

LEC (16)

CHEM 30A

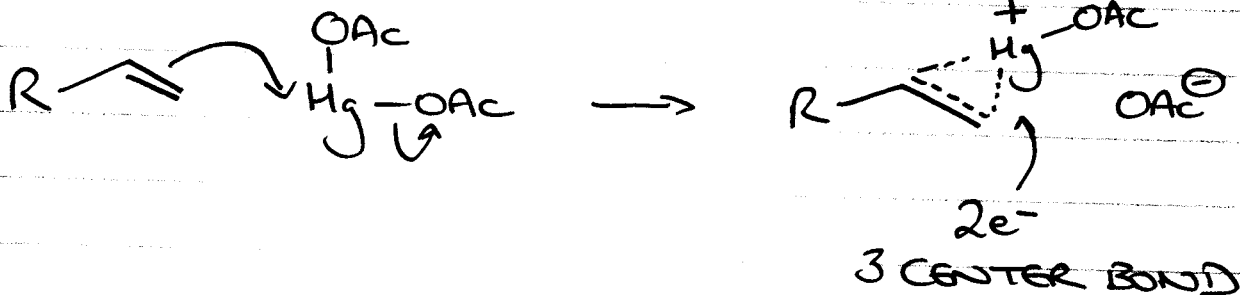
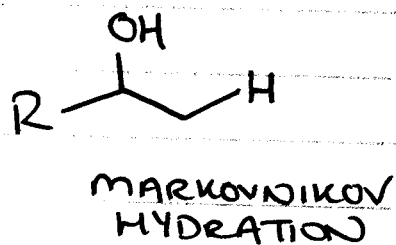
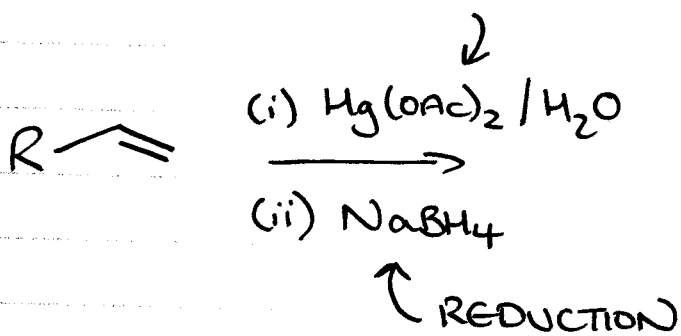
Nov 8th

(1)

- ① OXYMERCURATION
- ② HYDROBORATION
- ③ OXIDATION
- ④ REDUCTION

- Mechanism Guides / Problem Sets on WEB
- READ: Ch 6 esp 6.7
- PROBLEMS 6.13, 6.37-6.49
- QUIZ ON WEDNESDAY

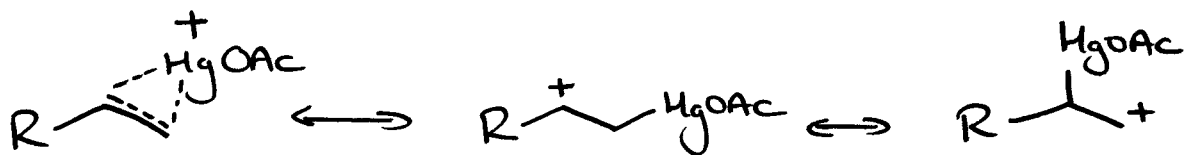
① OXYMERCURATION



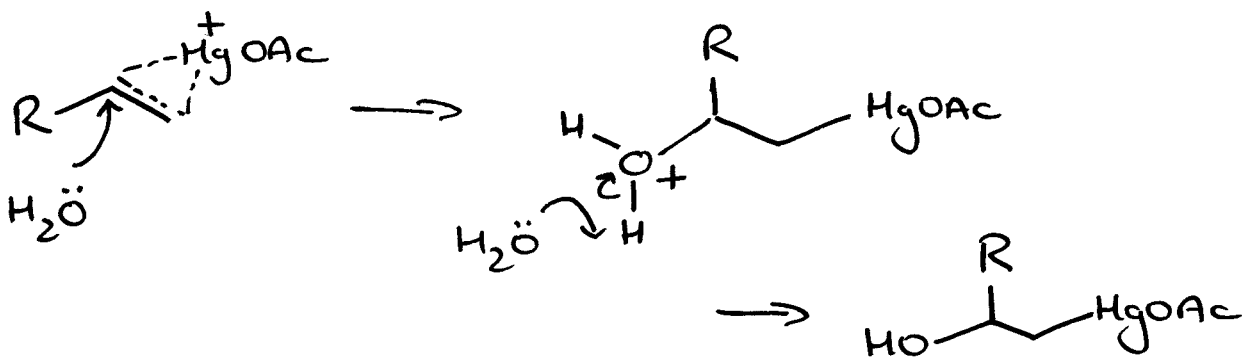
CYCLOC MERCURINIUM ION

(2)

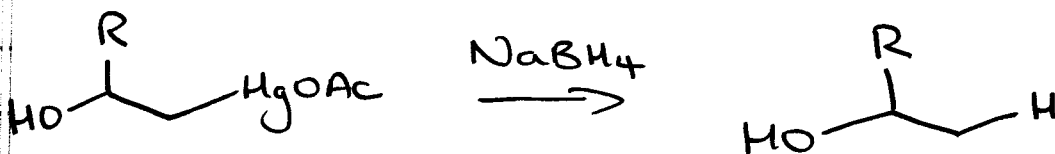
Consider resonance forms



opens via most stable  $\text{C}^+$



IN SECOND STEP, ORGANOMERCURY IS REDUCED WITH  $\text{NaBH}_4$



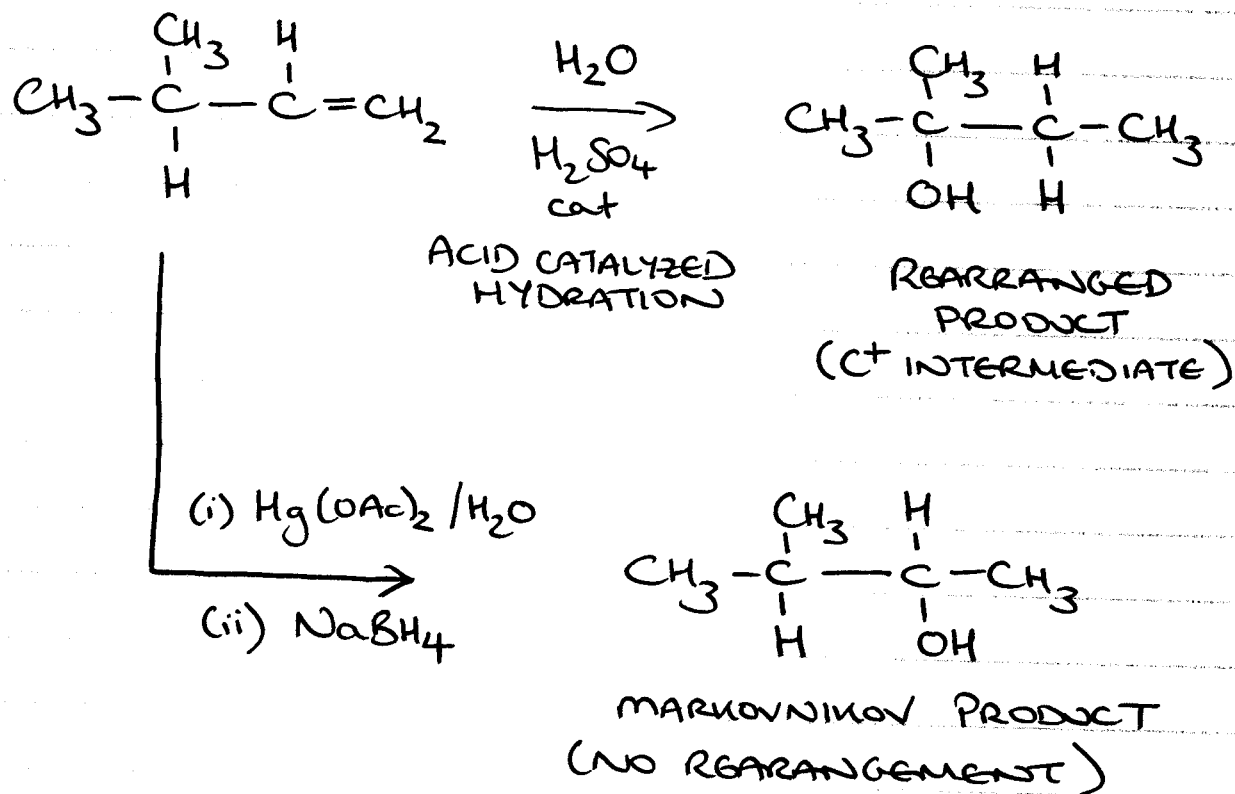
Replaces  $\text{HgOAc}$  with  $\text{H}$

REGIOSPECIFIC w/ ANTI STEREOSPECIFIC  
OPENING OF MERCURINIUM ION

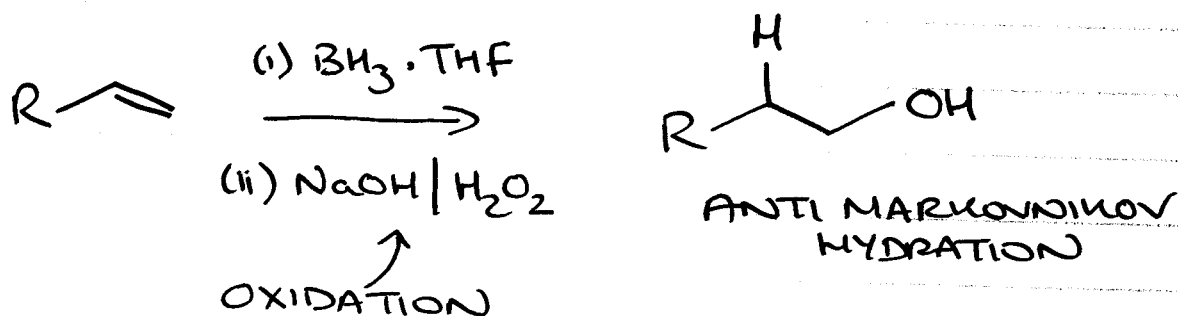
NO  $\text{C}^+$  INTERMEDIATE  $\Rightarrow$  NO REARRANGEMENT

3

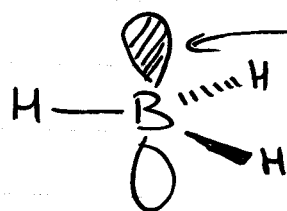
Why is this useful



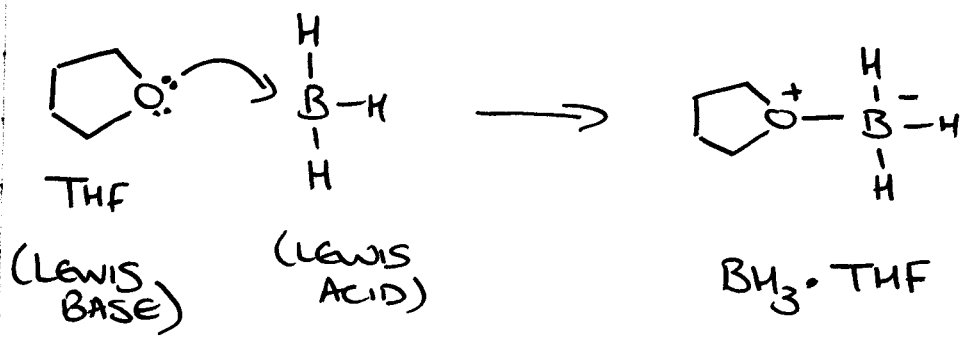
## ② HYDROBORATION



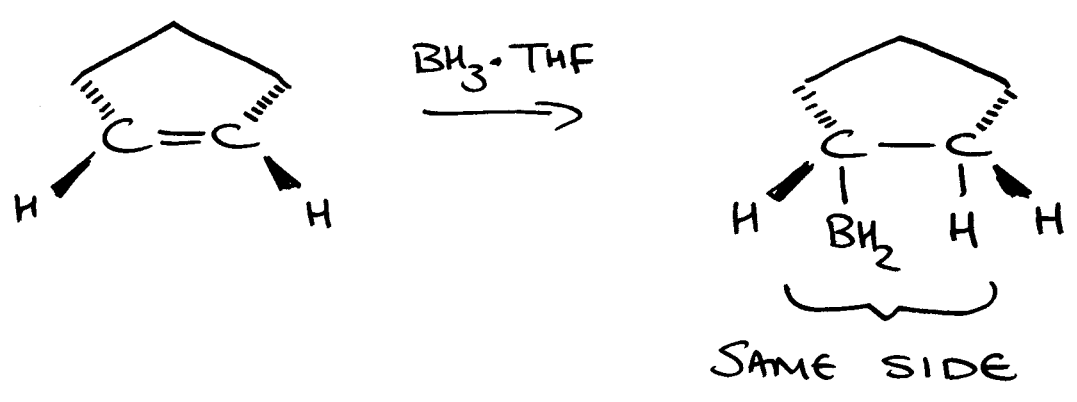
BORANE (BH<sub>3</sub>)



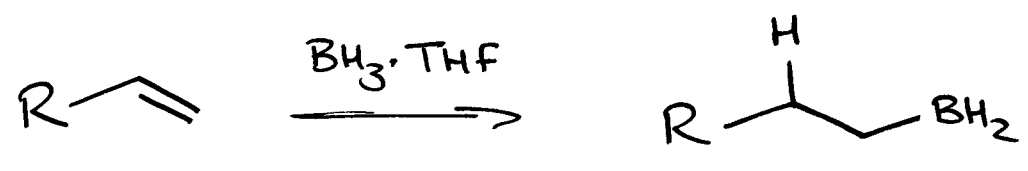
(actually exists as  
B<sub>2</sub>H<sub>6</sub> - DIBORANE)  
STRUCTURE?



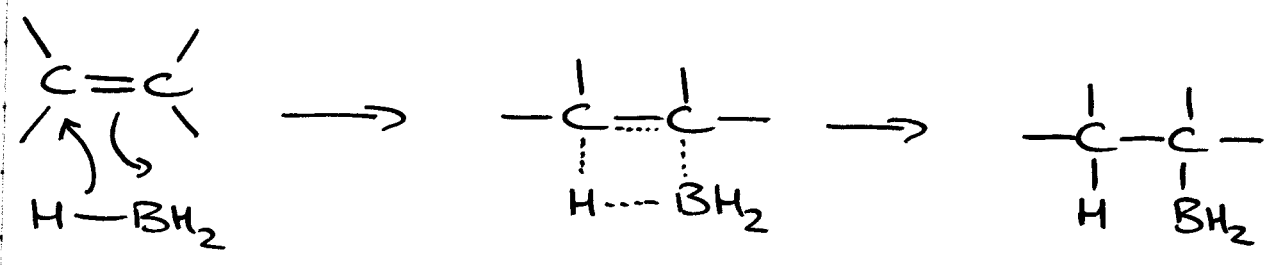
— SYN-STEREOSPECIFIC



— REGIOSELECTIVE



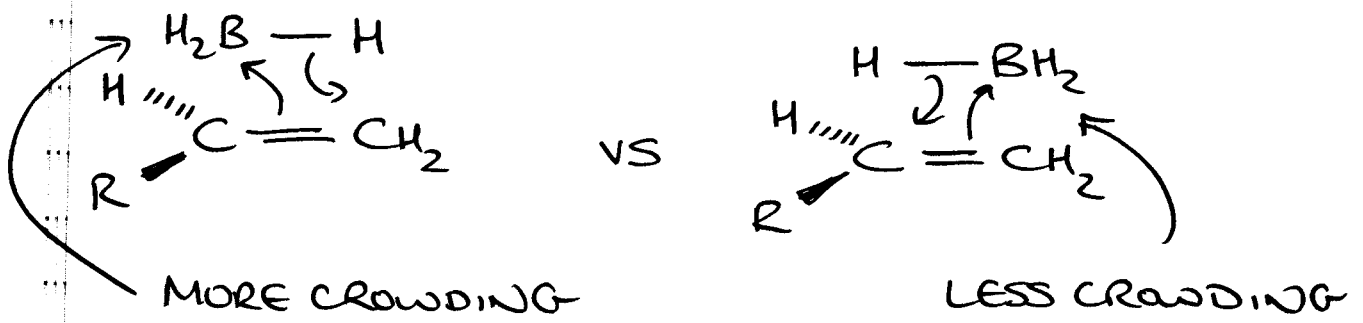
BORON ADDS TO LESS SUBSTITUTED C ATOM



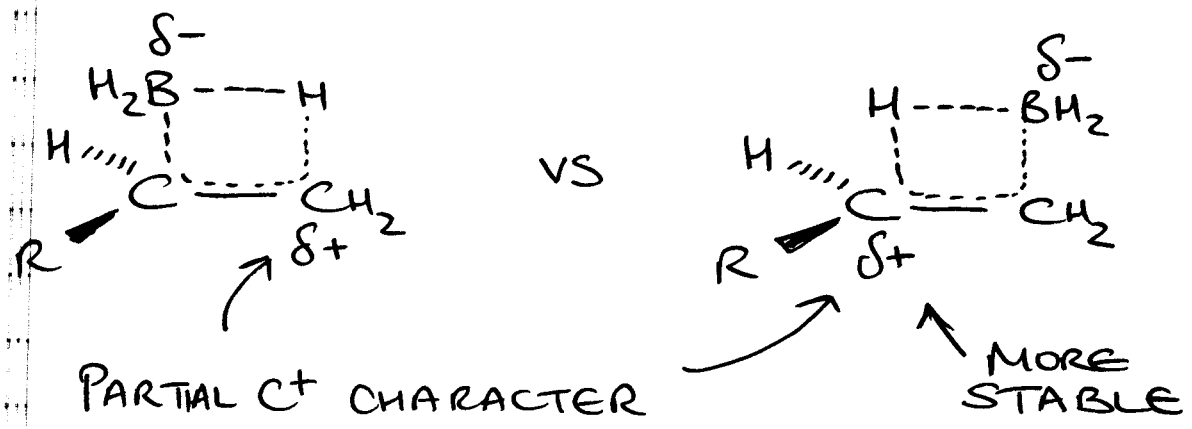
DOES NOT GO THROUGH C<sup>+</sup> INTERMEDIATE  
⇒ NO REARRANGEMENTS

# WHY REGIOSELECTIVE?

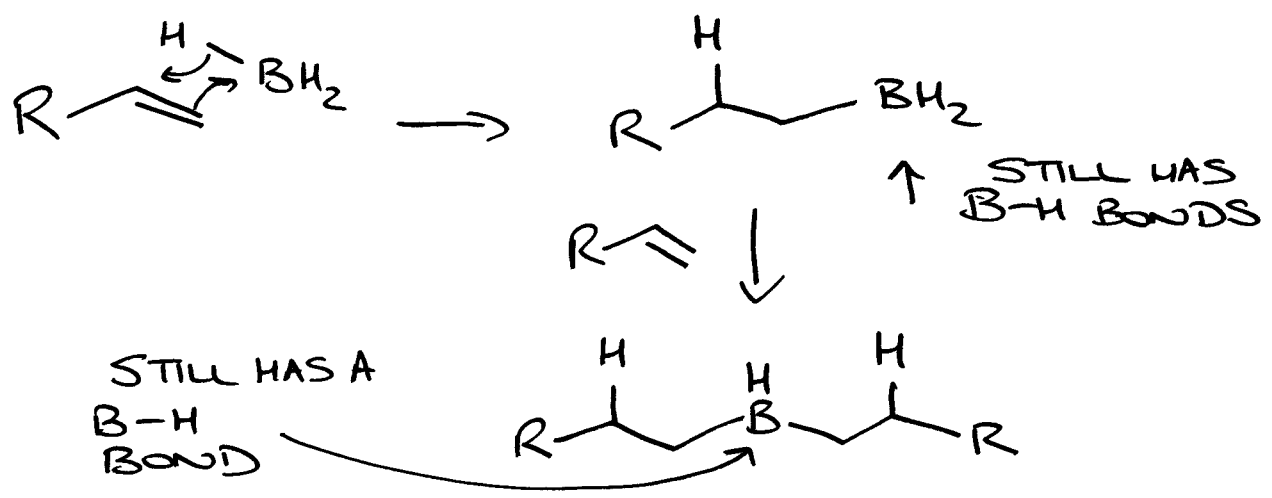
## (i) STERIC



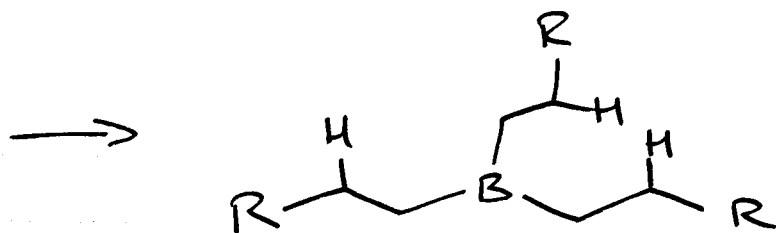
## (ii) ELECTRONICS



## FULL MECHANISM

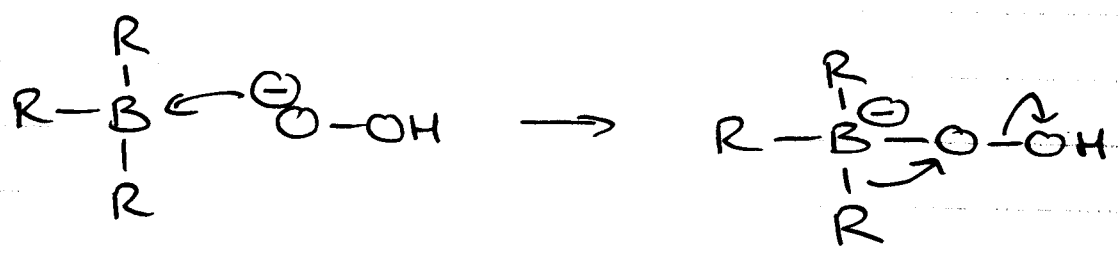
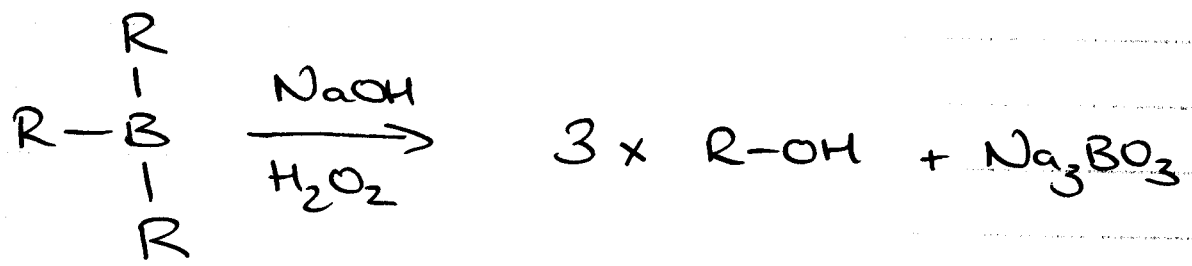


6

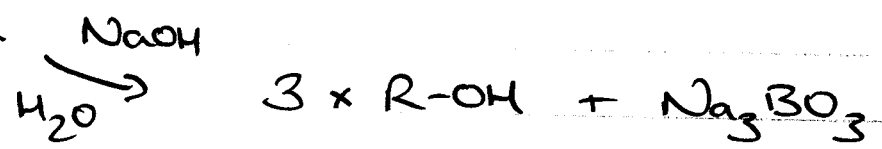
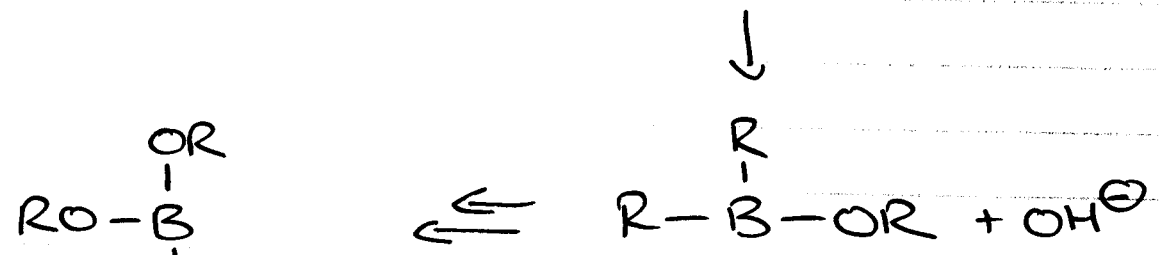


TRIALKYLBORANE

OXIDATION STEP

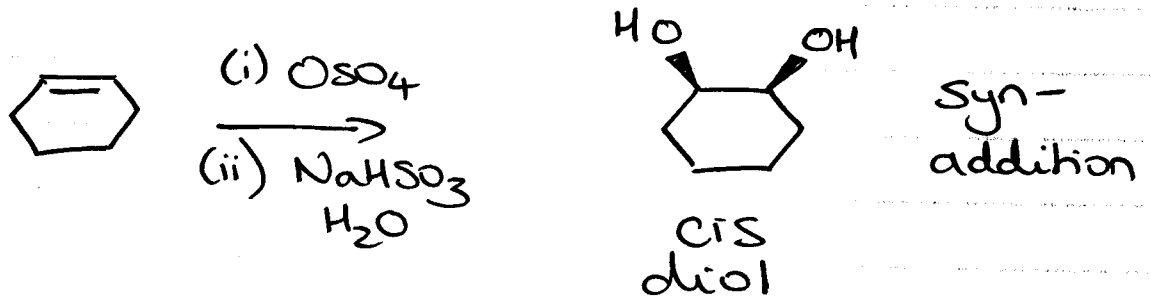


TRIALKYL BORATE

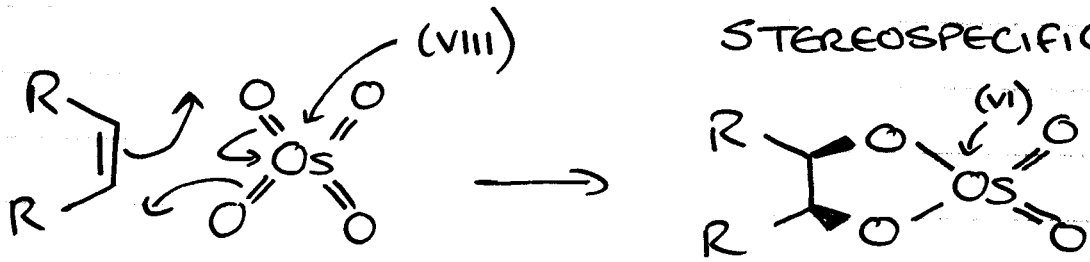


### ③ OXIDATION

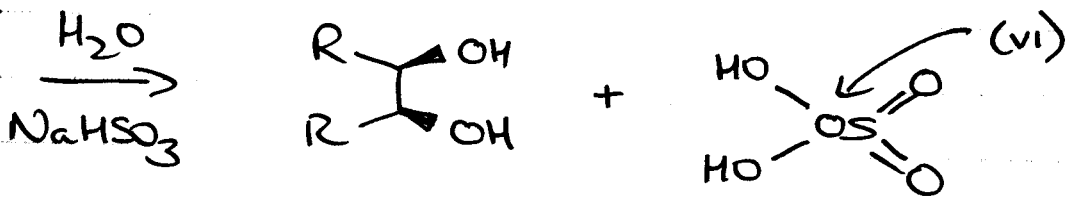
#### (i) $OsO_4$ OSMIUM TETROXIDE



STEREOSPECIFIC



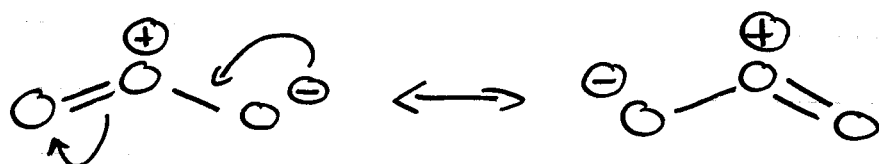
cyclic osmate ester



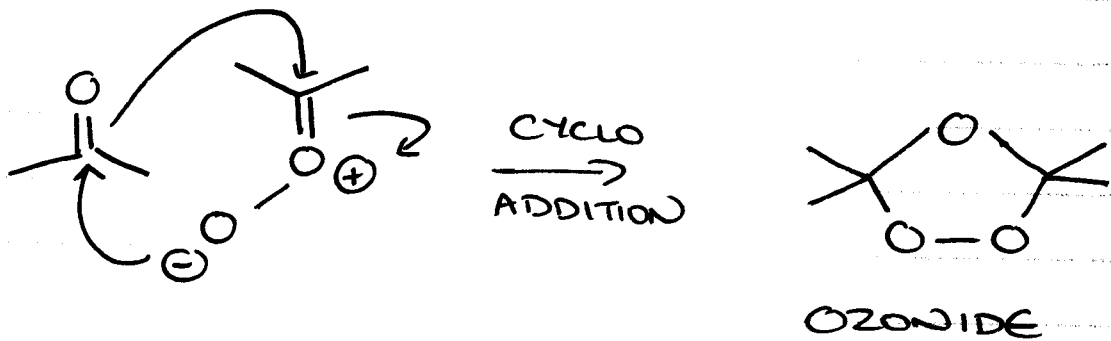
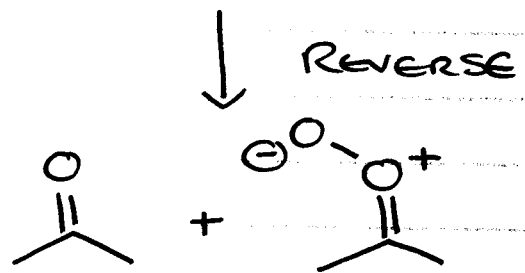
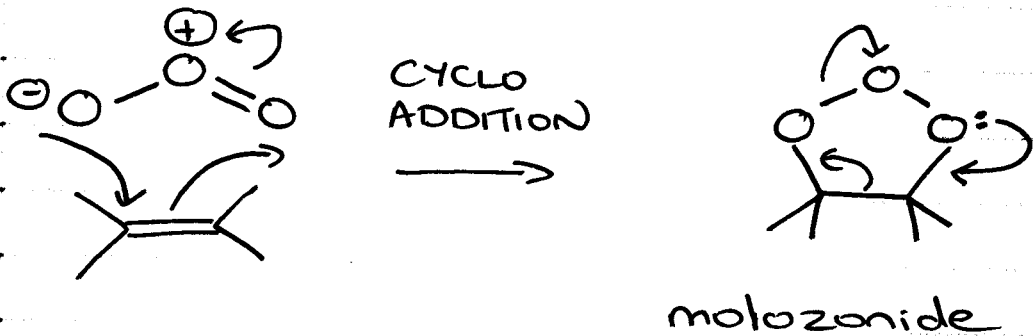
Os reduced (VIII  $\rightarrow$  VI) Alkene oxidized.

#### (ii) OZONOLYSIS

OZONE  $O_3$

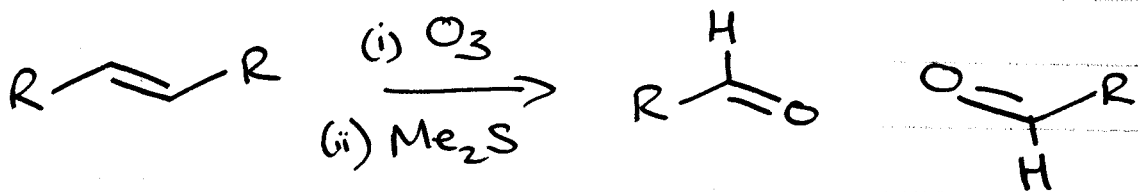


### ... Mechanism



... PRODUCT DEPENDS UPON 2nd REAGENT

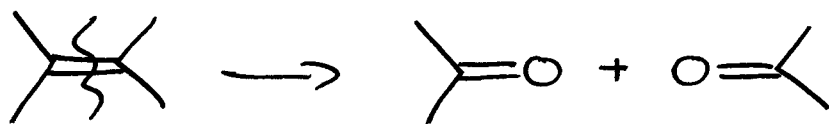
- most common Me<sub>2</sub>S



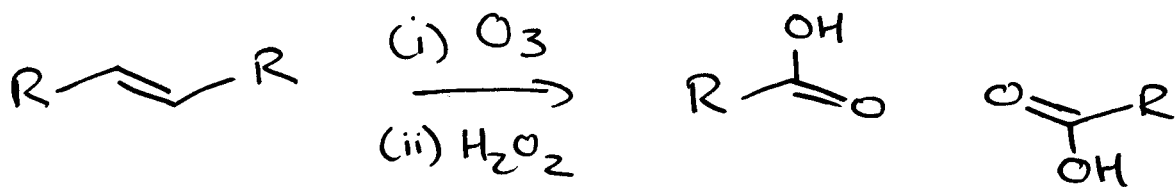
ALDEHYDES  
(OR KETONES)



9



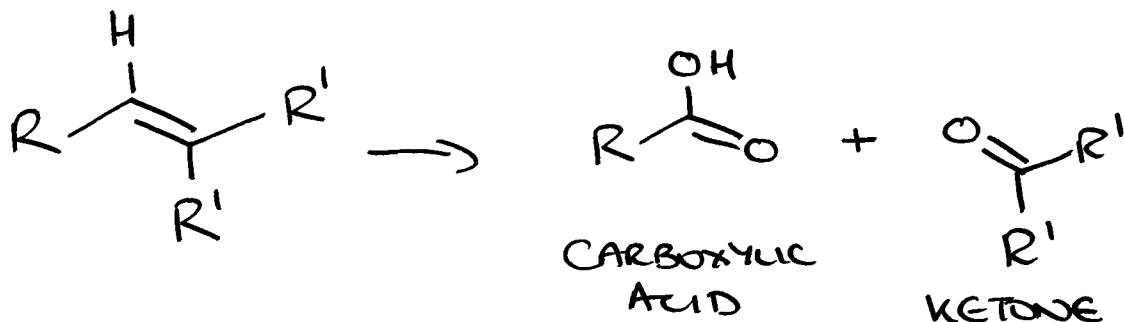
-  $\text{H}_2\text{O}_2$



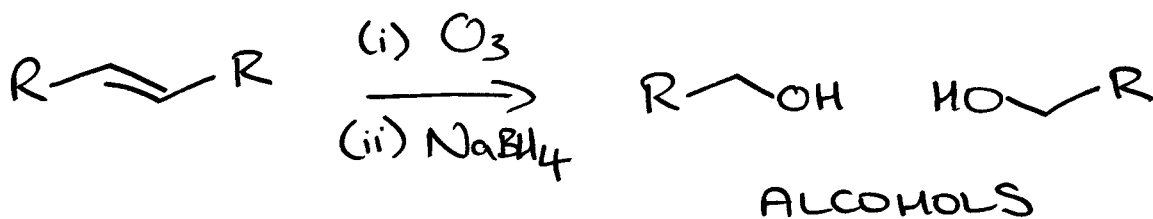
CARBOXYLIC ACIDS  
(or KETONES)

(must have H on C=C to get ACID)

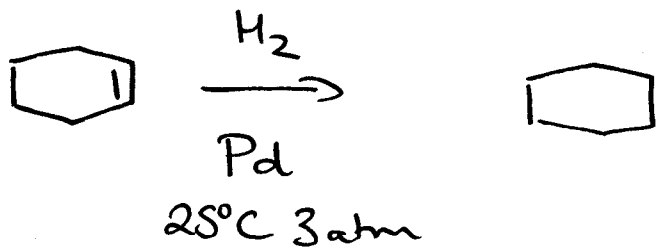
i.e.



-  $\text{NaBH}_4$



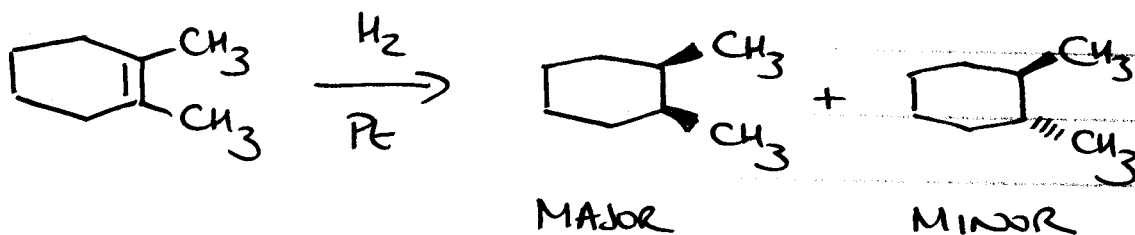
### ④ REDUCTION



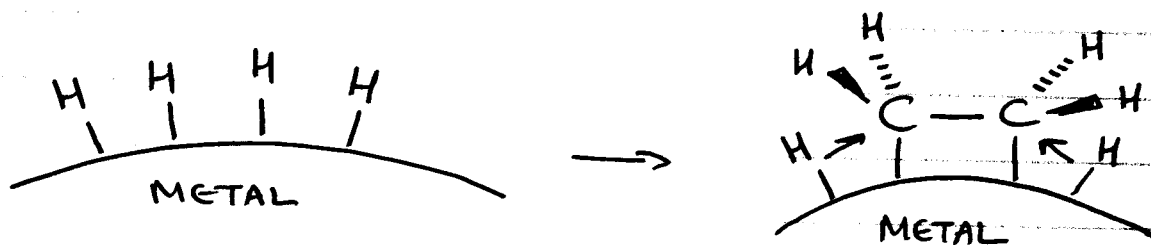
Transition metal catalyst Pt, Pd, Ru, Ni

CATALYTIC REDUCTION / HYDROGENATION

- STEREoselective



Mechanism



ADDS SAME SIDE  
(SYN ADDITION)