



SYNTHETIC APPLICATIONS OF ORGANOBORANES

A Thesis

Presented for the Degree of

Doctor of Philosophy

in

The University of Adelaide

by

Roger Murphy, B.Sc. (Hons.)

Department of Organic Chemistry

1976.

CONTENTS

	<u>Page</u>
SUMMARY	(i)
STATEMENT	(iii)
PUBLICATIONS	(iv)
ACKNOWLEDGEMENTS	(v)
CHAPTER 1. Synthesis of Products Isolated from the Hydroboration-Cyanidation of Unsaturated Terpenes.	
1.1 Introduction.	1
1.2 Synthesis of Products Derived from Geraniol.	12
1.3 Synthesis of Products Derived from Linalyl Acetate.	17
1.4 Synthesis of Products Derived from Myrcene.	22
CHAPTER 2. Cyanidation of Dialkylboranes and Borinic Acids and Esters.	
2.1 Introduction.	43
2.2 Cyanidation of Dialkylboranes.	50
2.3 Cyanidation of Borinic Acids and Esters.	65

CHAPTER 3. Silver(I) Oxidation of Organoboranes.	
3.1 Introduction.	70
3.2 Cyclization of Dienes via Intramolecular Alkyl Coupling.	76
3.3 Attempted Reduction of Intermediates Obtained by Reaction of Organoboranes with Alkaline Silver nitrate.	84
CHAPTER 4. Asymmetric Induction by Hydroboration with Optically Active Dialkylboranes.	
4.1 Introduction.	88
4.2 Attempted Resolution of (±)-4,4,6-Trimethylcaprolactam and (±)-4,6,6-Trimethylcaprolactam.	96
4.3 Attempted Resolution of (±)-3,5,5-Trimethylcyclohexanone.	100
4.4 Asymmetric Hydroboration of 6,7-Dihydro-4,6,6-trimethyl-5H-azepinone and 3,5,5-Trimethylcyclohex-2-enone (Isophorone).	110

CHAPTER 5. Experimental.

5.1 General.	118
5.2 Work described in chapter 1.	121
5.3 Work described in chapter 2.	163
5.4 Work described in chapter 3.	178
5.5 Work described in chapter 4.	184

REFERENCES.	197
-------------	-----

(i)

SUMMARY

An investigation of the synthetic utility of organoboranes has been carried out, and this investigation is presented in four parts.

Firstly, a number of novel compounds have been obtained by application of the cyanidation procedure to the products of hydroboration of various unsaturated terpenes. The structures of these products are confirmed herein by synthesis of each product via unambiguous means.

Secondly, an attempt has been made to facilitate the synthesis of secondary carbinols and ketones by application of the cyanidation procedure to dialkylboranes, and borinic acids and esters, respectively. The scope and limitations of such procedures are discussed.

Thirdly, the coupling reaction of organoboranes in the presence of silver (I) salts has been applied to organoboranes derived from dienes, and again the scope and limitations of the reaction are discussed. In the light of products obtained from this investigation, the mechanism of the coupling reaction is re-examined.

(11)

Fourthly, an attempt has been made to apply the known ability of optically active dialkylboranes to induce asymmetry in substrates with which they react to a specific synthetic problem. An attempt has also been made to utilize what was formerly an undesirable side-reaction in the hydroboration of allylically substituted olefins to induce asymmetry in a specific substrate. Both of these investigations have also been compared to the more conventional methods of resolution of the optical isomers of asymmetric compounds.

(iii)

STATEMENT

This thesis contains no material previously submitted for a degree or diploma 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.

Roger Murphy.

(iv)

PUBLICATIONS

Part of the work described in this thesis has been reported in the following publications:

"Annulation of Organoboranes Derived from Geraniol". R. Murphy and R.H. Prager, Aust.J.Chem., 1976, 29, 617.

"Cyclization of Dienes via Hydroboration: Silver Ion Induced Intramolecular Alkyl Coupling". R. Murphy and R.H. Prager, Tet. Letters, 1976, 463.

(v)

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to Dr. R.H. Prager for his enthusiastic supervision and guidance throughout the course of this work.

My thanks also to Dr. G.E. Gream for many helpful discussions, and to other members of the department, particularly my colleagues in laboratory six, for their advice and encouragement.

Finally, I am indebted to my family and my friends for their patience and support during the course of my candidature.