SYNTHESIS OF SOME AROMATIC AND HETEROCYCLIC COMPOUNDS CONTAINING NITROGEN ATOM

A Thesis

Submitted in Partial Fulfillment of the Requirements

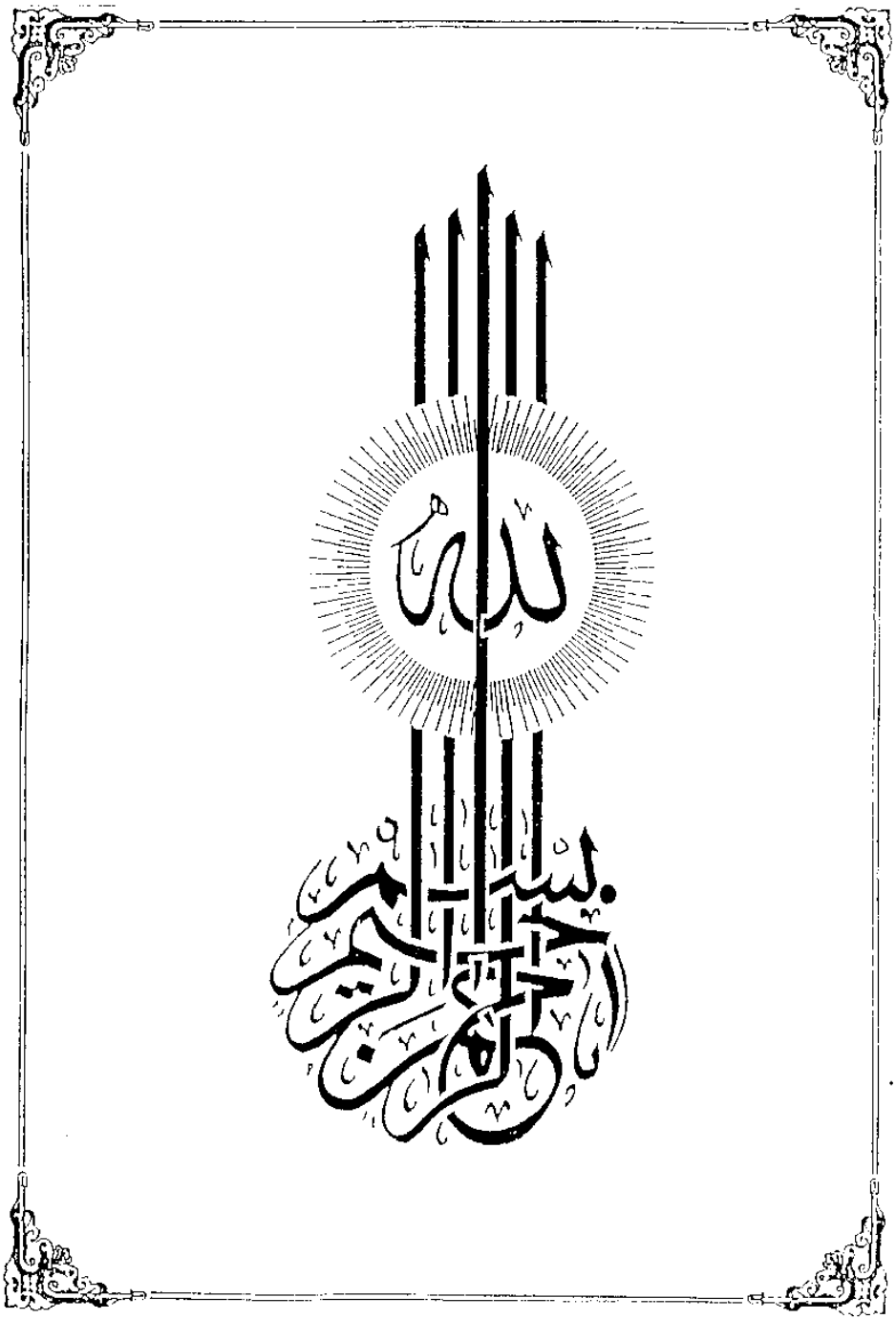
for the Degree of

DOCTOR OF PHILOSOPHY IN CHEMISTRY

Presented by

WALEED ELSAYED BORAIE

Department of Chemistry
Faculty of Science
Ain shams University
Cairo, Egypt
1997



SYNTHESIS OF SOME AROMATIC AND HETEROCYCLIC COMPOUNDS CONTAINING NITROGEN ATOM

Thesis advisors

Prof. Dr. G.H. Sayed

Prof.Dr.Ashraf A.M. Hamed

Prof.Dr. A.S Abd-El- Aziz

Thesis approved

Head of Chemistry Department

Prof.Dr. Fahmy , A.F.M .

ABSTRACT

Time-dependent oxidation reactions of η^6-alkylaniline-η^5-cyclopentadienyliron hexafluorophosphate, allowed for the preparation of nitrobenzene complexes with alkyl or keto substituents. Alkyl nitroarene complexes were prepared by the oxidation of their corresponding aniline complexes with H_2O_2 in CF_3COOH for 20 minutes. Increasing the reaction time to 24 hours gave rise to nitroarene complexes with keto substituents in lower yields. The use of nitroarenes as starting materials in the synthesis of alkanoic acid esters is of importance since it allows for the preparation of a large number of this class of compounds with a variety of alkyl substituents. Two different approaches were utilized to allow for the synthesis of alkanoic acid esters. The first approach involved nucleophilic aromatic substitution reactions of alkyl nitrobenzene complexes with ethyl alkylacetoacetates followed by demetallation to give alkanoic acid esters. This methodology allowed for the preparation of these esters with a variety of alkyl substituents in either the meta or para positions. Another route outlined the reaction of phenylsulphonylacetonitrile with nitroarene complexes to prepare alkanoic acid precursors with alkyl substituents in the ortho, meta, and para positions. The preparation of a large pool of nitroarene complexes clearly demonstrates the advantage of using the cyclopentadienyliron arene complexes in the synthesis of alkanoic acid esters or their precursors, arylated phenylsulphonylacetonitriles, over traditional synthetic routes. Also, addition of cyanide anions to substituted arene cyclopentadienyliron complexes

containing electron-donating group like alkyl and electron-withdrawing group such as nitrogroup, was investigated. Cyanide addition with these complexes proved to be highly selective, allowing for the formation of one adduct while in the case of sec-butyl group in p-position for nitroarene iron complex gave rise to two isomers due to the asymmetric carbon. Also, the reaction of cyanide anion with p-keto nitroarene complex gave rise to two isomers; one is ortho addition and the other is ipso addition. Selective addition of the cyanide anion with various alkylarylsulphonyl di-iron complexes gave rise to one adduct ortho to the electron-withdrawing sulphonyl group.

Formation of cyanide adducts of poly-iron systems were achieved by selective addition to ortho position of methyl group in polycyclopentadienyliron arene complex with etheric bridges. The nature of some of these adduct were identified by HH COSY NMR techniques. Oxidative demetallation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) yielded the substituted benzonitrile and the functionalized uncomplexed polyaromatic ether with cyano groups in good yield and free diaromatic sulphoxide alkane with cyano group in good yield.

Formation of cinnolines cyclopentadienyliron complexes was carried out in two steps. First formation of the hydrazone on a keto group in position 2 of the side chain of o-chloro (substituted benzene) cyclopentadienyliron complex. Second, the nucleophilic substitution carried out on the o-chloro group by the second amino group of hydrazone gave rise the CpFe complexes of 3-mono-, or 3,4-disubstituted 1,4-dihydrocinnoline.

ACKNOWLEDGEMENTS

I would like to thank my supervisors, Professor Dr. Galal Hosni Sayed, Professor of Organic Chemistry, Faculty of Science, Ain Shams University, Professor Dr. Ashraf A.M. Hamed, Professor of Organic Chemistry, Faculty of Science, Ain Shams University, and Professor Dr. Alaa S. Abd-El-Aziz, Professor of Chemistry, Faculty of Arts and Science, University of Winnipeg, for their support, guidance, and patience throughout the course of my work. I wish to express my sincere gratitude and deep indebtedness to Dr. Alaa S. Abd-El-Aziz for his continual help, guidance, and valuable criticism. I wish to thank all the people who provided moral support and patience through the duration of my thesis: C.R. de Denus, K. Epp, S. Bernardin, K. Tran, D. Armstrong, S. Smith, A. White, and A. Peter.

I would like to thank the Department of Chemistry, Faculty of Science, Ain Shams University and the Department of Chemistry, University of Winnipeg for providing me with the facilities necessary to pursue this project. I would also like to acknowledge Dr. Ahmed El-Zonfly and the Egyptian Cultural and Educational Bureau in Montreal for their support during my scientific mission at the University of Winnipeg. Finally, special thanks to all my family for all their support and encouragement.

TABLE OF CONTENTS

LIST OF FIGURES