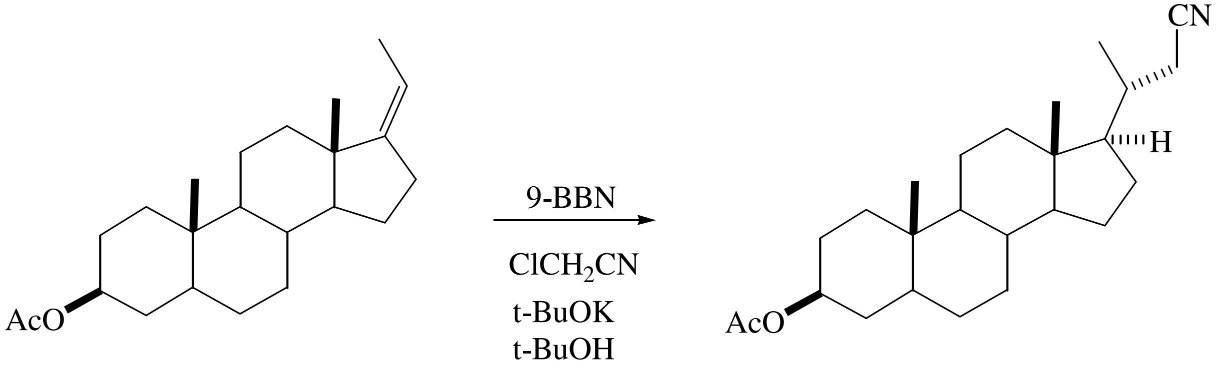
Heteroatoms in Organic Chemistry

Second Year

Professor T. J. Donohoe (lectures 1-4)

HT 2006 : 8 Lectures: Thursday at 10 am (weeks 1-8)
DP: Lecture Theatre

HANDOUT 1: Boron Reagents in Organic Synthesis



A copy of this handout is available at:

http://users.ox.ac.uk/%7Emagd1571/finalpage/teaching2.html

Heteroatoms in Organic chemistry

Synopsis

Lectures 1 & 2 Boron

1) General features and general reactions

2) Hydroboration

3) Reaction of Organoboranes (oxygenation, amination, halogenation, protonation, carbon-carbon bond formation)

4) Alkene synthesis using organoboron reagents

5) Allyl addition using boron reagents

Recommended books:
General: Organic Chemistry (Warren et al)
Organic Synthesis: The Role of Boron and Silicon, S. E. Thomas (Oxford Primer)
Some Modern Methods of Organic Synthesis, W. Carruthers (Cambridge)

1) General Features of Organoboron Compounds

a) Electronic configuration is

b) ie 6

c) electron

d) isoelectronic with

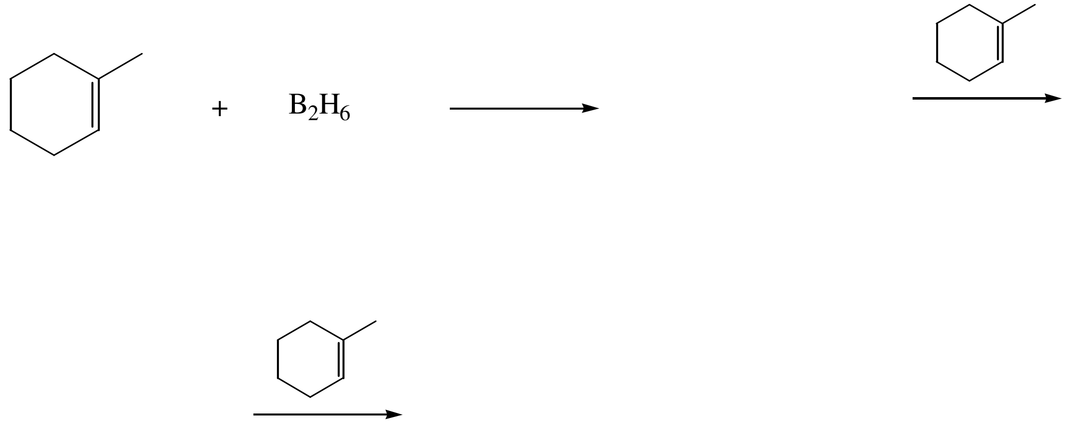
e) trigonal complexes

f) tetrahedral complexes

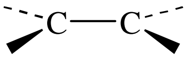
g) electronegativity C= H= B=

2. General Reactions of Organoboranes

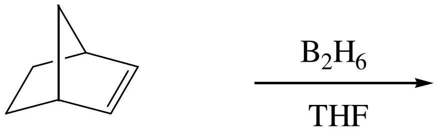
A. Hydroboration:

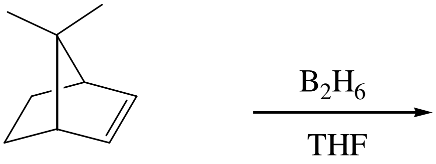


Consider the STEREOCHEMISTRY of this reaction.



Not only is the addition concerted but also it can be DIASTEREOSELECTIVE

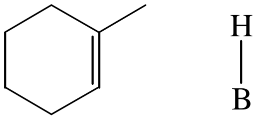




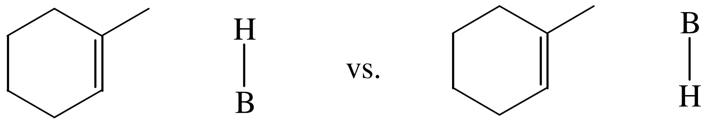
and the REGIOCHEMISTRY

Regioisomers are:

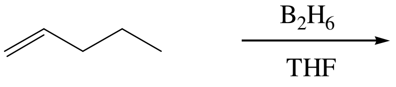
(i) Electronic



(ii) Steric



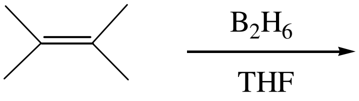
However, the regioselectivity is not always



94 : 6

60 : 40

The solution involves using a



(Thex-BH_2)

9-BBN

These reagents, especially

94 : 6 (BH_3)

(9-BBN)

(BH_3)

(9-BBN)

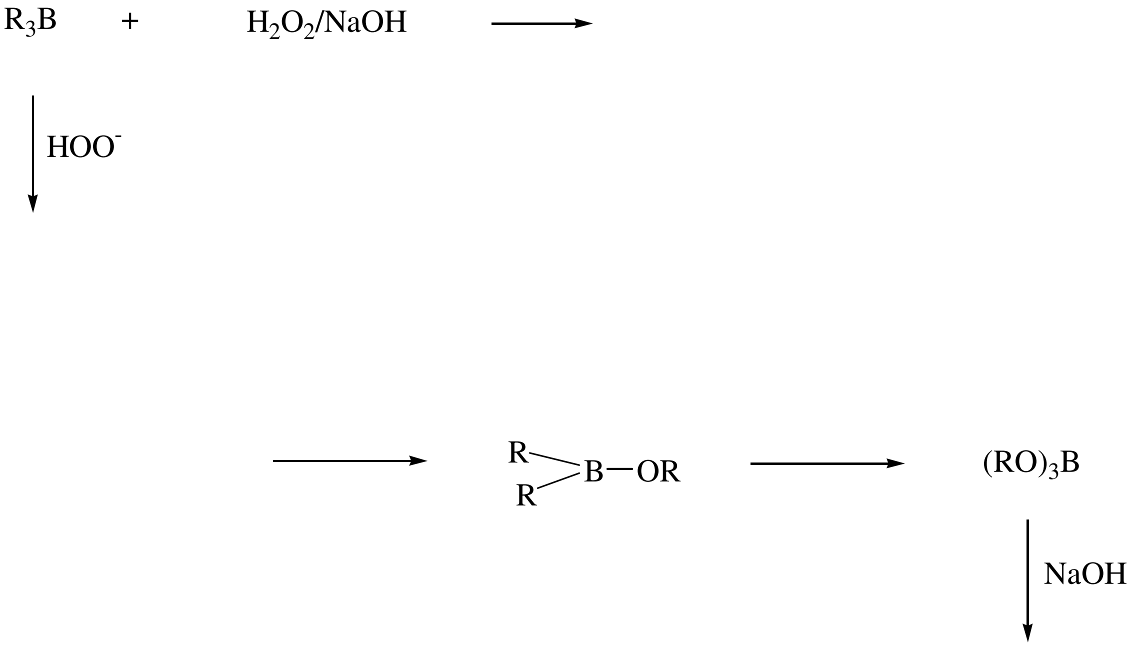
B. Reactions of Organoboranes

General:

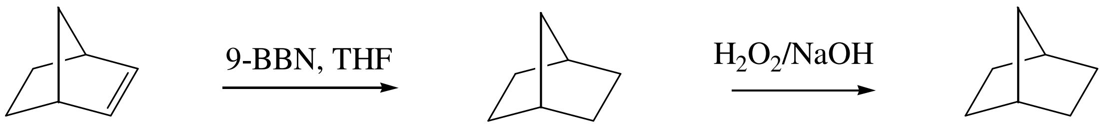
$B{-}R \dashrightarrow$

$R_3{-}B \dashrightarrow$ 3x R-X

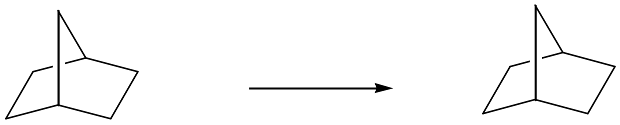
i) Introduction of oxygen



This reaction involves RETENTION

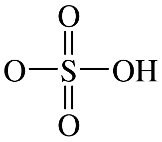


By using a stronger oxidant then



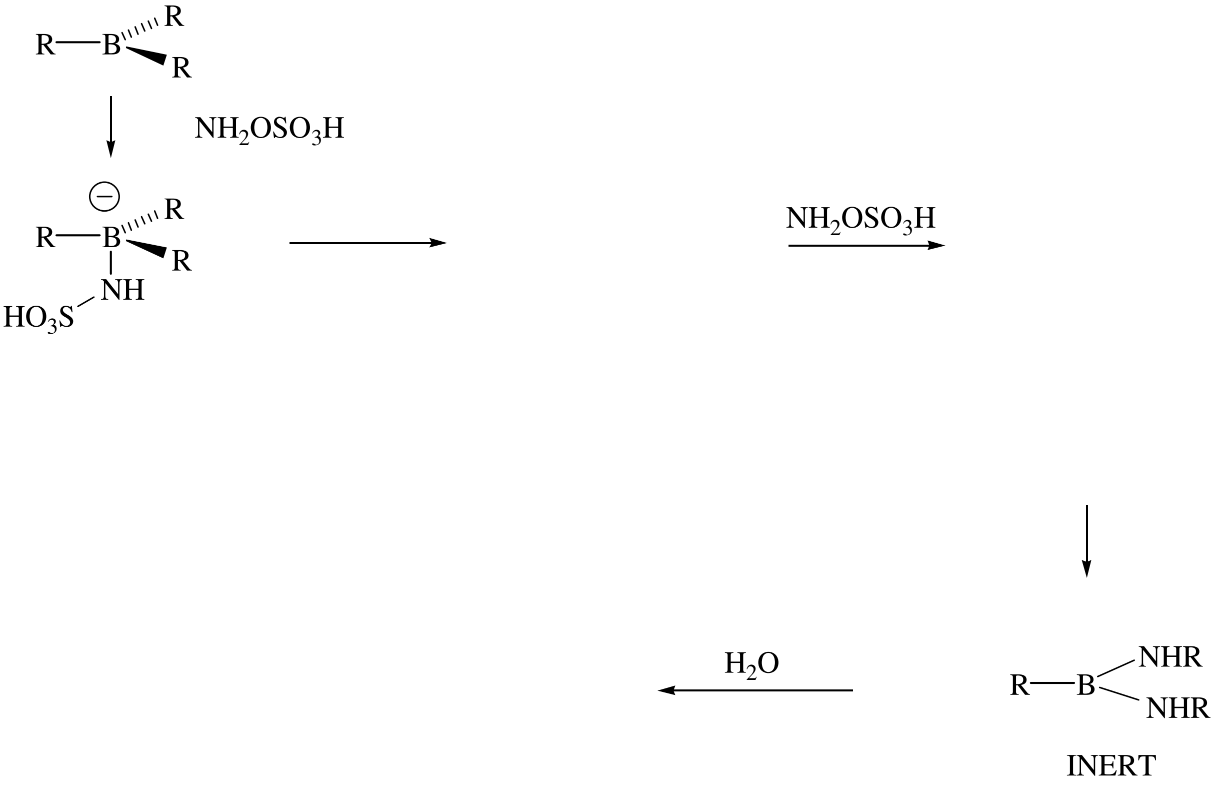
ii) Introduction of nitrogen

Use H_2N-X

X= Cl, 

$O-S(=O)_2-OH$

Mechanism



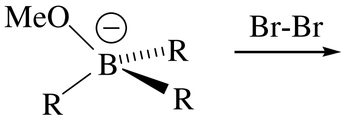
iii) Introduction of a halogen

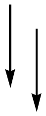
$R{-}B \dashrightarrow R{-}X$

Use methoxide as an additive:

INVERSION

Mechanism





$(MeO)_3B + 3x\ RBr$

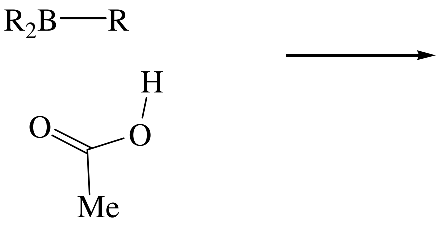
iv) Introduction of a proton

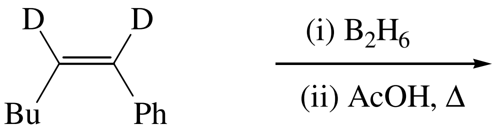
$R\text{-}B \dashrightarrow R\text{-}H$

$R_3B \xrightarrow{AcOH}$

RETENTION
ALL 3

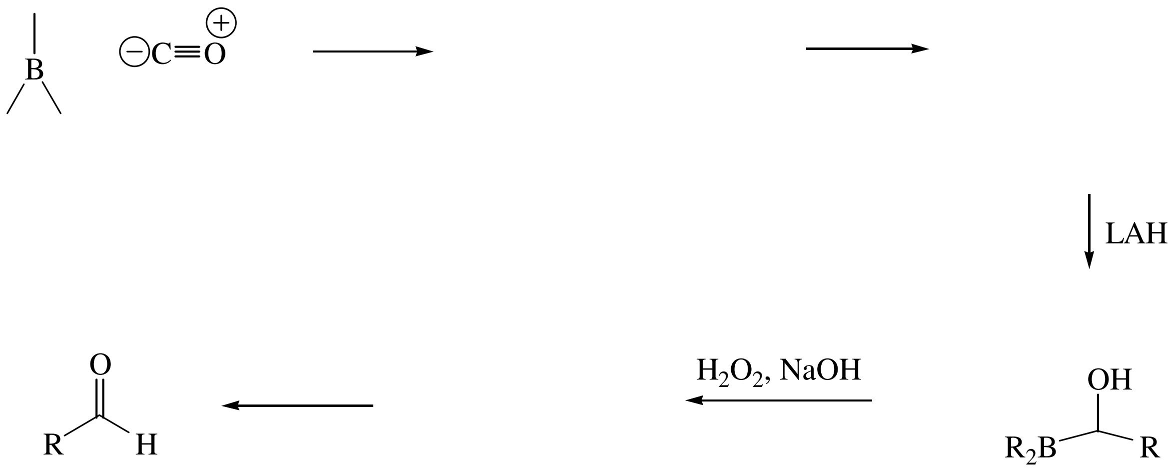
Mechanism





v. Carbon-Carbon Bond Formation

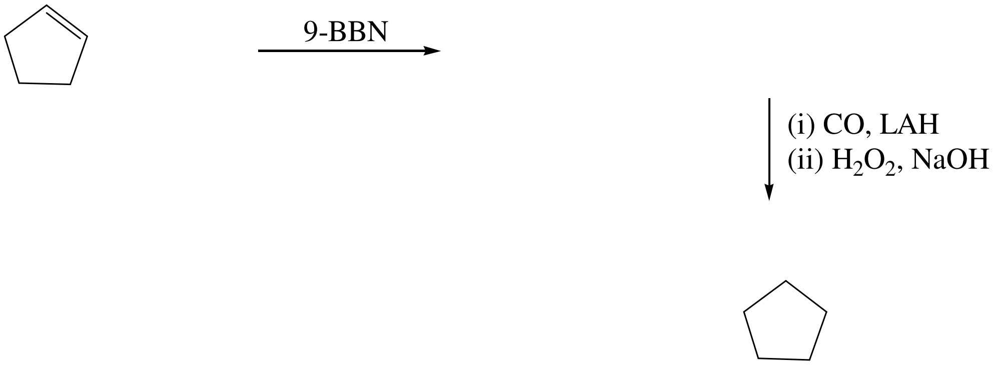
(a) Carbonylation



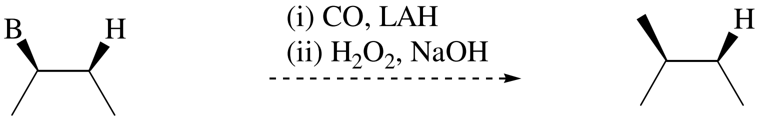
Clearly, only ONE

This can be best utilised in conjunction with 9-BBN

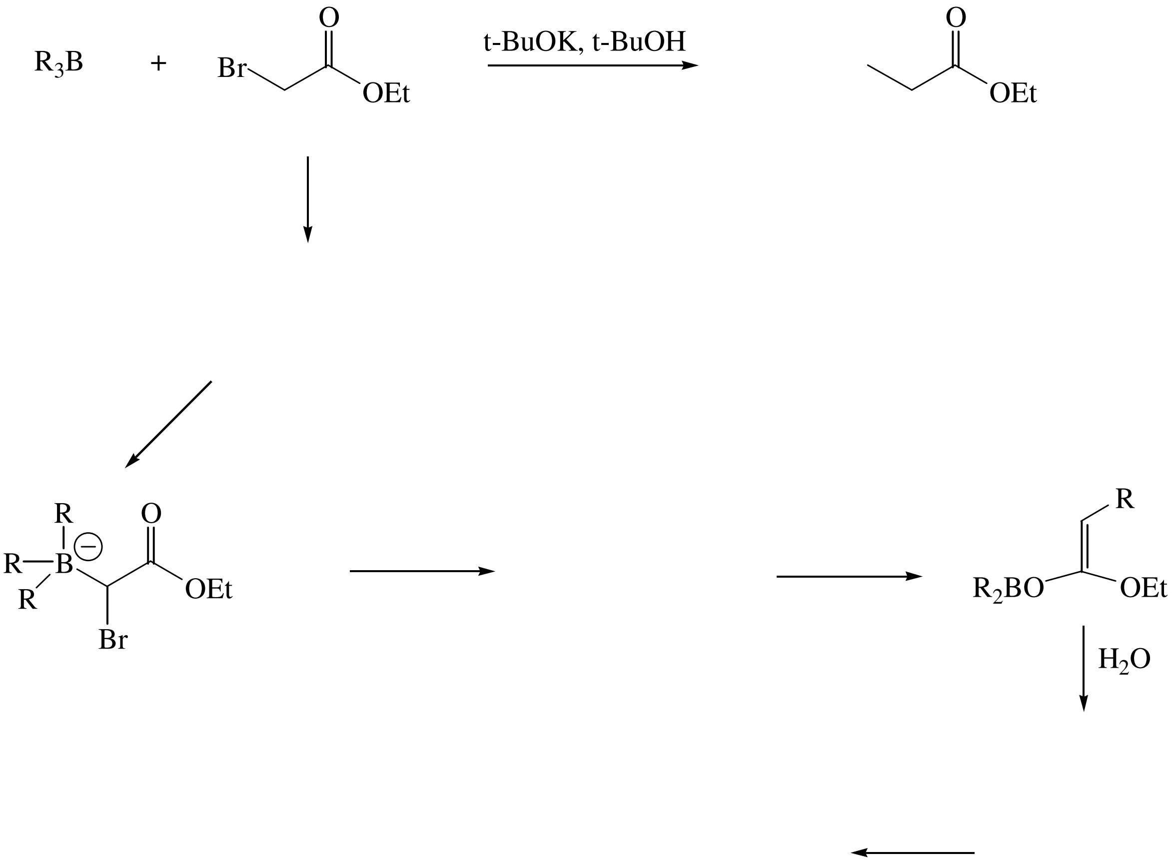
So



All occurs with RETENTION



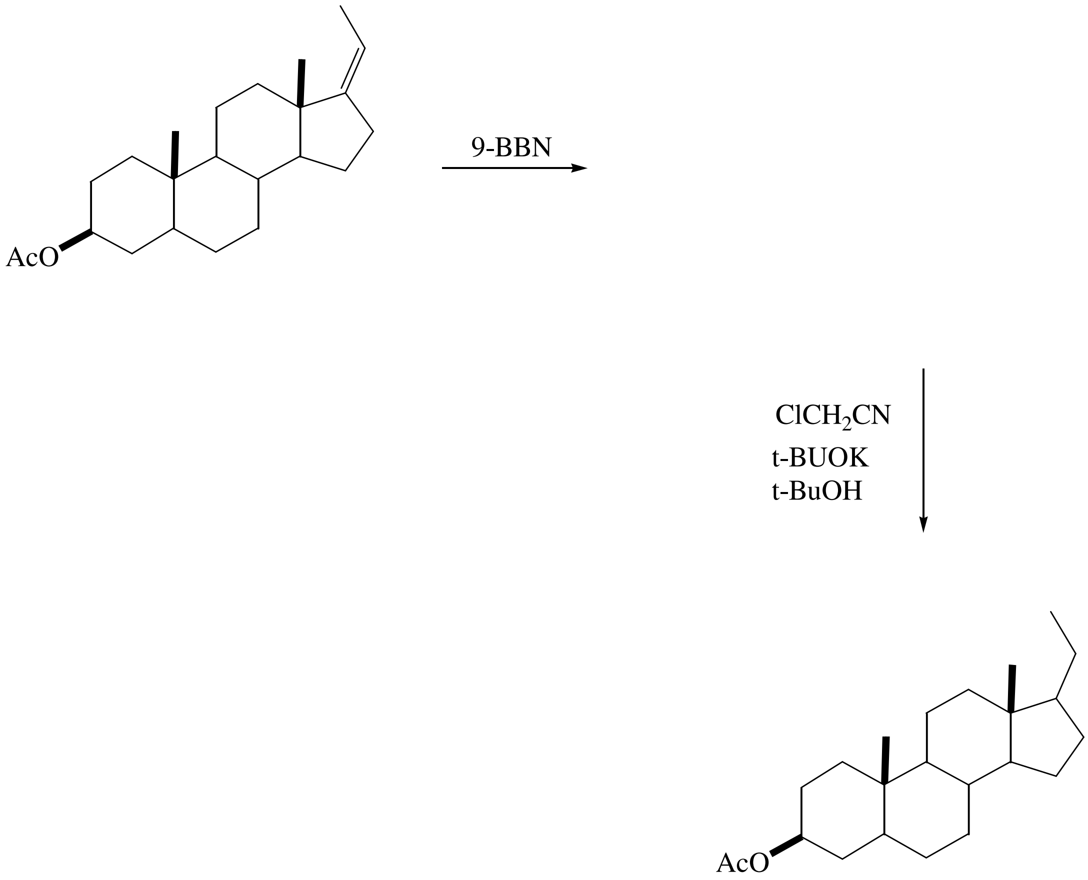
(b) α-Haloesters (Darzens Reaction)



BUT, Only 1 R migrates

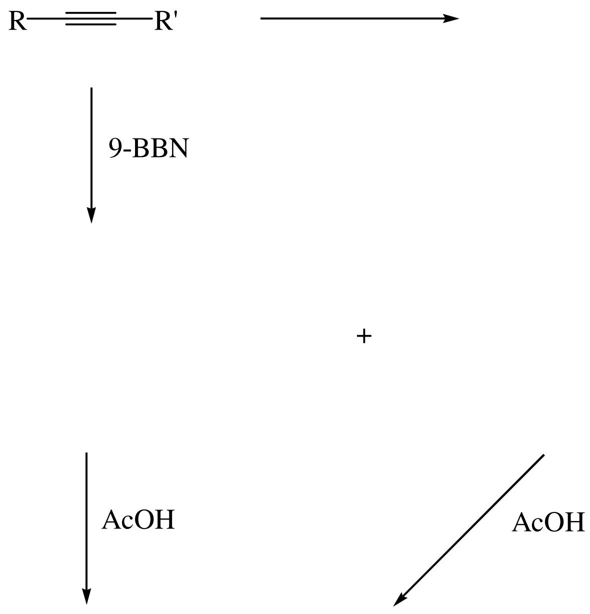
Use, 9-BBN

Example from steroid synthesis

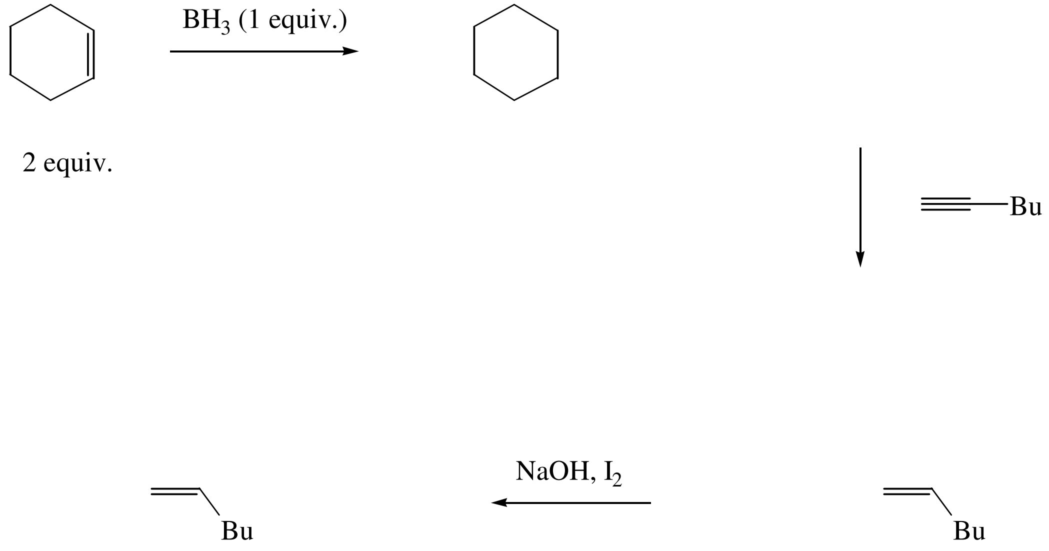


Alkene Synthesis Using OrganoBoron Reagents

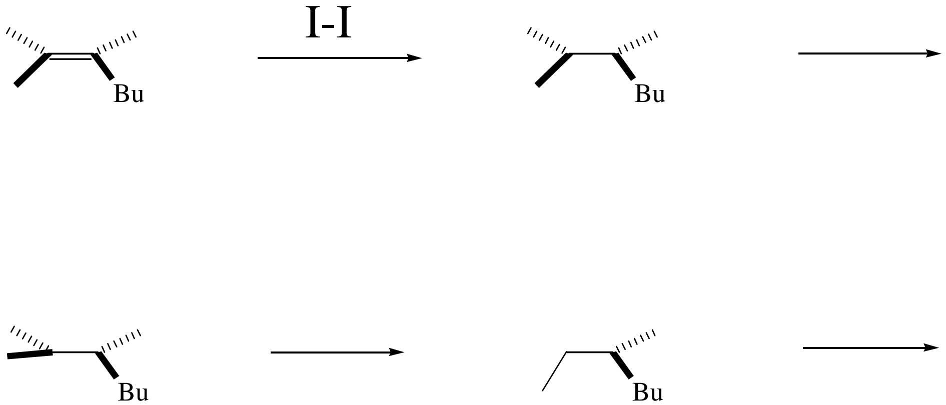
1) Cis (*Z*)-Alkenes from disubstituted acetylenes



2) Cis (*Z*)-Alkenes from monosubstituted acetylenes



Now the alkene is

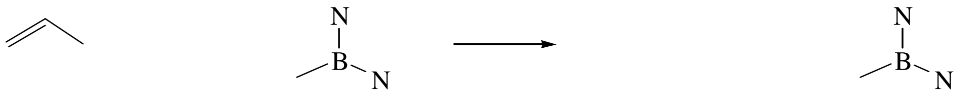


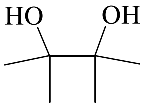
Allyl Addition Using Allyl-Boron Compounds

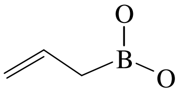
Allylboranes are very reactive:

Also- substituted allylboranes rearrange easily: limits

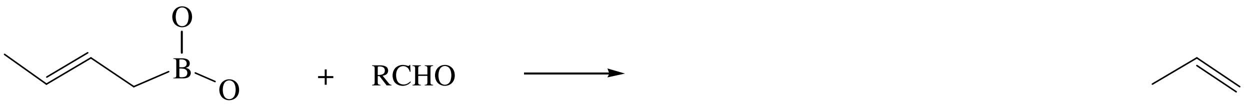
So, the use of dialkoxyallylboranes

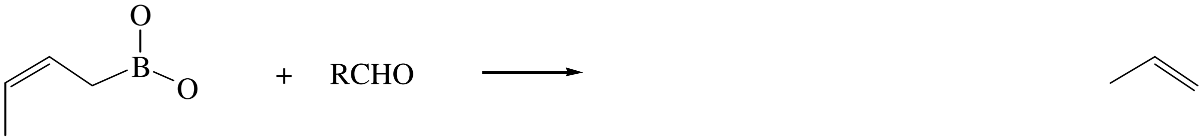






These have the advantage that rearrangement is SLOW and this allows





There is a big advantage over allylic anions