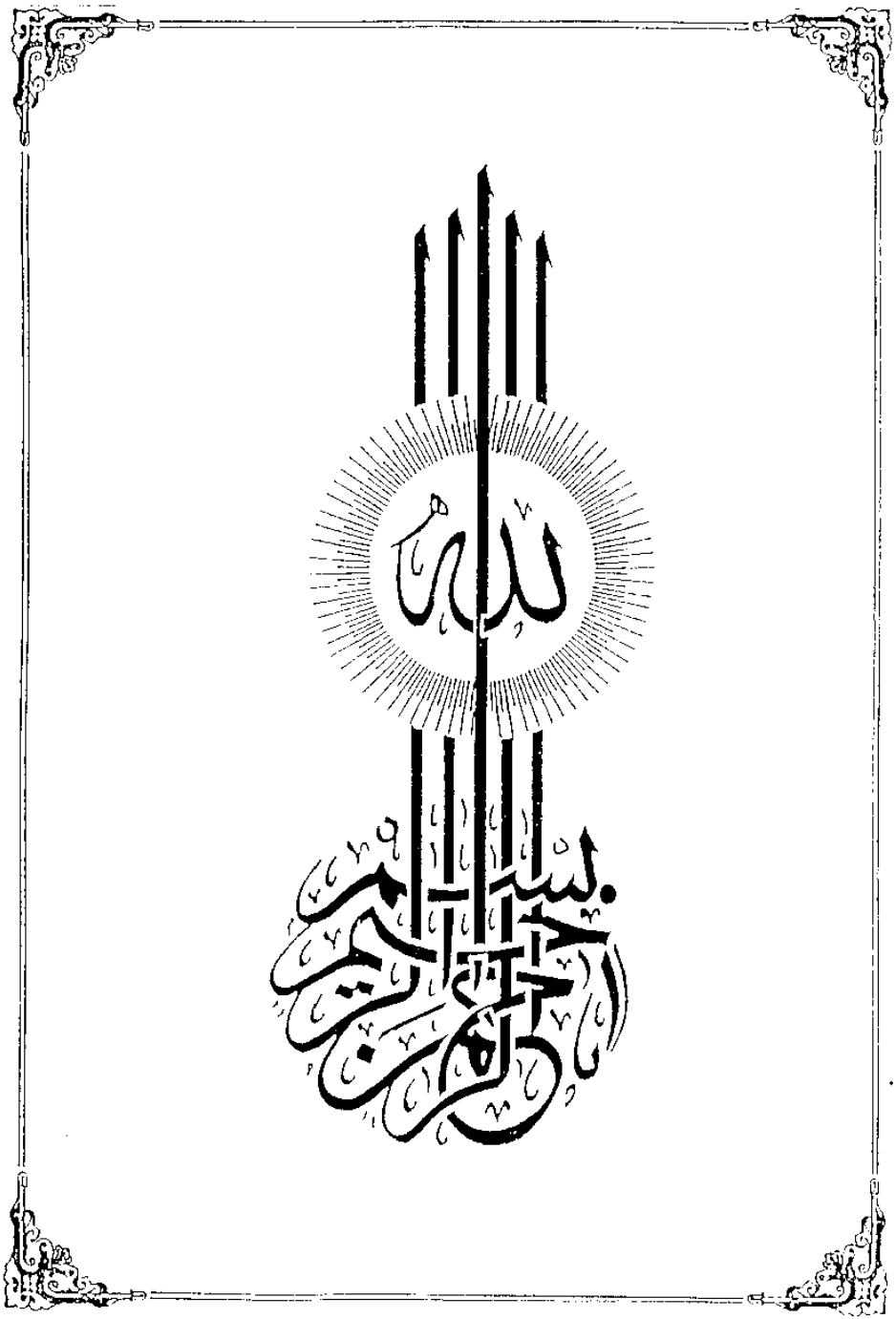
University College for Women

Ain Shams University

(Cairo)

1992





وَعَلَّمَكَ مَا لَمْ تَكُنْ تَعْلَمُ

وَكَانَ فَضْلُ اللَّهِ عَلَيْكَ عَظِيمًا

صَدَقَ اللَّهُ الْعَظِيمُ

سورة النساء آية ١١٣

TO

MY FAMILY AND MY HUSBAND

STUDIES ON SOME ORGANOMETALLIC COMPOUNDS

THESIS SUPERVISORS

Prof. Dr. EMTITHAL A. EL-SAWI

LATE Prof. Dr. ATEF-SHALABY

APPROVED

.....E. El-Sawi.....

Prof. Dr. M.A. WASSEF

Marguerite A. Wassef

Head of Chemistry Department

ACKNOWLEDGEMENT

The authoress wishes to express her deepest gratitude to Prof. Dr. Emtithal A. El-Sawi, Professor of organic chemistry, University College for Women, Ain Shams University, not only for suggesting the problem investigated, but also for her continuous supervision, help, encouragement, advices and valuable criticism.

Sincere appreciation are also extended to the Late Prof. Dr. Atef A. Shalaby, Professor of plant physiology, Desert Res. Centre for his cooperation and valuable advice.

Many thanks are also due to Dr. Tahia B. Mostafa, Lecturer of organic chemistry, University College for Women, Ain Shams University for her interest in this work.

N O T E

The candidate has attended courses for one year, covering the following topics :

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.

She has successfully passed a written examination in these courses, in partial fulfilment for the degree of Master of Science.

CONTENTS

SUMMARY

SUMMARY

The work recorded in this thesis deals with metalation of some organic compounds (benzimidazole and phenylthiohydantoic acid) by some metalating agents such as Nickel (II), cobalt (II), copper (II), acetate and chloride and mercuric acetate under different conditions, (solvent and temperature).

The thesis is divided into four chapters, literature survey (Chapter I) which is covered by 218 references, dealing with synthesis of metal alkyl and aryl, metalation reaction, metal hydrogen exchange, mercuration of aliphatic and alicyclic structures, mercuration of aromatic hydrocarbons, mercuration of aromatic hydroxy compounds, mercuration of aromatic amines and mercuration of the aromatic carboxylic and sulphonic acids and their derivatives.

Results and discussion are divided into two chapters (II,III). Chapter II deals with metalation of benzimidazole with metalating agents in (1:1 molar ratio). The reaction of nickel acetate with benzimidazole in toluene as non-polar solvent at its boiling point gives rise to a monometalated product (I), while it gives with methanol at room temperature two monometalated products (II,III) and a monometalated product (IV) at its boiling point.

Nickel chloride reacts with benzimidazole in boiling toluene and methanol at room temperature and at their boiling points to give (Va), (Vb) and (Vc) via replacement of the

active monometalated products methine group. The reactions of cobalt acetate with benzimidazole in toluene at its boiling point and in methanol at room temperature and at its boiling point give a monometalted product (VIa); cobalt bis-products (VIIa), (VIb); a monometalated product VIII and cobalt bis-product (VIIb). Cobalt chloride reacts with benzimidazole in toluene and in methanol at different temperatures to give a dicobaltated product (IX), monometalted products (Xa) and (XI); products (XIIc) and (Xb) respectively. With copper acetate in boiling toluene, methanol at room temperature and at its boiling point products (XII) as dicopperated; (XIIIa) and (XIV) as Cu-bis- , a mono-metalated products, and Cu-bis-product (XIIIb) respectively. However, copper chloride reacts with benzimidazole in toluene and methanol to give (XVa); (XVb), (XVI), where (XVa,b) are dicopperated products formed via ring cleavage. Mercuric acetate under the same conditions in toluene and methanol gives a dimercurated product (XVII) via ring cleavage and by the same mechanism discussed for (XVa,b); (XVIIIa) and (XVIIIb) as monomercurated products.

Chapter III describes the reaction of phenyl-thiohydantoic acid with Ni^{++}, Co^{++}, Cu^{++} and Hg^{++} acetates under different conditions. These reactions leads to the formation of a dinickelated product (XIX); a nickel bis-product via C-S, N-C bond cleavages; (XXI) product via S-C bond cleavage; a dicobaltated product with the formation of vie-membered

ring containing cobalt (XXII); (XXIII) and (XXIV); a monocopperated product with the formation of a five-membered ring (XXV)(; a monometalated product (XXVI) formed via cyclisation to give a five-membered fused ring with the aromatic ring accompanied by C-S, and C-N and cleavages; a monocopperated product XXVII formed via S-C and N-C bond cleavages, whereas mercuric acetate gives, a monomercurated product (XXVIII) containing a five-membered ring; (XXIX), (XXX) as mercuri-bis-products; dimercurated products; (XXXI) product formed via C-N and S-C bond cleavages.

The mechanism of some reactions are studied and structures are confirmed by the different data,elemental analysis, IR, UV, MS, NMR and some chemical tests.

Chapter (IV) (experimental part), deals with the conditions of the reactions, procedures, yields, melting points of the new compounds and their chemical analysis.

CHAPTER I

INTRODUCTION

Relatively new systematic study in the field of organometallic chemistry by large numbers of people did not really begin until the 1950's. When this systematic work did get underway, chemists naturally worked on the chemistry of a particular element or groups of elements, and, furthermore, divided themselves rather naturally into main group or transition metal chemists. Therefore, the literature of the field and texts in the area have often sub-divided organometallic chemistry by the part of the periodic table being studied e.g. Fig. (1) and Fig. (2).