SUDAN UNIVERSITY OF SCIENCE AND TECHNOLOGY COLLEGE OF POSTGRADUATE STUDIES

Reactions of diazonium salts

A THESIS SUBMITED AS PARTIAL FULFILLMENT OF REQUIRMENT FOR THE DEGREE OF M.Sc. In Chemistry By

Mubasher Hashim Awad Alkarim

:Supervisor

Dr. Dafaalla Mohamed Hag Ali

Dedication

I dedicate this thesis

To my father

To my mother

And

To my fiancée

Contents

List of Tables	i
List of Figures	ii
Abstract (Arabic)	iii
Abstract (English)	iv
Chapter One	
Introduction and literature review	
Introduction 1	
1	
Structure of aryl diazonium salts	2 1.1
Properties of aryl diazonium salts	3 1.2
Stability of aryl diazonium salts	3 1.3
The effects of solvent and pH on the reactions of aryl diazonium salts .	5 1.4
Reactions of aryl diazonium salts	8 1.5
Reactions of aryl diazonium salts without loss of nitrogen	8 1.5.1
Preparation of aryl hydrazines	8 1.5.1.1
Preparation of aryl azides	10 1.5.1.2
Preparation of Azo-compounds	10 3 .1.5.1
Preparation of diazoamino compounds	15 1.5.1.4
Reactions of aryl diazonium salts with loss of nitrogen	17 1.5.2
Replacement of diazonium group by iodide	18 1.5.2.1
Replacement of diazonium group by chloride	18 1.5.2.2
Replacement of diazonium group by a hydroxyl group	19 1.5.2.3
Replacement of diazonium group by hydrogen	19 1.5.2.4
Reaction of diazonium salts with artesunate	22 1.5.3
Objective of this work	24 1.6

Chapter Two

Experiments

Instrumental 2.1

Chemicals and reagents
Melting points
2.1.3Infrared spectroscopy (IR)26
Ultraviolet spectroscopy (UV)26 2.1.4
Reactions of aryl diazonium salts without loss of nitrogen
Preparations of azo- compounds
. Reaction of benzene diazonium chloride with β –naphthol
Reaction of o-anthranilic acid diazonium chloride with β -naphthol28 2.2.1.2
Reaction of o-toluidine diazonium chloride with β -naphthol
Reaction of o-anthranilic acid diaznoium chloride with N, N-dimethyl 2.2.1.4
aniline29
Reaction of p-(diazonium phenyl sulphonic acid) with N,N-dimethyl 2.2.1.5
aniline30
Preparation of triazene compounds
Reaction of benzene diazonium chloride with aniline
Reaction of β -naphthalene diazonium chloride with β -naphthyl 2.2.2.2
amine32
Reaction of aryl diazonium salts with aliphatic compounds
Reaction of benzene diazonium chloride with acetyl acetone
Reaction of o-carboxybenzene diazonium chloride with acetyl 2.2.3.2
acetone

Reaction of m-nitrobenzene diazonium sulphate with ethyl 2.2.3.3
acetoacetate34
Reaction of p-phenylene bis (diazonium chloride) with acetyl 2.2.3.4
acetone
Reactions of aryl diazonium salts involving replacement of azo- group36 2.3
Reactions of aryl diazonium salts with a hydroxyl group
Hydrolysis of o-hydroxybenzene diazonium chloride
Hydrolysis of β-naphthalene diazonium chloride36 2.3.1.2
Reactions of aryl diazonium salts with iodide
Reaction of o-carboxybenzene diazonium chloride with potassium 2.3.2.1
iodide37
Reactions of aryl diazonium salts with chloride
Reaction of o-carboxybenzene diazonium chloride with cuprous 2.3.3.1
chloride

Chapter Three

Results and Discussion

Introduction	40 3.1
Synthesis of aryl diazonium salts40	3.1.1
Preparation of azo-compounds41	3.2.1
Mechanism of coupling reactions45 3	3.2.1.1
Preparation of Triazene compounds47	3.2.2
Reaction of aryl diazonium salts with aliphatic compounds50	3.2.3
Hydrolysis of aryl diazonium salts53	3.23.4
Reactions of aryl diazonium salts with iodide	3.2.5
Reactions of aryl diazonium salts with chloride57	3.2.6
Appendix A59	
Appendix B75	
Conclusion7	8 3.3
Reference80	

List of Tables

Table 3.1 The yield%, melting points and Ultraviolet spectra of the
prepared diazonium compounds
Table 3.2 Infrared spectral data of the products obtained from the
reaction between aryl diazonium chloride and β-naphthol45
Table 3.3 Infrared spectral data of the products obtained from the reaction
between aryl diazonium salts and N, N-dimethyl aniline46
Table 3.4 Infrared spectral data of the products obtained from the reaction
between aryl diazoniun salts and primary aromatic aniline49
Table3.5 Infrared spectral data of the products obtained from the reaction
between aryl diazonium chlorides and acetyl acetone51
Table 3.6 Infrared spectral data of the product obtained from the reaction
betwee m-nitroaniline and ethyl acetoacetate53
Table 3.7 Infrared spectral data of the products obtained from the reaction
between aryl diazonium salts and hydroxyl group55
Table 3.8 Infrared spectral data of the product obtained from the reaction
between o-carboxybenzene diazonium chloride and potassium
iodide56
Table 3.9 Infrared spectral data of the products obtained from reaction
between o-carboxybenzene diazonium chloride and coprous
chloride57

Fig.: 3.1.1 IR spectrum of the product obtained from the reaction
between benzene diazonium chloride and β -naphthol56
Fig.: 3.1.2 IR spectrum of the product obtained from the reaction
between o-anthranilic acid with β -naphthol57
Fig.: 3.1.3 IR spectrum of the product obtained from the reaction
between o-toluidine and $\beta\text{-naphthol}$
Fig.: 3.1.4 IR spectrum of the product obtained from the reaction
between p-diazonium phenyl sulphonic chloride and
N, N dimethyl aniline
IR spectrum of the product obtained from the reaction
between o-anthranilic acid diazonium chloride and
N,N dimethyl aniline60
Fig.: 3.1.6 IR spectrum of the product obtained from the reaction
between benzene diazonium chloride and aniline
(yellow prisms)61
Fig.: 3.1.7 IR absorption of the product obtained from the reaction
between benzene diazonium chloride and aniline
(gold prisms)62
Fig.: 3.1.8 IR spectrum of the product obtained from the reaction
between $\beta\text{-naphthalene}$ diazonium chloride and $\beta\text{-naphthyl}$
amine63
Fig.: 3.1.9 IR spectrum of the product obtained from the reaction
between benzene diazonium chloride and acetyl acetone64
Fig.: 3.1.10 IR spectrum of the product obtained from the reaction
between o-carboxybenzene diazonium chloride and
acetyl acetone65

Fig.: 3.2.5 UV spectrum of the product obtained from the reaction
between o-anthranilic acid diazonium chloride and
N,N dimethyl aniline72
Fig.: 3.2.6 UV spectrum of the product obtained from the reaction
between benzene diazonium chloride and aniline
(yellow prisms)72
Fig.: 3.2.7 UV absorption of the product obtained from the reaction
between benzene diazonium chloride and aniline
(gold prisms)
Fig.: 3.2.8 UV spectrum of the product obtained from the reaction
between β-naphthalene diazonium chloride and
β -naphthyl amine73
Fig.: 3.2.9 UV spectrum of the product obtained from the reaction
between benzene diazonium chloride and acetyl acetone73
Fig.: 3.2.10 UV spectrum of the product obtained from the reaction
between o-carboxybenzene diazonium chloride and
acetyl acetone73
Fig.: 3.2.11 UV spectrum of the product obtained from the reaction
between m-nitrobenzene diazonium sulphate and
ethyl acetoacetate73
Fig.: 3.2.12 UV spectrum of the product obtained from the reaction
between p-phenylene bis diazonium chloride and
acetyl acetone73
Fig.: 3.2.13 UV spectrum of the product obtained from the reaction
between o-carboxybenzene diazonium chloride and
hydroxyl group74

Fig.: 3.2.14 UV spectrum of the product obtained from the reaction
between naphthalene diazonium chloride and
hydroxyl group74
Fig.: 3.2.15 UV spectrum of the product obtained from the reaction
between o-carboxybenzene diazonium chloride and
potassium iodide74
Fig.: 3.2.16 UV spectrum of the product obtained from the reaction
between o-carboxybenzene diazonium chloride and
cuprous chloride74

الهدف من هذا العمل هو دراسة تفاعلات أملاح الدايزونيوم مع بعض الأمينات الأروماتية، الفينولات وبعض المجموعات الأيونية وتحديد العوامل التي تتحكم في طبيعة النواتج.

وقد اجريت الدراسه لبعض تفاعلات أملاح الدايزونيوم وتم التعرف على نواتج هذه التفاعلات بواسطة الأشعة تحت الحمراء ، الأشعة فوق البنفسجية ومقارنة درجات الانصهار.

ABSTRACT

The aim of this research is to study the reactions of some aryl diazonium salts with aryl amines, phenols and some nucleophilic groups and investigate the factors that control the nature of the products.

In this dissertation some samples of the diazonium salts reactions were studied and the result of these experiments were examined by infrared and ultraviolet radiations and comparing the melting points of these products with reported values in literature