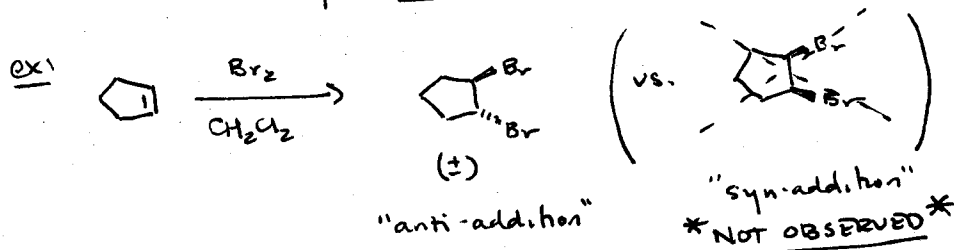
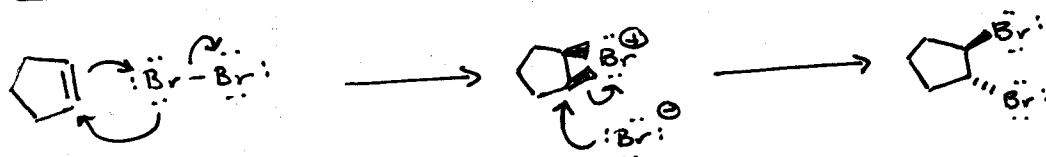


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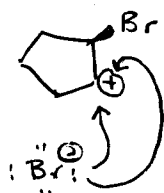
Recall: Interplay between reactivity & stereochemistry

Achiral SM $\longrightarrow$ Product w/ at least 2 stereocenters
can give diastereomers. $\rightarrow$ Mechanistic Rationale for Observed Diastereoselectivity:

*Br[⊖] Attack must occur from "back side"
of the C-Br bond

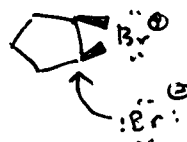
 $\rightarrow$ "Backside Attack" $\rightarrow$ Br[⊖] attack occurs with inversion
of configuration at Carbon

NOTE: The observed diastereoselectivity (only trans product, no cis product) rules out an alternative mechanism involving a carbocation intermediate



Br[⊖] could attack a carbocation
from either side $\rightarrow$ give cis & trans!

vs.



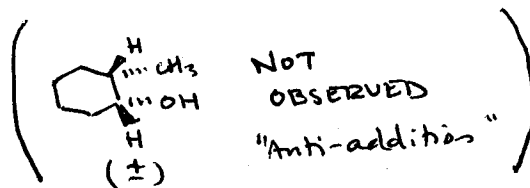
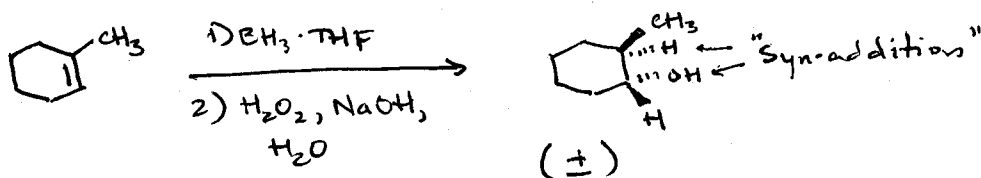
only backside
attack possible!

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Other Alkene Reactions - Stereochemical Insights

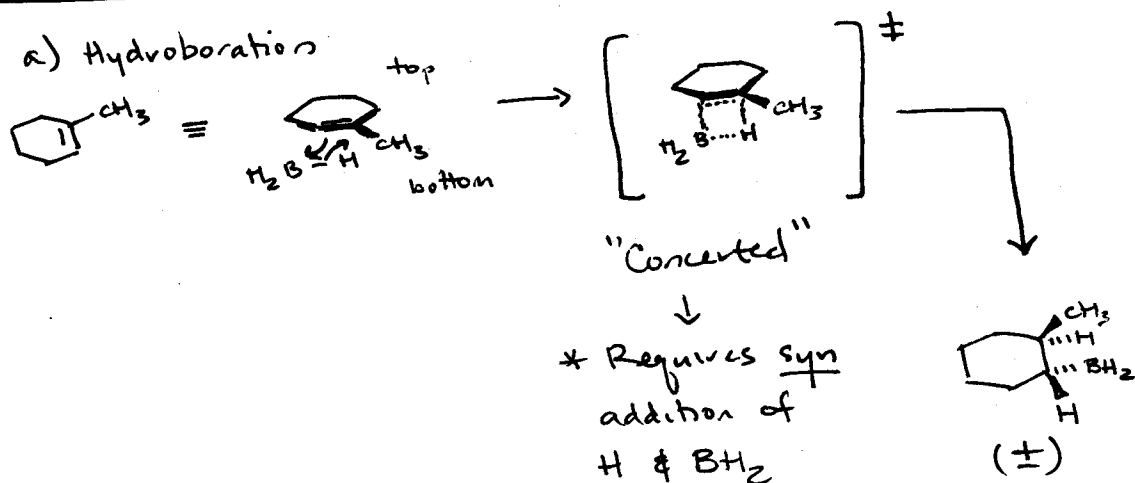
① Hydroboration - Oxidation

Overall: Syn addition of H & OH across alkene



Mechanistic Rationale - for observed diastereoselectivity

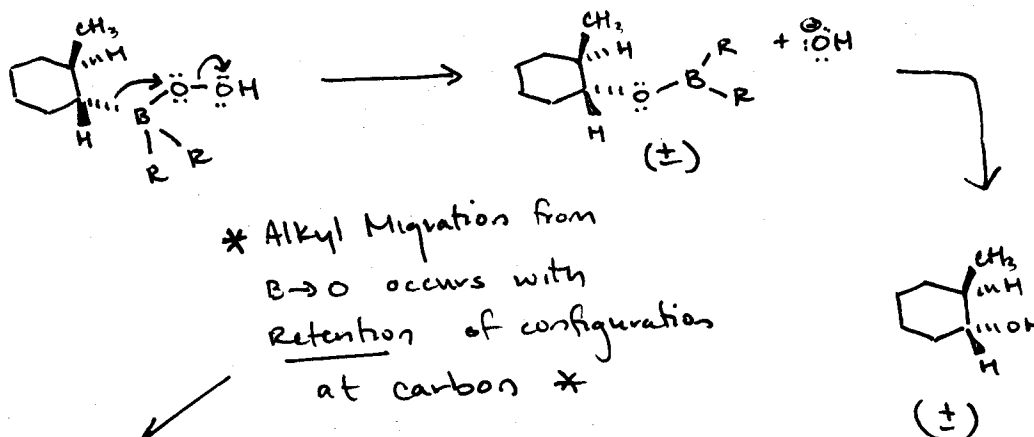
a) Hydroboration



(impossible for B & H to access both sides of the alkene at once...)

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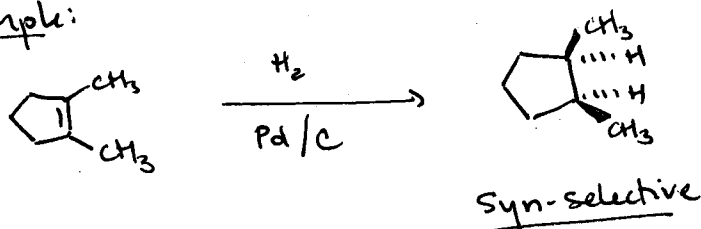
b) Oxidation



- Thus - overall Hydroboration-oxidation occurs with overall syn-addition.

② Catalytic Hydrogenation

Example:



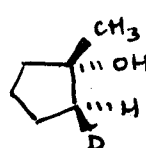
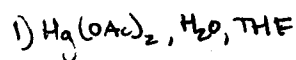
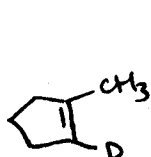
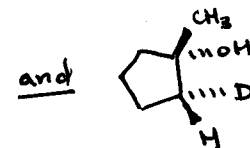
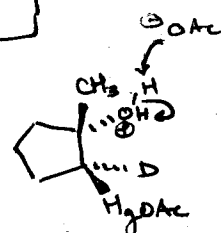
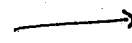
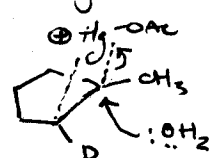
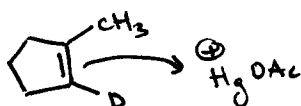
* Mechanism not perfectly understood & outside the scope of this course.

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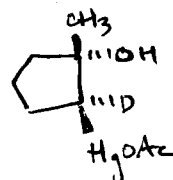
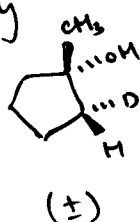
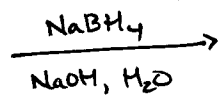
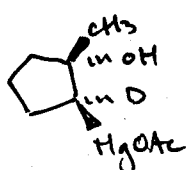
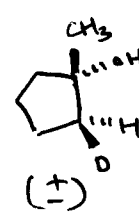
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③ Oxymercuration - Reduction

Ex:

 $(\pm)$  $(\pm)$ * D = Deuterium
(^2H)Both diastereomers form!
(Syn & Anti addition
products observed)Mechanistic Investigation:a) Oxymercuration:Stereospecific - Anti Addition of
 Hg & OH .Backside Attack
of OH_2 on carbon

Anti-Addition!

b) Reduction - No stereospecificity* $(\pm)$  $(\pm)$

** END OF EXAM MATERIAL **