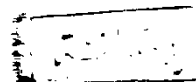


A THESIS
ENTITLED
STUDIES ON SOME ORGANOMETALLIC
NITROGENOUS COMPOUNDS

Submitted By
SAHAR MOSTAFA AHMED
(B.Sc. Special Chemistry)



In Partial Fulfillment
For The Degree of
MASTER OF SCIENCE

45324



University College for Women
Ain Shams University
(Cairo)

1992

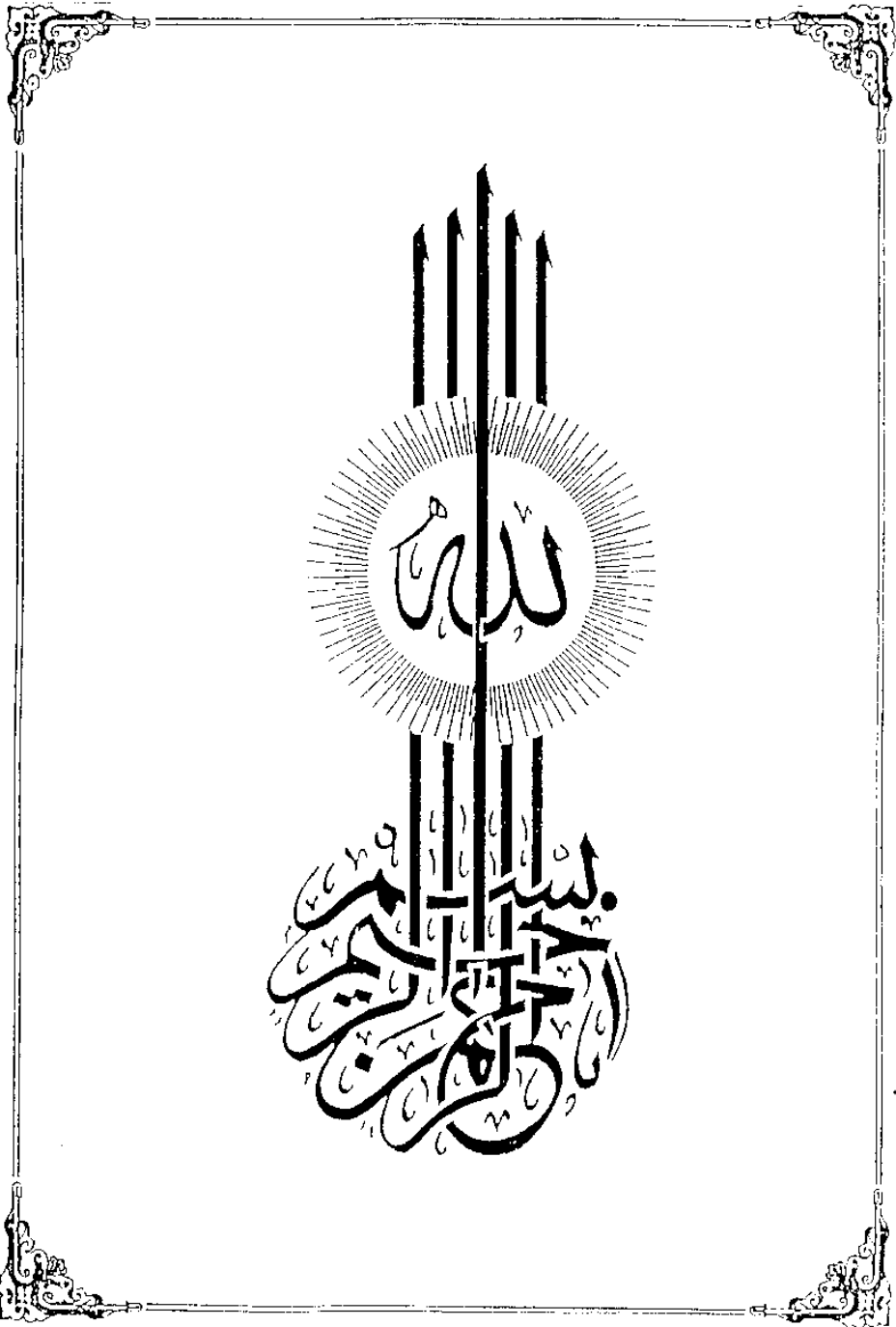
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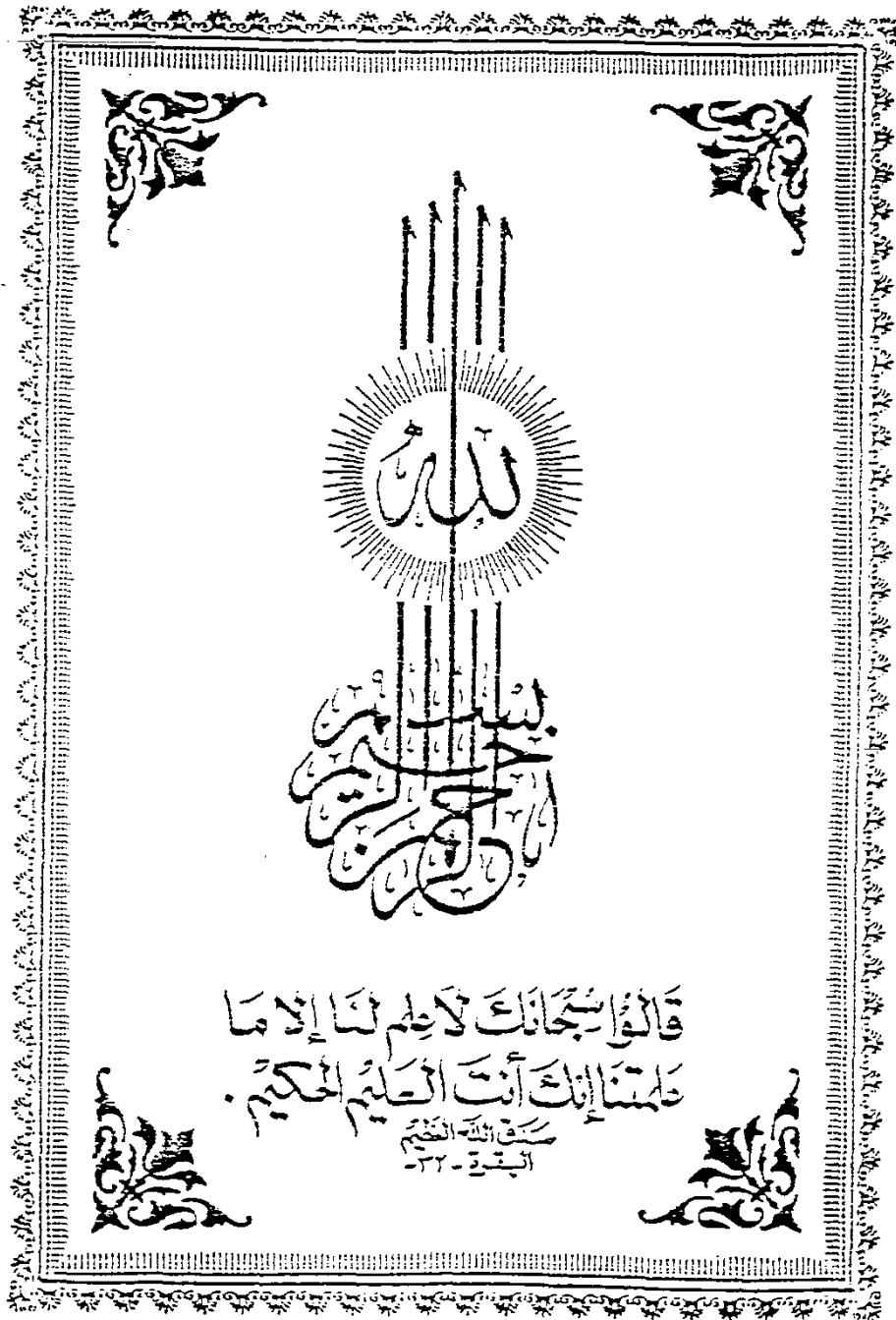
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STUDIES ON SOME ORGANOMETALLIC NITROGENOUS COMPOUNDS

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NOTE

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

- 1- Spectroscopy.
- 2- Heterocyclic compound.
- 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.

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SUMMARY

SUMMARY

The work recorded in this thesis deals with metalation of some organic compounds containing nitrogen by some metalating agents such as cobalt (II), Ni (II) and Cu (II) salts in polar solvents, (methanol and acetic acid) and in a non-polar solvent (toluene) at their boiling points. The thesis is divided into four chapters, literature survey (chapter I) which is covered by 86 references, dealing with synthesis of organometallic, direct reaction of metals with an organic halide, mercuration reactions, metal hydrogen exchange, metal carbon σ -bonded complexes, metal halogen exchange, oxidativel addition reactions, physical measurements and metal-metal exchange.

Results and discussion are divided into two chapters, II and III, chapter II deals with metalation of α -benzoinoxime with metalating agents. The reactions of cobalt acetate and chloride with α -benzoinoxime in methanol, acetic acid and toluene give different products, a monometalated product with the formation of five membered ring (1), a dimetalated (2), an organic compound, formed via condensation of 2 moles of the start under the reaction condition (3a,b), a monometalated product (4), a trimetalated product (5), and an organic product formed via bond cleavage and bond formation (6). The reaction with nickel salts gives a monometalated product accompanied with C-C(Ar) bond cleavage (7), a dimetalated product via C-C bond cleavage (8) and a product confirmed to

be a di-syn-form (9), a monometalated with C-C bond cleavage (10), a metal bis product (11), a dimetalated via C-C bond cleavage (12). However, copper salts react to give a dimetalated product with the formation of two five membered rings (13), a monometalated with the formation of five membered ring (14), an organic compounds (15), a monometalated product (16) via C-C bond cleavage and C-Cu-C bonds formation, a monometalated product (C-C cleavage and bond formation) (17), an organic compounds (18), and a monometalated product (19) (C-C bond cleavage). The structures are confirmed by analytical data, IR, UV/Vis, XS, and some chemical tests. Some reaction mechanisms are studied.

Chapter III describes the reactions of cobalt (II), nickel (II) and Cu (II) salts (acetate and chloride) with o-carboxyphenylazodiethylmalonate, in methanol, acetic acid (polar-solvent) and toluene (non-polar solvent) at their boiling points. The reaction with cobalt salts gives monometalated products (20), (21) via C-N, N-N bond cleavages, a dimetalated product formed via N-C bond cleavage (22), a monometalated product (23), a dimetalated product via N-N bond cleavage with the formation of six membered ring (24), and a metal bis-product (25). Nickel salts react to give a monometalated product via N-N, bond cleavage (26a), a monometalated product (27), a monometalated product (26b) and a metal bis-compound (28a,b).

The reaction with copper salts gives dimetalated product (29), monometalated product with the formation of six membered ring (30), metal bis-product (31) and monometalated product (32). Some reaction mechanisms are studied and structures are confirmed by the different data, elemental analysis, IR, Vis/UV and some chemical tests.

In chapter IV (experimental part), the conditions of the reactions, procedures, yields, melting points of the new products and their chemical analysis are included.

CHAPTER 1 **INTRODUCTION**

The field of organometallic chemistry is relatively new. Systematic study in the area large number of people did not really begin until the 1950's. When this systematic work did get under way, chemists naturally worked on the chemistry of particular element or group of elements, and, furthermore, divided themselves rather naturally into main group or transition metal chemists.

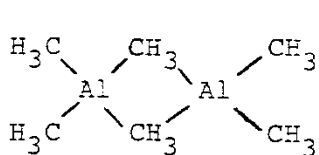
Therefore, the literature of the field and texts in area have often subdivided organometallic chemistry by the part of periodic table. Alkylaluminum compounds from the basis of the Ziegler-Natta catalyst system, which is widely used in industry for the homogeneous polymerization of ethylene and propylene. Trialkyl tin oxides and acetates have found wide application as fungicides, and dialkyl tin compounds are used as stabilizers anti-oxidants and ultraviolet radiation filters, for polyvinyl chloride or rubber⁽¹⁾, silicon compounds are extensively used in form of silicones, or organosilicon oxygen polymers, which haven among others, unique lubricating properties⁽²⁾.

Organometallic compounds formed from carbon σ -donor ligands may be subdivided into two classes σ -compounds in which the organic group can be considered an anionic σ -donor, and π -compounds which the organic group is neutral σ -donor and π acceptor.

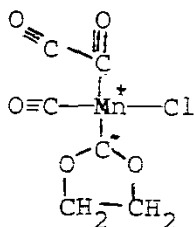
Compounds of the first type include metal alkyls and aryls such as phenyl sodium (an ionic compound); dimeric

trimethyl aluminium $[(CH_3)_6Al_2]$ (1). Volatile "electron deficient" compounds⁽³⁾; a volatile, covalent compound such as $(CH_3)_4Sn$; or an involatile transition metal compound such as $(\eta^5-C_5H_5)Fe(CO)_2(CH_3)$.

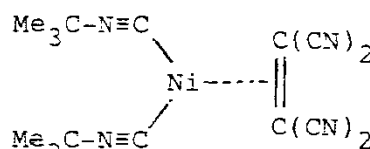
Type (b) compounds are almost exclusively formed by the transition metals in their low valence states, and they are exemplified by complexes with carbon monoxide and carbene (2)⁽⁴⁾ and with isonitriles⁽³⁾ (5).



(1)



(2)



(3)

1- Synthesis of organometallic compounds :

1- Direct reaction of metals with an organic halide :

The direct reaction of metals with alkyl and aryl halides may be used to produce numerous organometallic derivatives because of the simplicity of the reaction. The products are frequently of industrial importance. Furthermore, such reactions often produce many of more reactive representatives of each class of compounds. For example, direct reaction of alkyl halides with Li, Mg, Al, or Zn leads to some of the most reactive metal alkyls known. These compounds may then be used to produce alkyl derivatives of metals for which the direct reaction does not work.