A THESIS
ENTITLED
ACTION OF MERCURIC SALTS ON MUREXIDE AND XYLENOL ORANGE

Submitted by
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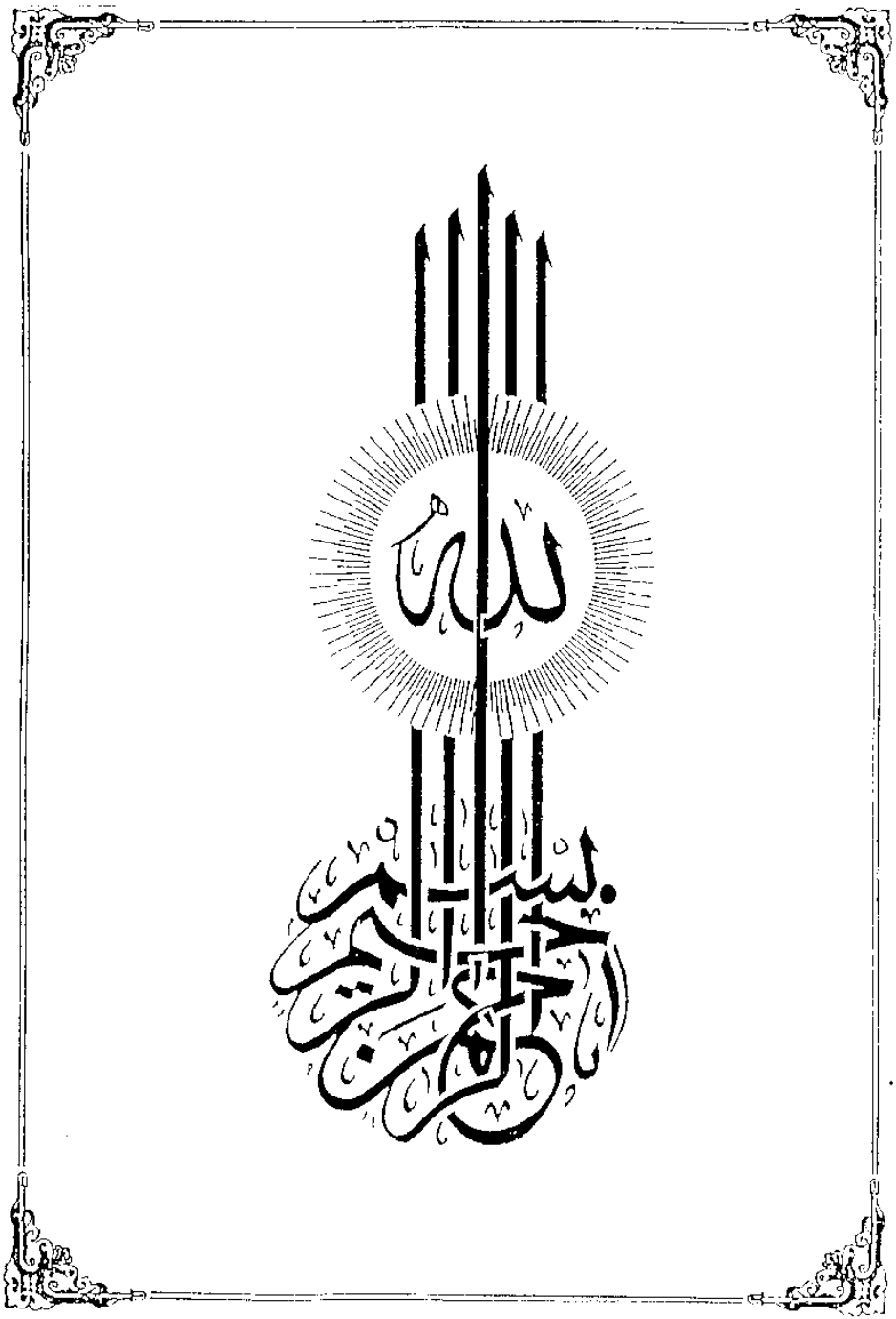

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NOTE

Besides the work carried out in this thesis, the candidate has attended postgraduate courses in the following topics :

1- Photochemistry.

2- Microanalysis.

3- Organometallic Compounds.

4- Quantum Chemistry.

5- Spectroscopy.

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C O N T E N T S

SUMMARY

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The work recorded in this thesis deals with mercuration of some metal indicators (xylenol orange and murexide) by some mercurating agents such as mercuric acetate, mercuric chloride and mercuric iodide in two different solvents, toluene and methanol as nonpolar and polar solvents respectively.

The thesis is divided into four chapters, literature survey (chapter I) which is covered by 122 references, dealing with mercuration reactions. Mass spectra, metallochromic indicators.

Results and discussion are divided into two chapters (II and III). Chapter II deals with mercuration of xylenol orange with mercurating agents in (1:1 molar ratios). The products obtained are monomercurated product where organo-metallic compounds is obtained via formation of acetoxy mercury salt followed by decarboxylation to form C-Hg bond and dimer-curated. The mass spectra fragmentation at different temperatures are schematically given. IR and electronic spectra at different pH are discussed to prove the structures.

Chapter III describes the reaction of murexide (in two forms mono- and pentahydrated) with some mercurating agents. In the former case (monohydrated) the products in nonpolar solvent (toluene) are formed via mercury-hydrogen exchange followed by coordination with central nitrogen, whereas in polar solvent

(methanol) adduct products are obtained. In the case of penta-hydrated another types of products are obtained by introduction of water or methanol as solvated intity. The mercuration with mercuric chloride takes place via C-N bond cleavage to form dimercurated product (XVI).

The mass spectra fragmentation, IR, NMR and electronic spectra are discussed to confirm all the products' structures.

Chapter IV gives detailed experimental conditions, yields, melting points and chemical analysis.

CHAPTER I

INTRODUCTION

CHAPTER II

EFFECT OF MERCURIC SALTS ON XYLENOL ORANGE AND THEIR HALOCHROMIC EFFECT

CHAPTER I

I N T R O D U C T I O N

The organic derivatives of mercury are among the most stable true organometallic compounds of the transition metal i.e. compounds in which the metal is bonded directly to the carbon. Although the stability of various organomercury derivatives fluctuates over a wide range, they are particularly noted for their inertness to oxygen and oxidising agents, water, and, to a certain degree, to weak acids.

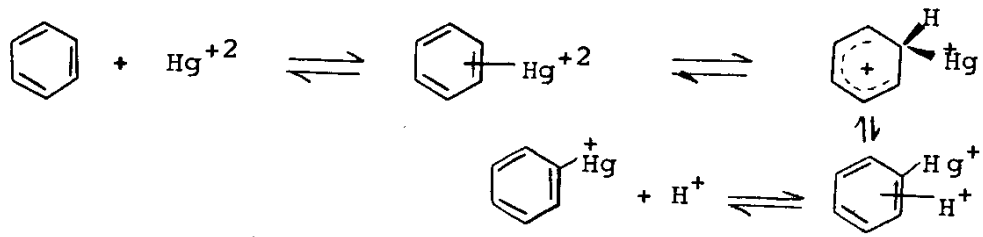
The organometallic compounds of mercury enter into two very important types of reaction.

1- Exchange of halides of metals and non metal resulting in a wide range of organometallic and organo-elemental compouds.

2- Replacement of the mercury in organomercury compounds under the action of the free metals. This method was found to be useful in the synthesis of organometallic compound of certin metals (Sodium, Aluminium etc) and is used to this day. Mercury combines with a wide range of organic molecules and is compatible with almost all funcationals groups intering into the structure of the radicals connected with it. Although there are only three basic types of organo-mercury compounds the fully symmetric R_2Hg, the non symmetric RHgR' and the mixed (organomercury salts) RHgX. The residue R may be saturated or unsaturated, alicyclic aromatic or heterocyclic. In the initial organic molecule RH, one or more hydrogen atoms linked with carbon may be replaced by mercury in the limiting case of complete mercuration, the products are the mercarbide_.

The same stability of the organometallic compounds of mercury is the reason for their case of formation and for the variety of methods available for introducing mercury into organic molecules, which in turn allows one to arrive at almost any combination in the resulting organomercury derivative.

Murcuration reactions are important example of metal hydrogen exchange[1] and they represent a particularly good way of introducing a metal into an aromatic molecule, the reaction of benzene with mercuric acetate in acetic acid at elevated temperature gives phenylmercuric acetate in good yield, ferrocene wherever gives ferrocenylmercuric acetate under much milder conditions.



A ferrocene is known to undergo electrophilic substitution was considerably more ease than benzene. These results and others, lead to that mercuration are electrophillic substitution.

Introduction of Mercury in Place of a Hydrogen Atom (Mercuration)

Direct displacement of hydrogen (formally as a proton) from its attachment to carbon by a metal ion to form a carbon-metal bond is not a common reaction. Mercuration is certainly the best known, although fragmentary examples of auration, thallation and plumbation have been reported (vide infra).

$$R\text{-}H + Hg^{++} \longrightarrow R\text{-}Hg^{+} + H^{+}$$

(The bare Hg^{++} ion is not intended to portray the actual nature of the kinetically active mercurating species).

Mercuration, like many other replacement of hydrogen attached to carbon is more facile with the aromatic hydrocarbons than with aliphatic molecules, and heterocycles such as furan and thiophene react more readily still. The monosubstitution stage is easily exceeded under certain conditions and polymercuration can be extensive.

The reaction of benzene with mercuric acetate in acetic acid at elevated temperatures leads to phenylmercuric acetate in good yield[2] and in the aromatic series it should be immediately apparent that mercuration has a strong formal resemblance to reactions such as nitration and halogenation.

Some authors either carelessly or unknowingly classify oxymercuration as a mercuration reaction, though as presently