



## Copyright Statement

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand). This thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author's right to be identified as the author of this thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material from their thesis.

To request permissions please use the Feedback form on our webpage.

<http://researchspace.auckland.ac.nz/feedback>

## General copyright and disclaimer

In addition to the above conditions, authors give their consent for the digital copy of their work to be used subject to the conditions specified on the Library

[Thesis Consent Form](#)

STUDIES OF SOME ELIMINATION AND  
SUBSTITUTION REACTIONS IN A SERIES OF  
1-ARYLNAPHTHALENE TETRACHLORIDES

A Thesis Presented to the  
University of Auckland  
for the Degree of  
Doctor of Philosophy

by

Keith Richard Bedford

University of Auckland

September, 1976

To my wife,

JENNY

ABSTRACT

The heterolytic chlorination of 1-arylnaphthalene (aryl = 1(p-nitrophenyl), 1(p-chlorophenyl), 1-phenyl, and 1(p-methylphenyl) ) yields the appropriate 1-aryl-r-1,c-2, t-3,t-4-tetrachloro-1,2,3,4-tetrahydronaphthalene as the major product of addition. The  $^1\text{H}$  n.m.r. spectra of these compounds show that there is no significant change in the conformation adopted in solution accompanying the change in the para-substituent.

The major product of the alkaline dehydrochlorination of each of these tetrachlorides using sodium methoxide in methanol-acetone (80:20 v/v) or benzene-methanol (75:25 v/v) is the 1-aryl-2,3-dichloronaphthalene. The first stage of the reaction is rate-controlling and both stages appear to be bimolecular. The observed rate-coefficients have been dissected to derive rates for the two competing elimination processes involving either initial loss of the 4-chlorine and 3-hydrogen or of the 1-chlorine and 2-hydrogen. The value of the Hammett reaction constant for the first of these processes was found to be 0.60 in methanol-acetone and 0.85 in benzene-methanol. The corresponding values for the second process were found to be 1.48 and 1.58. Both these results indicate that the effect of substituents in stabilizing the incipient negative charge developing at the  $\beta$ -carbon in the transition state is an important feature of the elimination processes involved.

A slow, unimolecular solvolysis at the 1-chlorine has been observed with 1-Ph-NTC and 1(p-Me-Ph)NTC in methanol-acetone. It is proposed that the major product of this solvolysis results from the replacement of the 1-chlorine by a methoxy-group with retention of configuration. In contrast, the major product of solvolysis assisted by silver (I) ions is that possessing the inverted configuration. Alkaline dehydrochlorination of the methoxy-substituted compounds derived from 1(p-Me-Ph)NTC leads to fully aromatic products. This requires the elimination of the components of a molecule of methanol under comparatively mild alkaline conditions.

Dehydrochlorination from the 1-arylnaphthalene tetrachlorides promoted by aluminium chloride in carbon disulphide at reflux temperature results in a mixture of the 1-aryl-2,3- and 2,4-dichloro- products. The proportion of 2,4-dichloro- product varies from 49% (1(p-NO<sub>2</sub>-Ph)NTC) to 65% (1-Ph-NTC).

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to Professor P.B.D. de la Mare for the opportunity of working under him. His guidance, encouragement and friendship during the course of this investigation have been deeply appreciated.

This study is a further contribution in a series which has involved a number of research workers under the guidance of Professor de la Mare. As such, it draws on the labours and insights of many others. In particular I wish to thank Dr G.W. Burton, formerly of this Department and now at the University of California, Berkeley, for his assistance and friendship during the early part of this work.

I am grateful for helpful discussions with members of staff and visitors to the Chemistry Department over the period I have spent at the University of Auckland. In this context I would particularly like to acknowledge the assistance of Dr D.J. McLennan. I would also like to thank the technical staff of the Department for their assistance.

The completion of this investigation is due, in no small measure, to the support and encouragement of my family and, more recently, of my wife. To them I express my very sincere thanks.

I wish to acknowledge the assistance of Mr D. Calvert in the running of some of the  $^1\text{H}$  n.m.r. spectra involved in

this investigation.

I am grateful to Miss Sue Brown for the careful way she has carried out the difficult task of typing this thesis.

The University Grants Committee is thanked for the provision of a Postgraduate Scholarship.

Finally, I would like to thank those whose friendships have made my time in the Chemistry Department so enjoyable.

## TABLE OF CONTENTS

	<u>Page</u>
Abstract	(i)
Acknowledgements	(iii)
Table of Contents	
List of Figures	
List of Tables	

### PART I. INTRODUCTION

1.1 Preamble	1
1.2 The Determination of Configuration and Conformation	2
1.3 The Naphthalene Tetrachlorides	11
1.4 Heterolytic Olefin-forming Elimination	29
1.5 Solvolysis Reactions	67
1.6 The Hammett Equation	80
1.7 The Aims and Scope of this Investigation	91

### PART II. EXPERIMENTAL

2.1 Materials and Methods	93
2.2 Syntheses	97
2.3 Computer-simulation of $^1\text{H}$ n.m.r. Spectra	110
2.4 Rates and Products of Alkaline Dehydrochlorination	114
2.5 Solvolysis Reactions	126
2.6 Alkaline Dehydrochlorination of Solvolysis Products	139
2.7 Catalytic Dehydrochlorination	148



PART III. DISCUSSION

	<u>Page</u>
3.1 Structures	153
3.2 The Alkaline Dehydrochlorination of the 1-Arylnaphthalene Tetrachlorides	157
3.3 Hammett Plots and Interpretation	163
3.4 Solvolysis Reactions	178
3.5 Elimination Reactions of Solvolysis Products	185
3.6 Catalytic Dehydrochlorination	192
3.7 Conclusions	195

APPENDICES

Appendix 1:	<sup>1</sup> H n.m.r. Spectra	197
Appendix 2:	Related Publications	208

LIST OF FIGURES

	<u>Page</u>
1-1 Plot of the Karplus relationship	9
1-2 The six stereoisomers of naphthalene tetrachloride	14
1-3 The dehydrochlorination of naphthalene- $\xi$ -tetrachloride	18
1-4 The dehydrochlorination of 1-chloronaphthalene tetrachloride	26
1-5 Schematic representation of the structure of the E2 transition state	42
1-6 Potential energy surface encompassing concerted and stepwise $\beta$ -elimination	46
1-7 Comparison of the predictions of the effect of structural variations in the reactants on the transition state of E2 eliminations	48
2-1 Graph of solvolysis rate-coefficient against percent reaction	135
3-1 Reaction scheme for the alkaline dehydrochlorination of the 1-arylnaphthalene tetrachlorides	158
3-2 A comparison of the rates of some elimination processes	187

3-3	A reaction scheme for dehydrochlorination promoted by aluminium chloride	192
-----	--	-----

LIST OF TABLES

	<u>Page</u>
2-1 The preparation of aryl halides	98
2-2 Summary of computer-simulated $^1\text{H}$ n.m.r. results	112
2-3 Product analysis; g.l.c. operating conditions	119
2-4 Rates of alkaline dehydrochlorination in 80:20 methanol-acetone	121
2-5 Products of alkaline dehydrochlorination in 80:20 methanol-acetone	122
2-6 Rates of alkaline dehydrochlorination in 75:25 benzene-methanol	123
2-7 Products of alkaline dehydrochlorination 75:25 benzene-methanol	124
2-8 The solvolysis of 1(p-Me-Ph)NTC in 80:20 methanol-acetone	134
2-9 Products of alkaline dehydrochlorination in 80:20 methanol-acetone	141
2-10 Rates of alkaline dehydrochlorination in 80:20 methanol-acetone	143
3-1 Analysis of results in methanol-acetone	165
3-2 Analysis of results in methanol-acetone	166
3-3 Analysis of results in benzene-methanol	167
3-4 Analysis of results in benzene-methanol	168

	<u>Page</u>
3-5 Reaction constants for various elimination reactions	170
3-6 Studies of $\alpha$ -carbon substituent effects	173
3-7 Miscellaneous solvolysis reactions	179