

12/10/76

SYNTHESIS OF ICEANE AND OXA-ICEANE

A THESIS  
PRESENTED FOR THE DEGREE OF  
DOCTOR OF PHILOSOPHY

in

THE UNIVERSITY OF ADELAIDE

by

GARRY FREDERICK TAYLOR, B.Sc.(Hons)

Department of Organic Chemistry

1975

## CONTENTS

	Page
SUMMARY	i
STATEMENT	iii
ACKNOWLEDGEMENTS	iv
PUBLICATIONS	v
CHAPTER 1 - Introduction	1
CHAPTER 2 - The Synthesis of Tricyclo[5.3.1.0 <sup>4,9</sup> ]undec-5-en-2-one (40).	24
CHAPTER 3 - The Synthesis of Iceane	37
CHAPTER 4 - The Synthesis of Oxaiceane and <i>Abeo</i> -oxaiceane.	61
CHAPTER 5 - An Investigation of the products obtained from the acid catalysed opening of the cyclopropyl ring of ketone (23).	85

	Page
CHAPTER 6 - Experimental:	
General Topics	91
Chapter 2	94
Chapter 3	102
Chapter 4	120
Chapter 5	133
REFERENCES	139

### Summary

Tetracyclo[5.3.1.1<sup>2</sup>,6<sup>0</sup><sup>4</sup>,9]dodecane (iceane) (1) and an oxygen analogue 3-oxa-tetracyclo[5.3.1.1<sup>2</sup>,6<sup>0</sup><sup>4</sup>,9]dodecane (oxaiceane) (46) have each been synthesized via the same key olefinic ketone (40).

Chapter 2 describes the synthesis of the bromo-cyclopropyl ketone (39) and its successful cleavage by means of a new efficient fragmentation reaction using liquid sodium-potassium alloy to give the olefinic ketone (40), the structure of which was confirmed by independent synthesis.

Chapter 3 details the synthesis of iceane. Because of complications due to intramolecular reactions, the carbon skeleton was developed first, via the diolefin (58), before the functionality necessary to continue the synthesis was introduced. In an attempt to optimize some of the reactions associated with the synthesis, limonene (70) was chosen as a model compound for the diolefin (58). Selective hydroboration of (58) gave the olefinic alcohol (59) which was cyclized using triphenylphosphine in carbon tetrachloride to give a mixture of the epimeric chlorides (83) and (85) of iceane.

Chapter 4 describes the synthesis of oxaiceane (46) and a structural isomer *abeo*-oxaiceane (89) by the oxymercuration-sodium borohydride reduction of the olefinic alcohol (45). The structures

of these cyclic ethers were differentiated by the use of a chiral nmr shift reagent. Sodium-amalgam reduction was used to show that the intermediate mercury compound in the preparation of oxaiceane had a mercury atom in the prow position of a ring in a boat configuration. The mercury salt was isolated and used to investigate the stereospecificity of its reduction with sodium borodeuteride.

Chapter 5 describes an investigation of the products obtained from the acid-catalysed opening of the cyclopropyl ring of tetracyclo[5.3.1.0<sup>3,5</sup>0<sup>4,9</sup>]undecan-2-one (23) in aqueous acetic acid.