



A STUDY OF SOME RANEY NICKEL

CATALYZED REACTIONS.

A thesis presented for the Degree of

Doctor of Philosophy

in

The University of Adelaide

by

Keith Oliver Wade, B.Sc.

Department of Organic Chemistry

December, 1966

## CONTENTS

	<u>Page</u>
Summary:	(i)
Statement:	(iii)
Acknowledgements:	(iv)
Introduction:	1
Chapter I: Hydrogenolysis of Group IVb-organo compounds.	
Discussion	21
Experimental	48
Chapter II: The action of Raney nickel on aniline and related compounds.	
Discussion	61
Experimental	96
Chapter III: Synthesis of monosubstituted 2,2'-bipyridyls.	
Discussion	115
Experimental	126
Appendix: Nomenclature of organosilicon compounds.	137
References:	138

\*\*\*

(i)

SUMMARY

This study of the mechanisms and synthetic applications of organic reactions with Raney nickel catalysts has been divided into three sections; the investigation of the cleavage of Group IVb-organo compounds with Raney nickel, the examination of the alkylation of amines catalyzed by Raney nickel, and the synthesis of several 2,2'-bipyridyl derivatives.

Twelve phenyl derivatives of silicon have been cleaved by treatment with several Raney nickel catalysts to give mixtures of benzene and cyclohexane and small quantities of by-products including biphenyl and tetracyclohexylsilane, Tetraphenylstannane, tetraphenylgermane, triphenylgermanol, and tetracyclohexylplumbane were similarly cleaved, while alkyl derivatives of silicon and tin were found to be stable under the conditions used. Phenylsubstituted siloxanes and silanols were less readily split than those silanes without oxygen functions. A mechanism for the cleavage of organosilicon bonds has been proposed, involving chemisorption of the silicon atom by accepting electrons into its empty  $3d$  orbitals, expulsion of a phenyl anion, and hydrogenolysis of the remaining groups. This mechanism has been discussed with respect to other Group IVb-organo derivatives.

The reactions of aniline and cyclohexylamine with Raney nickel giving N-cyclohexylaniline and other related secondary amines has been studied. These reactions have been extended to  $\alpha$ -naphthylamine, the toluidines, and compounds with two nitrogen atoms, including  $\beta$ -amino-

(ii)

pyridine, 3-aminopiperidine, 1,2-diaminocyclohexane, and the phenylene diamines. The reactions have been shown to be a useful synthetic pathway to N-alkylarylamines. The reaction pathways and mechanisms of these reactions are discussed with respect to the types of adsorptions possible between nitrogen and Raney nickel. The results of previous workers has been correlated by these conclusions.

Eighteen new 4-substituted 2,2'-bipyridyls and 2,2'-bipyridyl-1-oxides have been synthesized from 2,2'-bipyridyl by a synthetic route through 4-nitro-2,2'-bipyridyl-1-oxide.

\*\*\*

(iii)

STATEMENT

The work described in this thesis incorporates no material previously submitted for any degree in any University, and to the best of my knowledge and belief contains no material previously published or written by another person except where due reference is made in the text.

Keith Oliver Wade.

December, 1966.

(iv)

ACKNOWLEDGEMENTS

I sincerely thank Dr. W.H.F. Sasse for the inception of this project and for his enthusiastic guidance and help throughout the work. Thanks also go to Dr. A.D. Ward and Dr. R.A. Jones for their assistance and contribution of ideas to later stages of this project.

I gratefully acknowledge Dr. T. McL. Spotswood for helpful discussions on nuclear magnetic resonance spectra, Dr. J.H. Bowie for assistance with interpretation of mass spectra, and Dr. K. Norrish, Division of Soils, C.S.I.R.O., for silicon determinations.

I am deeply indebted to The University of Adelaide for the allocation of a Research Grant for the duration of this work.

\*\*\*